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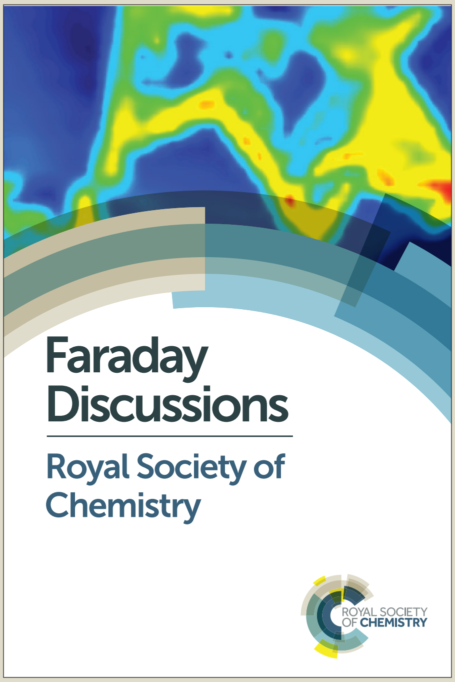

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ARTICLE

CO_2 Capture Systems Based on Saccharides and Organic Superbases

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In this report, novel systems, based on highly abundant saccharides, D-Mannose, D-Glucose, β-Cyclodextrin, Alginic Acid and Mannitol, in combination with an organic superbase, Tetramethylguanidine (TMG) or 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), are studied for carbon dioxide capture. With D-Mannose and D-Glucose, several ratios (equivalents of alcohol groups of saccharide):Superbase were tested, 1, 0.625, 0.5 and 0.25. High wt% values of CO_2 uptake were obtained with TMG-based systems. However, TMG itself can react directly with CO_2, and, in the presence of D-mannose, competition between carbonate and carbamate based products was established. In order to circunvent this competition and obtain exclusivelly the carbonate-based product, DBU was used instead as organic superbase. In the D-mannose series the highest result was obtained with a D-mannose:DBU ratio eq. = 0.625 (13.9 % CO_2 uptake, 3.3/5 alcohol groups converted into carbonates). A more effective stirring system, designed to overcome the high viscosity of the products, allowed the use of a D-glucose:DBU = 1:1 with 11.5 wt% of CO_2 uptake and 2.47/5 alcohol groups converted into carbonates). Additionally a DSC thermal study was performed in order to study stability/reversibility of the CO_2 loaded systems.

Introduction

Carbon dioxide capture and utilization is a fundamental concept to develop in the current environmental and energetic context[1]. The benchmark scrubbing systems for CO_2 capture available in the market for more than 60 years, aqueous solutions of alkanolamines, have as drawback the requirement of dilution of the capture agent in water (in order to avoid corrosion and mitigate excessive release of heat during reaction), leading to poor performances in CO_2 capture (7 wt% of CO_2 uptake in 30% aqueous solution of ethanolamine) and high energy demand for CO_2 stripping, due to the high heat capacity of water. Additionally, the solvent is lost during operations[2,3]. A competitive system should fulfil the criteria of high capacity to store this gas and sustainability from an energetic, economic and environmental point of view. The possibility to avoid water as reaction solvent made task specific ionic liquids (TSILs) interesting alternatives for CO_2 capture[4,5,6]. Ten years ago, Jessop and collaborators[7] developed the concept of reversible ionic liquid, using a mono-alcohol, an organic superbase and CO_2. These reagents led to an ionic liquid, formed by an alkylcarbonate and the protonated superbase cation. The reaction could be reverted bubbling an inert gas, like nitrogen or argon. The initial goal of this pioneer work was to develop solvents where polarity could be tuned by introduction or displacement of an acid gas such as CO_2. Following it, other studies with modification of several parameters such as the nucleophile (amines[8,9], amino-esters[10], amino-alcohols[11], amino-acids[12] and mono-saccharides[13]), type of organic superbase[9], element of reversibility[14] and number of functionalities in the same molecules able to react with CO_2[9,13] have been reported. In parallel, several applications based on the same principle of reversibility, such as media to promote reactions and extractions[15], dissolution of biomolecules[16], quenching of fluorescence[17], reversible manipulation of colour[14] and CO_2 capture have also been described. Regarding this last aspect, it is important to highlight that Heldebrant et al[2] could achieve a maximum of 19 wt% of CO_2 uptake using a system hexanol:Diazabicyclo[5.4.0]undec-7-ene (DBU), an excellent performance, compared with the conventional scrubbing system. The authors also state that alkyl carbonates are less stable than bicarbonates or carbamates, due to hydrogen bond interaction decrease. Naturally-occurring molecules with multiple alcohol groups could therefore become suitable platforms to reversibly capture CO_2. In agreement with these conjectures, Zhang et al. have recently reported a dramatic enhancement of the solubility of cellulose in DMSO after admission of CO_2 to cellulose:superbase

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systems[16]. The authors suggested that the reason for this behavior is related with the conversion of the alcohol groups of cellulose into carbonates. On the other hand, the order of alcohol reactivity is primary > secondary > tertiary, which may decrease the effectiveness of carbon capture by saccharides in comparison with primary alcohols. Herein, we present the study of saccharides and derived sugar structures containing multiple alcohol groups: D-glucose, D-mannose, alginic acid, mannitol and β-cyclodextrin, in combination with one of two organic superbases, Diazabicyclo[5.4.0]undec-7-ene (DBU) or tetramethyl guanidine (TMG). Considering reactivity constraints due to diffusion of CO_2 from gas to liquid phase associated to stirring efficiency[2,13] it was tested in the present work different ratios of saccharide to superbase, from equivalent amounts to large excesses of superbase - alcohol equivalents in saccharide/ mol of superbase from 1 to 0.25. Additionally, magnetic coupled stirring was tested as alternative method to conventional magnetic bar coupled system. Contrarily to our previous report[13], no solvents were used.

