Simulation of Hydrogen Adsorption on Modified Carbon Structures

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Abstract

The adsorption simulation of hydrogen molecules onto modified carbon structures has been carried out. The modifications have been done by rearranging carbon nanotube structure and also by replacing carbon molecules by impurities i.e. boron and nitrogen atoms. The aims of this simulation is finding an optimum adsorption delivery of each modified carbon structures leading to an effective gas storage system. The adsorption simulation has been carried by Grand Canonical Monte Carlo methods (GCMC). By this simulation, it was found that the optimum temperature for hydrogen adsorption delivery was still under room temperature.

Keywords: *adsorption, carbon nanotubes, gas storage, GCMC, adsorption delivery*

Introduction

One of the growing research fields in adsorption nowadays is its application for gas storages. The main purpose for the research is to find a better way in storing and delivering combustible gases. All those researches were trying to meet the standard for an effective storage, which was set by US Department of Energy (DOE) at ~6 wt% for gravimetric and 60 kg m^{-3} for volumetric densities.

Many attempts had been made to improve the conventional adsorbents to be able to store more gas molecules. Doping an adsorbent with impurities which can increase the affinity to a specific adsorbate was one of the ways. For example, alkali doped carbon nanotubes has been become a potential adsorbent to be developed (Chen *et al.*, 1999), as well as boron and nitrogen doping (Gai *et.al.*, 2004).

In this paper, several manipulations of pure graphite nanotubes has been made and observed intensively. The first part of the simulation has been revealing a new arrangement of nanotubes performance in storing hydrogen by computer simulations. Then, the second part of the research has succeeded in obtaining Lennard-Jones parameters, written in eq 1, for boron and nitrogen by experiments coupled with simulations, and then using the parameters for measuring boron nitride nanotubes performance in storing hydrogen.

Theoretical Background and Methodology

Several new structures of carbon nanotubes have been studied about their properties. The main purpose of searching a new structure is to improve the properties and capabilities of conventional nanocarbons. For instance, Y shaped carbon nanotubes has been reported by several researchers (Latgé *et al.*, 2005). This shape was able to control the charge between the main channel and the two branches. Another variation of nanotubes was by adding fullerenes (C-60) inside the tubes (Ulbricht *et al.*, 2003). This modification also gained some characteristics improvements.

Boron is suggested to substitute several carbon atoms in nanotubes. Boron has only three electrons bonding, while for a normal graphite structure needs four electrons for its formation. By replacing carbon with boron makes nonotube structure stability decrease. Then, the unstable graphite structure is expected having a greater potential to attract other molecules to recover its stability rather than original graphite. Boron existences will charge nanotubes excessively, which the excess charge is predicted could accelerate adsorption mechanism.

The optimum temperature for adsorption process will be calculated as well as the optimum spacing. The storage temperature is expected close to the ambient temperature by the modification attempts. Meanwhile, the upper pressure of adsorption should not exceed 10 bars; otherwise the modification is not worth implemented.

In this simulation, adsorption delivery term represents the amount of gas that can be released in the process of adsorption followed by desorption due to pressure swing mechanism at a specific temperature and pressure range. Gas adsorption for storage purpose should be carried in a high pressure but must not be exceeding 10 bars otherwise it will not compete with pressurized gas storage. Then, the adsorbed gas can be released by lowering the pressure until the lowest possible pressure at atmospheric pressure. However, there must be some gases still captured inside the adsorbent at ambient pressure due to molecule interactions. So that, adsorption delivery

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terms considered as the most important variable, since that term represents the amount of gas than can be utilized for particular purposes. Thus, in gas storage mechanism not only capability in adsorbing gas is important but also how much gas can be released when decreasing the pressure is also significant.

