Supplementary Materials for

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]

[a]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China
[b]School 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

*Author to whom correspondence should be addressed:

Dr. Weixing Wang, Tel: (+86) 20-22236985; Fax: (+86) 20-22236985; Email: cewxwang@scut.edu.cn

Dr. Luyi Sun, Tel: (860) 486-6895; Fax: (860) 486-4745; Email: luyi.sun@uconn.edu

Materials and Methods

Teas (green tea, Longjing; oolong tea, Tieguanyin; black tea, Yunnan) were purchased from the Peking Supermarket in Guangzhou, China. Green tea polyphenol (99%) was purchased from Hangzhou Gosun Biotechnologies Co. Ltd., China. Tea saponin was purchased from Aladdin Co. Ltd., China. *Bauhinia purpurea* and *Mallotus apelta* leaves were collected from the campus of the South China University of Technology (Guangzhou, China, in June). Methane (99.95%) was purchased from Zhuozheng Gas Co. Ltd., China. To extract the water soluble compounds, 1.0 g of the dry tea (2.0 g of dry *Bauhinia purpurea* leaves or *Mallotus apelta* leaves (378.2 K over night)) were infused in 100 g of water at a temperature of 353.2 K for 60 min. Then, the extracted suspension was filtered to obtain a clear solution. The concentration of the green tea, oolong tea, black tea, *Bauhinia purpurea* leaves extract, and *Mallotus apelta* leaves extract is 0.37 wt%, 0.29 wt%, 0.30 wt%, 0.28 wt%, and 0.40 wt%, respectively.

Methane Gas Hydrates Formation

To carry out the methane uptake kinetic experiments, 20.0 g of sample solution was loaded into a high pressure stainless steel vessel with a volume of 82 cm^3 (Kerui Instruments Co., Gongyi, Henan, China). The temperature of the coolant was controlled by a programmable thermal circulator (DWHW-10, Kerui Instruments Co., Gongyi, Henan, China). The sample temperature in the high pressure cell was measured using a type K thermocouple (-250 to 400 ℃, Tianyi Cekong Co., Henan, China). The methane gas pressure was monitored using a High-Accuracy Gauge Pressure Transmitter (0-20 MPa, Tianyi Cekong Co., Henan, China). Both the

thermocouple and the transmitter were connected to a Digital Universal Input Panel Meter (ZNHW, Kerui Instruments Co., Gongyi, Henan, China), which communicates with a computer. Prior to each experiment, the cell was purged with methane three times to remove the air, and then pressurized to the desired pressure (starting pressure is 9.5 MPa without special statement) at the designated temperature. The temperature (*T*, K), pressure (*P*, MPa), and time (t, min) were automatically interval-logged using SuperCx 3.0 software (Kerui Instruments Co., Gongyi, Henan, China). The apparatus is shown schematically in Figure S1.

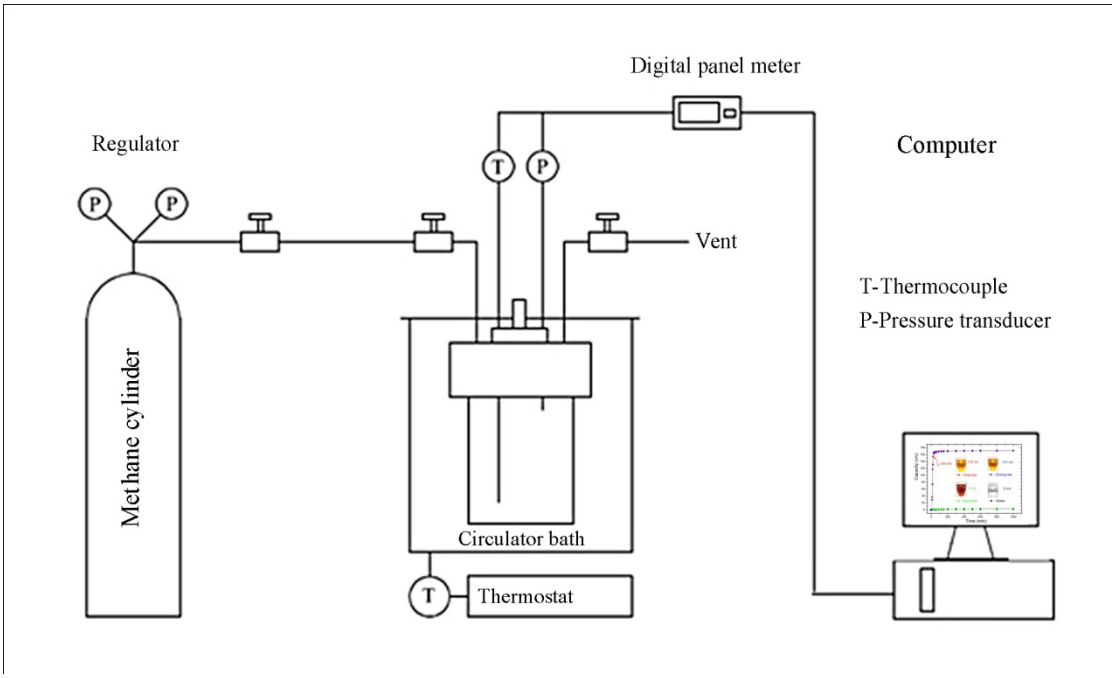

Figure S1. Schematic diagram of the experimental apparatus.

Calculation of Capacity

In this work, capacity is defined volumetrically in terms of the number of volumes of methane gas released per unit volume of methane clathrate hydrate (v/v). The capacity was calculated relative to the pressure change within the reaction vessel. The free

space volume of the vessel was obtained by subtracting the sum volume of methane clathrate hydrate, unreacted water and solid extract. Taking the non-ideality factors into account, GASPAK v3.41 software (Horizon Technologies, USA) was employed to calculate the methane enclathration capacity, according to the pressure and the temperature. We assume that the liquid and gas phases inside the vessel are exclusively formed from the water and the gas, respectively, neglecting any dissolution of the gas into the liquid phase and any mixing of the water vapor in the gas phase.

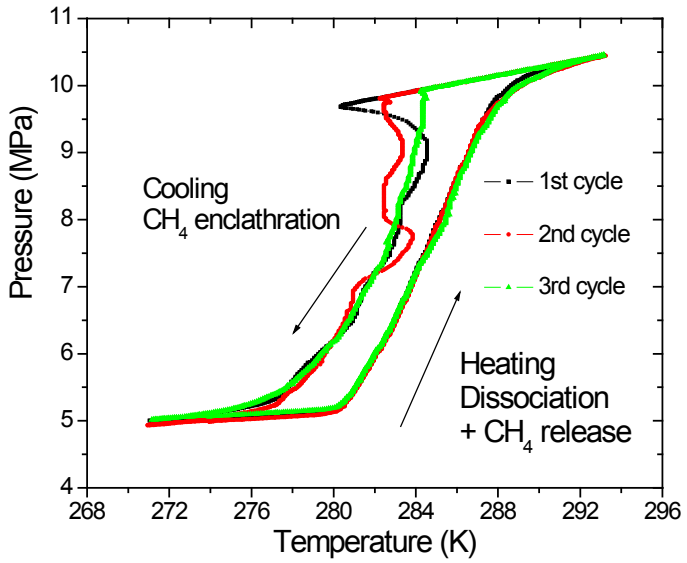

Figure S2. Recyclability of green tea (Longjing) during cooling and heating under CH_4 pressure (temperature ramp: 4.0 K/h).