

## REFERENCES

- Al-Juaied, M. (2004). Carbon dioxide removal from natural gas by membranes in the presence of heavy hydrocarbons and by aqueous diglycolamine/morpholine. Austin: The University of Texas at Austin.
- Alper, E. (1990). Kinetics of reactions of carbon dioxide with diglycolamine and morpholine. Chemical Engineering Journal (Amsterdam, Neth.), 44, 107-111.
- Arbatskii, A.P., Traktina, E.P. and Smirnova, L.A. (2006). A titrimetric study of chemical properties of chitosan. Russian Journal of Applied Chemistry, 79(2), 272-274.
- Amaz, I., Mengibar, M., Harris, R., Paños, I., Miralles, B., Acosta, N., Galed, G. and Heras, A. (2009). Functional characterization of chitin and chitosan. Current Chemical Biology, 3, 203-230.
- Aroonwilas, A., and Veawab, A. (2007). Integration of CO<sub>2</sub> capture unit using single- and blended- amines into supercritical coal-fired power plants: implications for emission and energy management. International Journal of Greenhouse Gas Control, 1, 143–150.
- Avadi, M.R., Sadeghi, A.M., Tahzibi, A., Bayati, Kh., Pouladzadeh, M., Zohuriaan-Mehr, M.J. and Rafiee-Tehrani, M., (2004). Diethylmethyl chitosan as an antimicrobial agent: Synthesis, characterization and antibacterial effects. European Polymer Journal, 40, 1355–1361.
- Bhattacharai, N., Ramay, H.R., Chou, S.H. and Zhang, M. (2006). Chitosan and lactic acid-grafted chitosan nanoparticles as carriers for prolonged drug delivery. International Journal of Nanomedicine, 1(2), 181-187.
- Bishnoi, S. and Rochelle, G.T. (2002). Absorption of carbon dioxide in aqueous Piperazine/Methyldiethanolamine. AIChE Journal, 48(12), 2788-2799.
- Chang, F.Y., Chao, K.J., Cheng, H.H. and Chung, S.T. (2009). Adsorption of CO<sub>2</sub> onto amine-grafted mesoporous silicas. Separation and Purification Technology, 70, 87–95

- Chatti, R. ,Bansiwal, A.K., Thote, J.A., Kumar, V., Jadhav, P., Lokhande, S.K., Biniwale, R.B., Labhsetwar, N.K. and Rayalu, S.S. (2009). Amine loaded zeolites for carbon dioxide capture: Amine loading and adsorption studies. Microporous and Mesoporous Materials, 18, 167-172.
- Christensen, J.J., Izatt, R. M., Wrathall, D.P. and Hansen, L.D. (1969). Thermodynamics of proton ionization in dilute aqueous solution. XI.  $pK$ ,  $DH^\circ$ , and  $DS^\circ$  values for proton ionization from protonated amines at  $25^\circ$ . Journal of The American Chemical Society, 90, 1212-1223.
- Cullinane, J.T. and Rochelle, G.T. (2006). Kinetics of carbon dioxide absorption into aqueous potassium carbonate and piperazine. Industrial and Engineering Chemistry Research. 45, 2531-2545.
- Dash, M. ,Chiellini , F. , Ottenbrite, R.M. and Chiellini, E. (2011). Chitosan—A versatile semi-synthetic polymer in biomedical applications. Progress in Polymer Science , 36, 981–1014
- Dugas, R. and Rochelle, G.T. (2009). Absorption and desorption rates of carbon dioxide with monoethanolamine and piperazine. Energy Procedia, 1, 1163-1169.
- Figueroa, J.D., Fout, T., Plasynski, S., McIlvried, H. and Srivastava, R. D. (2008). Advances in CO<sub>2</sub> capture technology—The U.S. department of energy’s carbon sequestration program. International Journal of Greenhouse Gas Control, 2 (1), 9-20.
- Freeman, S.A., Dugas, R., Wagener, D.V., Nguyen, T. and Rochelle, G.T. (2010). Carbon dioxide capture with concentrated, aqueous piperazine. EnergyProcedia, 1, 1489-1496.
- Gargiulo,N., Caputo, D. and Colella,C. (2007). Preparation and characterization of polyethylenimine-modified mesoporous silicas as CO<sub>2</sub> sorbents. Studies in Surface Science and Catalysis, 170, 1938-1943.
- Gibbins, J., and Chalmers, H. (2008). Carbon capture and storage . Energy Policy, 36(12), 4317-4322.

