RESULTS AND DISCUSSION

In this section, the simulation results will be discussed. It includes all geometrical parameters, the electronic property and the proton transfer mechanism in chitosan membrane for PEM fuel cell.

1. Geometrical Parameters

Optimized bond lengths and angles of chitosan monomer calculated with the semiempirical PM3, AM1, HF/3-21G* and HF/6-31G* are concluded in Table 1. Structural data obtained from X-ray crystallographical study are also used for comparison. In general, the results have a good agreement to these X-ray data.

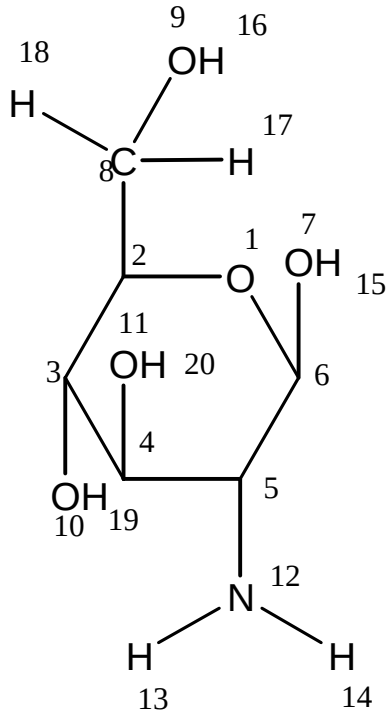


Figure 5 Atomic Numbering of Chitosan Structure.

Table 1 Equilibrium geometrical parameters of chitosan monomer in the ground sate

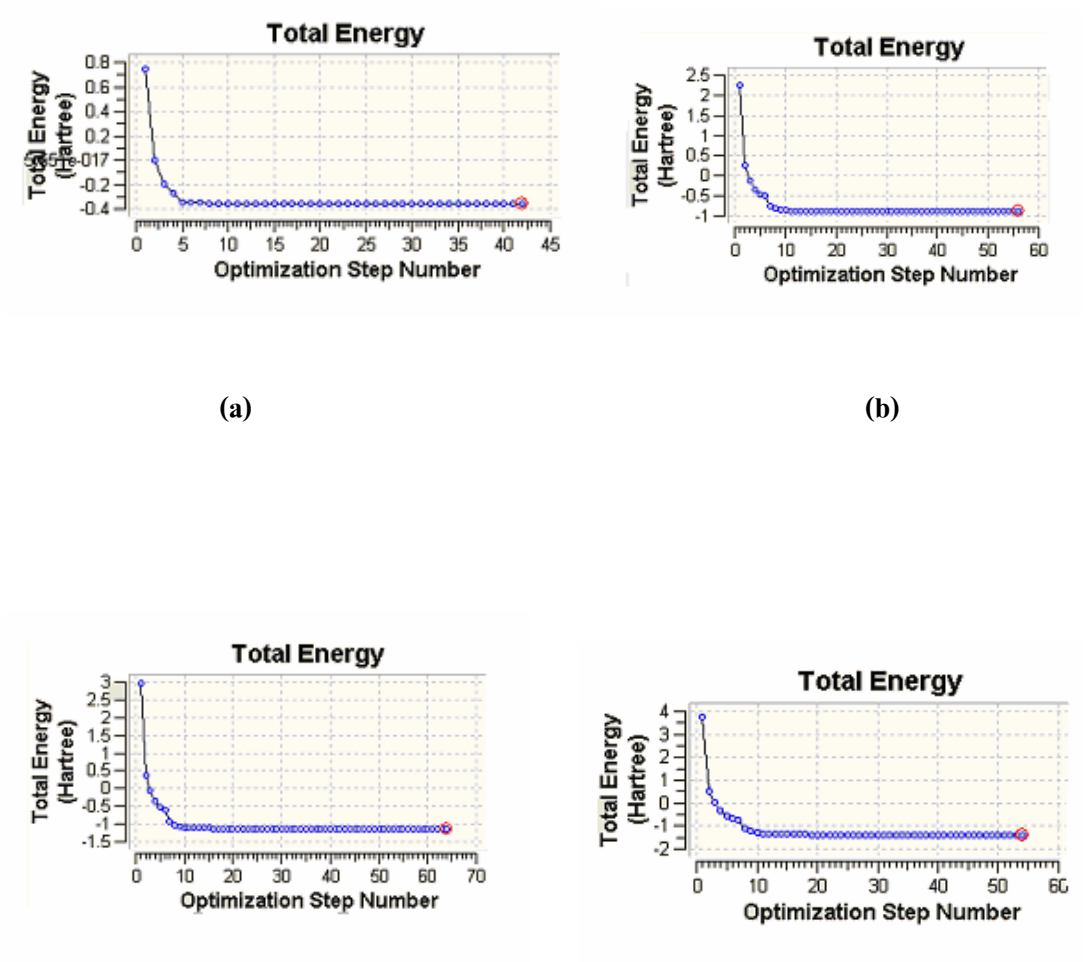
Parameter	PM3	AM1	HF/3-21G*	HF/6-31G*	X-ray
	Bond Lengths (Angstrom)				
O1-C2	1.400	1.398	1.219	1.266	1.394
C2-C3	1.099	1.121	1.196	1.188	1.113
C3-C4	1.385	1.406	1.203	1.232	1.404
C4-C5	1.402	1.555	1.328	1.381	1.412
C5-N12	0.996	1.017	1.101	1.089	1.005
N12-H13	1.504	1.551	1.559	1.523	1.500
N12-H14	1.513	1.503	1.513	1.509	1.509
C5-C6	1.402	1.555	1.309	1.381	1.412
C6-O1	1.262	1.326	1.202	1.222	1.262
O7-H15	1.461	1.488	1.415	1.424	1.460
C2-H8	1.116	1.217	1.399	1.371	1.119
C8-O9	1.429	1.420	1.569	1.556	1.423
C8-H17	1.120	1.335	1.224	1.210	1.120
C8-H18	1.382	1.412	1.321	1.300	1.396
O9-H16	1.360	1.204	1.288	1.243	1.353

Table 1 (Cont'd)

Parameter	PM3	AM1	HF/3-21G*	HF/6-31G*	X-ray
	Bond Angles (Degree)				
C2-O1-C6	120.9	120.5	120.7	120.6	120.6
O1-C2-C3	120.5	120.4	120.4	120.5	118.5
C2-C3-C4	120.9	120.6	120.6	120.7	122.1
C3-C4-C5	118.7	119.1	119.0	118.9	119.2
C4-C5-N1	118.6	118.9	118.6	118.6	116.5
C5-C6-O1	120.4	120.4	120.5	120.7	122.3
C2-C8-O9	131.2	131.4	131.3	130.8	109.4
C6-O7-H15	110.3	110.0	109.7	110.1	105.4
C8-O9-H16	103.3	102.8	103.1	102.7	107.3
C3-O10-H13	108.3	108.6	108.5	108.5	109.8
C4-O11-H20	120.9	120.8	120.9	121.0	122.3
C5-N12-H13	119.8	119.7	119.8	119.6	119.0
C5-N12-H14	119.3	119.7	119.2	119.0	120.5

The bond lengths and bond angles of chitosan monomer considered by semiempirical PM3, AM1, HF/3-21G* and HF/6-31G*. It can be noticed that the results obtained from PM3 and AM1 methods are closer to the X-ray crystallographical data than HF/3-21G* and HF/6-31G* because the PM1 and AM3 methods come from semiemprical while HF/6-31G* is based on the quantum chemical calculations and also has weak point in geometric properties.

The HF/3-21G* and 6-31G* ware used in this study for comparison, Hartree-Fock-3-21G* and 6-31G* are known to have some painful shortcomings, In general, the treatment of the correlation between the motions of electrons in adequate. Due to this, HF can never describe fully the exact energy and the difference is called the correlation energy (Here et al, 1999).



(a) **(b)**

(c) **(d)**

Figure 6 Total energy of chitosan oligomers optimization: (a) monomer (b) dimer (c) trimer (d) tetramer

