Angewandte
Zuschriften

Waste Heat Chemistry

DOI: 10.1002/ange.201306928

A Microvascular System for Chemical Reactions Using Surface Waste Heat**

Du Thai Nguyen and Aaron P. Esser-Kahn*

Every year, nearly 29 billion metric tons of CO_2 are released into the atmosphere from human activities.[1] Research into carbon capture and sequestration (CCS) technologies is a key element in reducing CO_2 emissions.[2,3] A set of CCS methods uses chemical reactions between CO_2 and liquid agents for the capture and controlled release of CO_2. Current CCS technologies, however, are estimated to increase the cost of energy for a power plant by 80–85 %.[4] Much of this increased cost is due to the high enthalpy associated with heating a CO_2-rich capture agent to "strip" it and release the captured CO_2.[5–8] This "parasitic" energy loss might be lowered by coupling these chemical reactions to low-grade waste heat already present on the surfaces of many combustion systems generating CO_2. To date, no material system has used surface waste heat to provide the energy for a CO_2 stripping process, although latent heat systems have been successfully implemented.[9]

Herein we demonstrate a system that uses low-grade waste heat from surfaces to provide energy for chemical reactions. To access the waste heat, we fabricated a microvascular stripping system composed of microchannels, up to meters in length, conformed to heated ceramic and metal surfaces in complex three-dimensional configurations. Our initial system released CO_2 from a saturated monoethanolamine (MEA) solution. MEA is a capture reagent currently used in pilot-scale plants, but is often cited as too energetically expensive for large-scale use.[4] In our microvascular system, we found that increased CO_2 release resulted from: 1) decreasing the diameter of the microchannel; 2) increasing the surface temperature; and 3) increasing the solution residence time. Using high-speed photography, we observed a two-phase flow phenomenon in the form of bubbly, slug, and annular flow.[10,11] We report a stripping rate of 1.9 $\mathrm{mg\,min^{-1}}$ for MEA in a 300 μm diameter microchannel conformed onto a surface heated to 125 °C.

The micrometer-scale features in large, distributed systems are essential for accessing heat-transfer characteristics of two-phase release.[12–18] Methods of microvascular fabrication, such as the vaporization of a sacrificial component (VaSC), lithographic techniques, direct-write approaches, and many others, can form these micrometer-sized features.[19–27] At the micrometer scale, differences from the macroscale arise, as surface tension counteracts gravitational effects and laminar rather than turbulent flows are dominant.[28] The mechanisms of two-phase heat transfer and its relationship to gas nucleation is not yet fully understood, as the methods of characterizing these systems can vary widely.[29] However, we observed rapid and complete CO_2 release occurring only with channels below 300 μm in diameter, indicating the advantages of using microscale heat exchangers.

We fabricated our microvascular waste-heat system using the VaSC process.[30] VaSC is a sacrificial polymer process to create long, cylindrical microchannels and vasculature conformed directly to a surface. The non-lithographic nature of VaSC is particularly suited for the formation of microvasculature directly on surfaces with complex 3D contours that allow direct access to waste heat. Most other microvascular fabrication processes require initially flat substrates, restricting their direct access to many surfaces. Others, such as 3D printing, can be well-suited for fabricating solid structures, but are less capable of forming hollow structures. In contrast to other heat exchanger fabrication techniques, the length, ease, and conformability of VaSC allow this technique to adapt microchannels to pre-fabricated surfaces. However, VaSC has limitations in that it does not obtain the same structural precision as lithographic techniques. The fabrication process is also limited to materials which polymerize or set at temperatures below 120 °C and can withstand temperatures above 200 °C.

In a generalized model of our experiments, VaSC is used to fabricate cylindrical microchannels on a heated surface. MEA (4.9 M) is saturated with CO_2 (0.5 mol CO_2/mol MEA). CO_2 is captured by MEA as the reaction between MEA and CO_2 forms carbamates via a zwitterionic intermediate (Supporting Information, Section S2.1). The saturated MEA flows through the microchannels at a controlled flow rate and surface temperature (Figure 1). The high temperature reverses the reaction, leading to the release of CO_2. As CO_2 releases from MEA, two phases appear within the microchannel and can be separated for future use or sequestration.