- Glasscock, D. A., Critchfield, J. E. and Rochelle, G. T. (1991). CO<sub>2</sub> absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine and diethanolamine. Chemical engineering science, 46(11), 2829-2845.
- Granite, E.J. and Brien, T.O. (2005). Review of novel methods for carbon dioxide separation from flue and fuel gases. Fuel Processing Technology, 86, 1423–1434.
- Gray, M.L., Soong, T.Y., Champagne, K.J., Pennline, H., Baltrus, J.P., Stevens, R.W.Jr., Khatri, R., Chuang, S.S.C. and Filburn, T. (2005). Improved immobilized carbon dioxide capture sorbents. Fuel Processing Technology, 86, 1449–1455.
- Guerrero R.S., Belmabkhout Y., and Sayari A. (2010). Further investigations of CO<sub>2</sub> capture using triamine-grafted pore-expanded mesoporous silica. Chemical Engineering Science, 158, 513-519.
- Hao, S., Xiao, Q., Yang, H., Zhong, Y., Pepe, F. and Zhu, W. (2010). Synthesis and CO<sub>2</sub> adsorption property of amino-functionalized silica nanospheres with centrosymmetric radial mesopores. Microporous and Mesoporous Materials, 132, 552-558.
- Herzog, H., (1989). An introduction to CO<sub>2</sub> separation and capture technologies. Cambridge : Massachusetts Institute of Technology.
- Hikita, H., Asai, S., Ishikawa, H. and Honda, M. (1977). The kinetics of reactions of carbon dioxide with monoethanolamine, diethanolamine and triethanolamine by a rapid mixing method, Chemical Engineering Journal, 13, 7-12.
- Hoenich, N., (2006) Cellulose for medical application, bioresource, 1(2), 270-280.
- Holappa, J., Nevalainen, T., Safin, R., Soininen, P., Asplund, T., Luttikhedde, T., Masson, M. and Jarvinen, T. (2006). Novel water-soluble quaternary Piperazine Derivatives of Chitosan: Synthesis and Characterization. Macromolecular Bioscience, 6 (2), 139–144, February 10, 2006.

- Hook, R.J. (1997). An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds. Industrial and Engineering Chemistry Research, 36, 1779-1790
- Hsu, S.C., Lu, C., Su, F., Zeng, W. and Chen, W. (2010). Thermodynamics and regeneration studies of CO<sub>2</sub> adsorption on multiwalled carbon nanotubes. Chemical Engineering Science, 65, 1354–1361
- Idem, R., Wilson, M., Tontiwachwuthikul, P., Chakma, A., Veawab, A., Aroonwilas, A. and Gelowitz, D. (2006). Pilot plant studies of the CO<sub>2</sub> capture performance of aqueous MEA and mixed MEA/MDEA solvents at the university of regina CO<sub>2</sub> capture technology development plant and the boundary dam CO<sub>2</sub> capture demonstration plant. Industrial and Engineering Chemistry Research, 45(8): 2414–2420.
- Jekins, D.W. and Hudson, S.M. (2001). Heterogeneous Chloroacetylation of Chitosan Powder in the Presence of Sodium Bicarbonate. Journal of Polymer Science: Part A: Polymer Chemistry, 39, 4174–4181.
- Jensen, A. and Christensen, R. (1995). Study on Carbamates. XI. The carbamate of ethylenediamine. Acta Chemica Scandinavica, 9, 486-492.
- Jensen, A., Jensen, M. B. and Faurholt, C. (1952). Study on Carbamates. VIII. The carbamates of benzylamine, piperidine, and alanine. Acta Chemica Scandinavica, 6, 1073-1085.
- Littel, R. J., Bos, M. and Knoop, G. J. (1990). Dissociation constants of some alkanolamines at 293, 303, 318, and 333 K. Journal of Chemical & Engineering Data, 35, 276-277.
- López, F.A., Merê, A.L.R., Alguacil, F.J., and López-Delgado, A., A kinetics study on the thermal behaviors of chitosan. Carbohydrate Polymers, 80, 394-800
- Lu, C., Su, C., Hsu, S.C., Chen, W., Bai, H., Hwang, J.F. and Lee, H.H. (2009). Thermodynamics and regeneration of CO<sub>2</sub> adsorption on mesoporous spherical-silica particles. Fuel Processing Technology, 90, 1543–1549.