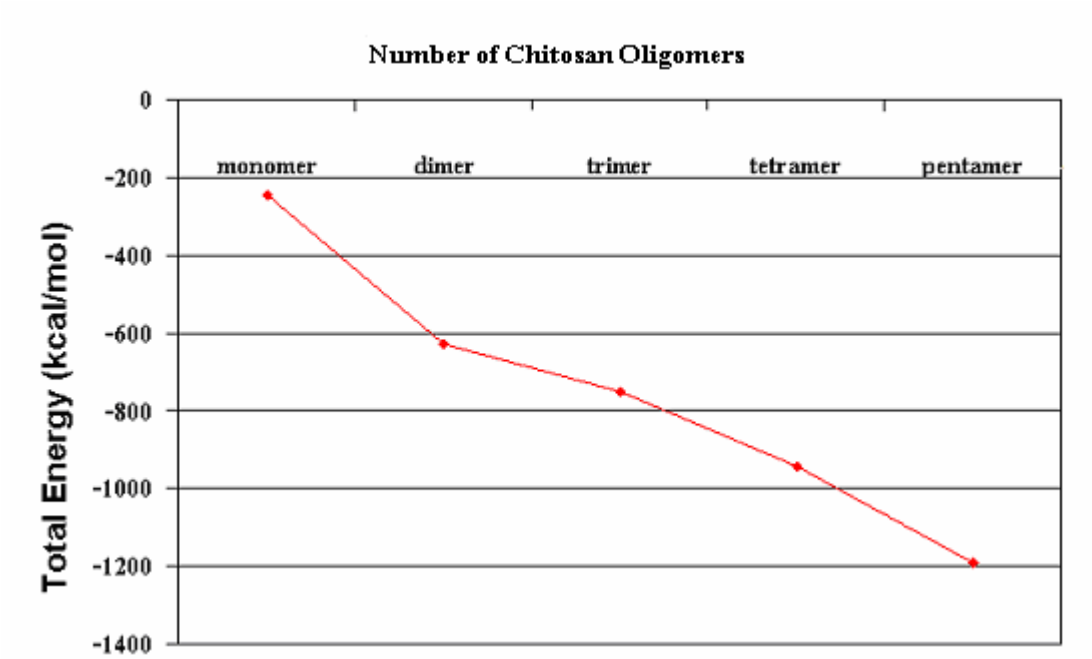


Figure 7 The relative total energy of Chitosan oligomers

The total energy of each chitosan oligomers is shown in figure 6 during their adjustment to the optimum stage. This figure shows the behavior of molecular energy throughout the step of optimization in the range of 40-80 depending on the conformation before optimization. The molecular energy decreases because chitosan oligomers normally adjust their molecular structure to the best stability. The relative total energy of chitosan oligomers is shown in figure 7 in kcal/mol unit. This figure shows that chitosan pentamer has the lowest total energy in this group of oligomers. It is concluded that increasing number of mer of chitosan will decrease the total energy to lower. Thus, this figure could ensure that optimized chitosan polymer will obtain the lowest total energy.

Table 2 summarizes the optimized bond lengths and angles of chitosan dimer; chitosan trimer; chitosan tetramer; and chitosan pentamer by PM3.

Table 2 Equilibrium geometrical parameters of chitosan oligomers in the ground state by semiempirical PM3

Parameter	**dimer**	**trimer**	**tetramer**	**pentamer**
	Bond Lengths (Angstrom)			
O1-C2	1.400	1.399	1.398	1.394
C2-C3	1.099	1.112	1.111	1.113
C3-C4	1.385	1.402	1.400	1.404
C4-C5	0.996	1.049	1.002	1.005
C5-N12	1.504	1.501	1.504	1.500
N12-H13	1.513	1.514	1.512	1.509
N12-H14	1.498	1.500	1.496	1.497
C5-C6	1.402	1.413	1.415	1.412
C6-O1	1.262	1.266	1.264	1.262
O7-H15	1.461	1.462	1.464	1.460
C2-H8	1.116	1.124	1.113	1.119
C8-O9	1.429	1.423	1.423	1.423
C8-H17	1.120	1.125	1.119	1.120
O9-H16	1.382	1.400	1.398	1.396

Table 2 (Cont'd)

Parameter	dimer	trimer	tetramer	pentamer
	Bond Angles (Degree)			
C2-O1-C6	120.9	120.8	120.8	120.9
O1-C2-C3	120.5	120.5	120.6	120.4
C2-C3-C4	120.9	121.0	121.0	121.0
C3-C4-C5	118.7	118.7	118.9	118.8
C4-C5-N1	118.6	118.7	118.7	118.6
C5-C6-O1	120.4	120.5	120.4	120.5
C2-C8-O9	131.2	131.0	131.0	131.1
C6-O7-H15	110.3	110.5	110.3	110.4
C8-O9-H15	103.3	103.3	103.2	103.3
C3-O10-H13	108.3	108.3	108.3	108.2
C4-O11-H20	120.9	120.8	120.9	120.8
C5-N12-H13	119.8	120.0	120.0	120.1
C5-N12-H14	119.3	119.5	119.4	119.4

As can be seen, the bond lengths and bond angles of the first mer of these oligomers are in the same range. It can be concluded that this semiempirical method (PM3) can identify the geometrical parameters of chitosan oligomers. According to this, one can extrapolate the results into the geometrical parameters of chitosan polymer.

2. The electronic property of conducting polymer

In this part, the electronic property of chitosan membrane is discussed to ensure that chitosan membrane has a potential to be a conducting polymer. The application of this conducting polymer is the membrane for PEM fuel cell. This property can be investigated by the semiempirical PM3 and *ab inito* HF/6-31G*.

Table 3 shows the energy gap of chitosan oligomers. The results are plotted in relation between $\frac{1}{no.\ of\ mer}$ and HOMO-LUMO energy differences for determining the energy gap as shown in Figure 5.

Table 3 The Energy gap of chitosan oligomers using PM3 and HF/6-31G*

Method optimization	Oligomers(n)	energy (a.u.)		HOMO-LUMO energy differences	
		HOMO	LUMO	a.u.	eV
PM3	2	-0.17	-0.12	0.05	1.28
	3	-0.17	-0.14	0.03	0.97
	4	-0.16	-0.14	0.02	0.85
	5	-0.16	-0.14	0.02	0.76
HF/6-31G*	2	-0.19	-0.13	0.06	1.65
	3	-0.18	-0.13	0.05	1.39
	4	-0.18	-0.13	0.05	1.26
	5	-0.18	-0.13	0.04	1.20

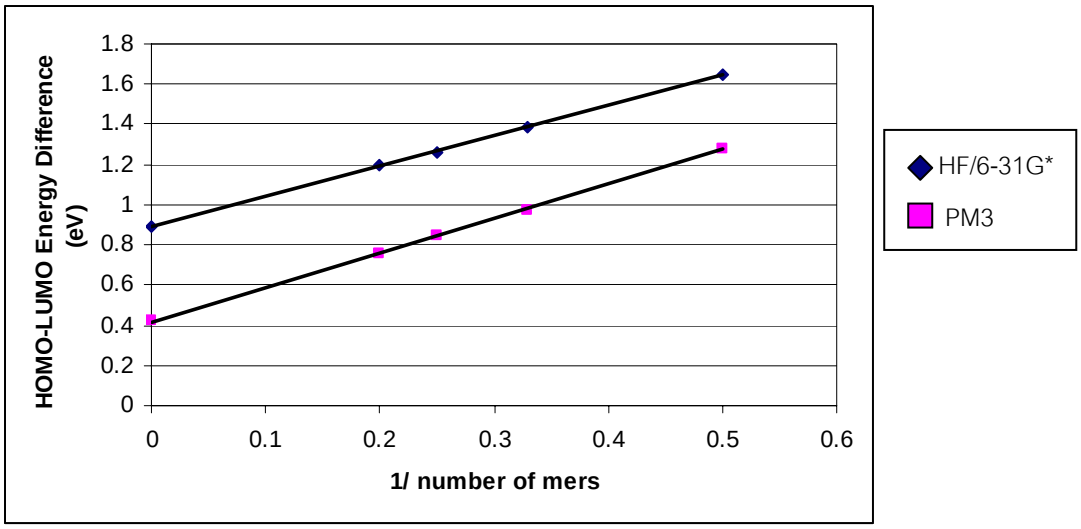


Figure 8 Relationship between $\frac{1}{no.\ of\ mer}$ and HOMO-LUMO energy differences for determining the energy gap

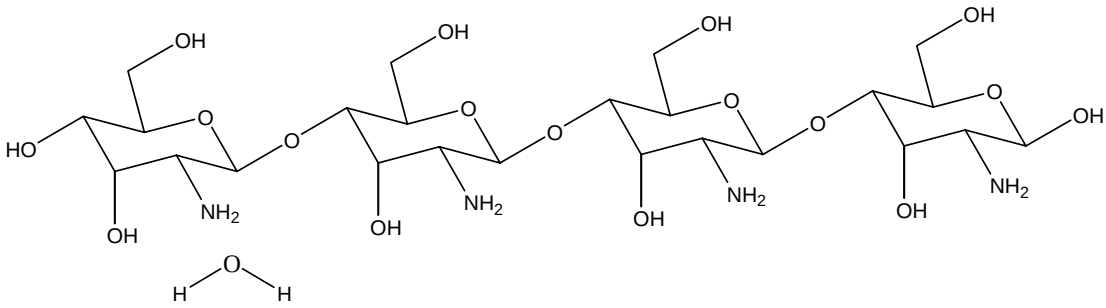
The results are extrapolated to $\frac{1}{\infty}$ or zero since the numbers of mer in polymer are assumed infinity as shown in Figure 8. The energy gap obtained from PM3 is 0.42 eV and from HF/6-1G* is 0.89 eV. This can be implied that the chitosan has enough potential to carry electron because of the near zero energy gap. Therefore, the chitosan can play an action as a conducting polymer.

