Carbon Dioxide Capture by Basic "Dry Water"

Robert Dawson,[a] Lee Stevens,[b] Weixing Wang,[c] Benjamin O. Carter,[a] Sam Sutton,[a] Trevor C. Drage,[b] Frédéric Blanc,[d] Dave J. Adams[a] and Andrew I. Cooper*[a]

[a] *Department of Chemistry and Centre for Materials Discovery, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom. Fax: +44 (0)151 794 2304; Tel: +44 (0)151 794 3539; E-mail: aicooper@liv.ac.uk*

[b] *Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK*

[c] *School of Chemical and Energy Engineering, South China University of Technology, Guangzhou, China.*

[d] *Department of Chemistry and Stephenson Institute for Renewable Energy, University of Liverpool, Crown Street, Liverpool, L69 7ZD, United Kingdom.*

Supporting information

Contents

S1. Experimental

Materials

Diethanolamine and PEI (750,000 Mw, 50 % solution in water) were obtained from Sigma-Aldrich. Potassium carbonate was obtained from Fisher Scientific. Hydrophobic silica nanoparticles (H18) were kindly supplied by Wacker-Chemie. High purity CO_2 (SCF grade) was obtained from BOC Gases.

Dry DEA

Hydrophobic silica (20 g) and diethanolamine (80 g) were added to a glass blender and blended for 30 sec. Samples were stored in a plastic bottle.

Dry K_2CO_3 solutions

Two solutions of K_2CO_3 were made from K_2CO_3 (45 g) and distilled water (45 g) or K_2CO_3 (30 g) and distillied water (60 g). Hydrophobic silica (10 g) and K_2CO_3 solutions (90 g) were added to a plastic blender and blended for 30 sec to yield two dry K_2CO_3 solutions: **DryK_2CO_3(45)** and **DryK_2CO_3(30)**. Samples were stored in plastic bottles.

Dry PEI

PEI (750,000 Mw, 50 % solution in water) (90 g) was blended with hydrophobic silica (10 g) for 30 seconds in a plastic blender. Samples were stored in plastic bottles.

CO_2 uptake experiments

5 g of dry base was weighed out into a 60 mL plastic bottle and sealed with a rubber septa and the mass recorded. A balloon fitted with a tap and needle was filled (approximate internal pressure 2-3 bar) with CO_2 gas. A second needle was inserted into the septa followed by the needle attached to the CO_2 filled balloon and the time was recorded. After 10 sec, during which time the bottle was purged with CO_2, the second needle was removed. The mass of the bottle and sample was recorded over 60 min. The balloon was topped up regularly throughout the experiment to roughly maintain the pressure.

Solid state NMR experiments

All solid-state NMR experiments were performed on a 9.4 T Bruker Avance III HD solid-state NMR spectrometer equipped with a 4 mm HXY triple-resonance MAS probe (in double resonance mode) at $n_0(^1H)$ = 400.13 MHz, with the X channel tuned to ^{13}C at $n_0(^{13}C)$ = 100.63 MHz. All experiments were performed under magic angle spinning (MAS) at n_r = 10 kHz at room temperature. All ^1H pulses and SPINAL-64 heteronuclear decoupling (Fung, B. M.; Khitrin, A. K.; Ermolaev, K. *J. Magn. Reson.* **2000**, *142*, 97) were performed at a radio-frequency (rf) field amplitude of 83 kHz. ^1H ^{13}C CP (Pines, A.; Gibby, M.; Waugh, J. *J. Chem. Phys.* **1973**, *59*, 569). MAS experiments were obtained with a ^{13}C

rf field of 40 kHz, while the ^{1}H rf field amplitude was ramped to obtain maximum signal at a ^{1}H rf field of approximately 50 kHz, and with a 3 s recycle delay. The ^{13}C direct excitation spectrum was obtained with a rotor synchronized Hahn echo sequence (one rotor period for the dephasing delays) with ^{13}C pulses performed at a rf field amplitude of 62.5 kHz, and a 10 s recycle delay. ^{13}C chemical shifts were externally referenced at room temperature to the CH_2 group of adamantane at 29.45 ppm (Morcombe, C. R.; Zilm, K. W. *J. Magn. Reson.* **2003**, *162*, 479).

S2. Microscope Images

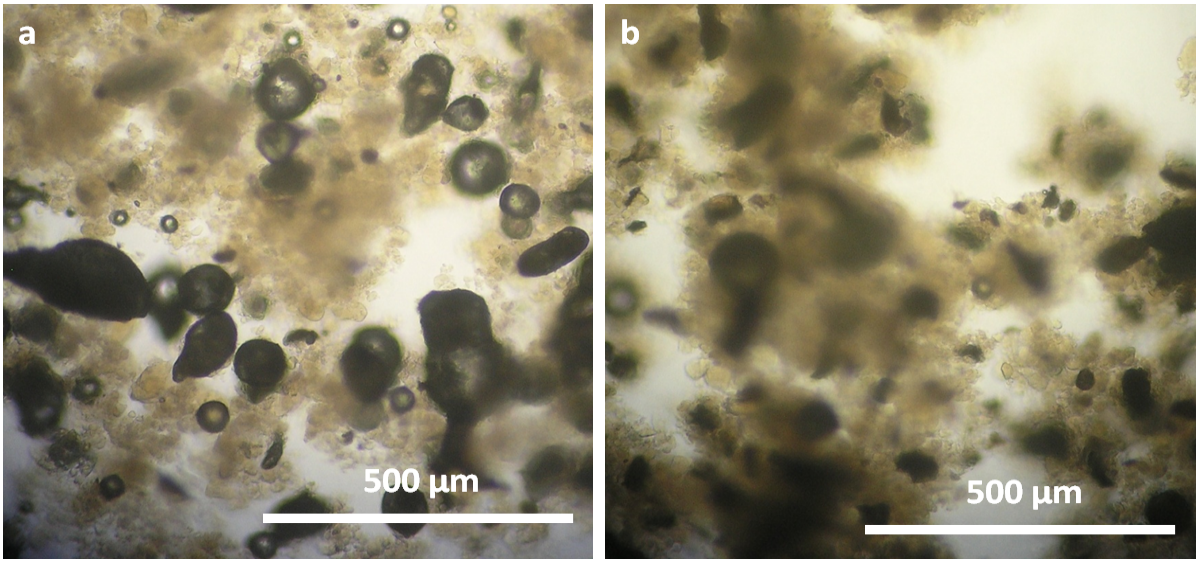


Figure S2.1 Microscope images of **DryDEA** (a) before and (b) after CO_2 absorption