Experimental

Materials. All chemicals were used as purchased, with the exception of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), with purity of at least 99%, provided by Fluka and 1,1,3,3 Tetramethylguanidine (TMG), supplied by Sigma-Aldrich (99%), where water was removed using molecular sieves. The remaining chemicals used were D-(+)-Mannose (99%), D-(+)-Glucose (99%), D-Mannitol (99%), Alginic Acid, β-Cyclodextrin from Alfa Aesar and Carbon Dioxide (Air Liquid, 99,998 mol%).

Methods. The prepared compounds were characterized by ^{1}H and ^{13}C-NMR, HMBC (Heteronuclear Multiple Bond Correlation) and HSQC (Heteronuclear Single Quantum Coherence) and in specific cases by TOCSY (TOtal Correlated SpectroscopY) on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million from a tetramethylsilane reference, using d_6-DMSO as deuterated solvent. IR spectra were recorded on a Perkin Elmer FTIR Spectrometer, Spectrum 1000. The samples were prepared in a KBr matrix. DSC analysis was carried out by using a TA Instruments Q-series TM Q2000 DSC with a refrigerated cooling system. The sample is continuously purged with 50 mL/min nitrogen gas and 2-20 mg of salt was crimped into an aluminum standard sample pan with lid. The samples were submitted to an isothermal step (40ºC, 1 minute), cooled to -90^{o}C (20^{o}C/min, isothermal step 1 minute at -90^{o}C) and then heated to 150^{o}C (20^{o}C /min, isothermal step 1 minute at 150^{o}C). Following another cycle of cooling (-90^{o}C, 20^{o}C/min) and heat (150^{o}C, 20^{o}C/min). The glass transition temperature, the melting point and the decomposition temperature were determined on the heating process of the first cycle.

Synthetic procedures. The syntheses were performed in a cylindrical high pressure steel reactor (11 mL) with sapphire windows at both ends– Figure 2, allowing a full view of the contents of the cell. In each experiment, 2.5 g. of superbase (DBU or TMG) were used, alone or in combination with the proper number of equivalents (alcohol or carboxylic acid groups) of each saccharide. In the case of D-mannose and D-glucose, the ratios (in equivalents) Saccharide:DBU were 1, 0.625, 0.5 and 0.25, whereas for β-Cyclodextrin, Alginic Acid and Mannitol, they were 0.5, 1 and 0.5 respectively. Stirring of the saccharide + superbase mixtures was done with a small magnetic bar, coupled to a common laboratory plate, for at least 20 min. until complete dissolution of the saccharide in the (liquid) base. CO_2 was then introduced into the cell, at room temperature, normally until a pressure of 5 MPa was reached (exceptions were 2 MPa for TMG alone, and 4 MPa for TMG in combination with D-Mannose). The pressure dropped continuously until reaching a stable minimum, usually in less than 3 hours. In some situations was necessary to refill the cell with CO_2 in order to complete the reaction. Decompression of the reactor was then carried out slowly, in order to avoid the release of any fine powder. The reactor was weighed previously to CO_2 supply and after decompression, in order to measure the carbon dioxide uptake. The products were stored in a freezer at temperatures below 0°C to their analysis.

Visual observations of the reactions as they proceeded indicated that a solid progressively formed and separated from the liquid mixture. In the cases of higher concentration of saccharide in the superbase (1:1 ratio), the solid could even block the magnetic bar and stop stirring. In order to check whether in these cases the kinetics of the reaction were significantly decreased; one experiment was carried out in a different apparatus, with a more effective stirring system. A 250 mL reactor with a magnetically coupled stirring, built by Thar, was used. This stirring system is often used in high-pressure reactions, and consists of a powerful external electromagnet that rotates, and couples its movement with permanent magnets attached to the top of a rod, located inside the reactor, with a stirring helix at the bottom. The nominal torque exerted by this configuration is at least 5 times higher than what we could obtain with the magnetic bar in the reactor of Figure 2.

Although several disadvantages would not allow the systematic use of that experimental apparatus for our purposes, continuous stirring throughout the whole time of reaction was obtained for a (1:1) DBU + glucose mixture**,** consisting of 20.36 g. of DBU combined with an equivalent amount of D-glucose. The mixture was stirred 35 min. previous to the reaction with CO_2.

Results and discussion

Saccharides or derived sugar structures with different numbers of OH groups were sudied (Figure 1). In the cases of D-glucose and D-mannose (five OH groups per molecule), two highly abundant natural compounds, several number of equivalents of OH groups in mono-saccharides per number of superbase molecules ratios (nr. -OH eq./nr. SB : 0.25, 0.5, 0.625 and 1) were tested. Considering this approach, mixtures of monosaccharide:superbase with different viscosities were achieved for CO_2 capture studies. Moreover, other saccharide-based structures such as alginic acid (two OH groups and one carboxylic acid group per monomer), β-cyclodextrin (three OH groups per unit and twenty-one per molecule) and D-mannitol (six OH groups per molecule). For these last saccharide scaffolds the saccharide: superbase ratios (nr. –OH and COOH eq./nr. SB) were 1, 0.5 and 0.5 respectively. In the case of alginic acid, the carboxylic group was also considered to be deprotonated by the superbase, along with the alcohol groups, in order to determine the ratio under discussion.

