Using Clathrate Hydrates for Gas Storage and Gas-Mixture Separations: Experimental and Computational Studies at Multiple Length Scales

Supplemental Information

Ioannis N. Tsimpanogiannis[1,*], Joseph Costandy[2,a], Panagiotis Kastanidis[3], Sally El Meragawi[2,b], Vasileios K. Michalis[2,3], Nikolaos I. Papadimitriou[1,c], Stylianos N. Karozis[1], Nikolaos I. Diamantonis[2], Othonas A. Moultos[4], George E. Romanos[3], Athanassios K. Stubos[1] and Ioannis G. Economou[2,*]

[1] Environmental Research Laboratory,
National Center for Scientific Research "Demokritos",
15310 Aghia Paraskevi Attikis, Greece.

[2] Chemical Engineering Program,
Texas A&M University at Qatar,
PO Box 23874, Doha, Qatar.

[3] Institute of Nanoscience and Nanotechnology,
National Center for Scientific Research "Demokritos",
15310 Aghia Paraskevi Attikis, Greece.

[4] Engineering Thermodynamics, Process & Energy Department,
Faculty of Mechanical, Maritime and Materials Engineering,
Delft University of Technology,
Leeghwaterstraat 39, 2628CB Delft, The Netherlands.

(*) Corresponding authors at: i.tsimpanogiannis@qatar.tamu.edu (I.N. Tsimpanogiannis); ioannis.economou@qatar.tamu.edu (I.G. Economou).

(a) Current address: McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, 78712, USA.

(b) Current address: Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia.

(c) Current address: Public Power Corporation, Testing Research and Standards Center, Leontariou 9, Kantza, 15351 Pallini, Greece

Web-based gas storage calculator

The user can select the case to examine, among the following five cases of storing CH_4 in solid clathrate hydrates that are currently available:

[A] Pure CH_4 hydrates.

[B] Binary hydrates with the promoter in the large (*L*) cages.

[C] Binary hydrates with the promoter in the medium (*M*) cages (applicable only for the case of sH hydrates).

[D] Binary hydrates with tuning of promoter in large cages.

[E] Binary hydrates with tuning of promoter in medium cages (applicable only for the case of sH hydrates).

Note that cases A, B and D consider all the three common hydrate structures (i.e., sI, sII, and sH). On the other hand, cases C and E are applicable only for the case of sH hydrates, since only the sH structure has a third type of (i.e., medium-sized) cavity.

Figure SI–1 shows a snapshot of the entry page of the web-based calculator. Once the user selects the case to examine, the next page appears where the user can define the particular conditions where the CH_4 storage capacity will be estimated. All fields with the required information that needs to be inserted are gathered in a separate zone (also depicted with different colour) towards the bottom of the web-page. Namely, in that zone the user can define the pressure range, the specific temperature, the structure, and the number of points, where the storage calculations are performed.

Case A is the simplest case examined and has the least input required to perform a calculation. Furthermore, for Case A the user can either select a particular structure to examine [i.e., sI, sII, or sH], or alternatively can compare the storage capacities of all the three hydrate structures. For the remaining cases additional information needs to be introduced. That includes the molecular weight of the promoter (required for cases B, C, D, and E), and the degree of cage tuning (required for cases D and E). Figure SI–2 shows a partial snapshot of the web page depicting only the required fields to be completed for cases A, B, and D.

During the development of the web-calculator it was assumed that for cases B and C the large cages are occupied completely by the promoter (100 %), while for cases D and E the large cages are occupied partially by the promoter (i.e., less than 100 %), while the remaining cages can be occupied by the guest gas. Such behaviour results in increasing the storage capacity of the hydrate structure and is known as hydrate tuning [1, 1]. Significant discussion is available in the literature regarding the existence of tuning [1–4]. The scope of the current study is not to confirm or refute the possibility of hydrate tuning. This study examines the issue as a possibility to increase storage capacity that is worth exploring.

Once the input parameters for the calculation are inserted the next page shows the visualization of the CH_4 storage capacity estimated results. Two options are available:

(i) The results are shown as a figure where the gas storage capacity (expressed in *wt* % of the stored gas in the hydrate structure) is plotted as a function of pressure for the particular temperature considered, and

(ii) the same results are given as a table that can be downloaded for further use.

When examining cases D and E the possibility of tuning [1] the hydrate structure is considered. In order to account for tuning a parameter, *F*, taking values in the range [0, 1], is introduced denoting the degree of tuning. The storage capacity tool performs calculations in a range of upper and lower CH_4 storage capacity values, plotting five different curves in total. The upper storage limit corresponds to the case of pure CH_4 hydrate (*F*=0). The lower storage limit corresponds to the case of binary CH_4–Promoter hydrate (*F*=1) where the promoter occupies 100 % of the promoter-designated cages (i.e., large cages for case D, and medium cages for case E). Cases with *F* having values in the range (0–1) correspond to some degree of tuning, where part of the promoter-designated cages is occupied by CH_4, increasing therefore, the storage capacity of the structure. Figure SI–3 shows a snapshot of the results for a particular example of case D with the input information shown in Figure SI–2. For this example the molecular weight of the promoter corresponds to the case of methylcyclohexane (MCH).

References

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Figure SI–1. Snapshot of the entry page of the web-based calculator. Initial selection of the case to examine.

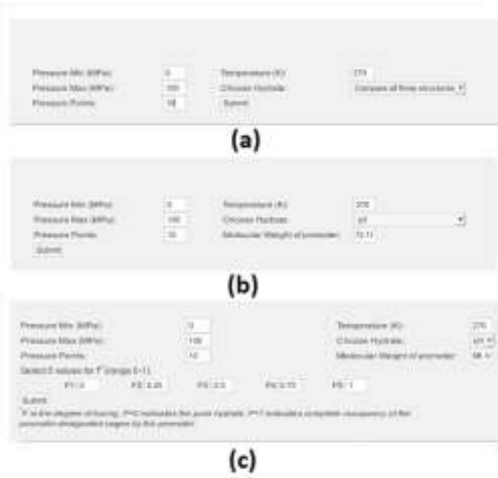

Figure SI–2. Partial snapshot of the second page of the web-based calculator where the user defines the conditions of the calculations: **(a)** comparison of all three structures for case A, **(b)** structure sII for case B (molecular weight of promoter corresponds to the case of THF), and **(c)** structure sH for case D (molecular weight of promoter corresponds to the case of MCH).

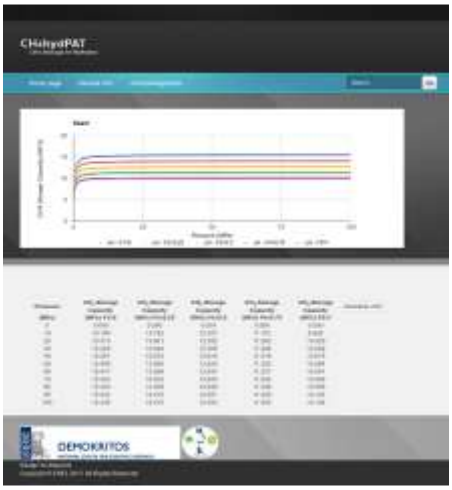

Figure SI–3. Snapshot of the third page of the web-based calculator. Example of results (given as a figure and tabulated) for case D. Parameters used: binary CH_4–Promoter hydrate at *T*=270 K, molecular weight of promoter 98.186 corresponding to the case of MCH, structure sH.