

Pectin as an Extraordinary Natural Kinetic Hydrate Inhibitor

Shurui Xu, Shuanshi Fan, Songtian Fang, Xuemei Lang, Yanhong Wang & Jun Chen

Pectin as a novel natural kinetic hydrate inhibitor, expected to be eco-friendly and sufficiently biodegradable, was studied in this paper. The novel crystal growth inhibition (CGI) and standard induction time methods were used to evaluate its effect as hydrate inhibitor. It could successfully inhibit methane hydrate formation at subcooling temperature up to 12.5 °C and dramatically slowed the hydrate crystal growth. The dosage of pectin decreased by 66% and effective time extended 10 times than typical kinetic inhibitor. Besides, its maximum growth rate was no more than 2.0%/h, which was far less than 5.5%/h of growth rate for PVCap at the same dosage. The most prominent feature was that it totally inhibited methane hydrate crystal rapid growth when hydrate crystalline occurred. Moreover, in terms of typical natural inhibitors, the inhibition activity of pectin increased 10.0-fold in induction time and 2.5-fold in subcooling temperature. The extraordinary inhibition activity is closely related to its hydrogen bonding interaction with water molecules and the hydrophilic structure. Finally, the biodegradability and economical efficiency of pectin were also taken into consideration. The results showed the biodegradability improved 75.0% and the cost reduced by more than 73.3% compared to typical commercial kinetic inhibitors.

Pectin, a kind of polysaccharides, widely exists in ripe fruits and certain vegetables. As possessing eco-friendly biodegradable natural product, pectin is widely used in medicine and food industry. Recently, we found another important application of pectin in oil and gas industry. It can solve one of the most vexing problems of gas industry, which are hydrate blockages during transportation in pipeline. Natural gas hydrate, an ice-like crystalline compounds formed by natural gas molecules and water molecules at high pressure and relatively low temperature¹. Gas hydrate formation in pipelines will lead to pipeline plugged, stopping production. In extreme cases, it will result in abandonment and replacement of well^{2,3} and bring great potential risks to the oil and gas industry in flow assurance area. A serious hydrate plugs occurred at the leaking well on May 7 during accident of the BP Deep Water Horizon Oil Spill in 2010 when methane gas bubbles come in contact with cold seawater. Then, the cofferdam filled with hydrates, gas and oil and lost control. Until June 3, methanol injection was started and hydrate plugging was avoided⁴. Based on the events of the Deep Water Horizon disaster, hydrates blockages in any future containment operation have been emphasized highly. In order to avoid this kind of large scale gas hydrate for-

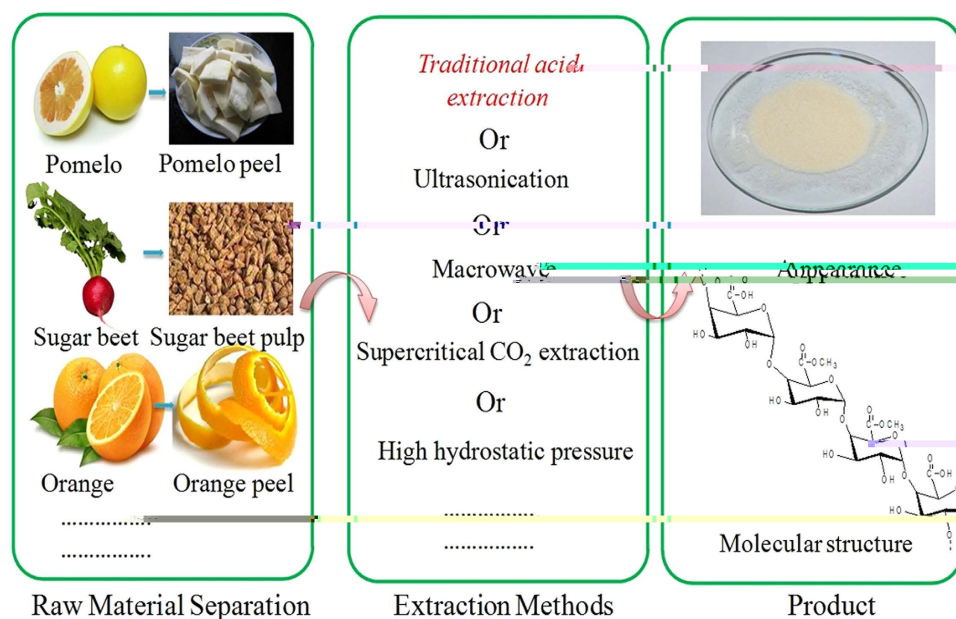


Figure 1. Simple extracted process and main chain structure of pectin. The traditional acid extraction method was used in this paper (These photographs of the figure were provided by Songtian Fang and this figure was created by shurui Xu).