- Maroto-Valer ,M.M., Lub, Z., Zhang,Y and Tang, Z. (2008). Sorbents for CO<sub>2</sub> capture from high carbon fly ashes. Waste Management, 28 , 2320–2328.
- Meisen, A. and Shuai, X. (1997). Research and development issues in CO<sub>2</sub> capture .Energy Conversion and Management, 38(1), S37-S42.
- Meyers, R.A.(Ed.) Encyclopedia of Analytical Chemistry. (2000) Chichester: John Wiley & Sons
- Miya, M., Iwamoto, R., Yoshikawa, S. and Mima, S.(1980) I.r. spectroscopic determinationof CONH content in highlydeacylatedchitosan. International Journal of Biological Macromolecules, 2, 323-324.
- Olajire, A.A. (2010). CO<sub>2</sub> capture and separation technologies for end-of-pipe applications - A review, Energy, 35, 2610-2628.
- Perrin, D.D., Dempsey, B. and Serjeant, E.P. (1981) pKa Prediction for Organic Acids and Bases.London : Chapman and Hall.
- Plaza, M.G. ,Pevida, C. , Arenillas, A., Rubiera, F. and Pis ,J.J. (2007). CO<sub>2</sub> capture by adsorption with nitrogen enriched carbons. Fuel, 86, 2204–2212
- Polasek, J. and Bullin, J.A. (2006). Selecting amines for sweetening units. Bryan Research and Engineering, 1-9.
- Qu, X., Wirsén, A. and Albertsson, C.H.(1999). Synthesis and Characterization of pH-Sensitive Hydrogels Based on Chitosan and D,L-Lactic Acid. Journal of Applied Polymer Science,74, 13, 3193–3202
- Ramanathan, E. (2006).TNPCEE Chemistry Newsyllabus.Chennai: Sara College of Competition.
- Ritter, J. A. and Ebner, A. D. (2004). “Evaluating Internet Research Sources.” Carbon dioxide separation technology:R&D Needs For the Chemical and Petrochemical Industries . 19 Jan 2006. 6 June 2011  
<[http://www.chemicalvision2020.org/pdfs/h2\\_report.pdf](http://www.chemicalvision2020.org/pdfs/h2_report.pdf)>
- Ruthven, D.M. (1938). Principles of adsorption and adsorption processes. Canada: Wiley-Interscience.
- Sharma, M. M. (1965). Kinetics of reactions of carbonyl sulphide and carbon dioxide with amines and catalysis by Bronsted bases of the hydrolysis of COS. Transactions of the Faraday Society , 61, 681-687.