3. The proton transfer mechanism

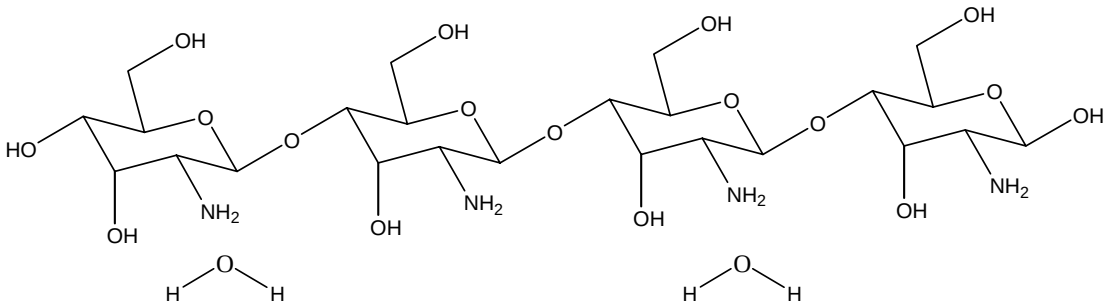
The proton transfer mechanism in this study focused on proton hopping mechanism. The mechanism is an important key to determine the phenomenon occurring during the operation of the fuel cell. The proton will hop from one water molecule in form of hydronium ion to conducting ion in chitosan molecule, in this case is NH_2. The efficiency of the mechanism depends upon the amount of water. In the other hand, the water content influences the performance of the cell. Hence, this research will be classified into 3 cases; 10, 35 and 90% water, to study the suitable water content which will give the best performance of the cell in term

of proton transfer. In addition, each water content will be for chitosan oligomers; from monomer to pentamer.

First, Chitosan tetramer will be studied by varying the amount of water from 1 water molecule to 8 water molecules for searching for the suitable water molecules which give the lowest total energy. This will be the guideline for choosing the amount of water to study for the proton hopping mechanism. Figure 9 shows the schematic for Chitosan tetramer with the varying amount of water.



(a)



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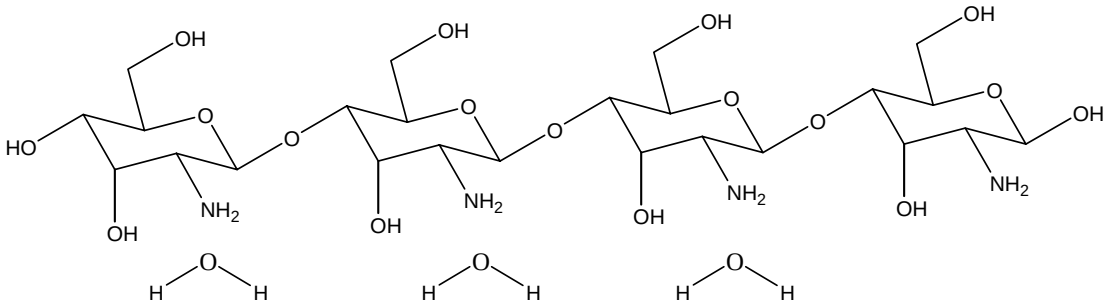

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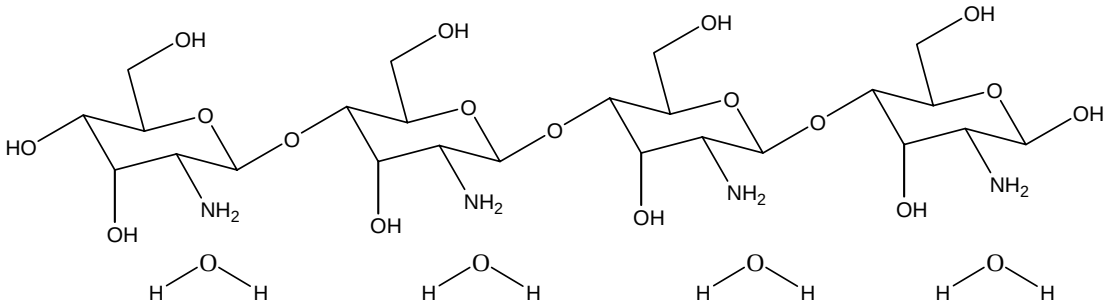

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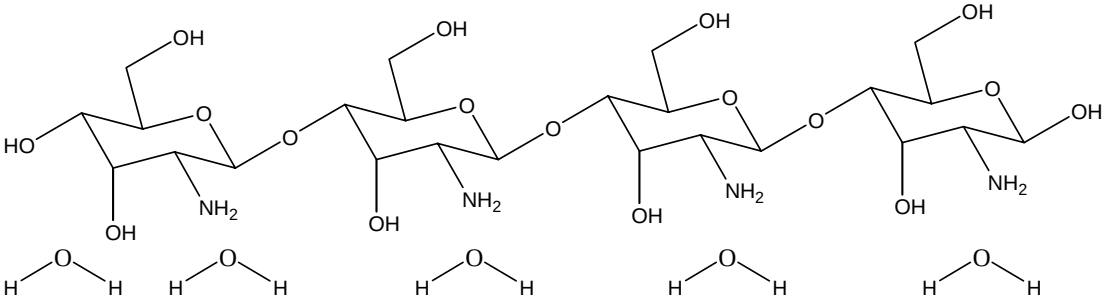

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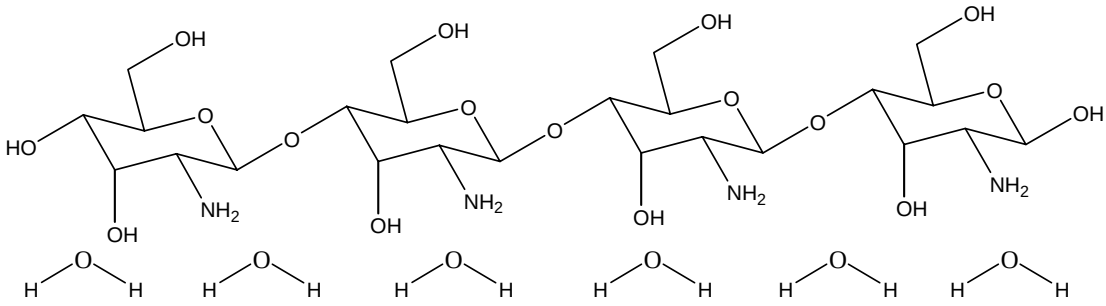
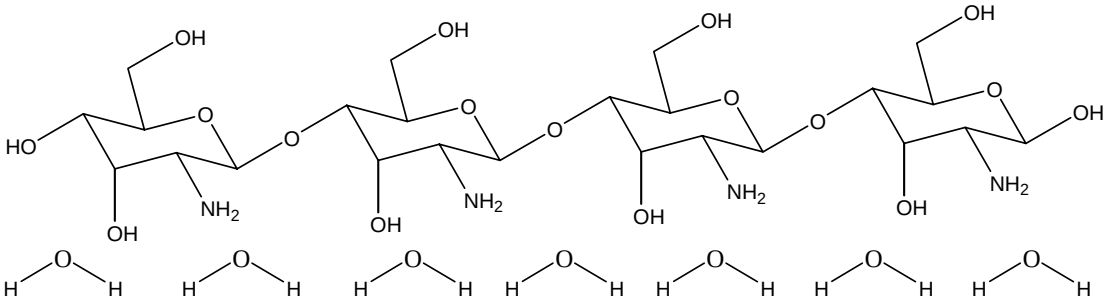


(f)



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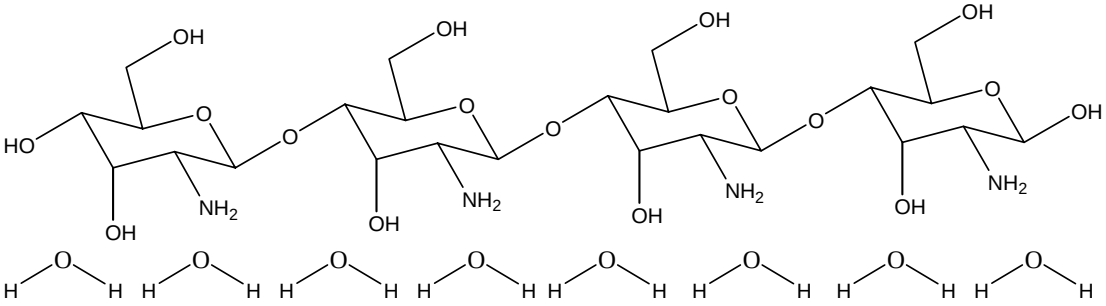


(h)

Figure 9 The schematic of Chitosan tetramer with the different amount of water;

(a) 1 water molecule (b) 2 water molecules (c) 3 water molecules

(d) 4 water molecules (e) 5 water molecules (f) 6 water molecules

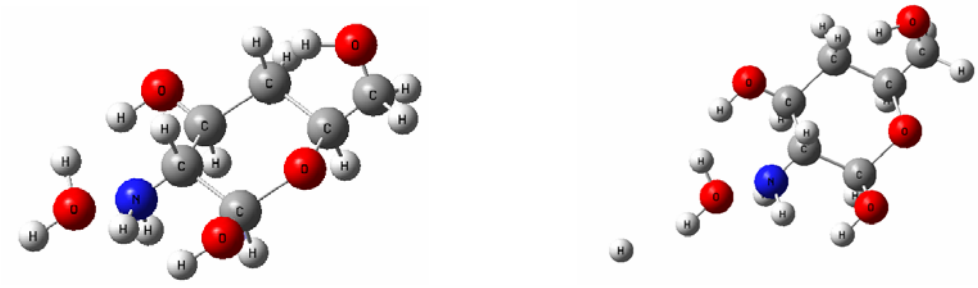
(g) 7 water molecules (h) 8 water molecules