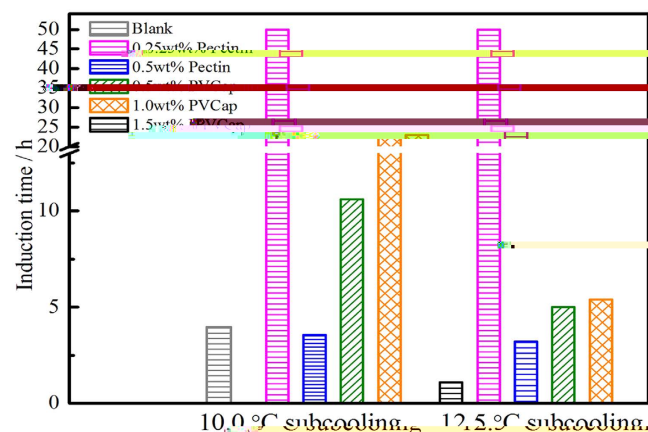


Figure 2. Onset time of methane hydrate formation in pure water system (the values in this figure are all based on 5 measurements).

Results and Discussion

The inhibitory performance.

As the structural unit of plant cells and the junction between the plant cell-wall, pectin can be easily extracted from citrus peel, apple pomace, orange peel, sugar beet pulp by various methods¹⁵. The process was shown in Fig. 1. We used traditional acid extraction extract pectin (Mw:264.624 KDa) from pomelo peel and investigated the inhibition effect of pectin on methane hydrate, and compared with the recognized effective KHI (PVCap, Mw:1.41 KDa) at the same conditions.

As expected, the results proved that the pectin performed a powerful inhibition for methane hydrate formation. Figure 2 summarized the induction time of different concentrations of pectin and PVCap at two subcooling temperatures. Induction time was the time from the start cooling to the first detected hydrate formation and was the acknowledged evaluation parameter^{16,17}, at which time hydrate had nucleated and started growing. Figure 3 displayed the gas consumption change with hydration time with the pectin or PVCap existence.

Compared with blank sample, both additives not only can prolong the induction time of methane hydrate but also can retard hydrate crystal growth. The inhibitory performance of PVCap was tested in the concentration range of 0.5 mass% to 1.5 mass%. The results showed that PVCap performed best at 1.5 mass%, which induction time is longest. When the methane hydrate appeared, it can keep a slow growth and the total gas consumption is less than that of experiment without additives. In the cases of pectin, it showed a much better inhibitory performance than PVCap. At 10.0 °C subcooling (9.5 MPa), the inhibitory performance of pectin at

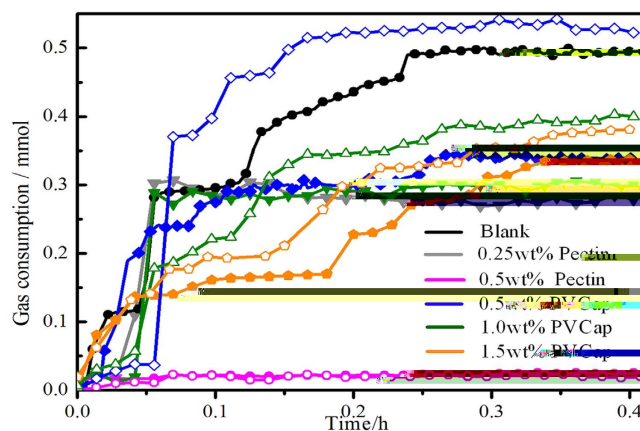


Figure 3. Gas consumption vs time profiles after initial hydrate formation in pure water system (the open and close symbol indicated 12.5°C and 10.0°C subcooling temperature, respectively).