A waste-heat stripping system using this process can be formed around many heated surfaces, including those already present in combustion processes. We demonstrate coupling of

---

[*] Dr. A. P. Esser-Kahn
Dept. of Chemistry, Dept. of Chemical Engineering and Materials Science, Dept. Of Biomedical Engineering, University of California, Irvine
3038A Frederick Reines Hall, Irvine, CA 92697 (USA)
E-mail: aesserka@uci.edu

D. T. Nguyen
Dept. of Physics and Astronomy, University of California, Irvine
3038A Frederick Reines Hall, Irvine, CA 92697 (USA)

[**] A.P.E.-K. acknowledges an AFOSR Young Investigator Grant under FA9550-12-1-0352 and a 3M non-tenured faculty award. We would like to thank Lalisa Stutts, Janine Tom, Jade Warren, and Jessica Kim for helpful discussion. We thank Dr. Peter Taborek and Robert Joachim for the use of their high-speed photography equipment.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306928.

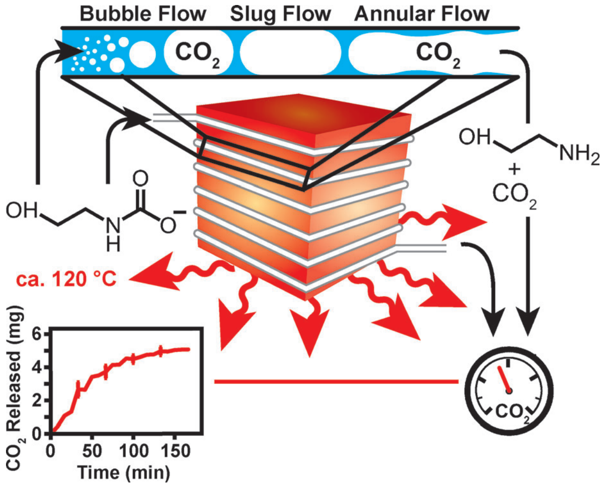

Figure 1. Representation of CO_2 stripping. Monoethanolamine (MEA) saturated with CO_2 flows through a microvascular channel surrounding a heated surface and embedded within PDMS. The channel is heated to about 120 °C, which removes CO_2 from the solution. A two-phase flow profile develops within the microchannel from the released CO_2. The flow rate and concentration of CO_2 exiting the system are measured to calculate the total release of CO_2. A sample data set is provided.

VaSC with two-phase release through the microvascular retrofitting of a pre-existing and lab-available waste-heat source: a coffee mug (Figure 2 a). Using multiple polydimethylsiloxane (PDMS) coatings as the microvascular embedding material, a 1.2 m long, 300 µm diameter microchannel was wrapped around a coffee mug five times and separated from the surface by 40 µm (Supporting Information, Section S1.1.1).

We released CO_2 from a saturated MEA solution (0.5 mol CO_2/mol MEA) by heating the mug as the solution flowed through the wrapped microchannel. As CO_2 reacts with MEA it lowers the pH of the solution.[31] We visualized the release of CO_2 by adding a pH-sensitive dye, namely phenolphthalein.[32] As CO_2 is recovered, the solution returns to its original pH, going from $pH \approx 8$ to $pH \approx 12$. The dye reflects this change by shifting from clear to pink. To regenerate the solution, the mug was heated until the average surface temperature was 120 °C. After the mug reached thermal equilibrium, the CO_2-saturated solution flowed through the microchannel at a rate of 0.1 $mL\,min^{-1}$. Within one cycle, the color of the solution shifted from clear to pink, indicating the release of CO_2 (Figure 2 b). The lean MEA solution was then re-saturated with CO_2 to quantify the amount of CO_2 released. This was calculated to be 0.10 mol CO_2/mol MEA (0.14 mol CO_2/mol MEA is released in conventional systems),[33] corresponding to a release rate of 1.9 mg CO_2/min.

Other stripping systems, such as packed columns and membrane contactors, achieve higher fluxes of CO_2. However, when the release rates of these systems are scaled relative to the flow rates in our system, similar values are found (ca. 1–3 $mg\,min^{-1}$ at 0.1 $mL\,min^{-1}$ MEA flow rate).[35] However, our system stands in contrast as it can use waste heat energy owing to its conformability to 3D contours.