Table 4 The total energy of Chitosan tetramer with the different amount of water

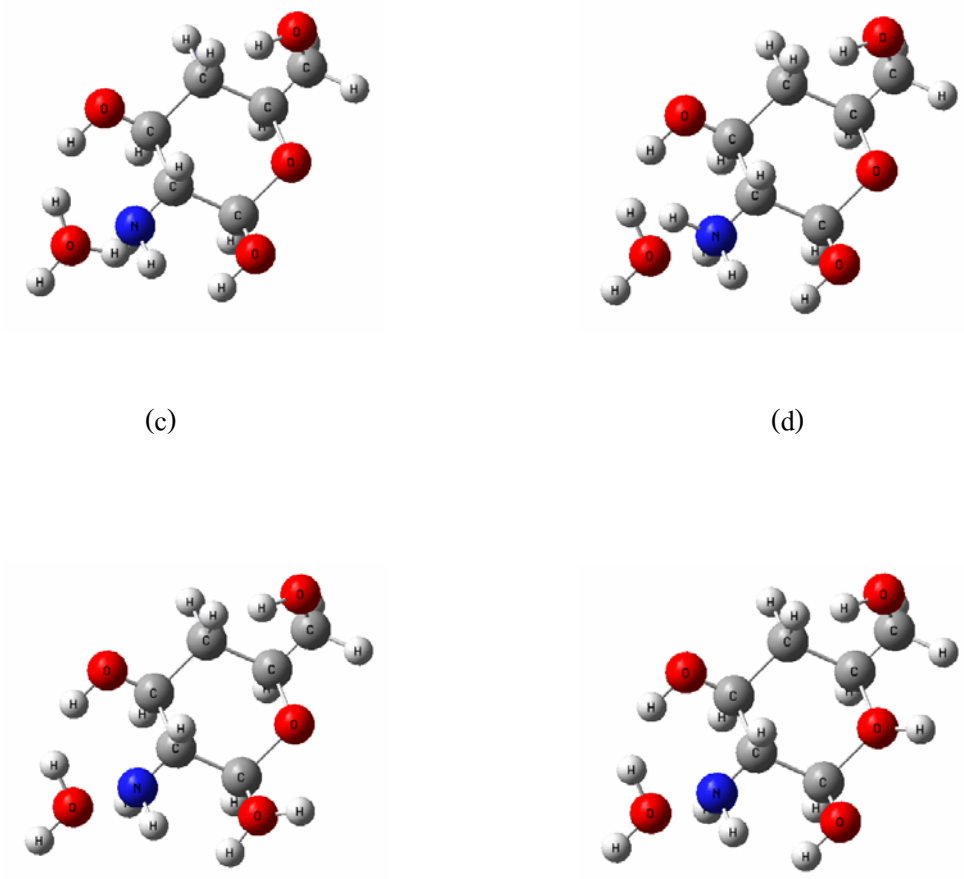
Chitosan tetramer with the different amount of water	Total Energy (kcal/mol)
1 water molecule	-712.6
2 water molecules	-796.4
3 water molecules	-845.2
4 water molecules	-915.6
5 water molecules	-1068.2
6 water molecules	-1102.6
7 water molecules	-870.5
8 water molecules	-455.9

Table 4 shows the total energy of Chitosan tetramer with the different amount of water. From the table, it will be noticed that Chitosan tetramer with 5 and 6 water molecules give the lowest total energy. It will be concluded that the suitable amount of water of Chitosan tetramer would be 5 or 6 molecules. When comparing the suitable amount of water with the 17 active sites of Chitosan tetramer, it will be found that the suitable one is about 35%.

3.1 Chitosan oligomers with 10% water content



(a) (b)



(c) (d)

(e) (f)

Figure 10 The schematic of proton transfer in chitosan monomer with 10 % water content

Figure 10 shows the schematic of proton transfer through chitosan monomer. Figure 10 (a) shows the chitosan with one molecule of water. The single proton begins to transfer through the monomer in Figure 10 (b). That proton interacts with water molecule to form Hydronium ion as shoen in Figure 10 (c). Then, it hops from water molecule to the active site of the chitosan monomer (NH_2) as shown in Figure 10 (d). Next, it hops again to other active sites of the monomer; OH and C-O-C as shown in Figure 10 (e) and (f). Finally, it will leave the monomer. It is noticed that the limitation of water molecule makes the transfer difficulty. The reason is the pathway of proton transfer depends on the distance between the water molecule and the active sites of the monomer or between the active sites within the monomer. From this figure the length

between water molecule and NH_2, NH_2 and OH, and OH and OH are about 1.35, 2.32, and 2.54 Angstrom respectively.

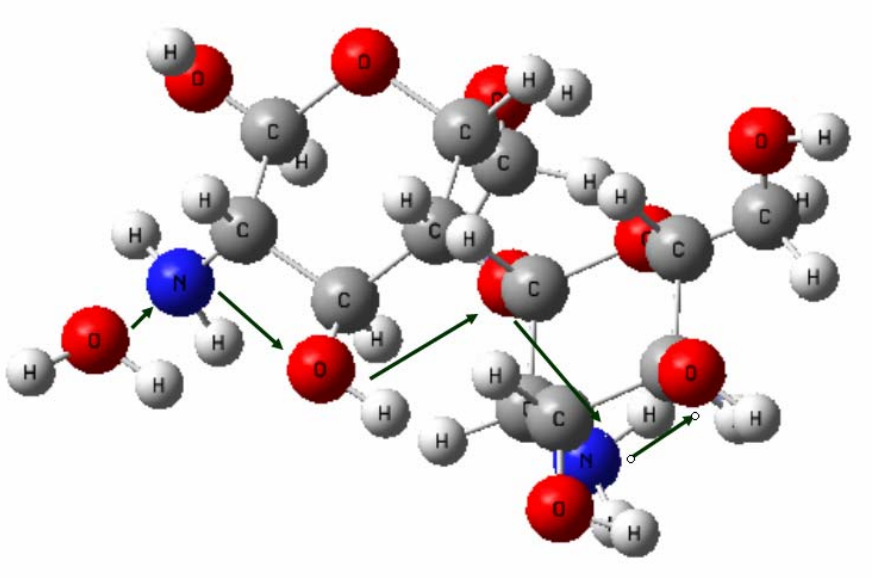


Figure 11 Chitosan dimer with 10 % water content

Refer to previous figure; the water molecule initiates the proton transfer in monomer. Next, the figure 11 shows chitosan dimer with one molecule of water at the first mer. From this figure the length between water molecule and NH_2, NH_2 and OH, and OH and OH are about 1.32, 2.42, and 2.44 Angstrom respectively. It is noticed that the dimer chain is longer than monomer but the amount of water is still the same. This reason makes the proton transfer difficulty in the dimer.

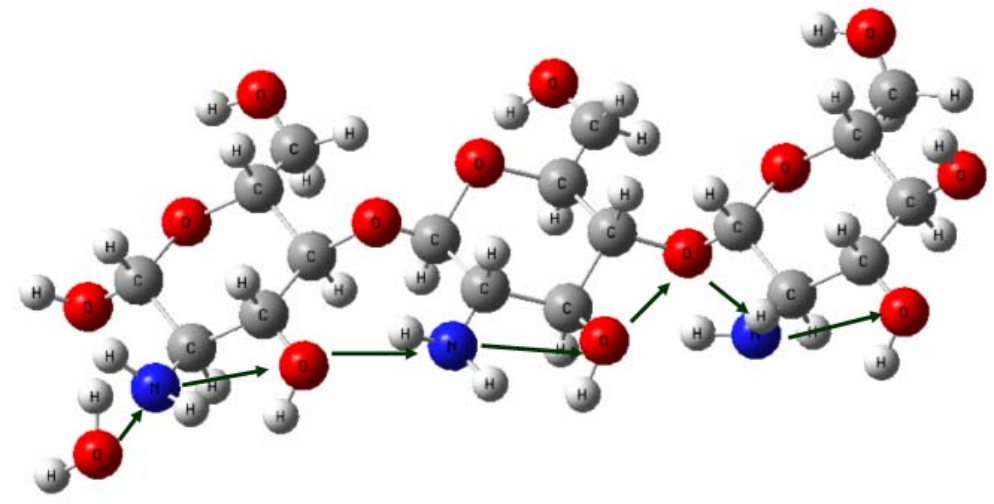


Figure 12 Chitosan trimer with 10% water content

Chitosan trimer with one molecule of water at the first mer is illustrated in Figure 12. From this figure the length between water molecule and NH_2, NH_2 and OH, and OH and OH are about 1.45, 2.36, and 2.39 Angstrom respectively.