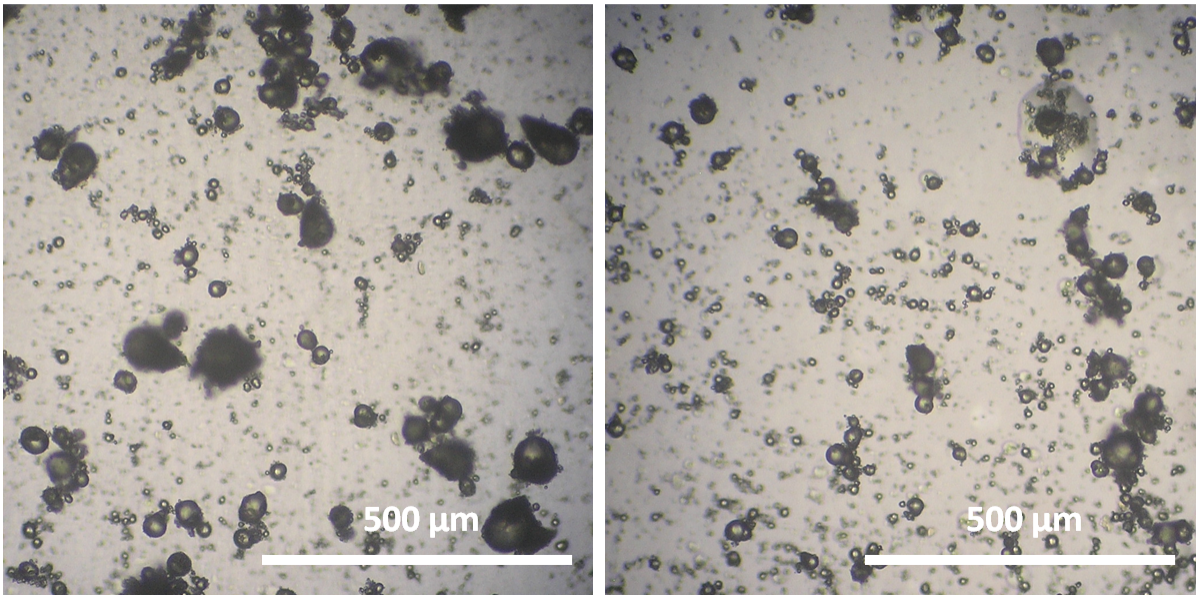


Figure S2.2 Microscope images of **DryK_2CO_3(45)** (a) before and (b) after CO_2 absorption

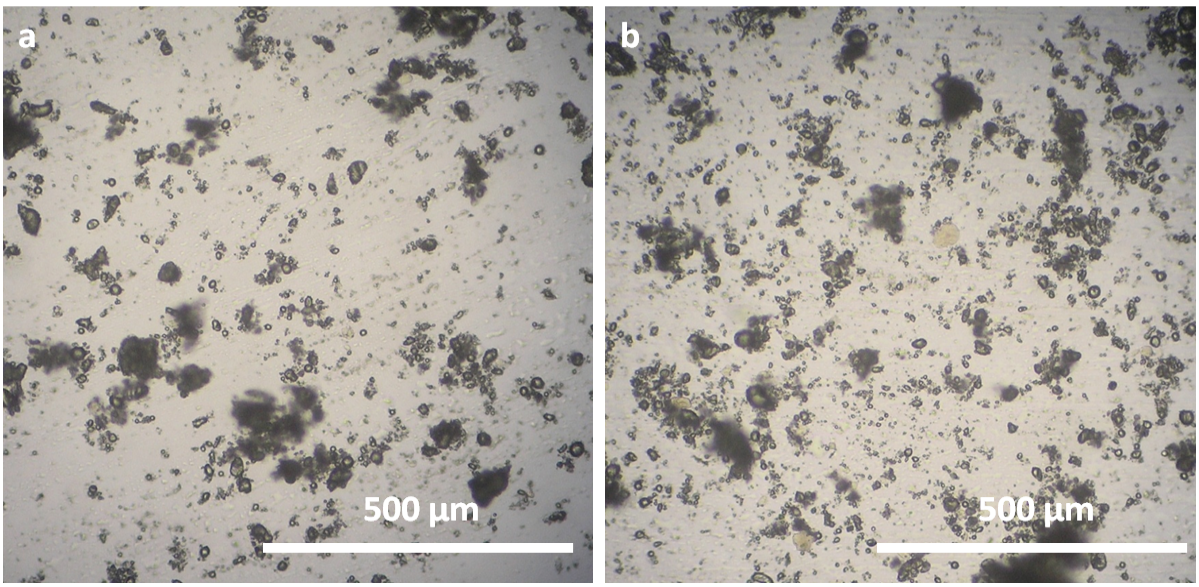


Figure S2.3 Microscope images of **DryK_2CO_3(30)** (a) before and (b) after CO_2 absorption

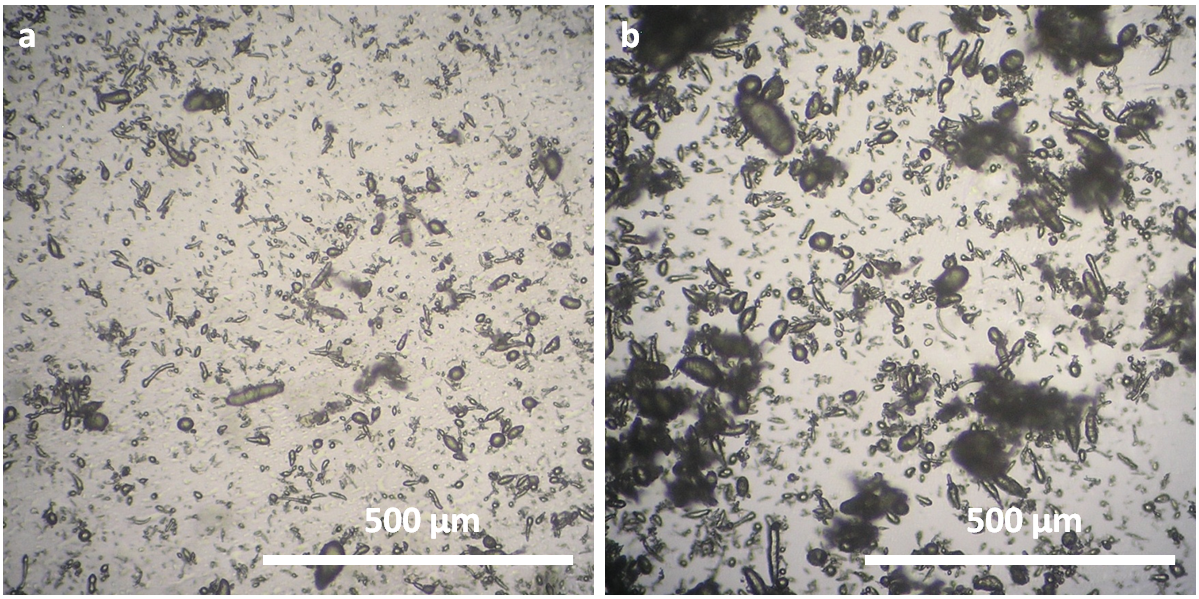


Figure S2.4 Microscope images of **DryPEI(750k)** (a) before and (b) after CO_2 absorption

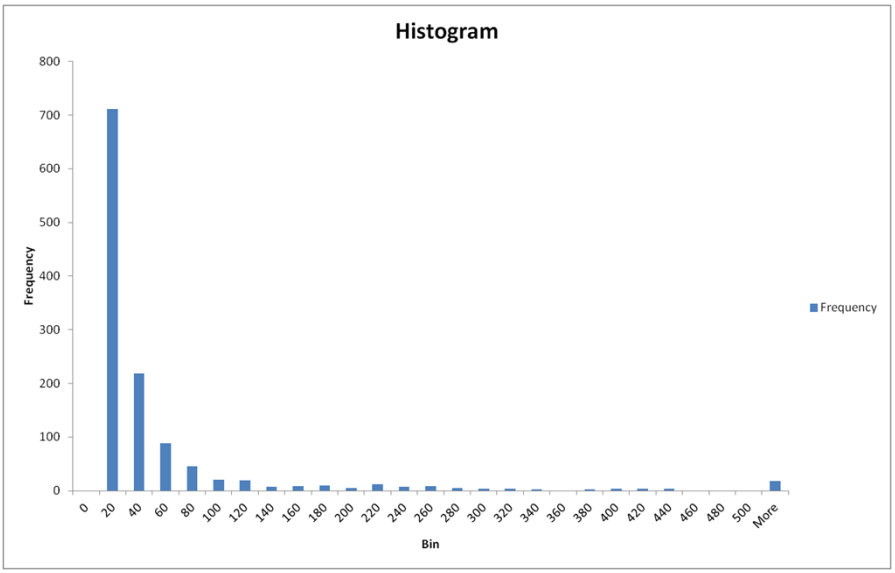


Figure S2.5 Histogram showing particle sizes of **DryDEA** before CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