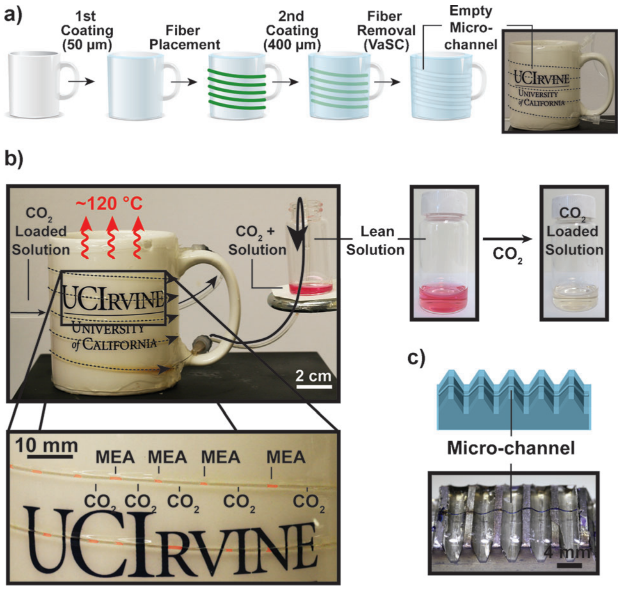

Figure 2. CO_2 stripping using waste heat. a) Fabrication of microchannels conformed to a coffee mug. First, a layer of PDMS coats the mug. Next, PLA elements are placed to match the contour of the mug. Another layer of PDMS then coats the fibers. Last, the PLA is depolymerized under heat and vacuum. The end result is a single microchannel conformed to the surface of the mug. b) CO_2 release with the mug. Phenolphthalein dye was added to a CO_2 saturated MEA solution, which changes from clear to pink when CO_2 is released from the solution. The solution flowed through the microchannel at a rate of 0.1 $mL\,min^{-1}$. The average surface temperature of the mug was 120 °C. After one pass through the microvascular mug, a color shift occurs, indicating the release of CO_2. Scale bar: 2 cm (image) and 10 mm (inset). c) Microchannel on a rough surface. Scale bar: 4 mm.

While the stripping mug demonstrated a practical surface for microstructure fabrication, not all heated surfaces are smooth and round. We verified the adaptability of the VaSC process by fabricating microchannels on a rough surface, a gear rack (Figure 2 c). The fabrication process was similar to that of the mug, using multiple PDMS coating layers (Supporting Information, Section S1.1.2). Using VaSC, many surfaces could provide energy for chemical reactions through waste-heat recovery.

We then studied parameters affecting the release efficiency including channel diameter, surface temperature, and residence time. A smaller system (4.4 cm) was developed to quantify the release of CO_2 (Supporting Information, Section S1.1.3). The exhaust gas flow rate and CO_2 concentration were used to calculate the total release of $CO_{2,}$ using an infrared CO_2 meter and mass flow-meter (Supporting Information, Section S1.2). Using thermocouples, we measured fluid input, fluid output, and surface temperatures to calculate the heat transfer coefficients (Table 1). Additional values such as Nusselt numbers and power input were also calculated (Supporting Information, Table S2).

First, we investigated the effect of channel diameter on the amount of CO_2 released from MEA using 100–300 µm diameter microchannels. We also examined a larger channel with a 1.59 mm diameter, as an example of a traditional size scale, and a hexagonally packed pattern of 200 µm diameter

Table 1: CO_2 release under experimental conditions.[a]