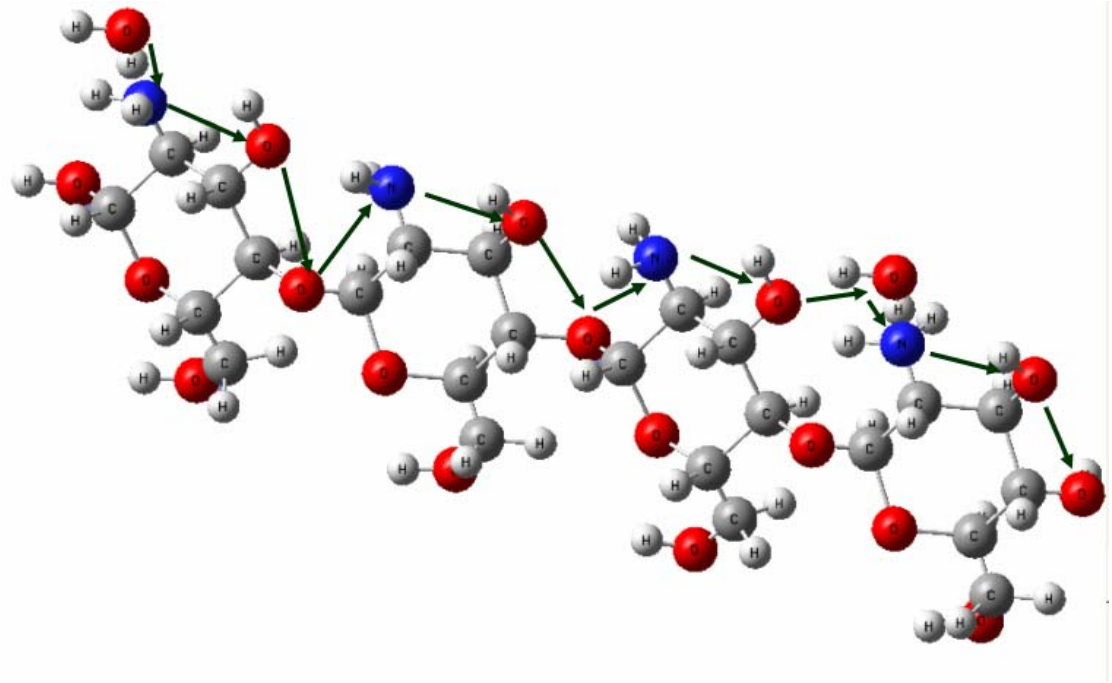


Figure 13 Chitosan tetramer with 10% water content

Figure 13 shows chitosan tetramer with two molecule of water, the first one is at the first mer and the latter is at the last mer of the tetramer. The length between the first water molecule and NH_2 of the first mer, NH_2 and OH of the first mer, OH and OH of the first mer, and NH_2 of the last mer and the second water molecule are about 1.45, 2.36, 2.39, 1.32 Angstrom respectively.

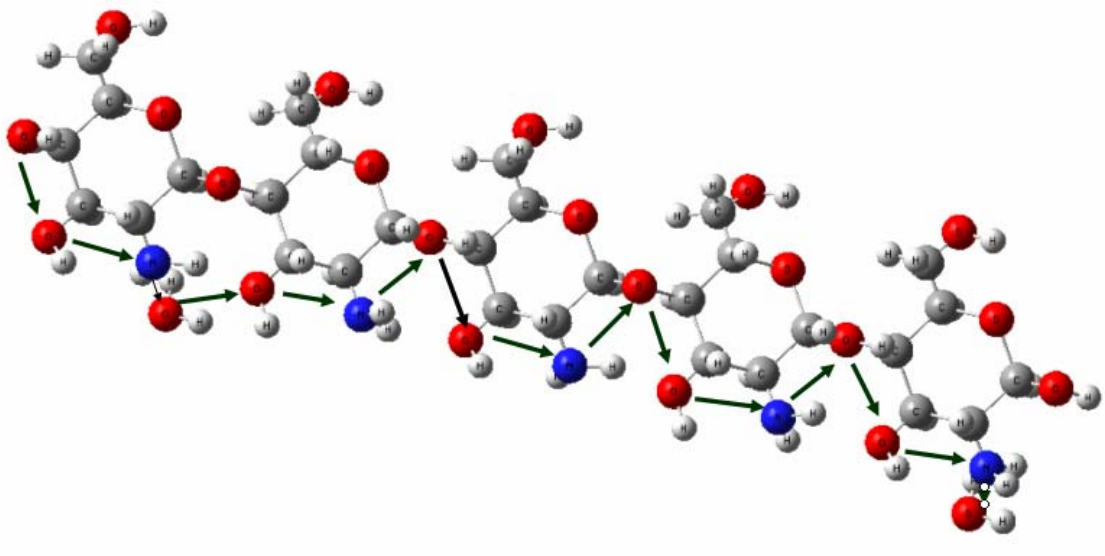
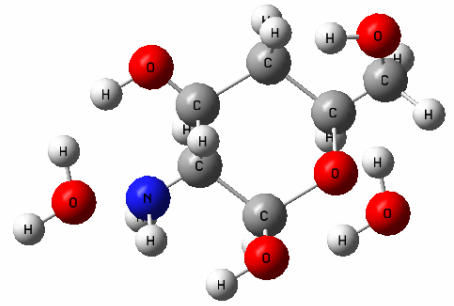


Figure 14 Chitosan pentamer with 10% water content

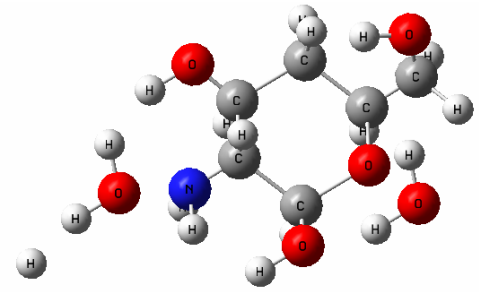
Chitosan pentamer with two molecule of water is illustrated in Figure 14, the first one is at the first mer and the latter is at the last mer of the tetramer. From this figure the length between the first water molecule and NH_2 of the first mer, NH_2 and OH of the first mer, OH and OH of the first mer, and NH_2 of the last mer and the second water molecule are about 1.39, 2.24, 2.15, 1.19 Angstrom respectively.

From the result, the proton transfer in chitosan oligomers with 10% water content is difficult to happen because of the small amount of water. It is noticed that the length between water molecule and the active site of the chitosan monomer is less than the length between the active sites within the monomer. Thus, the proton transfers between the active sites within the monomer will hardly occur compared to the proton hopping from water to the active site of chitosan.

3.2 Chitosan oligomers with 35% water content



(a)



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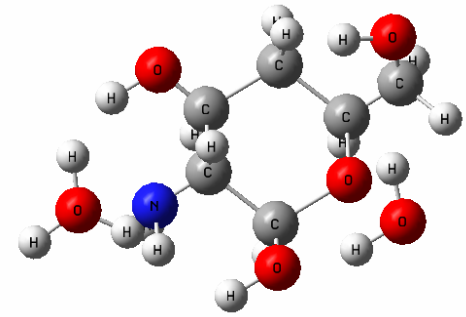

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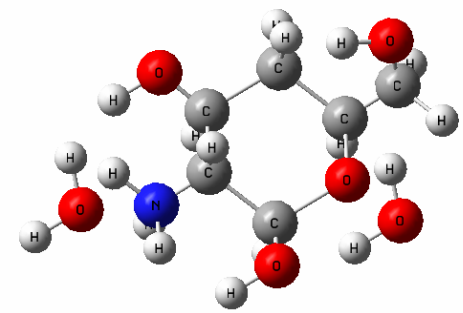
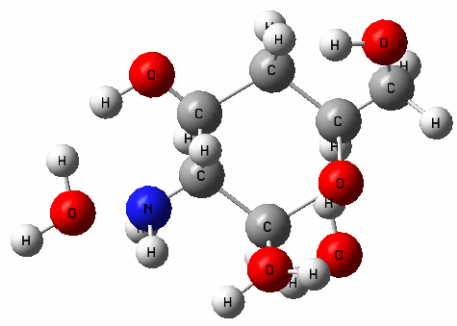


(d)



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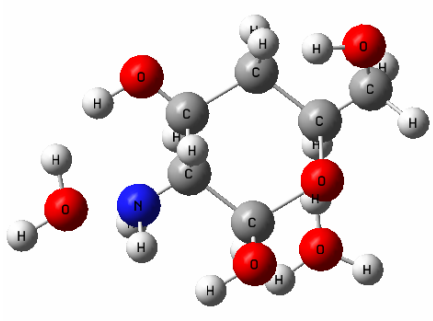

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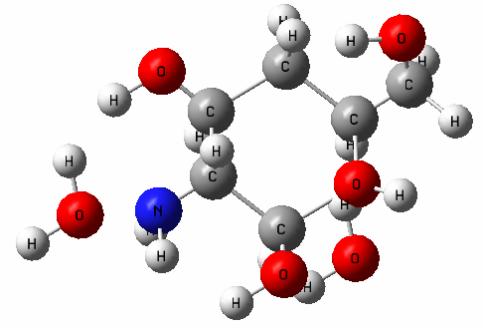


(g)

Figure 15 The schematic shots of proton transfer in chitosan monomer with 35 % water content

Figure 15 shows of proton transfer through chitosan monomer. Figure 15 (a) shows the chitosan with two molecules of water before the transfer. Figure 15 (b) shows that proton begins to transfer through the monomer. Figure 15 (c) shows that proton interacts with water molecule to form hydronium ion then it hops from water molecule to the active site of the chitosan monomer

(NH_2) as shown in figure 15 (d). Next, it hops again to other active sites of the monomer (OH). Figure 15 (f) shows that proton hops from the active site to another water molecule before it transfers to the other active site again which is C-O-C as shown in Figure 15 (g). Finally, it will leave the monomer. According to the proton transfer so called proton pathway, one is noticed that the amount of water molecule is sufficient to carry the proton. With this amount of water molecule, the proton transfer can move easier than that of 10% water content. From this figure the length between the first water molecule and NH_2 of the monomer, NH_2 and OH, OH and OH, and C-O-C and the second water molecule are about 1.39, 2.24, 2.15, and 1.19 Angstrom respectively.