- Singh, J., and Dutta, P.K. (2010). Antibacterial and physiochemical behavior of prepared chitosan/pyridine-3,5-di-carboxylic acid complex for biomedical applications. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 48, 246–253.
- Singh, J., Dutta, P.K, Dutta, J., Hunt, A.J., Macquarrie, D.J. and Clark, J.H. (2009). Preparation and properties of highly soluble chitosan–L-glutamic acid aerogel derivative, Carbohydrate Polymers. 76 , 188–195.
- Thiruvengkatachari, R., Su, S. and Yu., H.A.X.X. (2009). Post combustion CO<sub>2</sub> capture by carbon fibre monolithic adsorbents. Progress in Energy and Combustion Science, 35, 438–455.
- Vaidya, P.D., Kenig, E.Y. (2007). CO<sub>2</sub>-alkanolamine reaction kinetics: a review of recent studies. Chemical Engineering & Technology, 30(11), 1467–1474.
- Wan, Y., Peppley, B., Creber, K. A.M. and Buia, V.T., (2010). Anion-exchange membranes composed of quaternized-chitosan derivatives for alkaline fuel cells. Journal of Power Sources, 195, 3785–3793
- Wang, M., Lawal, A., Stephenson, P., Sidders, J., Ramshaw, C (2011). Post-combustion CO<sub>2</sub> capture with chemical absorption: A state-of-the-art review. Chemical Engineering Research and Design, 89(9), 1609-1624
- Xu, X., Zhao, X., Sun, L., Liu, X. (2009). Adsorption separation of carbon dioxide, methane and nitrogen on monoethanol amine modified  $\beta$ -zeolite. Journal of Natural Gas Chemistry, 18, 167–172
- Yan, X., Zhang, L., Zhang, Y., Qiao, K., Yan, Z. and Komarneni, S. (2011). Amine-modified mesocellular silica foams for CO<sub>2</sub> capture, Chemical Engineering Journal, 168 , 918–924
- Yoddee, P., Saiwan, C., Idem, R., Tontiwachwuthikul, P., and Wongpanit , P. (2004) Study of Modified Biopolymer for Adsorption of CO<sub>2</sub> in Flue Gas. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Zanganeh, K.E., Shafeen, A. and Salvador, C. (2009). CO<sub>2</sub> Capture and Development of an Advanced Pilot-Scale Cryogenic Separation and Compression Unit, Energy Procedia, 1(1), 247-252

- Zawadzki, J., and Kaczmarek, H. (2010). Thermal treatment of chitosan in various conditions, Carbohydrate Polymers, 80, 394–400
- Zhao, Z., Cui, X., Ma, J. and Li, R., (2007). Adsorption of carbon dioxide on alkali-modified zeolite 13X adsorbents. International Journal of Greenhouse Gas Control , 1, 355–359

## APPENDICES

### Appendix A Determination of Degree of Deacetylation of Purified Biopolymer by Fourier Transform Infrared Spectroscopy (FT-IR)

The degree of deacetylation (%DD) of purified biopolymer can be determined by Fourier Transform Infrared Spectroscopy (FTIR). This method which is purposed by Miya *et al.*, (1980) determined remaining N-acetyl glucosamine units in its structure by using the relation of the absorbance ratio of the amide I peak ( $1655\text{ cm}^{-1}$ ) to the CH stretching peak ( $2867\text{ cm}^{-1}$ ). The degree of deacetylation of purified biopolymer was calculated using equation 4.1, 4.2, 4.3 and Figure 4.3 which are shown in section 4.1.1.2. All values of parameters in these equations are shown in Table A1

For the example of calculation the purified biopolymer at batch #1, the relative intensities AB and AC of amide II were 57.72 and 77.54, respectively.

$$A_{C-H\text{ stretching},2867\text{ cm}^{-1}} = \log_{10}\left(\frac{77.54}{57.54}\right)$$

$$A_{C-H\text{ stretching},2867\text{ cm}^{-1}} = 0.128$$

And the relative intensities DE and DF of amide II were 57.72 and 77.54, respectively.

$$A_{amide,1655\text{ cm}^{-1}} = \log_{10}\left(\frac{76.12}{74.45}\right)$$

$$A_{amide,1655\text{ cm}^{-1}} = 0.009$$

$$Absorbance\ ratio = \frac{0.009}{0.128} = 0.075 \quad (4.3)$$

Finally, the degree of deacetylation was evaluated using Figure 4.3, the degree of deacetylation at absorbance ratio of 0.075 is 96.99%