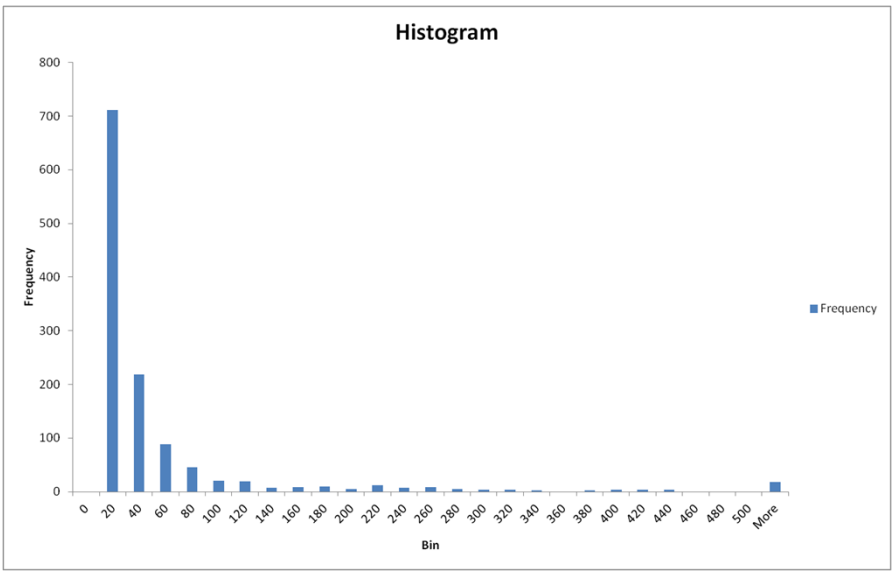


Figure S2.6 Histogram showing particle sizes of **DryDEA** after CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

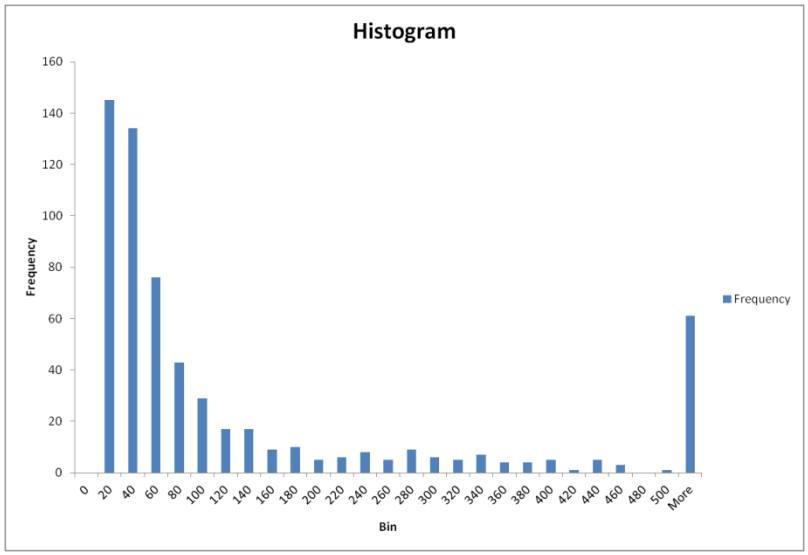


Figure S2.6 Histogram showing particle sizes of **DryK_2CO_3(30)** before CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

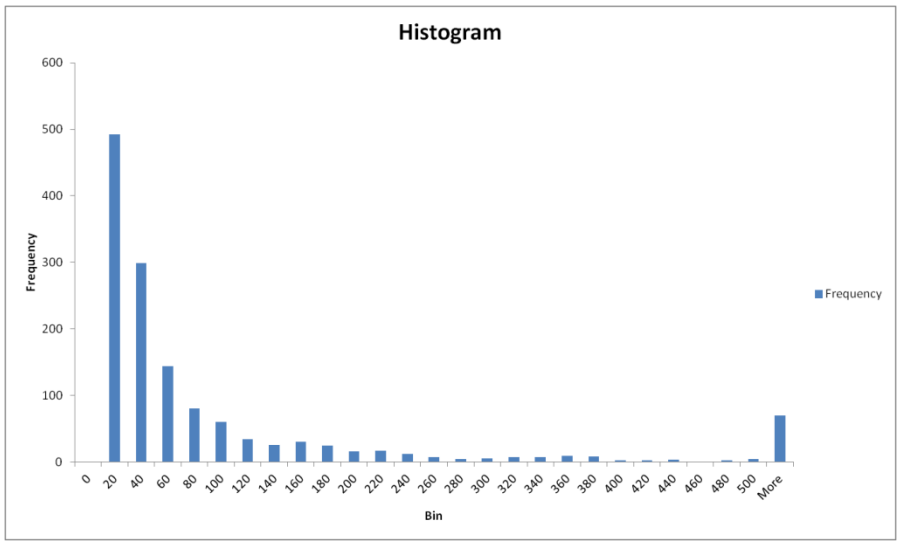


Figure S2.7 Histogram showing particle sizes of **DryK_2CO_3(30)** after CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

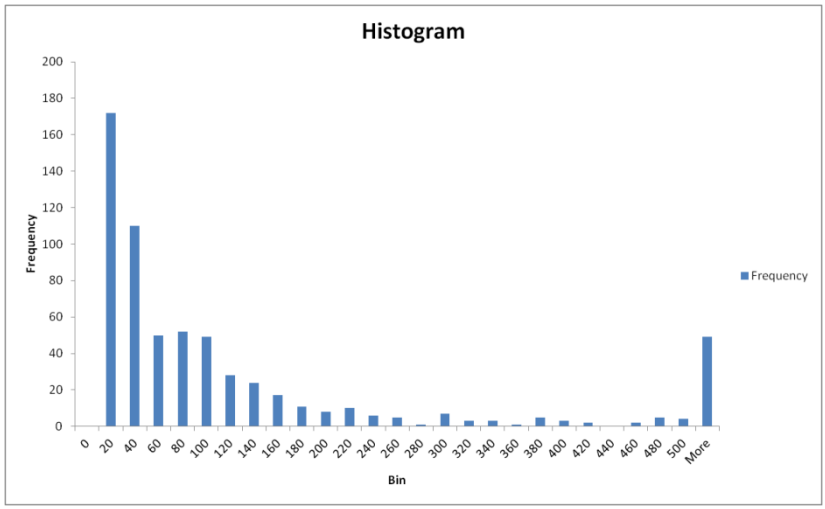


Figure S2.8 Histogram showing particle sizes of **DryK_2CO_3(45)** before CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

