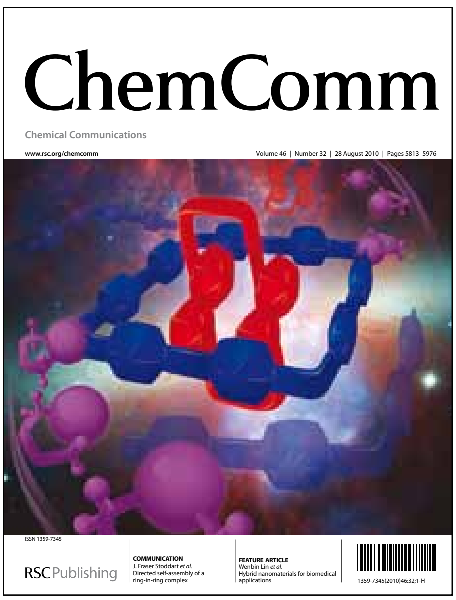
ChemComm
Chemical Communications
www.rsc.org/chemcomm
RSC Publishing

ChemComm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Methane Storage in Tea-Clathrates†

Weixing Wang,*[a] Peiyu Zeng,[a] Xiyi Long,[a] Jierong Huang,[a] Yao Liu,[a] Bien Tan,[b] and Luyi Sun*[c]

Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Methane can be stored in tea-clathrates, that is, methane clathrate formation kinetics can be significantly accelerated (90% saturation uptake in 20 min) by ingredients (polyphenols and saponin) in tea infusion with a volumetric capacity up to 172 v/v.

The main strategies for storing and transporting methane (CH_4) are compression and liquefaction. There has also been much attention recently in physical adsorption in synthetic porous materials, such as metal-organic frameworks and porous organic polymers.[1-6] While precise control of pore size in such materials has been achieved, few candidates can meet the demanding requirements in CH_4 storage in terms of performance, physical stability, sustainability, and cost.[1-10]

Gas clathrates, also known as gas hydrates, are non-stoichiometric, crystalline inclusion compounds composed of a hydrogen-bonded water lattice that traps gas molecules within polyhedral cavities.[11-15] One volume of CH_4 clathrate can yield approximately 180 v/v (under standard temperature and pressure, STP) CH_4, thus it has been suggested that it may be economically feasible to transport CH_4 in hydrated form.[12] A practical problem is that CH_4 clathrate forms slowly in bulk water. Formation rates can be accelerated by increasing contact between the gas and the liquid interface. Strategies for improving interface include vigorous mixing, grinding to produce small ice particles, use of fine water droplets in the form of dry water, or the addition of surfactants.[7, 12, 16-18] Such strategies require additional energy input and, very often, petrochemical-derived materials.

Through millions of years of evolution, Nature has become a treasure trove of valuable chemicals. What has been developed in the nature may provide inspiration in the research of gas clathrates. Herein, we report, to the best of our knowledge, for the first time regarding using teas or other cheap bio-extracts to accelerate CH_4 clathrate formation kinetics with a volumetric capacity up to 172 v/v.

Fig. 1 shows CH_4 uptake kinetics at 273.2 K for CH_4 clathrate formation in the samples of green tea (Longjing), oolong tea (Tieguanyin), and black tea (Yunnan), compared with bulk, unstirred water. The green and oolong tea samples exhibit much faster CH_4 absorption kinetics in comparison with the water, which does not absorb appreciable quantities of gas under these conditions. For the green tea sample, the CH_4 uptake reached a plateau of around 172 v/v CH_4 in 1000 min (t_{90}, the time to achieve 90% of this capacity, was only about 20 min). This storage capacity is close to the US Department of Energy (DOE) target for vehicular CH_4 storage (180 v/v, STP).[19] The CH_4 storage is reversible, and all of the CH_4 can be released upon warming back to 293 K (Figures 2 and S2).

