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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 (CH₄) 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. While precise control of pore size in such materials has been achieved, few candidates can meet the demanding requirements in CH₄ storage in terms of performance, physical stability, sustainability, and cost.

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. One volume of CH₄ clathrate can yield approximately 180 v/v (under standard temperature and pressure, STP) CH₄, thus it has been suggested that it may be economically feasible to transport CH₄ in hydrated form. A practical problem is that CH₄ 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. 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 CH₄ clathrate formation kinetics with a volumetric capacity up to 172 v/v.

Fig. 1 shows CH₄ uptake kinetics at 273.2 K for CH₄ clathrate formation in the samples of green tea (Longjing), oolong tea (Tieguanyin), and black tea (Yunnan), compared with bulk, unstripped water. The green and oolong tea samples exhibit much faster CH₄ absorption kinetics in comparison with the water, which does not absorb appreciable quantities of gas under these conditions. For the green tea sample, the CH₄ uptake reached a plateau of around 172 v/v CH₄ in 1000 min (tₙₐₓ, 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 CH₄ storage (180 v/v, STP). The CH₄ storage is reversible, and all of the CH₄ can be released upon warming back to 293 K (Figures 2 and S2).

As expected, not every type of tea is equally effective in promoting CH₄ clathrate formation. As shown in Fig. 1, the black tea (Yunnan) sample absorbs very little CH₄ 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 CH₄ 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. 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. This fact suggests that tea polyphenols might be a key promoter for the formation of CH₄ clathrates.

Our experiments have proved that tea polyphenols is a good CH₄ 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 \( \text{CH}_4 \) clathrate formation.

The synergistic effect of tea polyphenols and tea saponin might be the main reason why green tea is so effective in \( \text{CH}_4 \) 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 \( \text{CH}_4 \) hydrate with a volumetric capacity up to 170 v/v in 1000 min with a \( t_{90} \) of about 25 min.

Fig. 2 Pressure-Temperature (P-T) dependence during cooling and heating under \( \text{CH}_4 \) 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.

Commercial teas are of relatively high cost for \( \text{CH}_4 \) storage and transportation applications, we wish to find more effective \( \text{CH}_4 \) clathrate formation promoter from bio-extracts using inexpensive natural materials. As shown in Fig. 4, the extracts from \( \text{Bauhinia purpurea} \) and \( \text{Mallotus apelta} \) leaves can promote the formation of \( \text{CH}_4 \) clathrate with volumetric capacities up to 167 v/v and 170 v/v, respectively.

In summary, we have demonstrated that \( \text{CH}_4 \) 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 \( \text{CH}_4 \) clathrate to reach the target of DOE.

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