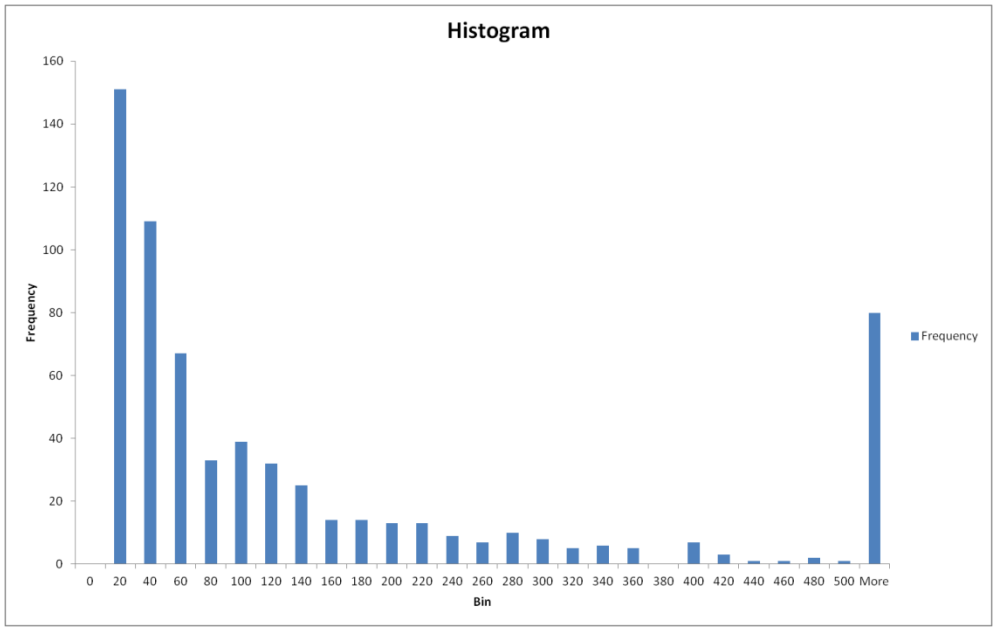


Figure S2.8 Histogram showing particle sizes of **DryK_2CO_3(30)** after CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

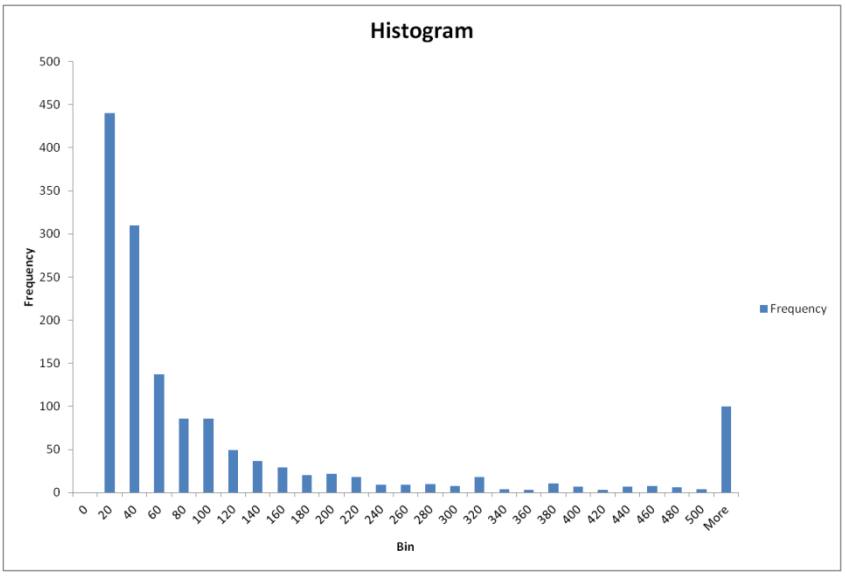


Figure S2.9 Histogram showing particle sizes of **DryPEI** before CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

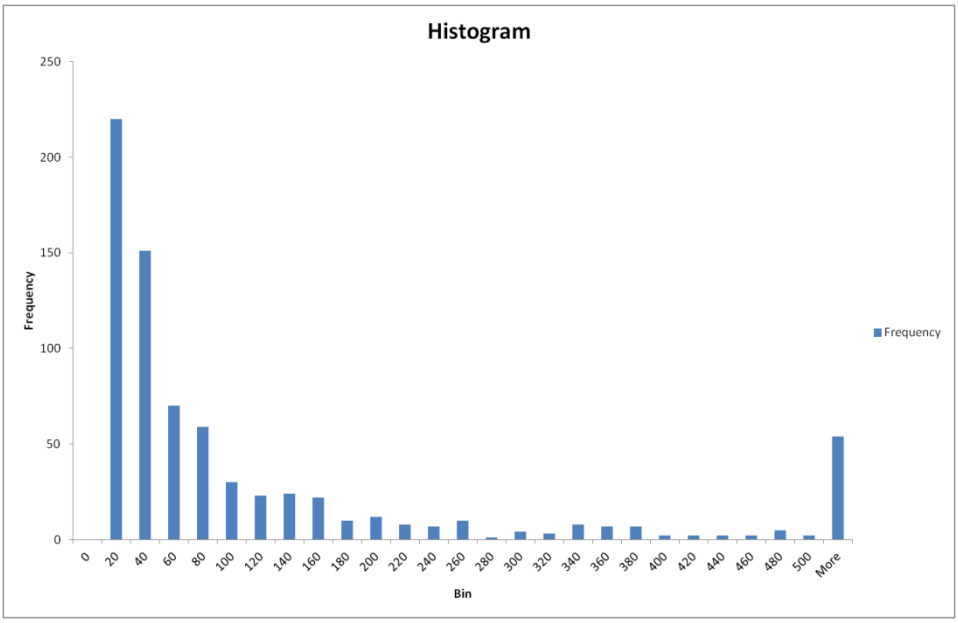
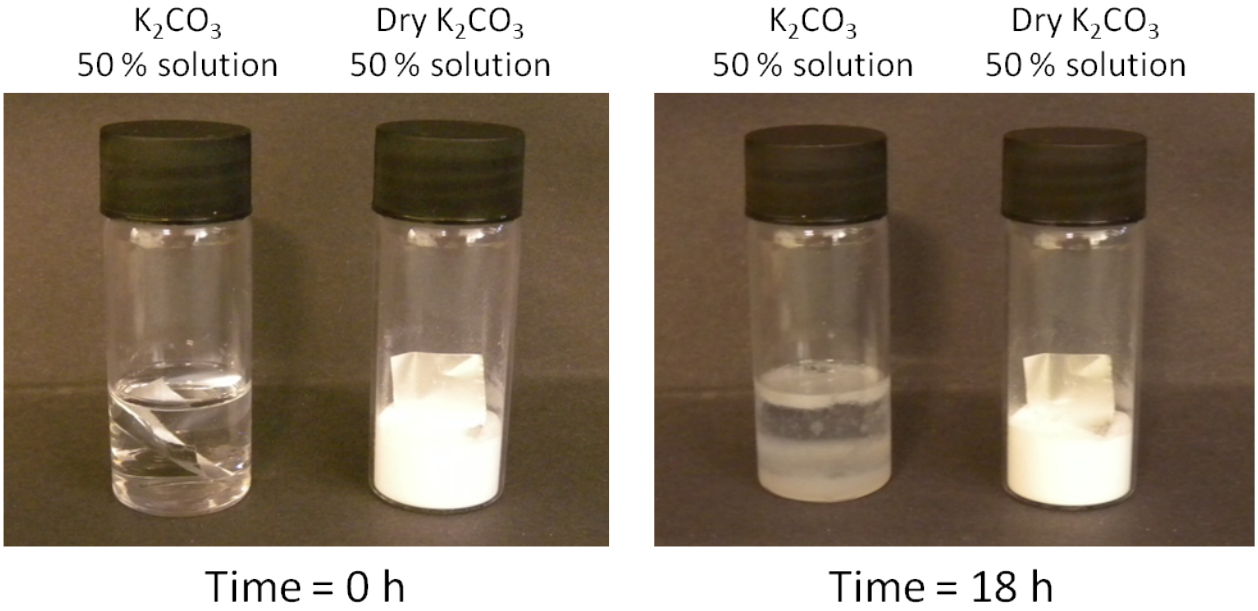


Figure S2.10 Histogram showing particle sizes of **DryPEI** after CO_2 capture. Data extracted by image analysis using ImageJ software from microscope images.