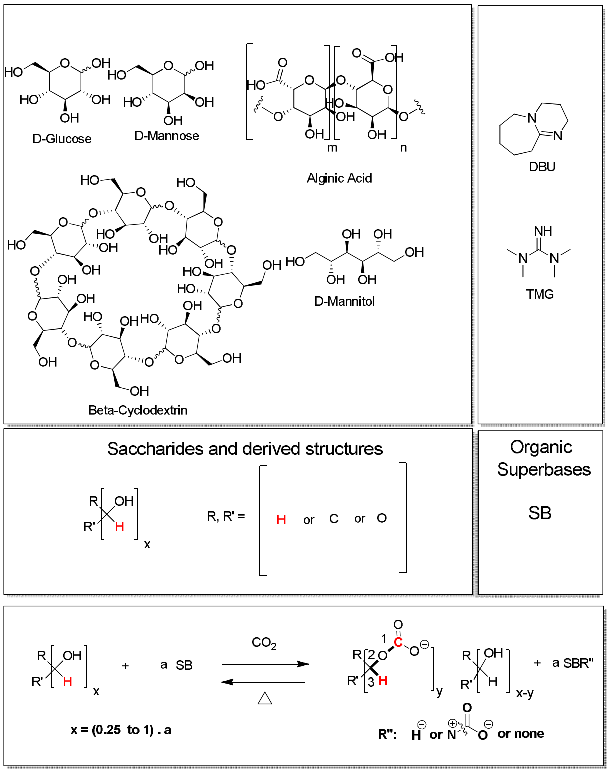

Figure 1: Saccharides and derived compounds used in combination with an organic superbase to capture CO_2 leading to organic carbonates and also a carbamate when TMG is employed as organic superbase. CO_2 is released after heating. According change of functionalization from alcohol to carbonate, modification of the chemical shift in ^{1}H-NMR of the protons at distance of three bonds from carbon from carbonate are detected as well as correlation by HMBC NMR spectroscopic technique.

In this context is fundamental to determine the percentage of CO_2 uptake respective to the capture system (superbase alone and superbase + saccharide) as well as the number of alcohol groups of the saccharide converted to carbonates.

The superbase TMG can by itself react with carbon dioxide, forming carbamates according the work of Pereira et al.[18] Considering this, in an initial stage of our studies, we measured the selectivity carbonate vs carbamate in a mixture D-mannose:TMG (ratio 1), using pressures of CO_2 up to 4 MPa, leading to 18 wt% of CO_2 uptake. The reaction was repeated, leading to 22.8 wt % of CO_2 uptake (Table 1) corresponding to 2.32 –OH groups of D-mannose (from 5 possible to be functionalized) converted into carbonates (determined by ^{1}H-NMR with aid of HMBC). 1.58 equivalents of TMG (from 5 possible) were converted into carbamates, as determined by weighing the mass of CO_2 uptake and considering the fraction converted into carbonates. This result is supported by the work of Ozturk et al[19] who performed a kinetic study of the reaction between CO_2, TMG and 1-hexanol, with the formation of a carbamate intermediate product (reaction with TMG), stabilized by the alcohol.

Table 1: Tetramethylguanidine (TMG) based systems in the capture of CO_2 and effect of the presence of D-mannose.

System	wt % CO_2	$[OH\ to\ CO_3^-]^b$ (=NH of TMG to $NCO_2^-)^c$	FTIR NCO_2^- bands (cm^{-1})	^{1}H-NMR H bond peak [TMG -C$\underline{H}_3$ peak] (δ, área)	^{1}H-NMR – CO_3^- peaks (δ, área)	^{13}C-NMR TMG Quat. carbon [TMG -$\underline{C}H_3$ peak]
TMG	-	[-] (-)	-	5.35, 0.94 [2.62, 12]	-	166.20 [39.04]
TMG w/CO_2	29.5[a]	[-] (0.775:1[a])	3282 3107 1667	5.93, 1.09 [2.64, 12]	-	165.82 [39.04]
Man: TMG 1:1 eq.	-	[-] (-)	-	5.16, 9.38 [2.62, 60]	-	166.23 [39.07]
Man: TMG w/CO_2 1:1 eq.	22.8[a]	[2.32:5[d]] (1.58:5[a])	3129 1685	6.06, 10.75 [2.70, 60]	(5.25, 0.15) (4.92, 0.05) (4.84, 0.25) (4.48, 0.05) (4.36, 0.05) (4.29, 0.18) (4.20, 0.01 (4.12, 0.02) (3.94, 0.18) (3.86, 0.08) (3.79, 0.2) (3.51, 1.36)	164.71 [39.14]

a - determined by weighed mass, b - number of OH groups from D-mannose converted to carbonates, c - number of =NH groups converted to carbamates, d - determined by 1H-NMR and HMBC. NMR spectra obtained in d6-DMSO.