All the efforts will be done in a computer simulation using Grand Canonical Monte Carlo (GCMC) method. The interactions between adsorbate and adsorbent molecules in this simulation were represented by Lennard-Jones 12-6 equation as described below.

$$V(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad (1)$$

For further adsorption capacity enhancement, some researches have proposed doping method of nanotubes by some impurities to enhance the adsorption capabilities. Alkali dopped nanotubed has been observed and reported could increase the hydrogen uptake. The similar way occurred in boron and nitrogen dopped carbon nanotubes. Furthermore, pure boron nitride nanotubes has been utilized to adsorb hydrogen and reported had a significant improvement compare to pure carbon nanotubes (Wu *et al.*, 2004).

For further study, in this paper, the LJ potential of boron and nitrogen has been measured. The method of measuring the parameters were comparing laboratory experiment isotherms data of boron nitride with data obtained from simulation using GCMC simulation by employing particular parameter values.

The reliable data of boron and nitrogen parameters will give benefits and confidence for further modeling simulation using boron and nitrogen in adsorption fields.

Table 1. Lennard-Jones Interaction Parameters Employed in the Simulations

Parameter	H_2-H_2	C-C
σ (Å)	2.96	3.4
ε (K)	34.2	28

The simulation in this paper used parameters that are listed in Table 1. Then, all procedures and assumptions applied in this paper based on an intensive simulation of gases onto carbonaceous adsorbent that has been well-performed elsewhere (Bhatia and Myers, 2006). One who is interested in the simulation equations and algorithms should refer to the document.

Results and Discussion

New Nanotubes Structure Performance. Even the new structures of any nanotubes have not been applied for adsorption applications, the idea of adding more molecules and changing the structure and arrangement are worthwhile to strive for finding a superb hydrogen adsorbent. This effort's expectation is to get a unique characteristic that can boost the particular properties of carbon as an adsorbent. In this project, the new arrangement of nanotubes will be observed intensively and measured in the potential of storing hydrogen. The project has been observed several structures as pictured below in Figures 1 and 2.

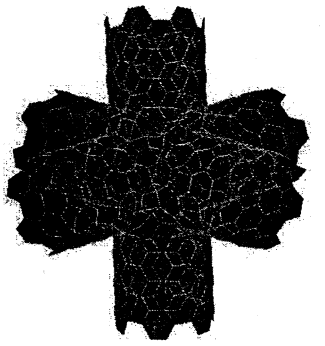

Figure 1. A new arrangement of 3 interconnecting nanotubes (3T).

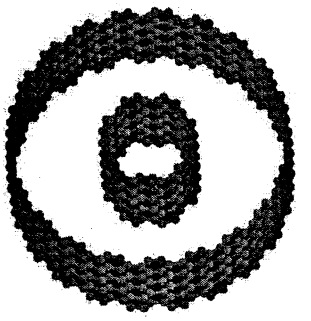

Figure 2. Multi walled nanotubes (MWNT) as one of the observed structures.

The first structure called 3T consists of 3 nanotubes interconnecting each other, while the second structure is made up by 2 nanotubes one inside the other. It is recognized as MWNT (multi walled nanotubes). All above structures has been studied in computer simulations to adsorb hydrogen. Then, the adsorption performance were measured and compared with the ordinary nanotubes arrangement. The comparison is expressed in terms of delivery capability of hydrogen pressure handling between 30 bars to 1.5 bars. Moreover, simulations had been conducted for several temperature points, thus the maximum temperature can be observed as well as the adsorption performance. The comparisons are described in the following figures and tables.

Figure 3 shows the comparison in hydrogen adsorption delivery between the first observed structure (3T) and a single nanotube. The number of carbon atoms that being used in adsorption simulation was slightly different, for the single tube it used 336 carbon atoms and 324 atoms for 3T structure. Then the distance between adjacent tubes was 9A for both structures. For the single tube, at low temperature

below 100 K the delivery is higher than 3T, but after 100 K the condition is change the way around. It is obvious that 3T structure perform better delivery at high temperature but when the temperature approaching 273 K the difference becomes insignificant.