S3. Stability tests



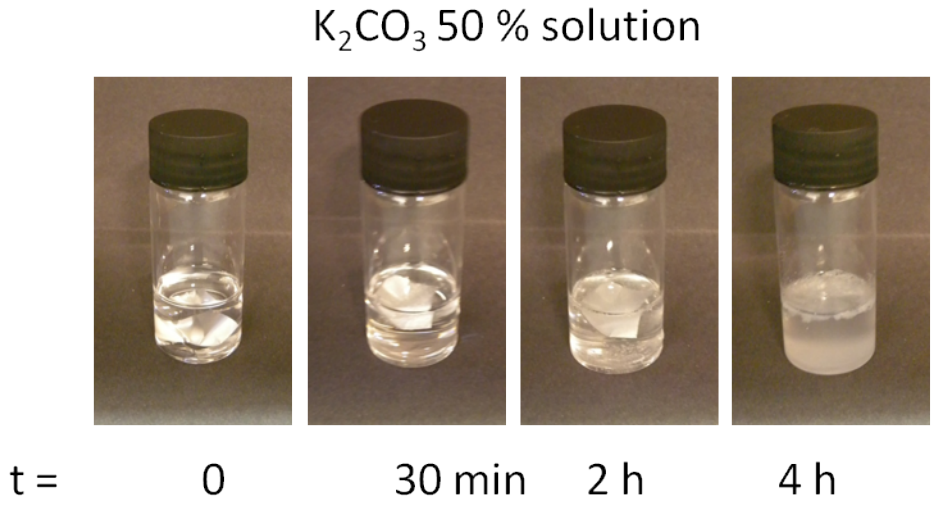


Figure S3.2 Aluminium foil in K_2CO_3 solution and DryK_2CO_3(45). As can be seen from the photographs, the aluminium dissolves in the solution quickly. However, after 18 hours in a dry base, the aluminium is visually unaffected.

S4. TGA Regeneration of DryDEA

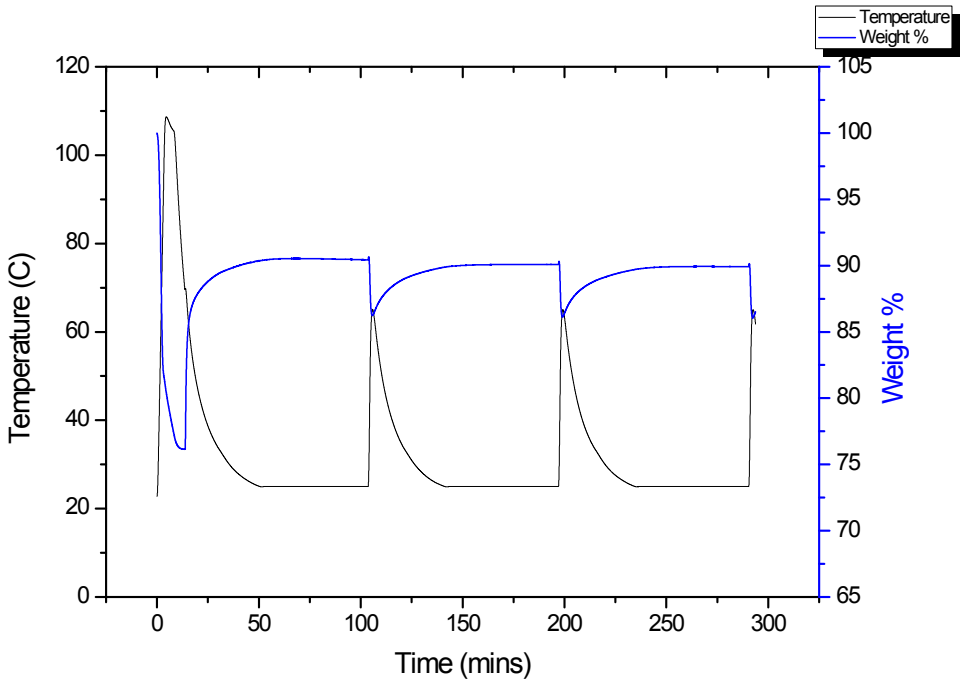


Figure S4.1 Cycling of absorption of CO_2 at 25 °C by DryDEA and regeneration at 60 °C

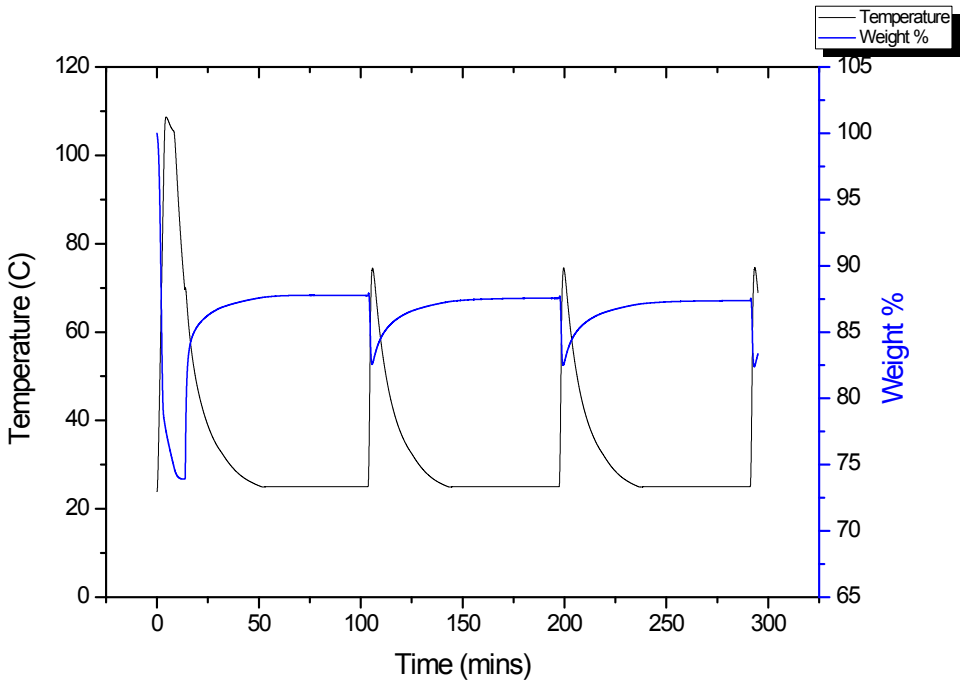


Figure S4.2 Cycling of absorption of CO_2 at 25 °C by DryDEA and regeneration at 70 °C

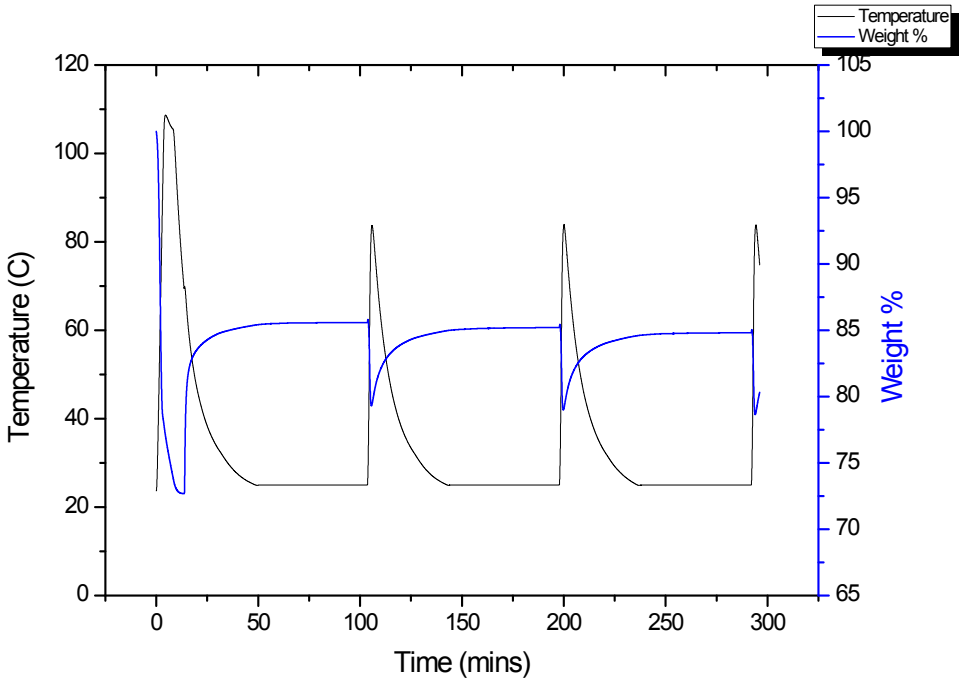


Figure S4.3 Cycling of absorption of CO_2 at 25 °C by DryDEA and regeneration at 80 °C