The authors proposed two alternative products: $TMGCO_2^-$ + $TMGH^+$ + hexanol and the other configuration $HexCO_3^-$ + $TMGH^+$ + hexanol. According the authors the second path is favoured and the carbonate product is preferred when compared with carbamate. In this context, we checked the reactivity of TMG towards CO_2, leading to 29.5% of CO_2 uptake (77.5% yield). It is important to note that the identity of the product was obtained by ^{1}H-NMR (by displacement of the $(N(CH_3)_2)_2C{=}N\underline{H}$ peak from 5.35 ppm in TMG to 5.93 ppm in the product $(N(CH_3)_2)_2C{=}N^+\underline{H}CO_2^-)$, TOCSY (see in supporting information; spectra of the product reveal a correlation $((C\underline{H}_3)_2N)_2C{=}N\underline{H}CO_2$ indication that the peak with chemical shift 5.93 ppm belongs to $TMGCO_2$), and ^{13}C-NMR spectra (the presence of an irregular peak at 165.8 ppm which can indicate us the presence of two different quaternary carbons: $((CH_3)_2N)_2\underline{C}{=}NHCO_2$, one from TMG and the other from carbamate functionality. Moreover the presence of carbamate functionality is confirmed by the presence of characteristic bands 3107, 3282 and 1667 cm^{-1} detected in FTIR spectra (bands at higher frequency giving indication of N-H stretch while the band of lower frequency is related with C=O stretch, both from carbamate functionality[5,20]). Differently from the work of Pereira et al[18], in our experimental work TMG was dried previously to its use in CO_2 capture.

In the case of the systems based on TMG or Mannose/TMG the weight percentages of CO_2 uptake are very high, nevertheless, besides the reactivity of the alcohol groups from D-mannose in the presence of CO_2, TMG also reacts, leading to the respective carbamate. In order to increase the average number of -OH groups of saccharides converted into carbonates and simplify the system, avoiding multiple products after reaction with CO_2, we decided to use DBU as organic superbase instead of TMG. Initially, only dry DBU was tested in CO_2 capture. After reaction a CO_2 uptake of 2.4%, was obtained with 13% of DBU protonated (by ^{1}H-NMR - slight shift of quaternary (N)*C*(C)(=N) carbon, 159.66 ppm comparing with initial DBU signal, 159.54 ppm). Moreover, it was not detected by HMBC any H/C correlation from a possible carbamate or even from bicarbonate. The only hypothesis that explains this residual CO_2 uptake and low protonation of DBU is the formation of carbonate $[CO_3]^{2-}$ by the reaction of residual water present in DBU with CO_2. From this assay we conclude that DBU don't react directly with CO_2 to originate the respective carbamate and it seems a good candidate to replace TMG in the activation of the alcohol groups of the saccharides and further reaction with CO_2, leading to carbonates. In the sequence of this reaction was used the mixture D-mannose:DBU (ratio of 1 in equivalents) to capture CO_2. Such mixture is very viscous precluding stirring during the reaction. As result the wt% of CO_2 uptake was approximately 0. In order to improve the efficiency of the system and attain maximum functionalization of the saccharide we tested different ratios D-mannose:DBU (0.25, 0.5, 0.625 – besides 1). Previous to reaction with CO_2, the mixture is liquid and afterwards the product is solid as shown in Figure 2.

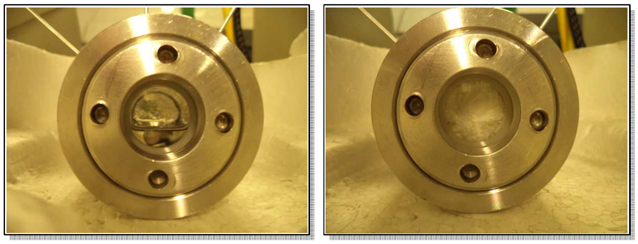

Figure 2: System D-Mannose:DBU (0.625 : 1 eq.). From left to right: before and after reaction with CO_2.

The possibility to have solids instead of viscous liquids facilitates the transport of captured CO_2. ^{1}H-NMR spectra was used to access the average number of alcohol groups of D-mannose converted into carbonates. The protons adjacent to carbonate functionality (Figure 1 – at a distance of three bonds from carbon of carbonate) have a different chemical shift when compared with equivalent protons when alcohol functionality is present. Considering this fact and comparing the ^{1}H-NMR spectra of the systems under discussion with the spectra of D-Mannose:DBU previous to its reaction with CO_2 is possible to highlight the differences (Figure 3) and account the areas of the protons with modified chemical shift and with the aid of HMBC spectra (H/C correlation– Figure 1 carbon of carbonate and protons at distance of three bonds) estimate the average number of alcohol groups converted into carbonates. Considering the results presented in Table 2, is possible to conclude that decreasing the proportion of saccharide respective to DBU leads to a much more effective CO_2 capture (13.9 wt% of CO_2 uptake in the case of the ratio Man:DBU = 0.625 in equivalents). In any case is not possible to establish a direct relationship between the ratio Man:DBU and the wt% of CO_2 uptake neither a relationship between the Man:DBU ratio and the number of alcohol groups converted into carbonates or an exact concordance between the two methodologies of calculation of the number of alcohol groups converted into carbonates (Table 2 – by mass or ^{1}H-NMR). In order to explain these results is important to consider that magnetic bar based stirring is not the ideal method to promote the reaction and also obtain reproducible results, moreover it may be present traces of water in DBU and/or even in D-mannose and partial precipitation of the product of reaction from d_6-DMSO solution during storage, delay and acquisition of the NMR spectra. Additionally, when weighing the reactor previous and after reaction with CO_2 we are detecting differences in the first or second decimal place when the total mass of the reactor with the mixtures is around 1200 g. Nevertheless is interesting to note by ^{1}H-NMR that the average number of alcohol groups converted into carbonates are ~3 out of 5 in all the systems studied except in the system Man:DBU (ratio 1 in equivalents).