Length scale [μm]	Flow rate [mL min^{-1}]	T [°C]	Total CO_2 release [mg]	Initial release rate [mg min^{-1}]	h [W m^{-2} K^{-1}]
Hex.	0.05	125	29.8 ± 2.6	1.00 ± 0.17	70 ± 10
Hex.	0.1	125	19.0 ± 3.6	1.11 ± 0.28	80 ± 20
Hex.	0.2	125	12.7 ± 0.9	1.68 ± 0.65	170 ± 50
100	0.1	125	9.1 ± 1.7	0.69 ± 0.14	910 ± 140
200	0.1	125	4.9 ± 0.3	0.46 ± 0.02	570 ± 90
300	0.05	125	9.0 ± 1.1	0.55 ± 0.05	320 ± 50
300	0.1	125	5.1 ± 0.2	0.43 ± 0.02	430 ± 80
300	0.2	125	1.4 ± 0.1	0.23 ± 0.03	870 ± 170
1590	0.05	125	9.2 ± 1.2	0.53 ± 0.04	41 ± 4
1590	0.1	125	2.8 ± 0.4	0.24 ± 0.02	23 ± 3
1590	0.2	125	1.6 ± 0.6	0.24 ± 0.14	21 ± 7
300	0.1	105	0.8 ± 0.4	0.06 ± 0.04	73 ± 19
300	0.1	115	2.5 ± 0.4	0.24 ± 0.08	310 ± 40
300	0.1	125	5.1 ± 0.2	0.43 ± 0.02	430 ± 80
300	0.1	135	8.7 ± 0.9	0.84 ± 0.19	560 ± 140

[a] After multiple cycles, no further CO_2 releases from the solution and the total CO_2 release is recorded. The first several cycles give the largest release rates. These initial release rates most closely mimic a continuous operation environment. Heat transfer coefficients were calculated from fluid input, fluid output, and surface temperatures, coupled with CO_2 release rates. Surface area for the hexagonal pattern uses all seven 200 μm diameter channels and the length scale is considered to be 200 μm.

channels. For each experiment, the surface temperature was 125 °C and the solution flowed at a rate of 0.1 mL min^{-1}. Computational models of the temperature profiles within the channels were also developed (Supporting Information, Section 2.2). As the channel diameters decreased, we saw an increase in the total amount of CO_2 released. The 100 μm diameter microchannel obtained the highest heat transfer coefficient (910 W m^{-2}K^{-1}). However, the dense, hexagonally packed arrangement of microchannels released the most CO_2 by more than a factor of two. Using packed patterns of microchannels provides more efficient release of CO_2 than millimeter-size channels. The result of the packed hexagonal structure also demonstrated that the release of CO_2 can be achieved while reducing the system footprint.

Next, we investigated the effect of surface temperature on the flow stripping process using a 300 μm diameter microchannel and a flow rate of 0.1 mL min^{-1}. We found that increasing the surface temperature also increased the total release of CO_2, with an increase from 125 °C to 135 °C nearly doubling the amount released. CO_2 is released from MEA at 100–120 °C in industrial processes, matching the release temperature of CO_2 detected in our system.[34] The ability to release CO_2 on surfaces with temperatures from 100 °C and higher may have practical applications, as heat pipes can reach temperatures in excess of 120 °C.[36]

The last effect we investigated was the solution residence time using our two most diverse cases for comparison: the hexagonally patterned 200 μm and 1.59 mm diameter channels. The residence time was investigated by the MEA flow rate. In both cases, decreasing the MEA flow rate in the channel resulted in greater CO_2 release. The hexagonal pattern at a flow rate of 0.05 mL min^{-1} obtained the highest release rate of any parameter set (1.7 mg min^{-1}). While the slower flow rate allows for increased CO_2 release, it also limits the throughput of the microvascular system. For a full system, a balance must be achieved between throughput and CO_2 release efficiency.

Interestingly, little correlation between heat transfer coefficients and either total CO_2 release or initial release rate was found. Instead, the gas release correlated more strongly with power entering the system (Supporting Information, Figure S10). This may be due to the chemical reaction taking place or the complex geometry of the system. An alternative calculation of the release rates was conducted through the visual analysis of the flow-stripping phenomenon using high-speed photography and a serpentine microchannel (Supporting Information, Section S1.1.4).[37,38] The release of CO_2 from MEA was observed predominantly as the slug flow profile under these conditions (Supporting Information, Movie S1). When a slug flow pattern develops, the velocities of the gas phase allow for measurement of the pressure of the gas. Combining this with the volume of the gas phase, the ideal gas law is used to calculate the release rate of CO_2 within the microvascular system (Supporting Information, Section S2.3). Using this visual analysis, the CO_2 release rate was calculated to be 0.8 ± 0.2 mg min^{-1} (100 μm microchannel, 125 °C, 0.1 mL min^{-1}), agreeing with the previously measured release rate.