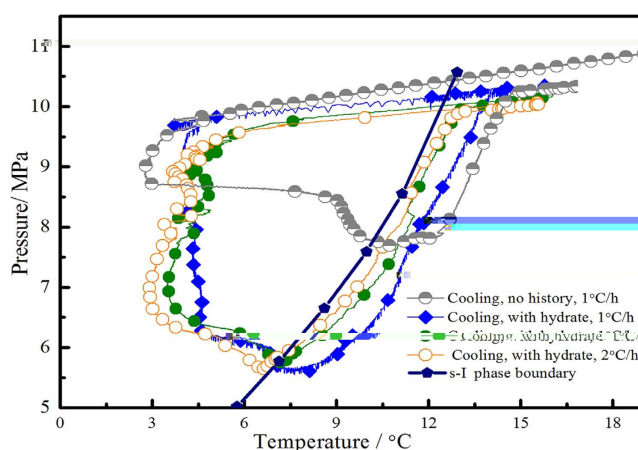


Figure 4. Pressure versus temperature plot showing example CGI method cooling/heating curves for methane-water system with 0.5 mass% pectin aqueous.

0.25 mass% concentration was similar to PVCap at 0.5 mass%. While the concentration increased to 0.5 mass%, pectin showed a remarkable inhibitory performance and no hydrate was observed during the whole experiment process at two different subcooling temperatures. It is shown in detail in Figure S8. At 10.0°C subcooling temperature, pectin showed extraordinary long inhibitory time and no gas consumed for methane hydrate formation. The induction time of pectin increased from 10.6 h to above 50.0 h, which surpassed 14.0 times than that of PVCap. Furthermore, pectin also showed powerful effect on inhibiting methane hydrate formation at relatively high subcooling temperature (subcooling 12.5°C). Even the dosage of pectin was one-third of PVCap, pectin also can totally inhibit hydrate crystal growth in 50.0 h. The results proved that inhibitory performance of pectin outperformed PVCap and the injection dosage decreased by 66.0%. Compared with other typical natural inhibitors, the inhibitory performance of pectin was also outstanding. The tapioca starch as KHI was evaluated at subcooling 2.0°C using methane (3.5 MPa). The results showed tapioca starch was able to delay the onset of hydrate formation by about 1.5 hours at 0.5 mass% concentration¹⁸. At about 4.5°C subcooling and 4.5 MPa, the induction time of chitosan was no more than 150.0 minutes in methane system¹⁵. Besides, in the presence of AFPs, the average conversion ratio of water converted to hydrate had been more than 20% after 30 h in methane gas system (11.7 MPa and 12.0°C subcooling)¹⁹. Above all, as a natural hydrate inhibitor, the inhibition activity of pectin to retard methane hydrate formation and reduce the crystal growth was efficient.

To further confirm the inhibitory of pectin on methane hydrate, crystal growth inhibition (CGI) method was used to determine crystal growth boundaries of pectin at 11.5 MPa. The CGI method, developed by Anderson *et al.* of Herriot Watt University²⁰ and proved to be rapidly and reliably^{7,21} in practice. CGI method consisted of several hydrate growth–dissociation cycles. Following the first hydrate formation, a little measurable hydrate crystal (typically 0.5 mass% of aqueous phase as hydrate) was left and then the system was cooled back into the hydrate region to measure growth rates. Inhibition regions would be quantified according to the crystal growth patterns. By this means, all stochastic nucleation process was avoided, and hydrate growth rates only represented the ability of the KHI hindered crystal growth. Figure 4 showed cooling and heating curves for methane system

with 0.5 mass% pectin aqueous plotted as pressure versus temperature. The s-I methane hydrate phase curve was shown for comparison²². On the first cooling run with no history (1.0 °C/h) nucleation eventually occurred after pressure and temperature conditions entered the hydrate region at 10.0 °C of subcooling. Then the cell temperature was heated rapidly to dissociate the hydrate present until only 0.74% the hydrate in cell.