These results represent an improvement in the functionalization of D-mannose when compared with similar system using TMG as organic superbase (2.32 out of 5 - Table 1). Additionally, FTIR spectra confirm the presence of carbonates, as bands at 1585, ~1400 and 1271 cm^{-1} appear in the studied systems, similarly as in the work of Heldebrant et al[21]. While in DBU a C=N stretch band centred at 1610 cm^{-1} is evident[22], in our systems DBU + D-Mannose, the two bands at ~1650 cm^{-1} and ~1610 cm^{-1}, are replaced by a single band at ~1650 cm^{-1} after reaction with CO_2 (Table 2), which, according Galezowski et al[23] is indication that DBU is protonated. Moreover, the value of the chemical shift of the quaternary carbon (C)(N)*C*(=N) is also indicative of the degree of protonation of DBU with the highest value (161.07 ppm) corresponding to the system Man:DBU = 0.625. Factors such as the proportion of D-mannose and percentage of incorporation of CO_2 increment the chemical shift of this carbon. The results obtained with D-mannose and DBU encourage us to study D-glucose based systems as this saccharide is highly abundant. Again, saccharide:DBU ratios (in equivalents) of 1, 0.625, 0.5 and 0.25 were tested (Table 3 and Figure 4). Differently from D-mannose case, with D-glucose based system in addition to the magnetic bar based stirring, was also tested magnetically coupled stirring in a much bigger reactor, as a clear influence of stirring on the outcome of reaction of carbonation was detected [2,13].

Table 2: Mannose series, effect of the Mannose: DBU ratio in the performance of CO_2 capture.

System	wt % CO_2	-OH to $CO_3^{-\,a}$ mass [NMR]	FTIR CO_3^- [DBU] bands (cm^{-1})	^{1}H-NMR H adjacent to CO_3^- (δ, area)^b	^{13}C-NMR DBU Quat. carbon peak^b	Man: SB eq. by ^{1}H-NMR
DBU	-	- [-]	- [1610]	-	159.54	-
DBU w/CO_2	2.4	- [-]	1372.18 1090.23 863.19 [1649.24] [1608.43]	-	159.66	-
Man: DBU 1:1 eq	-	- [-]	- [1648.89] [1611.13]	-	159.78	1
Man: DBU w/CO_2 1:1 eq	0	0 [0.21]	1585.77 1398.57 1271.80 [1651] [1615.08]	(3.74-3.89, 0.26)	160.12 160.05	1.008
Man: DBU w/CO_2 0.625:1 eq.	13.9	4.37 [3.3]	1585.47 1386.10 1271.69 [1645.60]	(4.83, 0.40) (4.51, 0.19) (4.34, 0.46) (4.19, 0.08) (4.07, 0.05) (3.97, 0.35) (3.87, 0.24) (3.75, 0.69) (3.52, 2.71)	161.07	0.814
Man: DBU w/CO_2 0.5:1 eq.	6.6	2.56 [3.06]	1585.79 1399.22 1271.89 [1642.71]	(4.84, 0.45) (4.46, 0.06) (4.36, 0.23) (4.19, 0.15) (3.98, 0.29) (3.86, 0.29) (3.74, 0.64) (3.52, 1.17)	160.69	0.492
Man: DBU w/CO_2 0.25:1 eq.	7.9	5.75 [2.61]	1585.33 1399.66 1271.66 [1645.45]	(4.82, 0.29) (4.50, 0.01) (4.30, 0.25) (4.17, 0.03) (3.99, 0.19) (3.86, 0.09) (3.74, 0.66) (3.51, 2.01)	160.24	0.281

a-number of OH groups of D-mannose converted into carbonates, b-NMR spectra obtained in d6-DMSO.. All the reactions were promoted using a magnetic bar.

With this test, we could obtain the maximum thermodynamically permitted number of alcohol groups converted into carbonates for a Glucose:DBU 1:1 equivalent ratio. In a previous report, we had indication that multi-anionic charged organic molecules, with the charges in close vicinity, obtained from functionalization with CO_2 are not very stable[6].

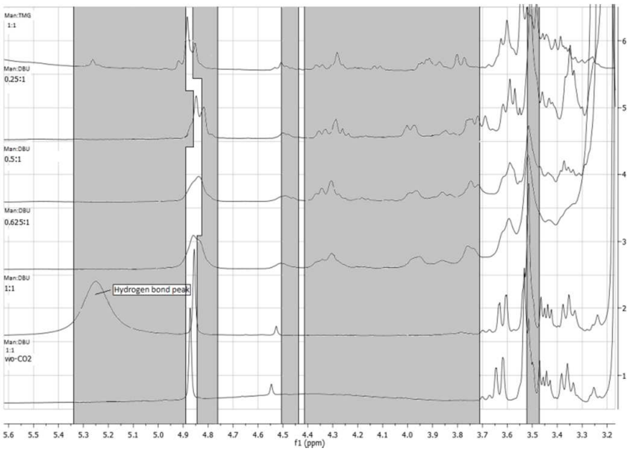

Figure 3: ^{1}H-NMR Spectra – Systems based on Mannose and an organic superbase (DBU or TMG). Highlight in grey of the new peaks obtained after reaction with CO_2. From up – down, Man:TMG (1:1), Man:DBU (0.25:1), Man:DBU (0.5:1), Man:DBU (0.625:1), Man:DBU (1:1) and Man:DBU (1:1) previous to reaction with CO_2.