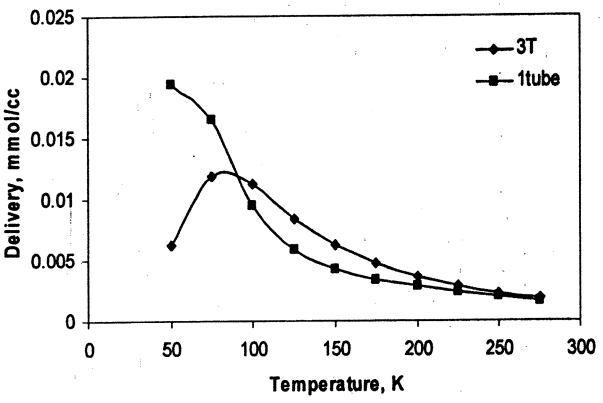

Figure 3. Delivery comparison of 3T with single nanotube at 9Å spacing in mmoles per cc.

Due to a compact structure, 3T structure only occupied smaller volume than an ordinary single tube for the same number of atoms and tube spacing. Thus when the delivery is expressed in terms of moles per grams of adsorbent the delivery of 3T is always below a single nanotube as shown in Figure 4.

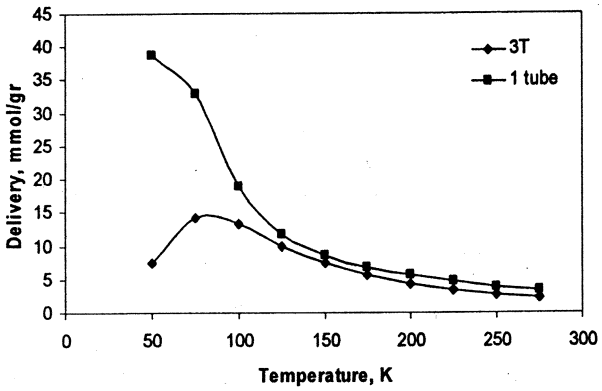

Figure 4. Delivery comparison of 3T with single nanotube at 9Å spacing in mmoles per grams.

The maximum delivery temperature for 3T structure is about 75 K, but for nanotubes it seems still increasing at temperature below 50 K.

The simulations have been conducted with several tube spacing. Below figures represent the results of adsorption simulation using 18Å tube spacing. The result includes the second observed structure (MWNT).

In the higher spacing, the 3T structure behaves similarly with single tube in the delivery performance. For MWNT, the line behaves a slightly different. It performs better delivery than the others at temperature between 75 and 200 K. The delivery expressed in mmoles per grams will be shown by Figure 6.

From Figure 6, it is obvious that the delivery of single tube is always higher than the other structures. MWNT has a close delivery performance to the single tube at 100 K up to 150 K. After that its delivery is lower than others.

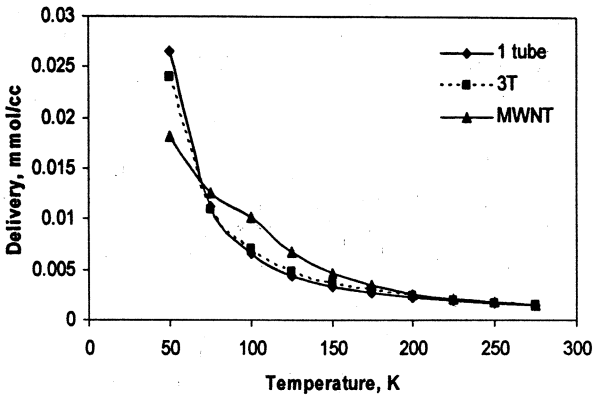

Figure 5. Delivery comparison of 3T and MWNT with single nanotube at 18Å spacing in mmoles per cc.