Following the above, the temperature of the system was then cooled (1.0 °C/h) back into the hydrate region with a small fraction of hydrate present. No growth was observed until 4.9 °C of subcooling, at which point hydrate started growing at a very slow speed (0.02% hydrate/h). When the temperature of cell reached 3.6 °C (10.4 °C subcooling), the hydrate crystal growth rate suddenly increased from 0.45%/h to 0.78%/h. The maximum growth rate was no more than 2.2%/h although the temperature decreased to 2.0 °C, at which point the subcooling reached to 12.0 °C. Subsequent heating to the temperature outside the thermodynamic hydrate stability region for the system, the hydrate dissociation continued at a speed of 0.04%/h, which value is only 3% of decomposition rate for no-KHI system. As shown in Fig. 4, four hydrate growth–dissociation cycles were conducted to obtain

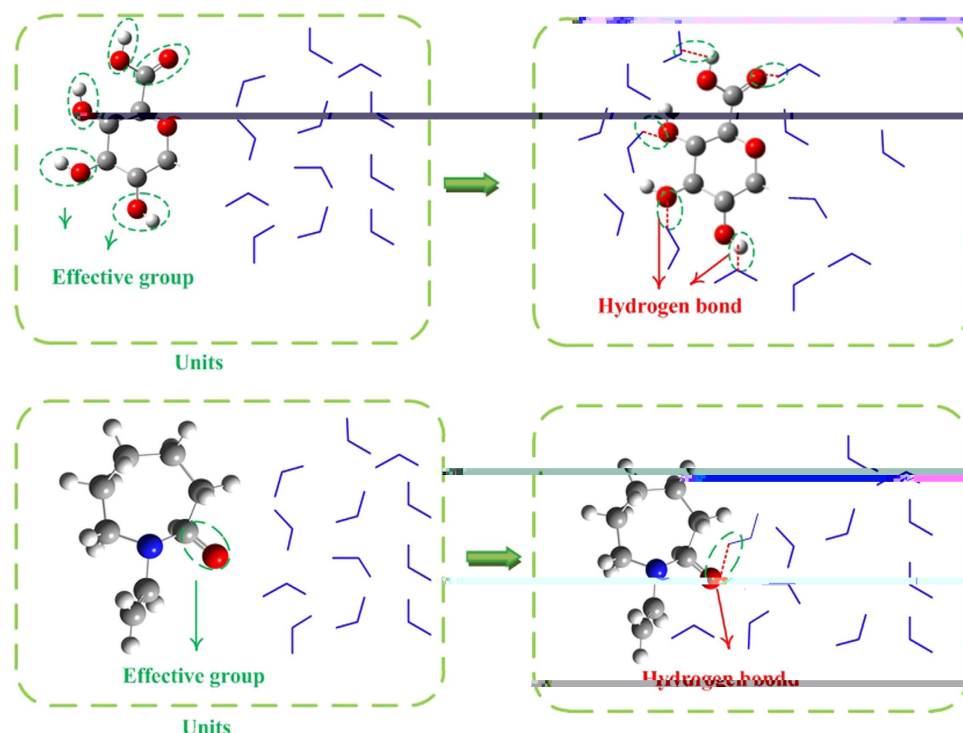


Figure 6. Schematic of active group of pectin and PVCap forming hydrogen bond with water molecules and perturbation of water molecules orders. Each monomer of pectin has five effective groups forming hydrogen bonds, while each monomer of PVCap has one effective group. Note that the graphic is intended for illustrative purposes and is not drawn to scale. (Red ball represent oxygen atom, blue ball represent nitrogen atom, gray ball represent carbon atom, white ball represent hydrogen atom, blue broken line represent water molecule, red dash line represent H-bond).

biodegradable in the case of the ratio lower than 0.20^{23,24}. From the above point, BOD_5/COD_{cr} value of the PVCap aqueous was 0.259, which was not easy to be biodegraded and pectin possesses easily biodegrade nature. The biodegradability pectin aqueous was higher and improved almost 75.0% compared with PVCap. Moreover, since pectin exist in many kinds of fruit and vegetables and its content in citrus peel is more than 20.0%²⁵ as well as its extract processing was mature, pectin is further cheaper than KHIs. Compared with using methanol (\$0.33/kg), typically used at 35.0 mass% of produced water, pectin (\$12.54/kg) provided a cost saving of approximately \$121,792 per month at the intermediate water flow rate of 500BWPD²⁶ and the cost was reduced by 45.7%. Besides, compared with the commercial KHIs (\$23.52/kg), 0.5 mass% pectin can replace 1.0 mass% KHIs, which usage can save almost \$397,834 per month²⁶ in the same water flow rate and make the cost decreased by 73.3%.