In this context this test could be an indication of the limits of glucose based systems to accommodate density of charge. Comparing identical systems (Glu:DBU of 1:1 ratio) differing in the type of stirring, was possible to obtain a much higher number of alcohol groups converted into carbonates with magnetically coupled than with magnetic bar based stirring (2.47/5 vs 1.08/5 – Table 3) as expected. Magnetically coupled stirred system is a 250 ml reactor that for obvious reasons could not be weighed previous and after reaction with CO_2. Considering this limitation, the value of 11.5 wt% of CO_2 uptake was estimated based on ^{1}H-NMR analysis. This was the maximum percentage obtained in this series highlighting the importance of the type of stirring.

Curiously, it was observed a clear trend for all the magnetic bar stirred systems, with the lower Glu:DBU ratios resulting in higher number of alcohol groups converted into carbonates (Table 3) with a maximum of 3.28 groups converted (estimated by ^{1}H-NMR) using the ratio Glu:DBU of 0.25:1 equivalents.

Two different arguments could explain the results: first, lower ratios of glucose in the system lead to lower viscosities, leading to a more effective mixing between gaseous CO_2 and the liquid phase until an extended functionalization is attained; differently, from a thermodynamic point of view, following the Le Châtelier principle, the increment of the reagents will shift the equilibrium towards the formation of more product. In this case an excess of DBU respective to the number of equivalents of alcohol groups in glucose if decreasing the Glucose:DBU ratio (eq.). Another relevant fact, the values of wt% uptake determined by different methods (weighing and NMR) are very similar, indication that the methodologies used are reliable.

Table 3: Glucose based systems using DBU as organic superbase in CO_2 atmosphere. Effect of the ratio Glucose:DBU (in number of equivalents) and type of stirring.

System	wt % CO_2	OH to CO_3^{-b} mass [NMR]	FTIR CO_3^- [DBU] bands (cm^{-1})	^{1}H-NMR H adjacent to CO_3^- peaks (δ, área)	^{13}C-NMR DBU Quat. carbon peak	Glu:SB eq. by ^{1}H-NMR
DBU	-	- [-]	- [1610]	-	159.54	-
DBU w/CO_2	2.4	- [-]	1372.18 1090.23 863.19 [1649.24] [1608.43]	-	159.66	-
Glu:DBU 1:1 eq.	-	- [-]	-	-	159.97	0.71
Glu:DBU w/CO_2 1:1 eq.	2.3	0.48 [1.08]	1589.12 1394 1274.55 [1645.99]	(5.01, 0.01) (4.86, 0.08) (3.99, 0.14) (3.90, 0.11) (3.82, 0.1) (3.77, 0.11) (3.54, 0.1)	160.38	0.5
Glu:DBU w/CO_2 1:1 eq. w/ magnetic coupled stirred.[a]	11.5[a]	- [2.47]	1585.97 1399.59 1271.89 [1642.34]	(5.04, 0.05) (4.87, 0.17) (4.30, 0.18) (3.96, 0.44) (3.86, 0.49) (3.55, 0.91)	161.31	0.75
Glu:DBU w/CO_2 0.625:1 eq.	6.1	1.94 [1.73]	1588.79 1378 1274.63 [1644.51]	(4.99, 0.02) (4.87, 0.1) (4.29, 0.19) (3.99, 0.28) (3.82, 0.24) (3.74, 0.29) (3.55, 0.25)	160.67	0.372
Glu:DBU w/CO_2 0.5:1 eq.	7.9	3.04 [2.85]	1588.84 1394 1274.59 [1645.17]	(5.03, 0.08) (4.86, 0.15) (4.29, 0.33) (3.99, 0.47) (3.86, 0.76) (3.75, 0.53) (3.55, 0.25)	160.81	0.375
Glu:DBU w/CO_2 0.25:1 eq.	4.9	3.59 [3.28]	1588.14 1365.92 1274.04 [1649.46] [1611.60]	(4.97, 0.02) (4.85, 0.13) (4.27, 0.23) (4.00, 0.24) (3.91, 0.09) (3.85, 0.08) (3.77, 0.42) (3.55, 0.24)	160.02	0.191

In all the entries, except when stated "magnetically coupled system", stirring was promoted using a magnetic bar., a: The value of wt % CO2 incorporation was estimated based on the number of equivalents of alcohol groups of glucose converted into carbonates. b: number of alcohol groups of D-glucose converted to carbonates.

The presence of carbonate based functionalities was confirmed by FTIR, with bands centred at ~1590, ~1400 and ~1270 cm^{-1} (similarly as in the case of D-mannose). Moreover it was also detected a shift of band from ~1610 to ~1650 cm^{-1} in Glu:DBU systems after reaction with CO_2, indication that DBU is protonated in the obtained products. It is also important to refer that the degree of protonation of DBU, influenced by the extension of CO_2 uptake and ratio of D-Glucose to DBU, is correlated with the chemical shift of the quaternary carbon (C)(N)*C*=N of DBU, which is inversely correlated with the frequency of the band ~1650 cm^{-1} detected by FTIR (R^2 = 0.91). This results, lead us to an empirical equation that relate the Glu:DBU ratio, number of OH groups converted into carbonates and number of alcohol groups that remained unchanged with a calculated factor that is well-correlated with the frequency of the band at ~1650 cm^{-1} in FTIR spectra (R^2 = 0.98).