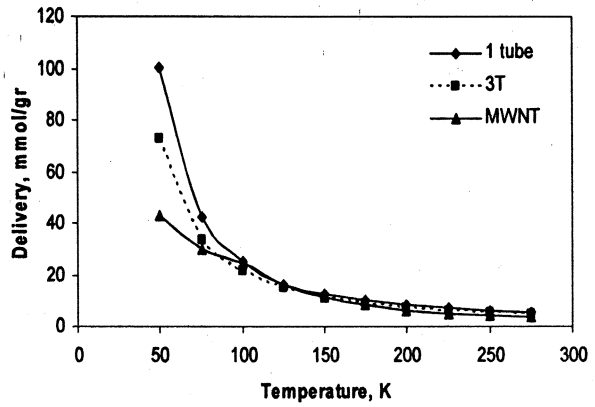

Figure 6. Delivery comparison of 3T and MWNT with single nanotube at 18Å spacing in mmoles per grams.

Bigger tube spacing has been simulated as well. For the 27Å, similar results with 18Å were obtained. The following figures show the results.

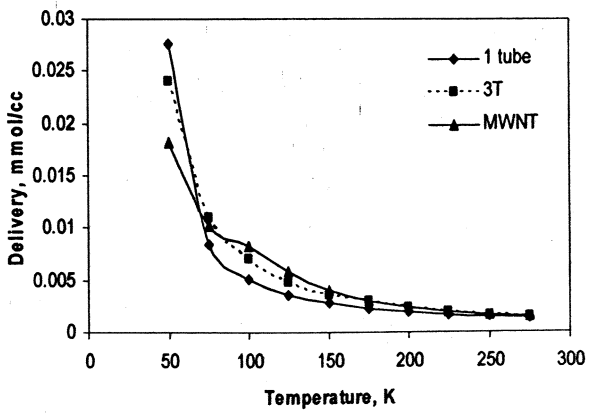

Figure 7. Delivery comparison of 3T and MWNT with single nanotube at 27Å spacing in mmoles per cc.

From the results above, it can be seen that the larger spacing used in the adsorption simulation produced in higher adsorption delivery. But when the largest spacing (27Å) was employed, it exhibited lower delivery than 18Å spacing in term of mmoles per grams. This fact happened due to lower molecular density in larger spacing.

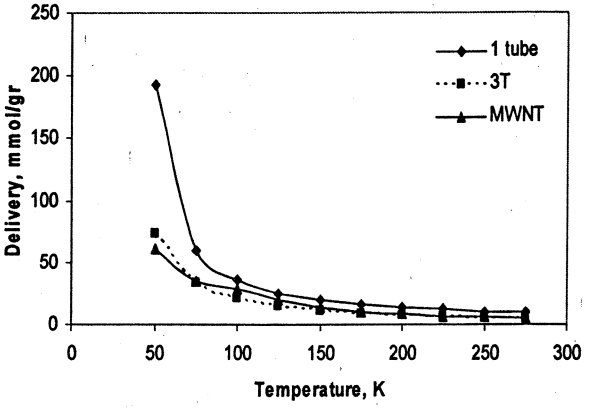

Figure 8. Delivery comparison of 3T and MWNT with single nanotube at 27Å spacing in mmoles per grams.

The number of atoms and the length of each box simulation for all the structure are summarized in the following table.

Table 2. The Summary of Tubes Properties

Tube spacing (Å)	Structure	No of C atoms	Box length (x*y*z) (Å)	Type of NT
9	1 tube	336	19.7*19.7*34.4	C(6,6)
	3T	324	19.7*19.7*19.7	C(6,6)
18	1 tube	576	27.1*27.1*59	C(6,6)
	3T	576	27.1*27.1*27.1	C(6,6)
	MWNT	560	46.5*46.5*12.3	C(7,21)
27	1 tube	816	36.9*36.9*83.6	C(6,6)
	3T	828	36.9*36.9*36.9	C(6,6)
	MWNT	784	55.5*55.5*17.2	C(7,21)