This calculation also applied to other batches of the purified biopolymer and the results are shown in table B1. The average degree of deacetylation is 96.05 % with 0.066 % standard deviation



**Table A1** All values of parameters in equations 4.1, 4.2, and 4.3 and the average of degree of deacetylation of purified biopolymer

No.	Relative intensity		$A_{2867}$	Relative intensity		$A_{1655}$	Absorbance ratio	%DD
	AB	AC		DE	DF			
1	57.72	77.54	0.128	74.45	76.12	0.009	0.075	96.99
2	59.85	79.23	0.122	73.23	74.83	0.009	0.077	96.39
3	58.76	81.34	0.141	74.44	76.15	0.009	0.070	97.03
Average								96.80±0.358

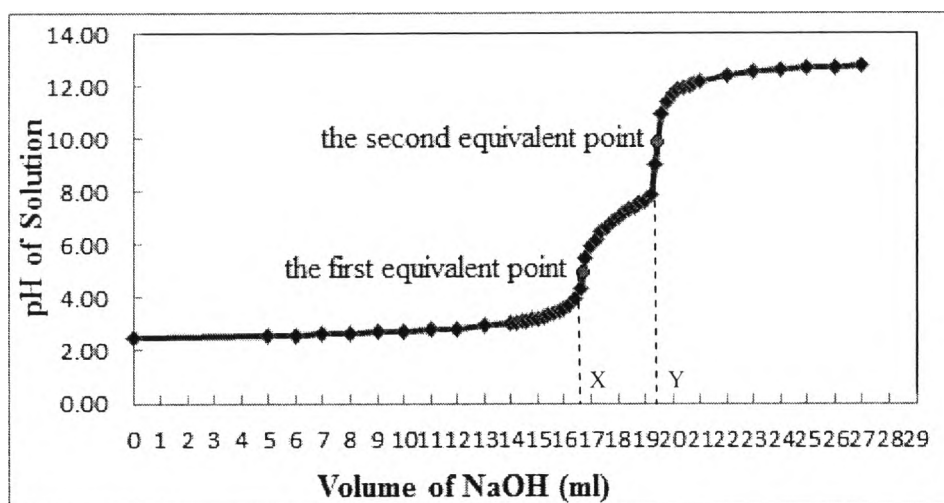
From Table A1, The average degree of deacetylation is 96.80 % with 0.358 % standard deviation

## Appendix B Determination of Degree of Deacetylation of Purified Biopolymer by pH-metrical Titration

Figure B1 illustrated the titration curve of purified biopolymer which has two equivalent points. The degree of deacetylation (%DD) is calculated using equation B1

$$\text{The degree of deacetylation}(\%DD) = 16.1(Y - X) \frac{f}{w} \quad (\text{B1})$$

Where Y and X are the consumed NaOH volume of the first and second equivalent points in Figure B1, respectively.  $f$  is the molarity of the NaOH solution and  $w$  is the initial purified biopolymer weight.



**Figure B1** Titration curve of purified biopolymer for determination of the degree of deacetylation.

Example of calculation the purified biopolymer at batch #1, 0.0502 g of purified biopolymer was dissolve in 0.1 N HCl and 0.1000 N NaOH solution is used as titrant So,

$$\text{The degree of deacetylation}(\%DD) = 16.1(19.5 - 16.505) \frac{0.1}{0.0502}$$