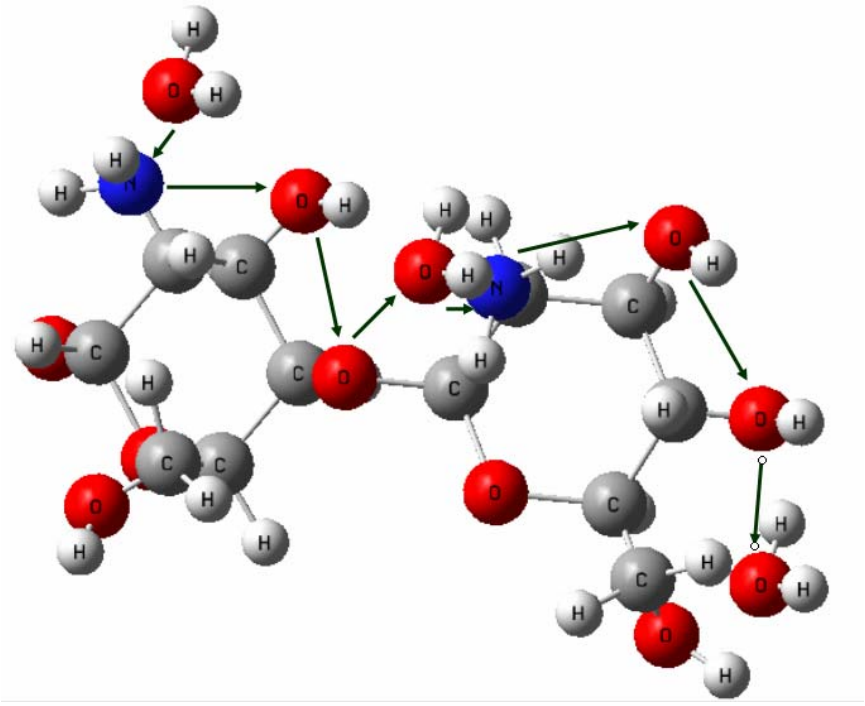


Figure 16 Chitosan dimer with 35 % water content

Figure 16 shows chitosan dimer with two water molecules, one is at the first mer and another is at the last mer. From this figure the length between the first water molecule and NH_2 of the first mer, NH_2 and OH, OH and C-O-C, C-O-C and OH, and OH and the second water

molecule are about 1.29, 2.36, 2.69, 1.96, and 1.23 Angstrom respectively. The result differs from that of 10% water content because of the different amount of water.

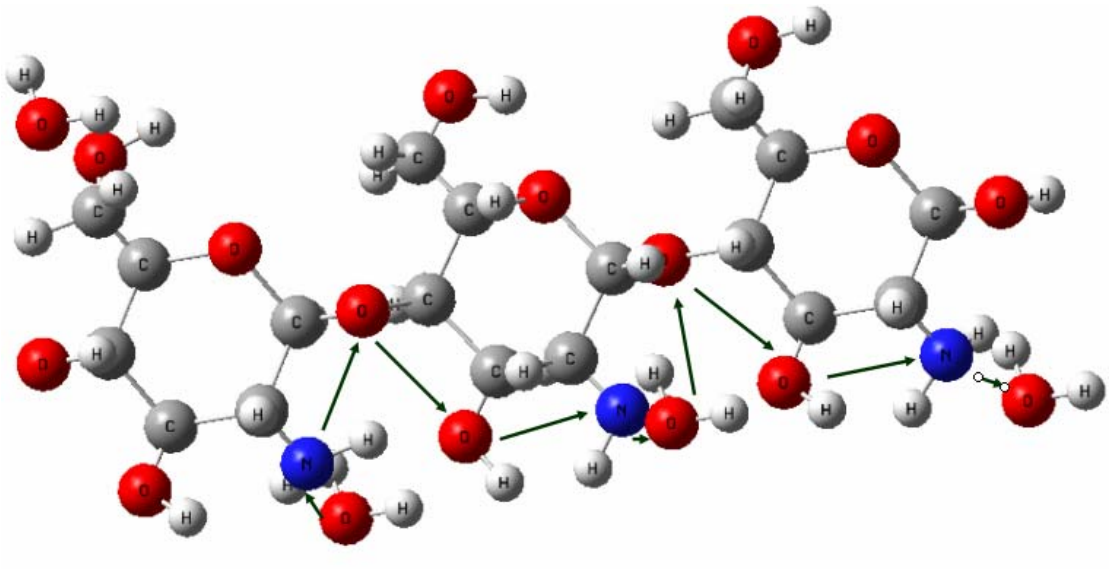


Figure 17 Chitosan trimer with 35% water content

The chitosan trimer with four water molecules due to the percentage of the water amount is shown in Figure 17. The length between the water molecule and OH of the first mer, the water molecule and NH_2 of the first mer, the water molecule and NH_2 of the second mer, and the water molecule and NH_2 of the third mer are about 1.18, 1.42, 1.36, and 1.23 Angstrom respectively.

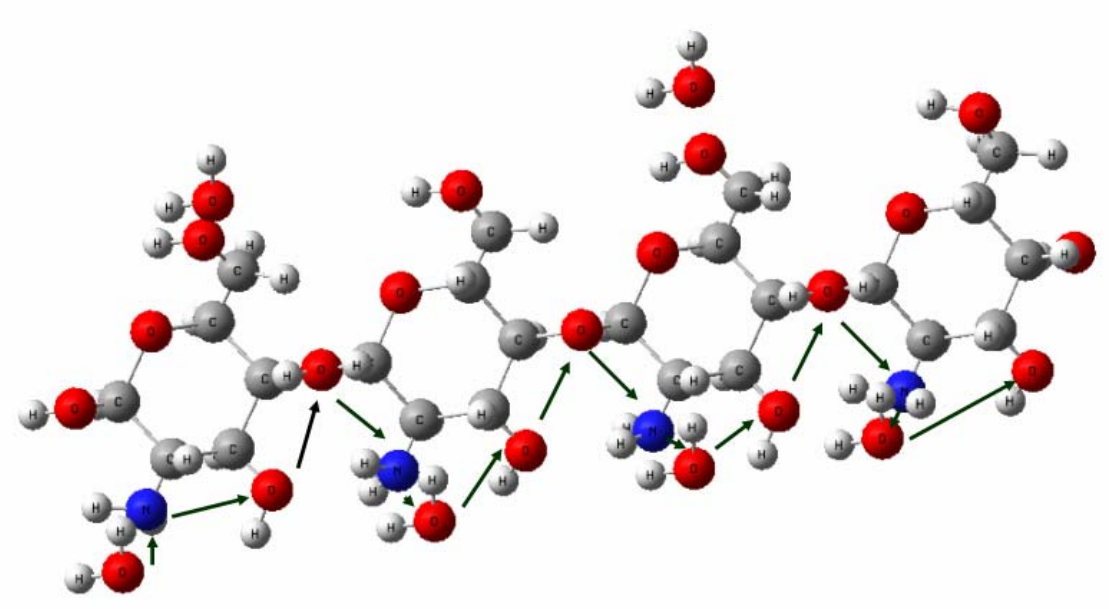


Figure 18 Chitosan tetramer with 35% water content

Figure 18 shows chitosan tetramer with six water molecules. Their length of particular bonds are

- water molecule and OH of the first mer = 1.28 Angstrom
- water molecule and NH_2 of the first mer = 1.42 Angstrom
- water molecule and NH_2 of the second mer = 1.54 Angstrom
- water molecule and NH_2 of the third mer = 1.74 Angstrom
- water molecule and OH of the third mer = 1.16 Angstrom
- water molecule and NH_2 of the fourth mer = 1.53 Angstrom

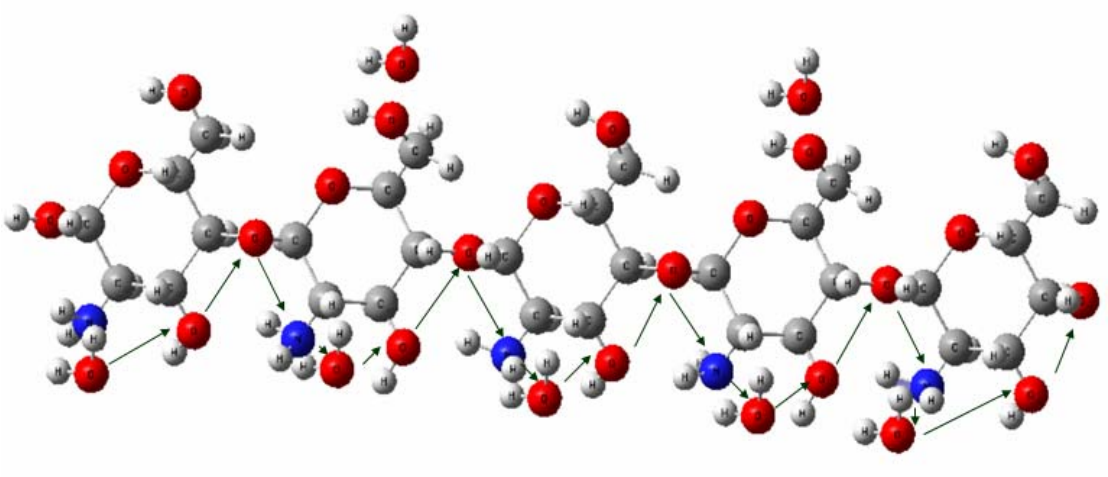


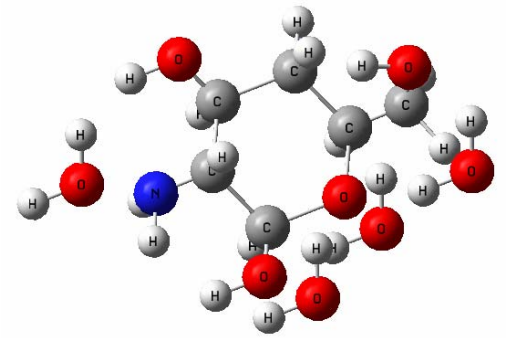
Figure 19 Chitosan pentamer with 35% water content