We wanted to determine, for potential applications, what our current stripping rates would translate to on a larger scale. To give a sense of what might be possible, we performed a calculation of how much heated area would be required to recover the CO_2 captured from an automobile. Assuming a square packed arrangement of microchannels and a release rate of 0.8 mg min^{-1} per channel, 0.0565 m^2 of surface area would be required to recover the amount of CO_2 emitted from an automobile (Supporting Information, Section S2.4). The total system dimensions required corresponds approximately to the size of a laboratory notebook. In contrast to other heat exchangers, this exchanger volume could also be conformed directly to a heated area rather than located in a separate region. However, this volume only accounts for the heat exchanger dimensions and does not consider other necessary system components that increase the size.

In conclusion, our results demonstrate the first adaptable system to use low-grade waste heat from a surface for powering the chemical reaction used in removing CO_2 from a saturated capture solution. This initial system has been shown to conform, on a lab scale, to both smooth, cylindrical surfaces and to uneven surfaces using the VaSC fabrication process. The system was demonstrated by flowing a CO_2 saturated solution as the surface was heated. The subsequent chemical reaction resulted in the release of CO_2 from the solution through a two-phase heat transfer phenomenon. This flow-release process was further characterized with respect to flow rates, temperatures, and channel diameters. Increasing the solution residence time, increasing the temperature, and decreasing the channel diameters have all resulted in increased CO_2 release capabilities. The heat transfer coefficients obtained by our microvascular systems (200–1000 W m^{-2}K^{-1}) are lower in comparison to other microscale heat exchangers (5–30 $\mathrm{kW\,m^{-2}\,K^{-1}}$).[16] However, our initial material (PDMS) is a partial insulator. Furthermore, these microvascular systems conform directly to surfaces which are incompatible with other microscale systems. In the future, we plan to use more conductive materials by integrating conductive elements into conformable polymers. The advantages of these conformal systems allow them to potentially find use in a variety of applications including flow chemistry, thermal management, and removal of CO_2 from saturated solutions. This microvascular system might easily interface with common heated surfaces such as a boiler, radiator, or other pre-existing waste-heat surfaces to power chemical reactions and lower parasitic energy loss. Further investigation into the exergy cost of the microvascular system will be required in order to determine the full energy loss of a wider implementation.

Received: August 7, 2013

Keywords: carbon dioxide fixation · energy transfer · microfluidics · waste heat

---

[1] P. Friedlingstein, R. A. Houghton, G. Marland, J. Hackler, T. A. Boden, T. J. Conway, J. G. Canadell, M. R. Raupach, P. Ciais, C. Le Quéré, *Nat. Geosci.* **2010**, *3*, 811 – 812.

[2] H. J. Herzog, *Environ. Sci. Technol.* **2001**, *35*, 148A – 153A.

[3] T. J. Skone, *Carbon Dioxide Capture from Existing Coal-Fired Power Plants*, U.S. Department Of Energy, **2007**.

[4] J. P. Ciferno, T. E. Fout, A. P. Jones, J. T. Murphy, *Chem. Eng. Prog.* **2009**, *105*, 33 – 41.

[5] M. R. M. Abu-Zahra, L. H. J. Schneiders, J. P. M. Niederer, P. H. M. Feron, G. F. Versteeg, *Int. J. Greenhouse Gas Control* **2007**, *1*, 37 – 46.

[6] O. J. Curnow, S. P. Krumdieck, E. M. Jenkins, *Ind. Eng. Chem. Res.* **2005**, *44*, 1085 – 1089.

[7] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon, *J. Membr. Sci.* **2011**, *376*, 110 – 118.

[8] S. Moazzem, M. G. Rasul, M. M. K. Khan in *Thermal Power Plants* (Ed.: M. Rasul), InTech, **2012**, pp. 227 – 254.

[9] R. P. Lively, R. R. Chance, W. J. Koros, *Ind. Eng. Chem. Res.* **2010**, *49*, 7550 – 7562.

[10] K. A. Triplett, S. M. Ghiaasiaan, S. I. Abdel-Khalik, D. L. Sadowski, *Int. J. Multiphase Flow* **1999**, *25*, 377 – 394.

[11] J. W. Coleman, S. Garimella, *Int. J. Heat Mass Transfer* **1999**, *42*, 2869 – 2881.