$$\text{The degree of deacetylation}(\%DD) = 96.05 \%$$

This calculation also applied to other batches of the purified biopolymer and

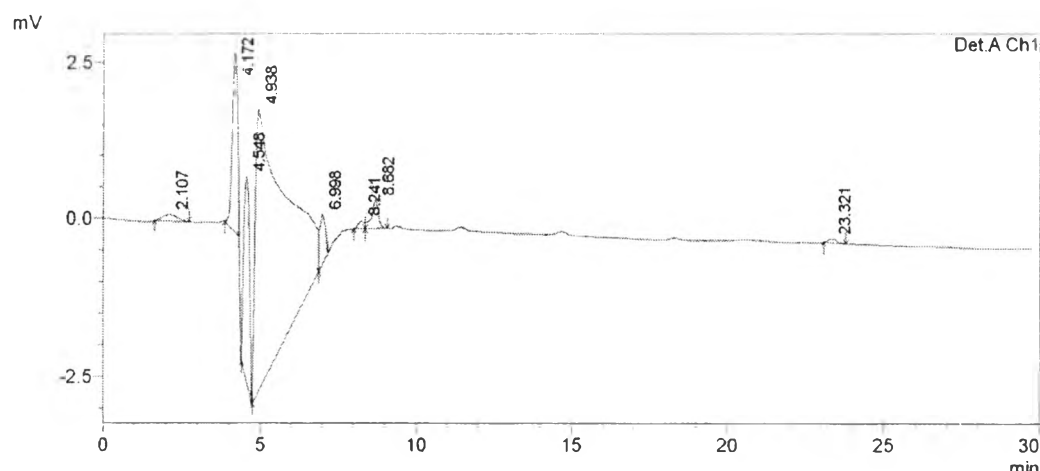
the results are shown in table B1. The average degree of deacetylation is 96.05 % with 0.066 % standard deviation

**Table B1** All values of parameters in equations B1 and the average of degree of deacetylation of purified biopolymer

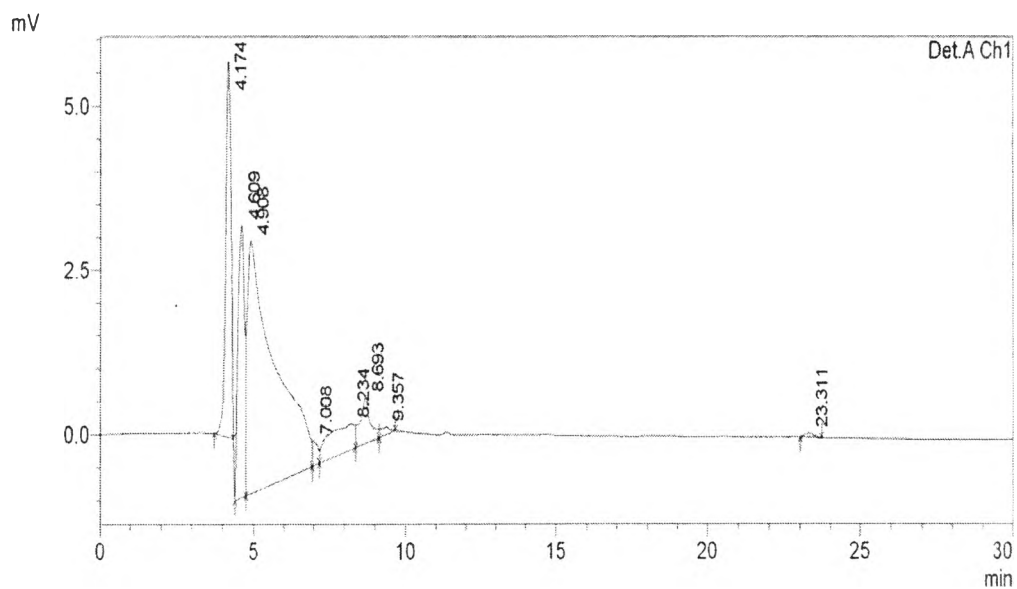
No.	the consumed NaOH at first equivalent point (mL)	the consumed NaOH at second equivalent point (mL)	the initial purified biopolymer(g)	the molarity of the NaOH (N)	%DD
1	16.505	19.5	0.0502	0.1	96.05
2	15.31488	18.3	0.0500	0.1	96.12
3	15.91303	18.9	0.0501	0.1	95.99
Average					96.05±0.066

### Appendix C Determination of Degree of Substitution of Modified Biopolymer by High-Performance Liquid Chromatography (HPLC)