Figure 19 shows chitosan tetramer with six water molecules. Their length of particular bonds are

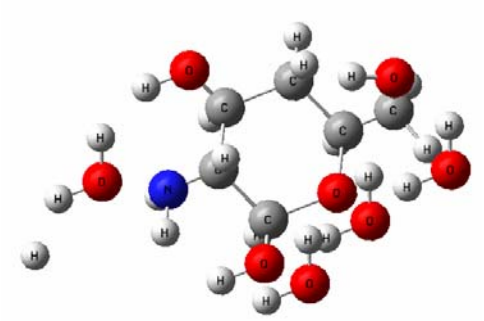
- water molecule and OH of the first mer = 1.14 Angstrom
- water molecule and NH_2 of the first mer = 1.23 Angstrom
- water molecule and NH_2 of the second mer = 1.22 Angstrom
- water molecule and NH_2 of the third mer = 1.40 Angstrom
- water molecule and OH of the third mer = 1.34 Angstrom
- water molecule and NH_2 of the fourth mer = 1.22 Angstrom
- water molecule and OH of the fourth mer = 1.53 Angstrom

The proton transfer in chitosan oligomers with 35% water content is consistent. The amount of water is in good range compared with the active sites of chitosan oligomers. The chitosan oligomers are surrounded by them, thus, proton can hop from one water molecule to the active site and then hop to another water molecule which is easier than that of 10% water content.

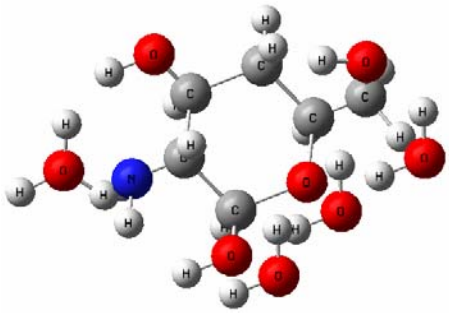
3.3 Chitosan oligomers with 90% water content



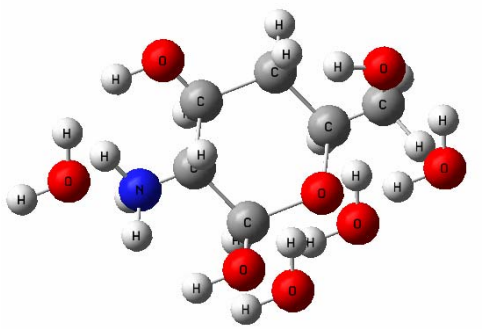
(a)



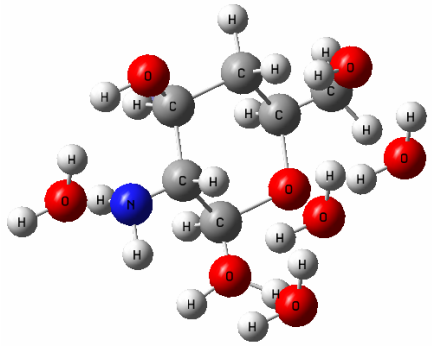
(b)



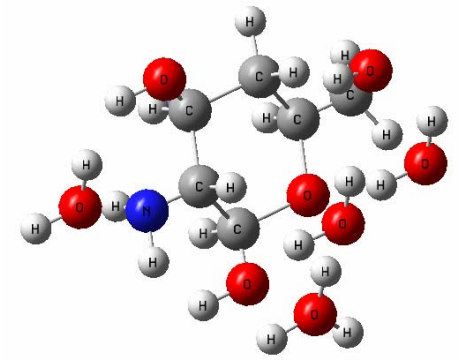
(c)



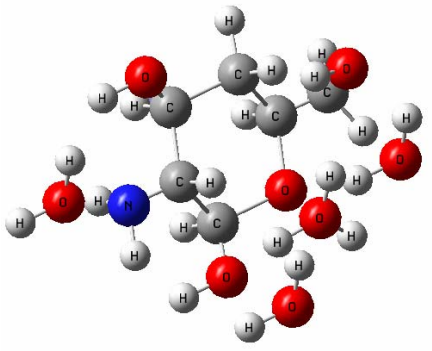
(d)



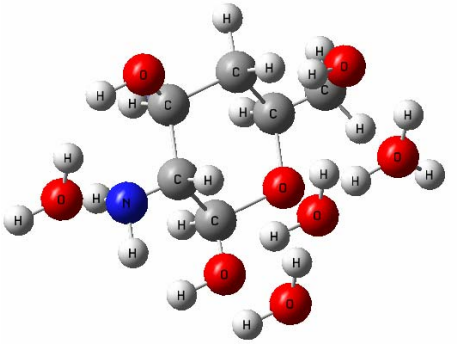
(e)



(f)



(g)



(h)

Figure 20 The schematic of proton transfer in chitosan monomer with 90 % water content

Figure 19 shows proton transfer through chitosan monomer. Figure 20 (a) shows the chitosan with four molecules of water before the transfer. Figure 20 (b) shows that proton begins to transfer through the monomer. Figure 20 (c) shows that proton interacts with water molecule to form hydronium ion then it hops from water molecule to the active site of the chitosan monomer which is NH_2 as shown in figure 20 (d), next it hops again to other active sites of the monomer; OH as shown in figure 20 (e). Figure 20 (f), (g) and (h) show that proton choose to hop form water molecule to the others because the distance between the water molecules are closer than the distance between the water molecule and the active sites of the monomer. Finally, it will leave the monomer. It is noticed from this figure that the large amount of water molecule can induce the hopping of proton from water to water. In addition, the large amount of water will cause flooding in the membrane which decreases the performance the proton transfer since the proton will interact with water in hydronium ion form easier than that of the active sites of the monomer.