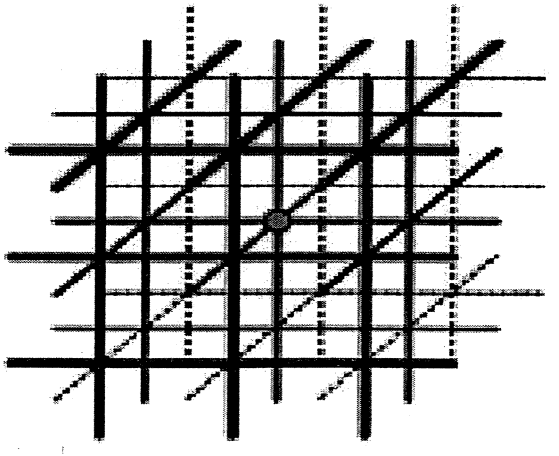

Figure 9. The 27 tubes structure with the circle showing the center.

For gaining confidence of hydrogen delivery of various tube structures, the first structure will be expanded in all directions becomes 27 tubes in connections. Then the 27 tubes structure will be compared with 9 tubes of conventional nanotubes structure, the structure of 27 tubes (27T) is displayed below.

The adsorption delivery of 27 tubes compared with 9 tubes in mole per cc is shown below.

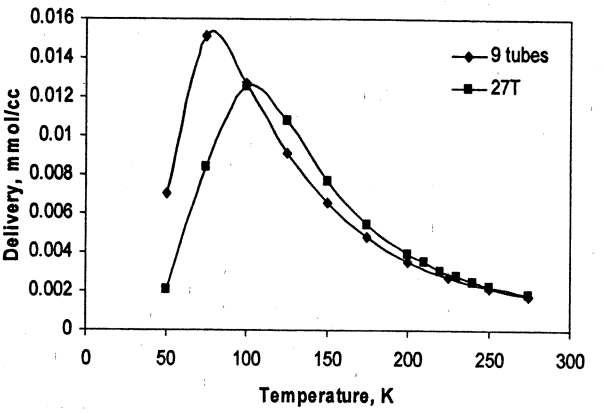

Figure 10. Delivery comparison of 27T with 9 nanotubes at 9Å tube spacing in mmoles per cc.

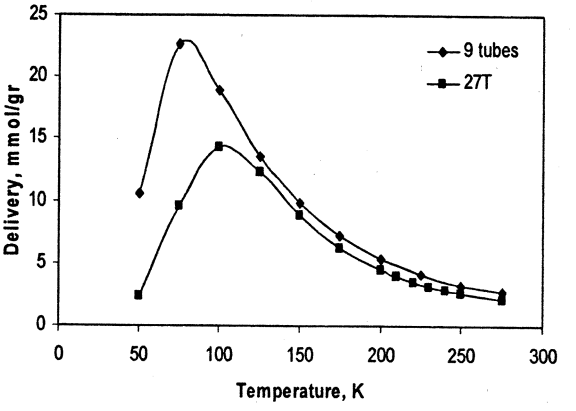

Figure 11. Delivery comparison of 27T with 9 nanotubes at 9Å tube spacing in mmoles per grams.

The result is consistent between 3T and 27T, this makes a sense since the 27 tubes structure is merely constructed from 3 tubes which repeated in every directions.

Boron Nitride Potential Energy Parameters. The result of adsorption experiment data gained using Micromeritic ASAP 2002 for finding adsorption isotherm of Argon at 87.3 K on boron nitride. Several variations of parameter have been used to fit the measurement data. The first trial was using the combination of ε_{boron} = 28 K and $\varepsilon_{nitrogen}$ = 40 K, σ_{boron}= 3.453Å and $\sigma_{nitrogen}$ = 3.367Å. The simulations were conducted in several pore sizes in consideration that a single pore will not satisfy the experiment isotherm (Table 2). The result is shown below.

From the above fitting attempt, the simulation results cannot fit well at low pressure. This fact

suggests that the epsilon values (LJ parameters) are higher than they should be. Thus by reducing the epsilon until its fitted better should be conducted. Another set of parameters has been used. The only changed parameter was $\varepsilon_{nitrogen}$ became 30 K, the new result is shown below.