[12] W. Qu, I. Mudawar, *Int. J. Heat Mass Transfer* **2003**, *46*, 2755 – 2771.

[13] D. Liu, S. V. Garimella, *J. Heat Transfer* **2007**, *129*, 1321 – 1331.

[14] V. Dupont, J. R. Thome, *Microfluid. Nanofluid.* **2004**, *1*, 119 – 127.

[15] C. L. Ong, J. R. Thome, *Exp. Therm. Fluid Sci.* **2011**, *35*, 873 – 886.

[16] S. S. Bertsch, E. A. Groll, S. V. Garimella, *Nanoscale Microscale Thermophys. Eng.* **2008**, *12*, 187 – 227.

[17] S. Garimella, J. D. Killion, J. W. Coleman, *J. Fluids Eng.* **2002**, *124*, 205 – 214.

[18] T. Harirchian, S. V. Garimella, *Int. J. Heat Mass Transfer* **2012**, *55*, 1246 – 1260.

[19] L. M. Bellan, M. Pearsall, D. M. Cropek, R. Langer, *Adv. Mater.* **2012**, *24*, 5187 – 5191.

[20] C. J. Bettinger, E. J. Weinberg, K. M. Kulig, J. P. Vacanti, Y. Wang, J. T. Borenstein, R. Langer, *Adv. Mater.* **2006**, *18*, 165 – 169.

[21] J. T. Borenstein, M. M. Tupper, P. J. Mack, E. J. Weinberg, A. S. Khalil, J. Hsiao, G. García-Cardeña, *Biomed. Microdevices* **2009**, *12*, 71 – 79.

[22] W. Wu, A. DeConinck, J. A. Lewis, *Adv. Mater.* **2011**, *23*, H178 – H183.

[23] W. Wu, C. J. Hansen, A. M. Aragón, P. H. Geubelle, S. R. White, J. A. Lewis, *Soft Matter* **2010**, *6*, 739 – 742.

[24] D. T. Nguyen, Y. T. Leho, A. P. Esser-Kahn, *Adv. Funct. Mater.* **2013**, *23*, 100 – 106.

[25] D. T. Nguyen, Y. T. Leho, A. P. Esser-Kahn, *Lab Chip* **2012**, *12*, 1246 – 1250.

[26] D. C. Duffy, J. C. McDonald, O. J. A. Schueller, G. M. Whitesides, *Anal. Chem.* **1998**, *70*, 4974 – 4984.

[27] J. C. McDonald, G. M. Whitesides, *Acc. Chem. Res.* **2002**, *35*, 491 – 499.

[28] S. G. Kandlikar, *J. Heat Transfer* **2004**, *126*, 8 – 16.

[29] W. Li, K. Liu, R. Simms, J. Greener, D. Jagadeesan, S. Pinto, A. Günther, E. Kumacheva, *J. Am. Chem. Soc.* **2012**, *134*, 3127 – 3132.

[30] A. P. Esser-Kahn, P. R. Thakre, H. Dong, J. F. Patrick, V. K. Vlasko-Vlasov, N. R. Sottos, J. S. Moore, S. R. White, *Adv. Mater.* **2011**, *23*, 3654 – 3658.

[31] N. McCann, D. Phan, X. Wang, W. Conway, R. Burns, M. Attalla, G. Puxty, M. Maeder, *J. Phys. Chem. A* **2009**, *113*, 5022 – 5029.

[32] R. W. Sabnis, *Handbook of Acid-base Indicators*, CRC Press, Boca Raton, FL, **2007**.

[33] M. S. Jassim, G. T. Rochelle, *Ind. Eng. Chem.* **2006**, *45*, 2465 – 2472.

[34] G. T. Rochelle, *Science* **2009**, *325*, 1652 – 1654.

[35] J. T. Yeh, H. W. Pennline, K. P. Resnik, *Energy Fuels* **2001**, *15*, 274 – 278.

[36] J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, **1988**.

[37] M. Abolhasani, M. Singh, E. Kumacheva, A. Günther, *Lab Chip* **2012**, *12*, 1611 – 1618.

[38] M. Abolhasani, M. Singh, E. Kumacheva, A. Günther, *Lab Chip* **2012**, *12*, 4787 – 4795.