Inhibition mechanism. With lots of oxygen or hydroxyl groups in the pectin structure, pectin could form hydrogen bonds with water molecules, perturbing the water structure. The literatures²⁷ indicated that water molecules could break the hydrogen bonds between hydroxyl and carbonyl groups of pectin through water and pectin molecules forming H-bonds. At same time, these effects result in the activity of water decreased²⁸. Pectin as a novel hydrate inhibitor, its extraordinary inhibition activity was closely related to its hydrogen bonds between water molecules. According to previous mechanism of kinetic inhibition^{29–31}, the oxygen atoms in carbonyl and hydroxyl groups of pectin (active group) can form hydrogen bonds with water molecules which will disrupt the water structure. This process hindered the water molecules to form hydrate cages and thus delayed the gas hydrate nucleation, as shown in Fig. 6. Furthermore, each monomer of pectin has five active groups. At the same mass, the active group amounts of pectin were about 2.6-fold of that of PVCap. That may be the reason why pectin has the better inhibitor performance than PVCap. Additionally, after nucleation, the hydrophilic structure enables pectin to retard hydrate crystal growth. Oxygen atoms of pectin bind to the surface of hydrate crystal through hydrogen bonds. Consequently, the α -D-galacturonosyl units of pectin can enhance the steric hindrance and thus suppress crystal growth²⁹.

Conclusion

In conclusion, as a kind of cheap natural material, pectin could tremendously improve induction time of methane hydrate nucleation and retard hydrate crystal growth. The induction time extended 10 times than the commercial hydrate inhibitor. Compared with other typical natural inhibitors, the inhibition activity of pectin increased 10.0-fold in induction time and 2.5-fold in subcooling temperature. Besides, it totally inhibited methane hydrate crystal rapid growth when hydrate crystalline occurred and the maximum growth rate was no more than 2.0%/h. Moreover, the biodegradability of pectin improved 75.0% and the cost reduced by more than 73.3%. With good inhibitory performance, high biodegradability and good economy, pectin is a good alternative KHI in gas and oil industry.

Methods

Traditional acid extraction of pectin from pomelo peel was shown in supporting information and the detailed characteristics of pectin can be seen in Figure S2 and S3. Free radical polymerization of N-vinyl caprolactam was also shown in supporting information and the detailed characteristics of pectin can be seen in Figure S4 and S5. The experimental apparatus and procedure used to measure the induction time of pectin were the same as those used in our previous study¹⁷. And the definition of induction time can be seen in Figure S6. Besides, the novel crystal growth inhibition (CGI) method developed by Anderson *et al.* was also used in our experiment. The detailed experimental apparatus and procedures can be seen in supporting information. Finally, the test procedures of biodegradation were also performed.