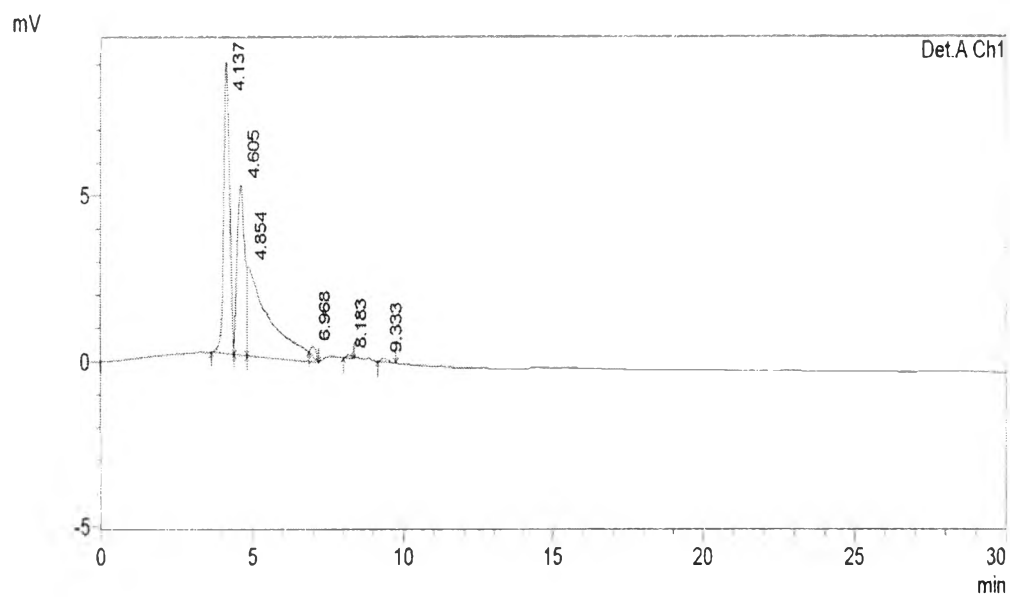
After the modification, the mixture solution of unreacted piperazine-2-carboxylic acid, isopropyl alcohol and water which is filtrated in order to get the modified biopolymer and get rid of impurity from product is was used for determination of degree of substitution by high-performance liquid chromatography (HPLC). The 40  $\mu$ L of sample (piperazine-2-carboxylic acid standard or the mixture solution of unreacted piperazine-2-carboxylic acid, isopropyl alcohol and water) was injected in to the column. The retention time of piperzine-2-carboxylic acid occurred approximately at 4.1 min. The chromatograms of pipereazine-2-carboxylic acid standard at 0.1%, 0.3%, 0.5%, 0.9% and 1.1% w/v were shown in Figure C1, C2, C3, C4, C5 and C6. Table C1 illustrated the peak area of piperazine-2-carboxylic acid at various concentrations. The peak area of piperazine-2-carboxylic acid indicated the quantity of unreacted piperazine-2-carboxylic acid in the mixture solution as shown in Figure C1.