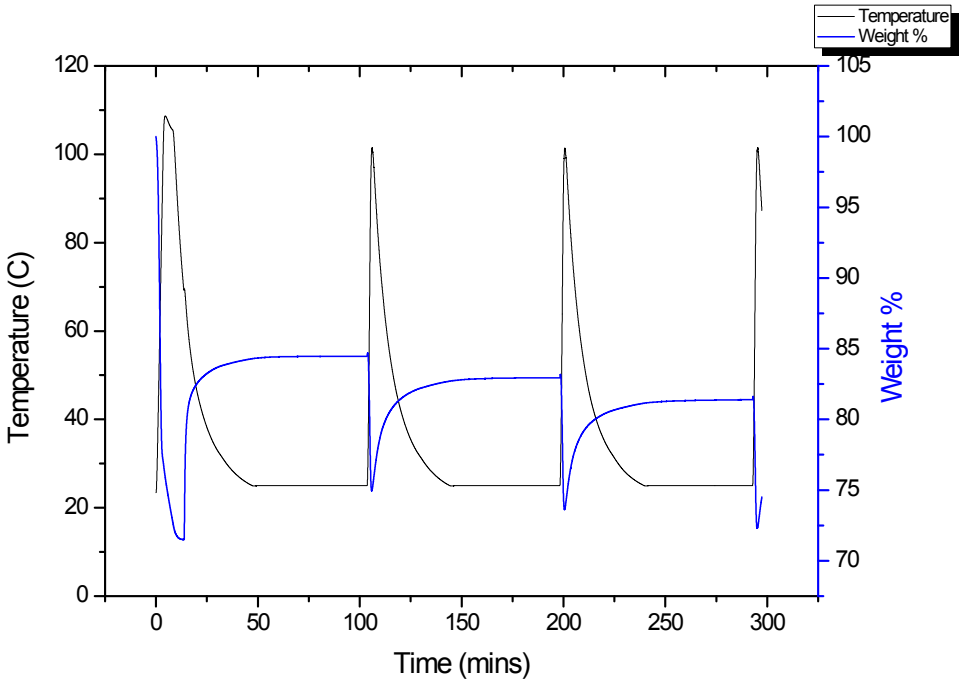


Figure S4.4 Cycling of absorption of CO_2 at 25 °C by DryDEA and regeneration at 90 °C

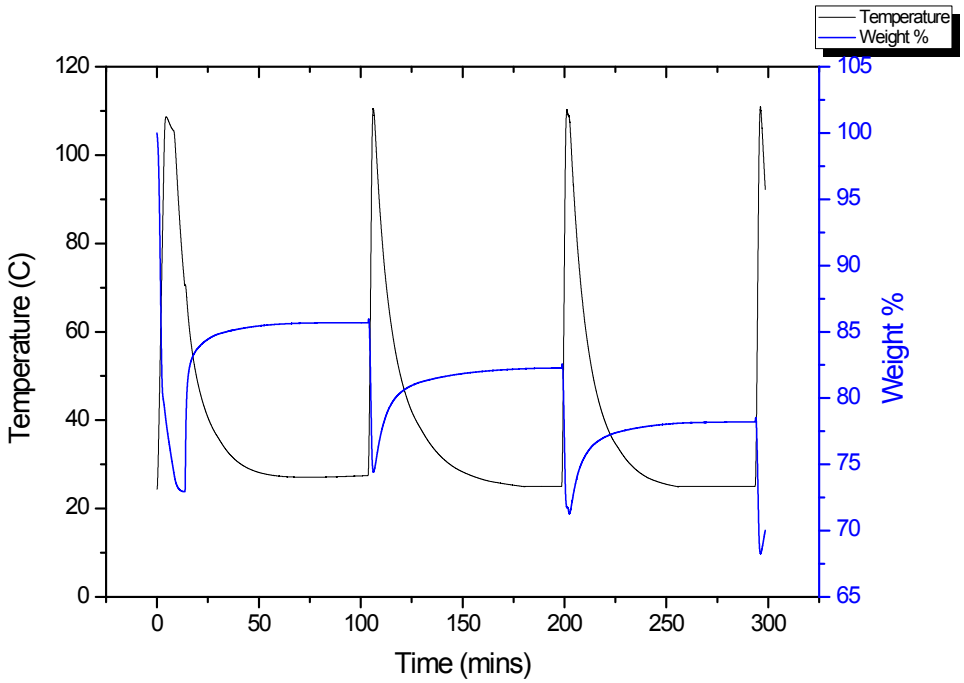


Figure S4.5 Cycling of absorption of CO_2 at 25 °C by DryDEA and regeneration at 100 °C

S5. TGA Regeneration of DryPEI

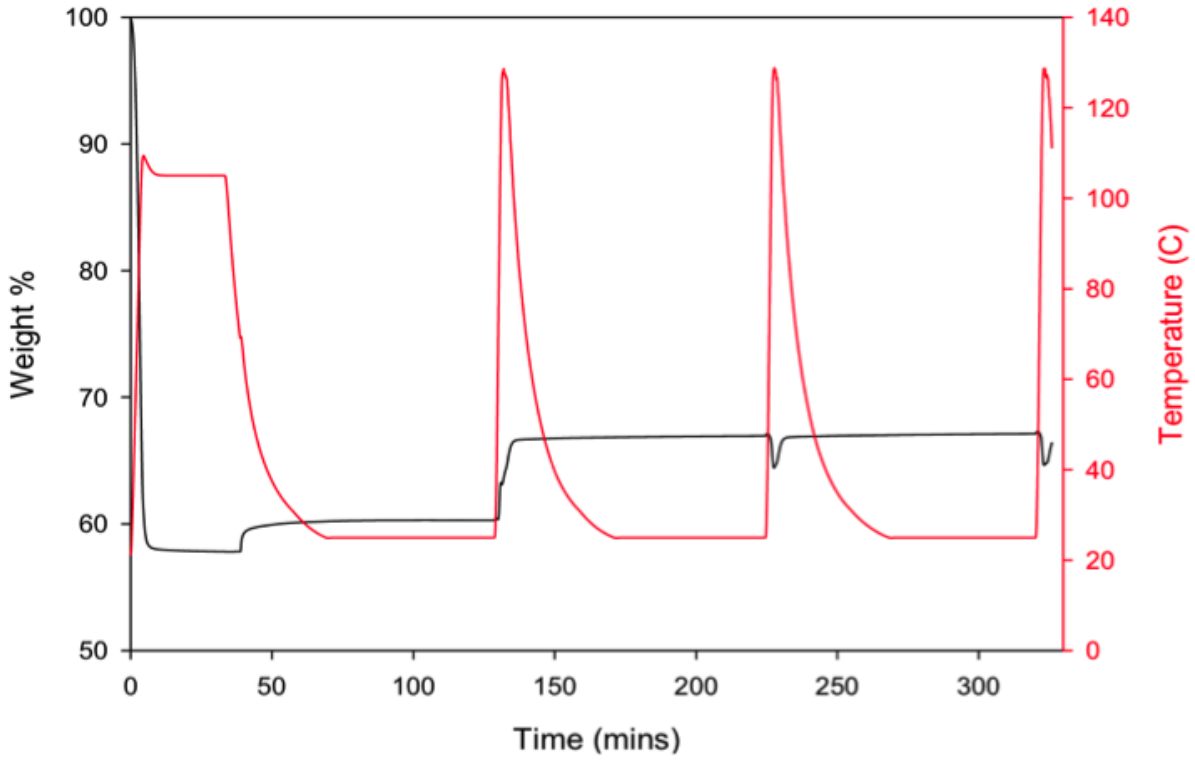


Figure S5.1 Cycling of absorption of CO_2 at 25 °C by DryPEI and regeneration at 120 °C