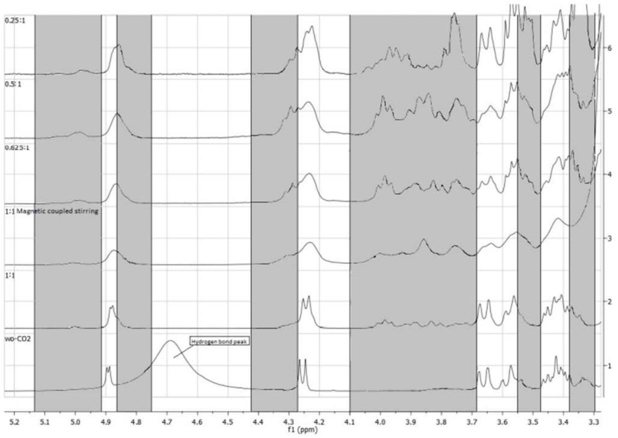

Figure 4: ^{1}H-NMR Spectra - Systems Glucose:DBU. Highlight of the new peaks obtained after reaction with CO_2. From up – down, Glu:DBU (0.25:1), Glu:DBU (0.5:1), Glu:DBU (0.625:1), Glu:DBU (1:1) with magnetically coupled stirrer, Glu:DBU (1:1) and Glu:DBU (1:1) previous to reaction with CO_2.

The empirical equation is:

$$Factor = (ratio\ Glu{:}DBU\ in\ eq.)^{0.24} \times nr.of - CO3\ \ per\ glucose^{0.7} \times nr\ of - OH\ per\ glucose^{0.81}$$

Equation 1

And the correlation equation that relates the FTIR frequency (cm^{-1}) with the determined factor in equation 1:

$$Frequency = -4.9939 \times Factor + 1661.9$$

Equation 2

With both equations is possible, by performing a FTIR spectra of the product of CO_2 capture and providing the Glu:DBU ratio (eq.), to access directly the average number of carbonate groups per molecule of functionalized glucose.

Similarly as in D-Mannose, with D-Glucose based systems, the estimation of the number of OH groups converted into carbonates was performed by highlighting the differences between Glu:DBU systems previous and after reaction of CO_2 (Figure 4) in ^{1}H-NMR spectra, with the aid of HMBC spectra (Supporting information - long times of acquisition were required and low intensity correlations were detected in most cases, and in specific cases no correlation was detected). Other saccharides and related structures were tested for CO_2 capture such as β-cyclodextrin, alginic acid and mannitol with three, two and six alcohol groups per unit or molecule respectively. Again due to high viscosities was necessary to use ratios saccharide:DBU in equivalents lower than 1 in most cases (Table 4).

Relatively low values of wt% of CO_2 uptake were attained with these saccharides, the main reasons behind these results are the considerable excess of superbase used (in the case of β-cyclodextrin and mannitol), inefficient stirring at a relative early stage of reaction (all the reactions were promoted by the use of a magnetic bar) and relatively low number of alcohol groups able to be functionalized (in the case of β-cyclodextrin and alginic acid). Again, the determination by NMR of the number of alcohol groups converted into carbonates was based on the area of protons adjacent to carbonate functionalities that were unveiled with the aid of HMBC spectra. In this context, it is important to highlight the relative resemblance between the values determined by NMR and mass. In all the cases tested, carbonate characteristic bands in FTIR spectra (Table 4) were detected similarly as in D-mannose and D-glucose series. In the same spectra is possible to verify that in the cases where the functionalization reaction is more extended (alginic acid and mannitol) a single band centred a ~1650 cm^{-1} is obtained). In the case of β-cyclodextrin two bands arise at ~1652 and 1613 cm^{-1} indication that DBU is partially protonated[23] and that the reaction was less extended when compared with other saccharides. The chemical shift of the quaternary carbon of DBU (C)(N)*C*=N give us the indication that DBU is more protonated in the system Mannitol:DBU ratio 0.5 (eq.).

Additionally, a DSC thermal study of the products of reaction with CO_2 was performed (Table 5). The experiment consisted in lowering the temperature of the sample until -90°C and increasing the temperature afterwards until 150°C. Tg (glass transition temperature), mp (melting point) and Td (decomposition temperature) measurement was performed, and finally a second cycle was performed to confirm CO_2 release by non-reproducibility of the second cycle respective to the first. In the case of TMG based system, two endothermic peaks were detected in the first cycle, one at 56.52°C and the other at 108.88°C. In the study of Pereira et al[18], two TGA losses are detected for the same system after CO_2 capture. According the authors, the release at lower temperature corresponds to carbamate, and the other is from bicarbonate. We agree with this interpretation however, considering also the result of Td of DBU system (118.01°C), that corresponds to CO_2 release from $[CO_3]^{2-}$ we hypothesise that instead of bicarbonate the reason behind the second peak of TMG system is CO_2 release from carbonate.

Considering Mannose:DBU series, is possible to verify that when the number of alcohol groups converted into carbonates is higher (Table 2 – by NMR) the value of Td decreases (Table 5), indication that higher density of charge in a small molecule like D-mannose lead to higher destabilization of the product and consequently lower temperature required for CO_2 release.

It is also important to note that at this point is premature to discard the influence of dilution of the functionalized saccharide respective to DBU in increasing the value of Td.

Table 4: Other saccharides combined with DBU to capture CO_2.