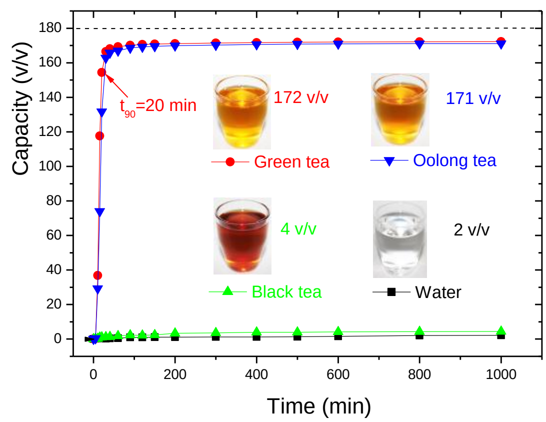

Fig. 1 Methane uptake kinetics for pure water, green tea (Longjing), oolong tea (Tieguanyin), and black tea (Yunnan) at 273.2 K.

As expected, not every type of tea is equally effective in promoting CH_4 clathrate formation. As shown in Fig. 1, the black tea (Yunnan) sample absorbs very little CH_4 over this timescale (4 v/v versus 171 v/v for oolong tea). Thus one can conclude that there must be some water soluble ingredients in green and oolong teas to promote the formation of CH_4 clathrate. Generally, commercial tea is manufactured in three basic forms: (1) Green tea is typically prepared in such a way as to preclude the oxidation of green leaf polyphenols; (2) During black tea production oxidation is promoted so that most of these substances are oxidized; (3) Oolong tea is a partially oxidized product.[20] Green tea contains the highest concentration of tea polyphenols (up to 30% of the dry weight). In comparison, the content of tea polyphenols in black tea is only 5% of the dry weight.[20-22] This fact suggests that tea polyphenols might be a key promoter for the formation of CH_4 clathrates.

Our experiments have proved that tea polyphenols is a good CH_4 clathrate formation promoter. As shown in Fig. 3, when the concentration of tea polyphenols is 0.2 wt%, the volumetric capacity reaches 160 v/v in 1000 min. However, the tea polyphenols' promoting effect is still lower than the sample of green tea, which indicated that there might be some other effective ingredients in green tea to promote CH_4 clathrate formation.

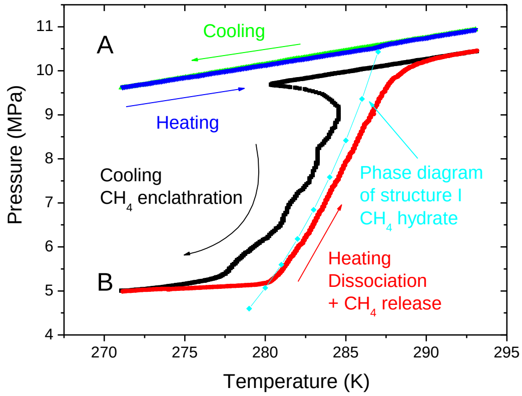

Fig. 2 Pressure-Temperature (P-T) dependence during cooling and heating under CH_4 pressure: (A) bulk water; (B) green tea (temperature ramp: 4.0 K/h).

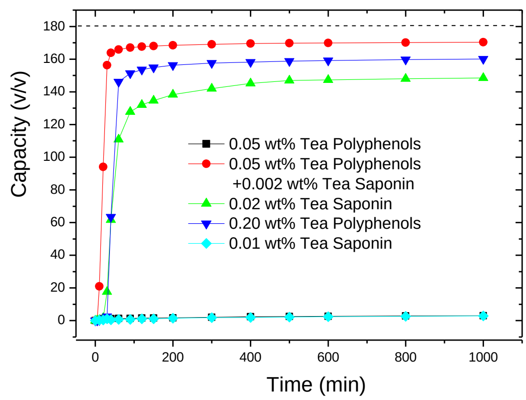

Fig. 3 Methane uptake kinetics for the aqueous solutions of tea polyphenols, tea saponin, and their mixture at 273.2 K.