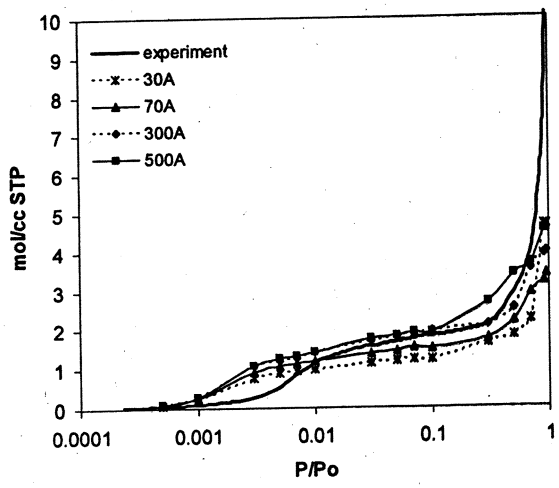

Figure 12. Isotherm fitting using ε_{boron} = 28 K; $\varepsilon_{nitrogen}$ = 40 K; σ_{boron} = 3.453Å and $\sigma_{nitrogen}$ = 3.367Å.

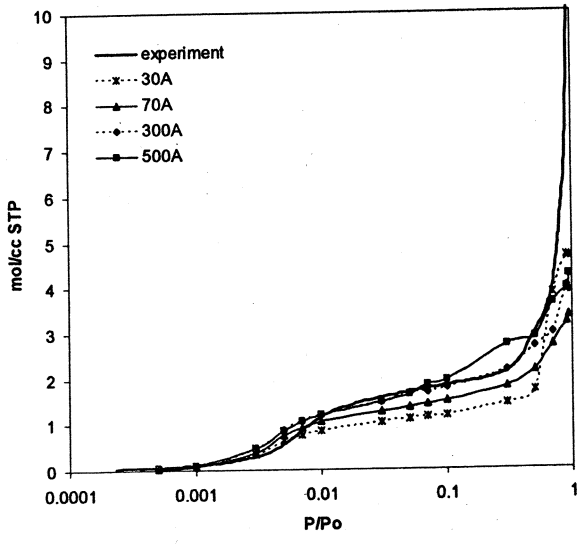

Figure 13. Isotherm fitting using ε_{boron} = 28 K; $\varepsilon_{nitrogen}$ = 30 K; σ_{boron} = 3.453Å and $\sigma_{nitrogen}$ = 3.367Å.

All above isotherms for each pore can be fitted to get close to the experimental isotherm. The fitting require an optimization program. In this optimization, the isotherm of each pore will be multiplied by a partial volume then summed to get total volume in each pressure point. The simulation will search the lowest error by varying the partial volume for each pore. The optimization was carried out then the result is shown in the following figure and table.

The above simulation shows that the solid even nonporous, it can be treated as a porous solid with has several pores. The chosen pore should range at mesopores and macropores region.

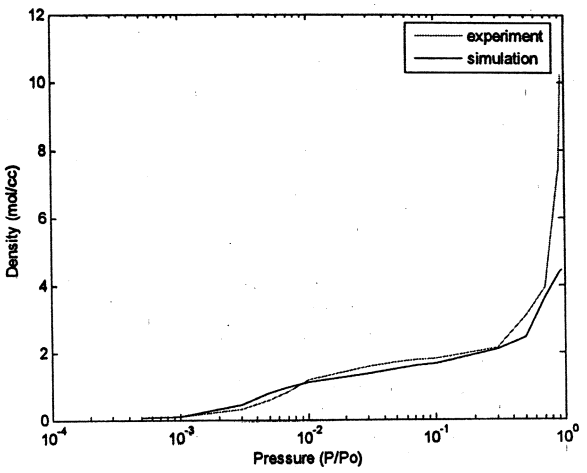

Figure 14. Isotherm fitting using ε_{boron} = 28 K; $\varepsilon_{nitrogen}$ = 30 K; σ_{boron} = 3.453Å and $\sigma_{nitrogen}$ = 3.367Å.