References

- Sum, A. K., Koh, C. A. & Sloan, E. D. Clathrate Hydrates From Laboratory Science to Engineering Practice. *Ind Eng Chem* doi: 10.1021/ie900679m (2009).
- Sloan, E. D., Koh, C. A. & Sum, A. K. *Natural gas hydrates in flow assurance*. Gulf Professional Publishing, doi: 10.1016/B978-1-85617-945-4.000001-7 (2010).
- Perrin, A., Musa, O. M. & Steed, J. W. The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. rev.* **42**, 1996–2015 (2013).
- Giavarini, C. & Hester, K. *Gas hydrates: Immense energy potential and environmental challenges*. Springer Science & Business Media, doi: 10.1007/978-0-85729-956-7 (2011).
- Nagappayya, S. K., Lucente-Schultz, R. M., Nace, V. M. & Ho, V. M. Antiagglomerant Hydrate Inhibitors: The Link between Hydrate-Philic Surfactant Behavior and Inhibition Performance. *J. Chem. Eng. Data*, **60**, 351–355 (2014).
- Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. rev.* **31**, 157–167 (2002).
- Luna-Ortiz, E., Healey, M., Anderson, R. & Sørhaug, E. Crystal Growth Inhibition Studies for the Qualification of a Kinetic Hydrate Inhibitor under Flowing and Shut-in Conditions. *Energy Fuels*, **28**, 2902–2913 (2014).
- Kang, S. P. *et al.* Unusual synergy effect on methane hydrate inhibition when ionic liquid meets polymer. *SC Advances*, **3**, 19920–19923 (2013).
- Bulbul, S., Kadoura, A. S. & Parlaktuna, M. M. Hydrate Inhibition with PEO (Poly 2-ethyl-2-oxazoline). *Energy Sources, Part A: recovery, Utilization, and Environmental Effects*, **36**, 2613–2620 (2014).
- Chua, P. C. & Kelland, M. A. Poly(N-vinyl azacyclooctanone): A More Powerful Structure II Kinetic Hydrate Inhibitor than Poly(N-vinyl caprolactam). *Energy Fuels*, **26**, 4481–4485 (2012).
- Sharifi, H., Walker, V. K., Ripmeester, J. A. & Englezos, P. Insights into the behaviour of biological clathrate hydrate inhibitors in aqueous saline solutions. *Cryst. Growth Des.* **14**, 2923–2930 (2014).
- Mady, M. F. & Kelland, M. A. N-N-Dimethylhydrazidoacrylamides. Part II: High Cloud Point Kinetic Hydrate Inhibitor Copolymers with N-Vinylcaprolactam and Effect of pH on Performance. *Energy Fuels*, **29**, 678–685 (2015).
- Zeng, H., Wilson, L. D., Walker, V. K. & Ripmeester, J. A. Effect of antifreeze proteins on the nucleation, growth, and the memory effect during tetrahydrofuran clathrate hydrate formation. *J. Am. Chem. Soc.* **128**, 2844–2850 (2006).
- Mangiacapra, P., Gorrasi, G., Sorrentino, A. & Vittoria, V. Biodegradable nanocomposites obtained by ball milling of pectin and montmorillonites. *Carbohydr Polym.* **64**, 516–523 (2006).
- Guo, X. *et al.* Emulsion stabilizing properties of pectins extracted by high hydrostatic pressure, high-speed shearing homogenization and traditional thermal methods: A comparative study. *Food Hydrocoll.* **35**, 217–225 (2014).
- Lone, A. & Kelland, M. A. Exploring Kinetic Hydrate Inhibitor Test Methods and Conditions Using a Multicell Steel Rocker Rig. *Energy Fuels*, **27**, 2536–2547 (2013).
- Xu, S. R., Fan, S. S., Wang, Y. H. & Lang, X. M. An Investigation of Kinetic Hydrate Inhibitors on the Natural Gas from the South China Sea. *J. Chem. Eng. Data*, **60**, 311–318 (2015).
- Lee, J. D., Wu, H. J. & Englezos, P. Cationic starches as gas hydrate kinetic inhibitors. *Chem. Eng. Sci.* **62**, 6548–6555 (2007).
- Zeng, H., Moudrakovski, I. L., Ripmeester, J. A. & Walker, V. K. Effect of antifreeze protein on nucleation, growth and memory of gas hydrates. *AIChE Journal*, **52**, 3304–3309 (2006).
- Tohidi, B., Anderson, R., Chapoy, A., Yang, J. & Burgass, R. W. Do We Have New Solutions to the Old Problem of Gas Hydrates? *Energy Fuels*, **26**, 4053–4058 (2012).
- Nazeri, M., Tohidi, B. & Chapoy, A. An Evaluation of Risk of Hydrate Formation at the Top of a Pipeline. *Oil Gas Facilities*, **3**, 67–72 (2014).
- Fan, S. S., Li, Q., Nie, J. H., Lang, X. M., Wen, Y. G. & Wang, Y. H. Semiclathrate Hydrate Phase Equilibrium for CO₂/CH₄ Gas Mixtures in the Presence of Tetrabutylammonium Halide (Bromide, Chloride, or Fluoride). *J. Chem. Eng. Data*, **8**, 3137–3141 (2013).
- He, Q., Yao, K., Sun, D. & Shi, B. Biodegradability of tannin-containing wastewater from leather industry. *Biodegradation*, **18**, 465–472 (2007).

24.

Author Contributions

S.S.Fan, Y.H.Wang and S.R.Xu proposed and supervised the entire project. S.R.Xu and S.T.Fang performed the experiments and analysis. S.S.Fan, Y.H.Wang, X.M.Lang and J.Chen contributed to the discussion the results. S.R.Xu and Y.H.Wang wrote this manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Xu, S. *et al.* Pectin as an Extraordinary Natural Kinetic Hydrate Inhibitor. *Sci. Rep.* **6**, 23220; doi: 10.1038/srep23220 (2016).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>