System	wt % CO_2	OH to CO_3^{-} [a] Mass [NMR]	FTIR CO_3^{-} [DBU] bands (cm^{-1})	^{1}H-NMR H adjacent to carbonate (δ, área)	^{13}C-NMR DBU Quat. carbon peak
DBU	-	- [-]	- [1610][d]	-	159.54
DBU w/CO_2	2.4	- [-]	1372.18 1090.23 863.19 [1649.24] [1608.43]	-	159.66
B-CD: DBU w/CO_2 0.5:1 eq.	1.8	3.08:21 [3.93:21]	1586.87 1384.56 1270.36 [1652.19] [1612.66]	(4.72, 1.69) (4.01, 0.85) (3.57, 1.98)	160.15
Alginic Acid:DBU w/CO_2 1:1 eq.	4.73	0.68:2 [-][a]	1586.62 1384.62 1270.18 [1651.65]	-[a]	-[a]
Mannitol :DBU w/CO_2 0.5:1 eq.	4.73	2.16:6 [1.95:6]	1585.87 1385.77 1272.17 [1646.05]	(3.37, 2.21) (3.58, 1.04)	160.53

a-number of OH groups of D-mannose converted into carbonates b: Solubility constraints didn't permit to obtain reliable NMR spectra. Magnetic bar stirring was used to promote reaction with CO2 in all the cases.

Considering Tg analysis is possible to observe that for all the cases that were detected, the value of Tg increases with the increment of the ratio Man:DBU (eq.) indication that a possible extended hydrogen bond network may lead to increased value of Tg. Regarding D-glucose series a similar approach can be performed, nevertheless and differently from D-mannose series, is possible to verify in the great majority of ratios a peak at >145°C that should correspond to melt/decomposition of glucose[24] after release of CO_2 from carbonate functionalized saccharide. In order to explain the values obtained at lower temperatures along the series we have to consider both the density of charge and the dilution of the functionalized saccharide, with the latest leading to an increased value of Td, and the former leading to a lower value of decomposition temperature, for the ratios, 1:1 (magnetically coupled), 0.625:1 and 0.5:1 the trend is clear because there's only one value of Td associated to CO_2 release from carbonates. Differently for the ratios 1:1 and 0.25:1 could be detected two peaks associated to CO_2 release from the different carbonates present in the mixture. An average of both peaks could lead to a value that is in agreement with the hypothesis of the influence of the effect of density of charge and dilution in the value of Td. Concerning Tg values, and similarly with D-mannose series, an extended hydrogen bond network provided by higher Glu:DBU ratios lead to higher values of Tg. Other saccharides lead to similar values of Td associated to CO_2 release.

Table 5: DSC thermal study of the saccharide based systems tested in this report after reaction with CO_2.

Systems	T_d(°C)	T_g (°C)
(TMG)	56.52, 108.88 [b]	-
(Man:TMG) 1:1 (eq.)	103.15[b]	-
(DBU)	118.01 [b]	-
(Man:DBU) 1:1 (eq.)	128.01 [b, d]	-44.39
(Man:DBU) 0.625:1 (eq.)	Td>107.10 [b]	-50.16
(Man:DBU) 0.5:1 (eq.)	122.1 [b]	-
(Man:DBU) 0.25:1 (eq.)	127.57[b]	-66.68
(Glu:DBU) 1:1 (eq.)	102.56, 122.25, 147.37 [b]	-51.49
(Glu:DBU) 1:1 (eq.) Magnetically coupled stirr	110.87, 145.48 [b]	-56.70
(Glu:DBU) 0.625:1 (eq.)	116.71, 146.26[b]	-
(Glu:DBU) 0.5:1 (eq.)	119.21, 146.68 [b]	-
(Glu:DBU) 0.25:1 (eq.)	108.22[b], 134 [c]	-74.78
(B-CD:DBU) 0.5:1 (eq.)	127.78[b]	-68.38
(Alginic Acid:DBU) 1:1 (eq.)	125.08[b]	-75.10
(Mannitol:DBU) 0.5:1 (eq.)	>112.70[a]	-66.16

a onset; b horizontal peak; c curve point; d exothermic peak. Td: decomposition temperature, Tg: glass transition temperature.

Conclusions

Effective systems for CO_2 capture based on a cheap organic superbase (TMG or DBU) and highly abundant natural saccharides were designed and tested. The main objectives of this work were to obtain maximal percentages of CO_2 uptake and number of alcohol groups of saccharides converted into carbonates. With TMG systems, very high percentages of CO_2 uptake were obtained, nevertheless when D-mannose is present a competition between carbonate and carbamate products was detected. In order to attain maximal conversion of alcohol groups into carbonates and to avoid competition with superbase to react with CO_2, DBU was tested as an alternative organic superbase. Moreover in the case of D-mannose and D-glucose different ratios saccharide:DBU were tested in order to find an optimal balance between average number of alcohol groups functionalized into carbonates and total wt% of CO_2 uptake. With D-mannose:DBU (ratio eq. = 0.625) was obtained an optimal wt% of CO_2 uptake of 13.9% corresponding to 3.3/5 alcohol groups converted into carbonates. In the case of Glucose:DBU (ratio eq. = 0.5) was obtained a maximum wt% of CO_2 uptake of 7.9%, corresponding to 3.04/5 alcohol groups converted into carbonates, with magnetic bar based stirring method. In order to test the thermodynamic limit of reaction and obtain maximal CO_2 uptake, a system Glu:DBU (ratio eq. = 1) was stirred in a magnetically coupled system. On that case 2.47/5 alcohol groups were converted into carbonates, corresponding to 11.5 wt% of CO_2 uptake. Factors, such as the stirring efficiency in promoting solubilisation of CO_2 gas into the liquid phase, saccharide:organic superbase ratio and type of superbase were unveiled as fundamental in the outcome of reaction. Other saccharide based structures were also tested with interesting indications, especially mannitol, with six alcohol groups per molecules, where it's expected that the obtained results could improve significantly if magnetically coupled stirring is used instead of magnetic bar. Thermal DSC analysis indicates us that the stability of the obtained products are dependent on the dilution of the saccharide and density of charge.

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