The ingredients in green tea are very complicated. A typical green tea contains as many as 500 chemical compounds, and their concentration and existence vary with location, harvesting season and processing procedures.[20-24] It's virtually impossible to separate and test every single ingredient for the CH_4 clathrate formation. But, the foaming phenomenon during infusing tea is well known. The surface activity of tea is coming from tea saponin which consists of hydrophilic groups (hydroxyl and ester groups) and hydrophobic groups (sterols or triterpenes).[25-27] The use of surfactants, such as sodium dodecyl sulfate to promote CH_4 clathrate formation has been widely investigated and shown to be effective.[15, 16] As shown in Fig. 3, tea saponin is also a good CH_4 clathrate formation promoter. When the content of tea saponin is as low as 0.02 wt%, the volumetric capacity reaches 148 v/v in 1000 min.

The synergistic effect of tea polyphenols and tea saponin might be the main reason why green tea is so effective in CH_4 clathrate formation. As shown in Fig. 3, a mixture of 0.05 wt% tea polyphenols and 0.002 wt% tea saponin can promote the formation of CH_4 hydrate with a volumetric capacity up to 170 v/v in 1000 min with a t_{90} of about 25 min.

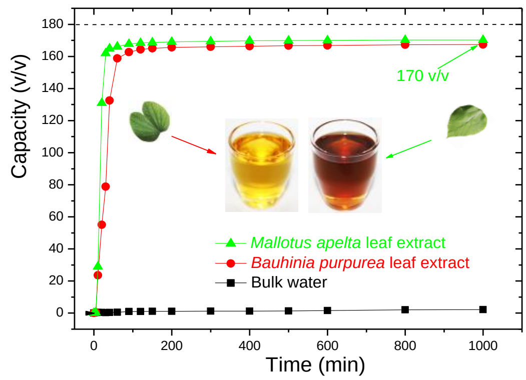

Fig. 4 Methane uptake kinetics for the *Bauhinia purpurea* and *Mallotus apelta* leaf extracts at 273.2 K.

Commercial teas are of relatively high cost for CH_4 storage and transportation applications, we wish to find more effective CH_4 clathrate formation promoter from bio-extracts using inexpensive natural materials. As shown in Fig. 4, the extracts from *Bauhinia purpurea* and *Mallotus apelta* leaves can promote the formation of CH_4 clathrate with volumetric capacities up to 167 v/v and 170 v/v, respectively.

In summary, we have demonstrated that CH_4 clathrate formation kinetics can be significantly accelerated (90% saturation uptake in 20 min) by ingredients (polyphenols and saponin) in tea infusion with a volumetric capacity up to 172 v/v. The maximum capacity of tea clathrates at present is still lower than the DOE's target. However, there are thousands of plants in nature, we may find more suitable bio-extracts from the plants to increase the formation kinetics and capacity of CH_4 clathrate to reach the target of DOE.

This project is sponsored by the National Natural Science Foundation of China (21176093), the National Undergraduate Innovation and Entrepreneurial Training Program (201310561087), and the U.S. Environmental Protection Agency (P3 Award, SU-83529201). L. S. acknowledges the Air Force Office of Scientific Research (No. FA9550-12-1-0159) and the National Science Foundation (Partnerships for Research and Education in Materials, DMR-1205670) for partial support for this research.

Notes and references

[a]*School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China Tel: (+86) 20-22236985; Fax: (+86) 20-22236985; Email: cewxwang@scut.edu.cn*
[b]*School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.*

[c]*Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States*
Tel: (860) 486-6895; Fax: (860) 486-4745; Email: luyi.sun@uconn.edu

† Electronic Supplementary Information (ESI) available: Experimental details,calculation of capacity, and recyclability plots. See DOI: 10.1039/b000000x/

References and Notes:

1 C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou and A. I. Cooper, *Adv. Mater.*, 2008, **20**, 1916-1921.
2 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472.
3 R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966-4981.
4 (*a*) Y. He, W. Zhou, T. Yildirim and B. Chen, *Energy Environ. Sci.*, 2013, **6**, 2735-2744; (*b*) Y. He, S. Xiang, Z. Zhang, S. Xiong, F. R. Fronczek, R. Krishna, M. O'Keeffe and B. Chen, *Chem. Commun.*, 2012, 48, 10856-10858.
5 T. A. Makal, J.-R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761-7779.
6 T. Düren, L. Sarkisov, O. M. Yaghi and R. Q. Snurr, *Langmuir*, 2004, **20**, 2683-2689.
7 W. Wang, C. L. Bray, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2008, **130**, 11608-11609.
8 W. Wang, B. O. Carter, C. L. Bray, A. Steiner, J. Bacsa, J. T. Jones, C. Cropper, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Chem. Mater.*, 2009, **21**, 3810-3815.
9 W. Wang, Z. Huang, H. Chen, Z. Tan, C. Chen and L. Sun, *Chem. Commun.*, 2012, **48**, 11638-11640.
10 W. Wang, C. Ma, P. Lin, L. Sun and A. I. Cooper, *Energy Environ. Sci.*, 2013, **6**, 105-107.
11 G. Rehder, R. Eckl, M. Elfgen, A. Falenty, R. Hamann, N. Kähler, W. F. Kuhs, H. Osterkamp and C. Windmeier, *Energies*, 2012, **5**, 2499-2523.
12 E. D. Sloan, *Nature*, 2003, **426**, 353-363.
13 L. A. Stern, S. Circone, S. H. Kirby and W. B. Durham, *J. Phys. Chem. B*, 2001, **105**, 1756-1762.
14 L. A. Stern, S. H. Kirby and W. B. Durham, *Science*, 1996, **273**, 1843-1848.
15 J. S. Zhang, S. Lee and J. W. Lee, *Ind. Eng. Chem. Res.h*, 2007, **46**, 6353-6359.
16 K. Okutani, Y. Kuwabara and Y. H. Mori, *Chem. Eng. Sci.*, 2008, **63**, 183-194.
17 R. Rogers, G. Zhang, J. Dearman and C. Woods, *J. Petrol. Sci. Eng.*, 2007, **56**, 82-88.
18 S. Takeya, W. Shimada, Y. Kamata, T. Ebinuma, T. Uchida, J. Nagao and H. Narita, *J. Phys. Chem. A*, 2001, **105**, 9756-9759.
19 T. Burchell, M. Rogers, *SAE Tech. Pap. Ser.*, 2000, 2000-01-2205.
20 H. N. Graham, *Prev. Med.*, 1992, **21**, 334-350.
21 C. Cabrera, R. Artacho and R. Giménez, *J. Am. Coll. Nutr.*, 2006, **25**, 79-99.
22 M. Reto, M. E. Figueira, H. M. Filipe and C. M. Almeida, *Plant Foods Hum. Nutr.*, 2007, **62**, 139-144.
23 Z. Y. Chen, Q. Y. Zhu, D. Tsang and Y. Huang, *J. Agric. Food Chem.*, 2001, **49**, 477-482.
24 Y. L. Su, L. K. Leung, Y. Huang and Z. Y. Chen, *Food Chem.*, 2003, **83**, 189-195.
25 Y. Sagesaka, T. Uemura, Y. Suzuki, T. Sugiura, M. Yoshida, K. Yamaguchi and K. Kyuki, *Yakugaku zasshi: J. Pharm. Soc. Jpn.*, 1996, **116**, 238-243.
26 Y.-F. Chen, C.-H. Yang, M.-S. Chang, Y.-P. Ciou and Y.-C. Huang, *Int. J. Mol. Sci.*, 2010, **11**, 4417-4425.
27 E. Wina, S. Muetzel and K. Becker, *J. Agric. Food Chem.*, 2005, **53**, 8093-8105.