Table 3. The Pores Volume Fraction

Pore width (Å)	Volume fraction
30	0.39
70	0.10
300	0.25
500	0.26

Boron Nitride Delivery Performance. The LJ parameters obtaining from the previous section will be used to simulate hydrogen adsorption and delivery on boron nitride nonatubes. Then the parameters obtained from a literature will be observed as well (Kang and Hwang, 2004). All the parameters are listed in Table 4 below.

Table 4. LJ Parameters

Adsorbent	Type of nanotubes	ε (K)	σ (Å)
Carbon	(6,6)	28	3.4
BN 1	(6,6)	B=28	B=3.45
		N=30	N=3.36
BN 2 (Kang and	(6,6)	B=47.8	B=3.45
Hwang, 2004)		N=72.9	N=3.36

Figure 15 shows the delivery of carbon and boron nitride nanotubes. For BN 1, as the parameters are not much different from carbon, the delivery will not change much as well. However, if the parameters are significantly above the carbon as in BN 2, the delivery shows some improvements (Figure 15).

From the finding above, actually the optimum parameters which lead to the optimum delivery can be determined by simulations. Even the optimum adsorbent which has those optimum parameters may not exist yet, but by simulating with those optimum parameters it can be a clue for seeking the best adsorbent in the future.

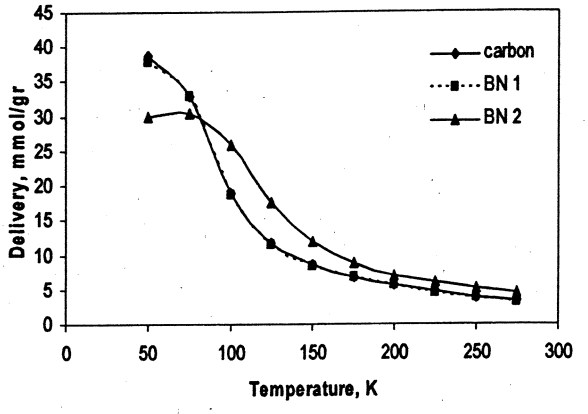

Figure 15. The delivery comparison between carbon and boron nanotubes.

Therefore, in the following section the optimum parameters will be measured. In this simulation the adsorbent structure is nanotubes with 9Å spacing between the tubes. The epsilon will be varied and sigma remains unchanged at 3.4Å. The result is shown in Figure 16.

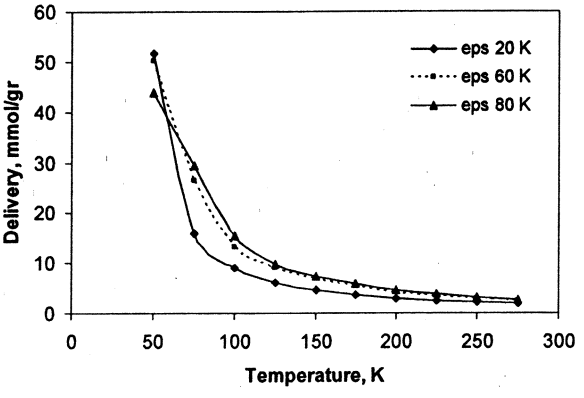

Figure 16. Adsorption delivery in various epsilon values.

From above figure, it shows that LJ parameter (ε) has a great influence in determining delivery of an adsorbent. Small epsilon has high delivery at very low temperature and decays very fast as the temperature goes up. On the other side, bigger epsilon has better delivery at high temperature. Even tough, at higher temperature the difference among the lines is invisible.

Conclusions

The observed structures especially boron nitride nanotubes have a potential to be a compact adsorbent since they occupied smaller volume than ordinary carbon nanotubes. The delivery in terms of moles per cc is better than carbon nanotubes at a particular range of temperature. Then, the tube spacing must be chosen at around 18A for optimum delivery performance.

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Notations

T = Temperature, K
P = Pressure, bar
ε = Lennard-Jones (LJ) parameter, K
σ = Atomic spacing, Å

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