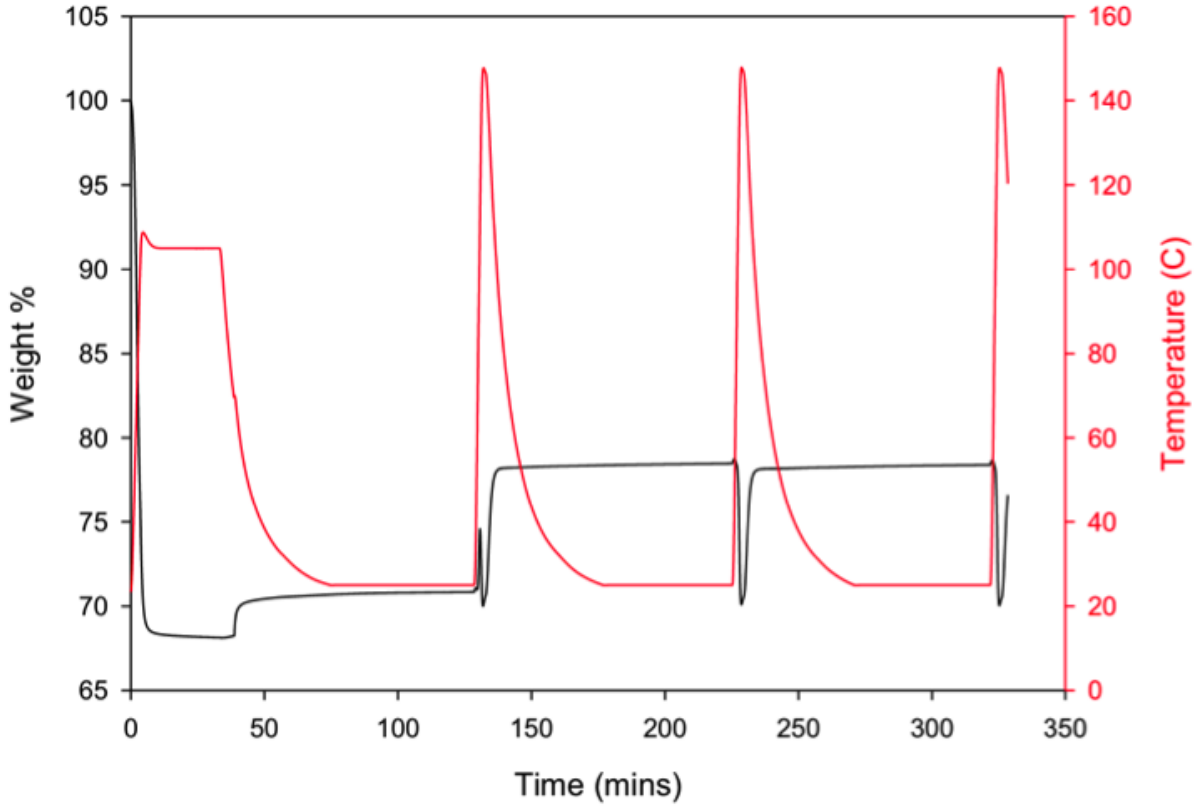


Figure S5.2 Cycling of absorption of CO_2 at 25 °C by DryPEI and regeneration at 140 °C

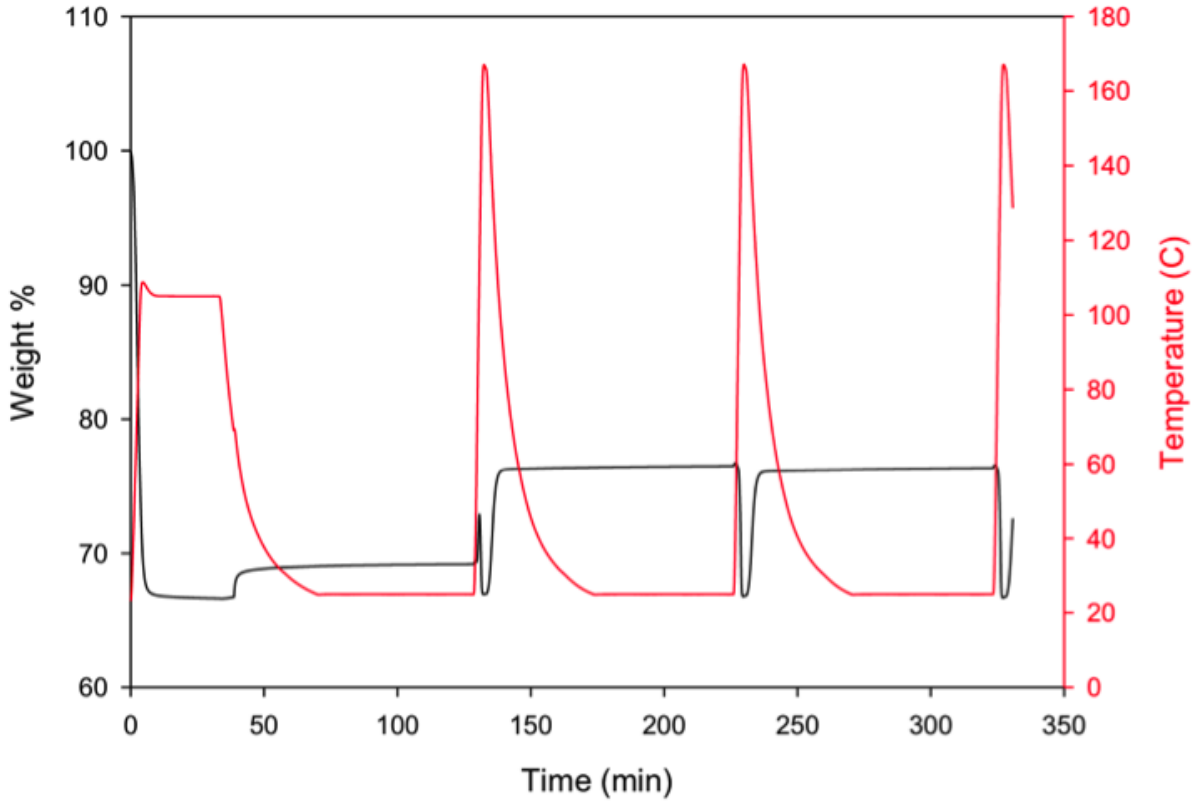


Figure S5.3 Cycling of absorption of CO_2 at 25 °C by DryPEI and regeneration at 160 °C