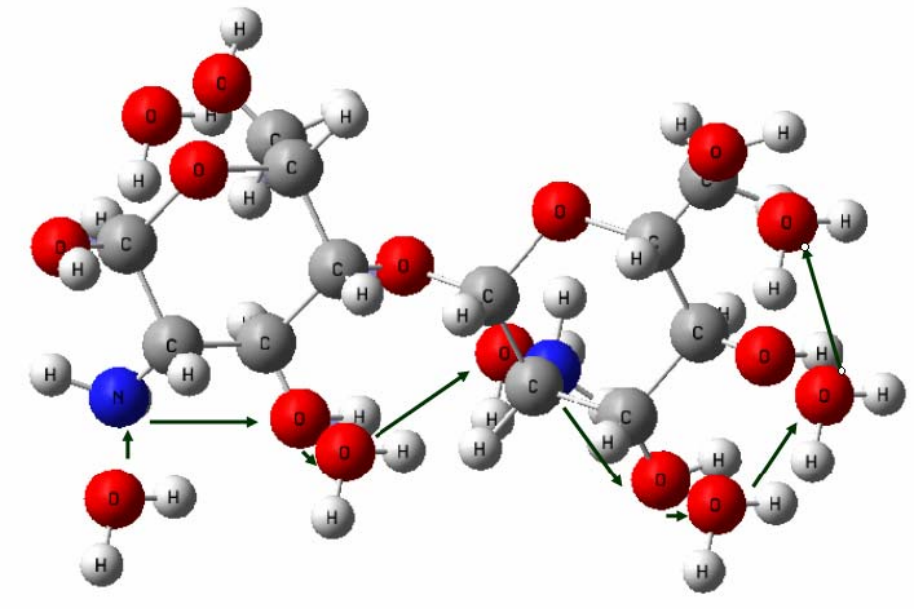


Figure 21 Chitosan dimer with 90 % water content

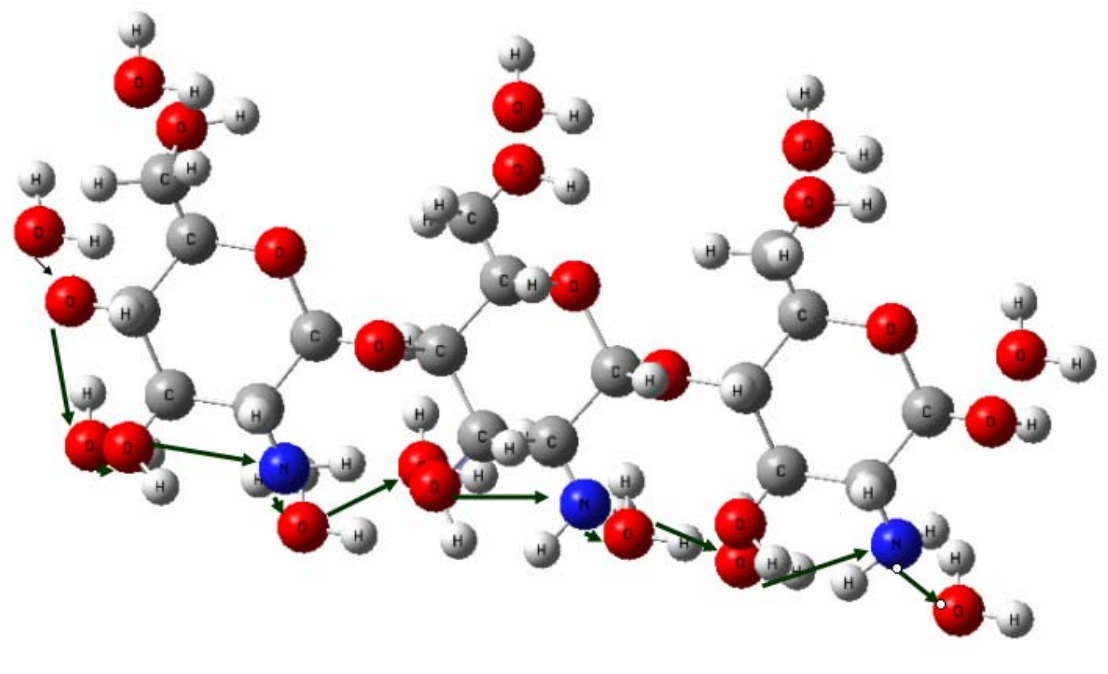


Figure 22 Chitosan trimer with 90% water content

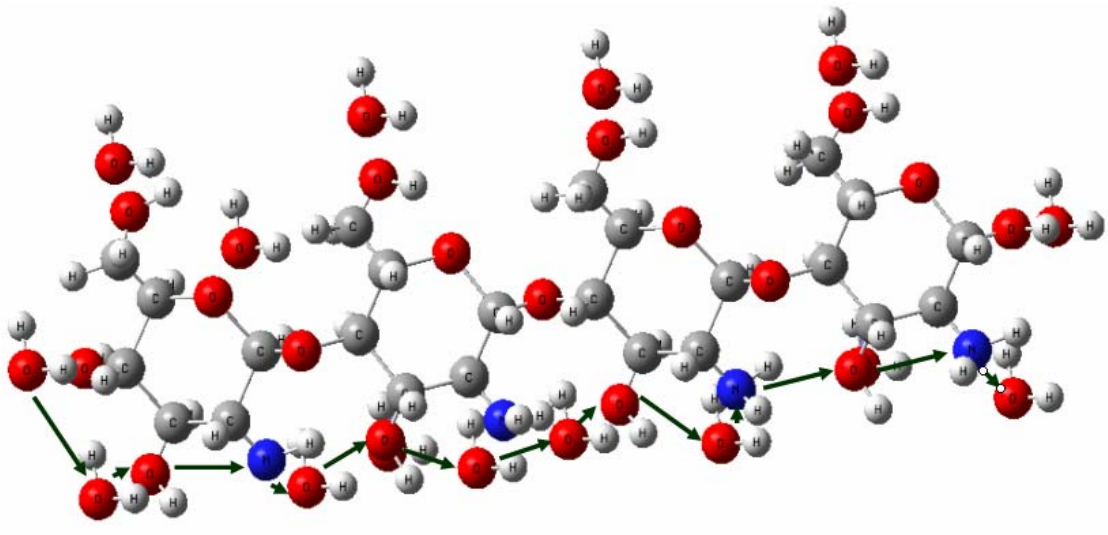


Figure 23 Chitosan tetramer with 90% water content

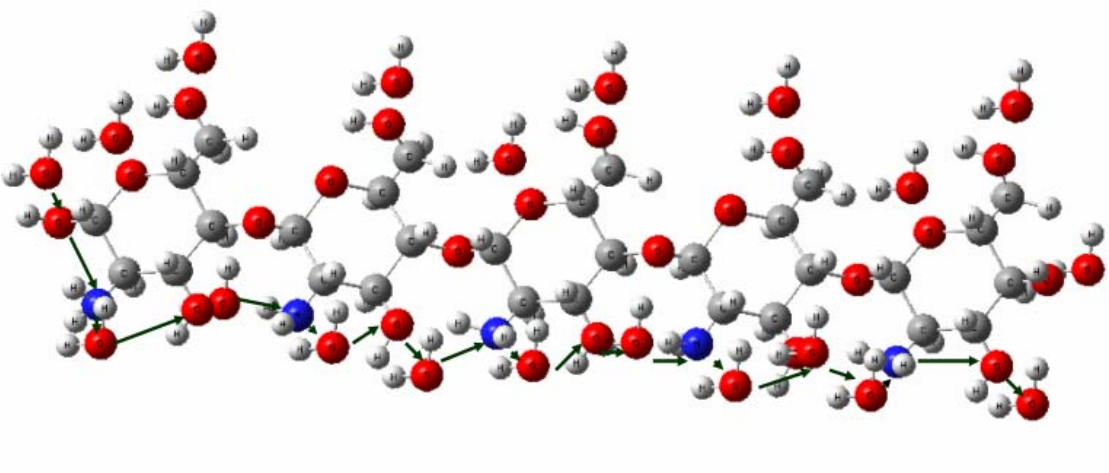


Figure 24 Chitosan pentamer with 90% water content

These figures (Figures 20-24) show chitosan oligomer with the large amount of water molecules, they surround the oligomerrs. From these figures, the lengths between the water molecule and the active sites of the oligomers are in the range of 1.1-1.6 Angstrom.

The proton transfer in chitosan oligomers with 90% water content is so difficult to really happen because of the large amount of water. It is noticed that the large amount of water affects the interaction between proton and the water molecule in form of hydronium ion. In addition, the 90% water content, the water molecules are closer than the distance between them and the active sites of the oligomers, thus, they prefer to keep their form of hydronium ion.

4. The Electricity Calculation

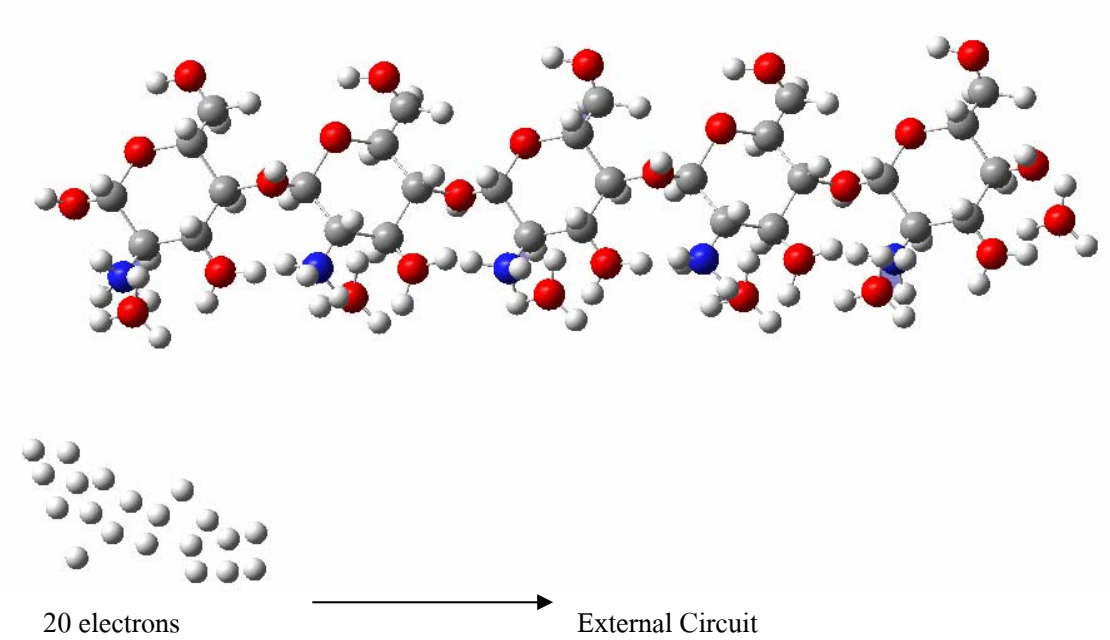


Figure 25 The chitosan pentamer with 35% water and released electron

Refer to Figure 25, the proton transfer mechanism through the chitosan membrane will release an equivalent number of electron. For example, the chitosan pentamer with 35% water content has 20 active sites, thus, the number of electron from this oligomer could be 20. This amount of electron can have some engineering potential sense. In principle, the current can be calculated from the number of electron. One electron has the charge of 1.6×10^{-19} Coulomb. The electrical current can be calculated from the number of charges per time in second. For instant, if 20 electrons which are released to the external circuit within 10 picosecond, then the current is 3.2×10^{-4} mA. This result comes from one chain of chitosan pentamer, in fact the membrane using for PEM fuel cell is the polymer, thus, the electron will release more than this result. Therefore, the current output must be greater than one chain of chitosan pentamer.