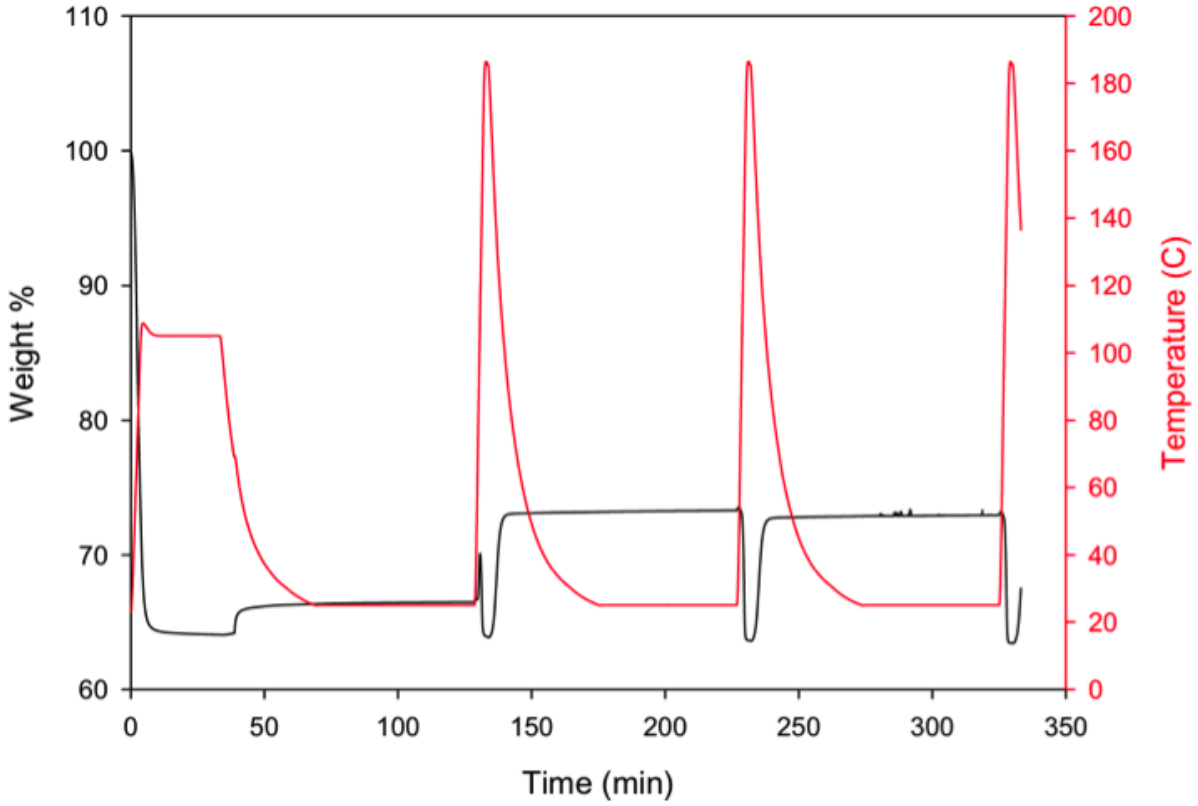


Figure S5.4 Reg Cycling of absorption of CO_2 at 25 °C by DryPEI and regeneration at 180 °C

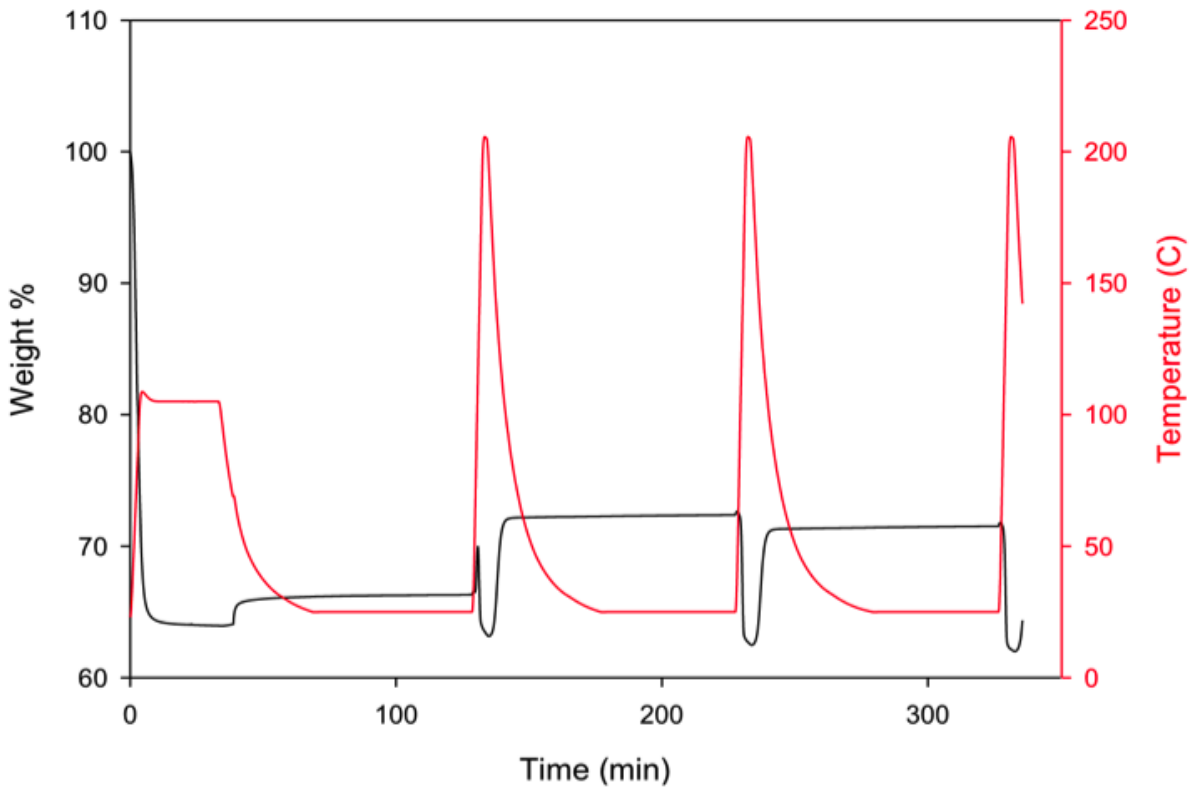


Figure S5.5 Cycling of absorption of CO_2 at 25 °C by DryPEI and regeneration at 200 °C

S6. Solid State NMR of DryDEA After CO_2 Adsorption

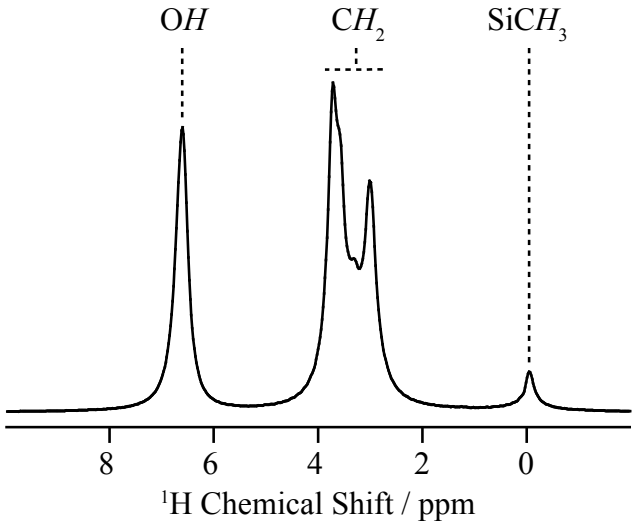


Figure S6.1 Solid-state ^{1}H NMR spectrum of **DryDEA** post CO_2 adsorption. The chemical shifts are 6.6, 3.7-3.0 and -0.1 ppm and assigned to OH (either water or $(OHCH_2CH_2)_2NCO_2H$ or $(OHCH_2CH_2)_2NH$), CH_2 and $SiCH_3$ respectively.