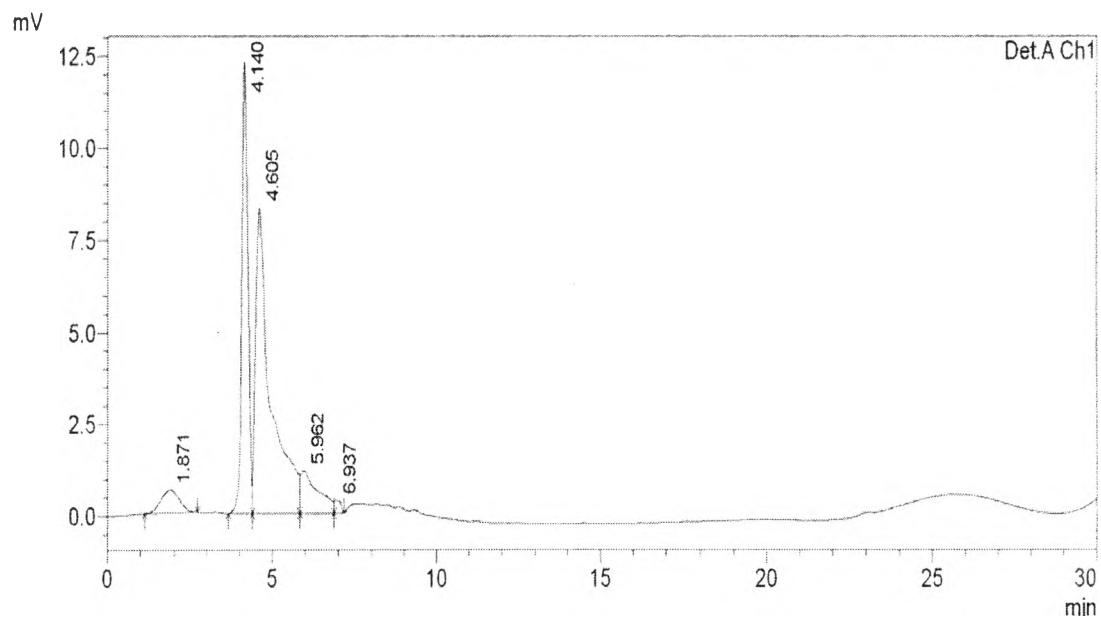
**Figure C1** Chromatogram of 0.1 % w/v piperazine-2-carboxylic acid standard.



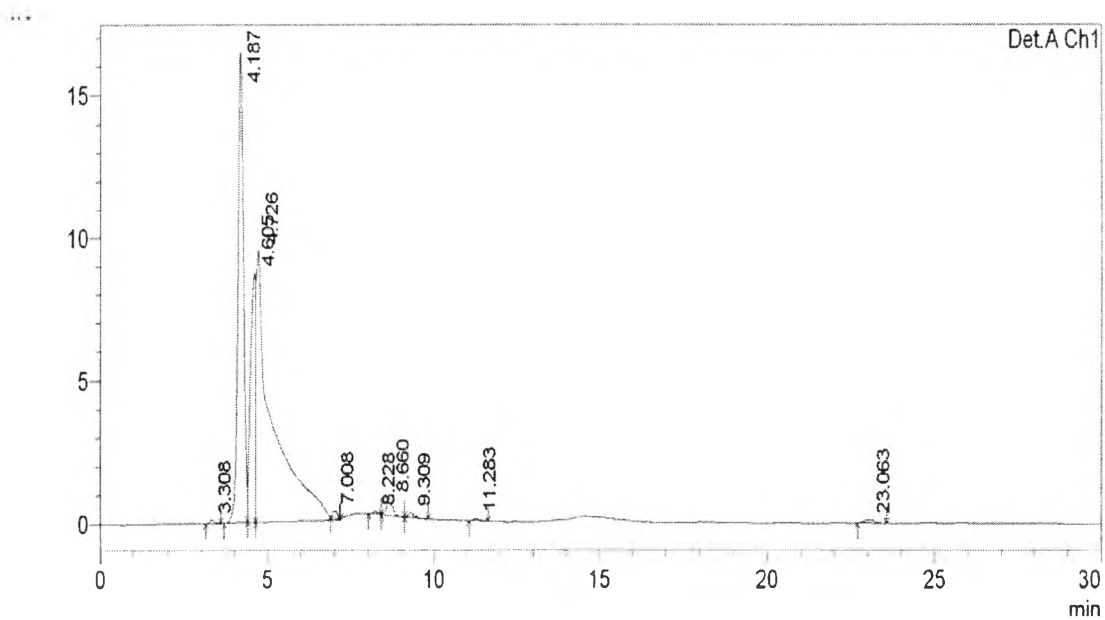
**Figure C2** Chromatogram of 0.3 % w/v piperazine-2-carboxylic acid standard.



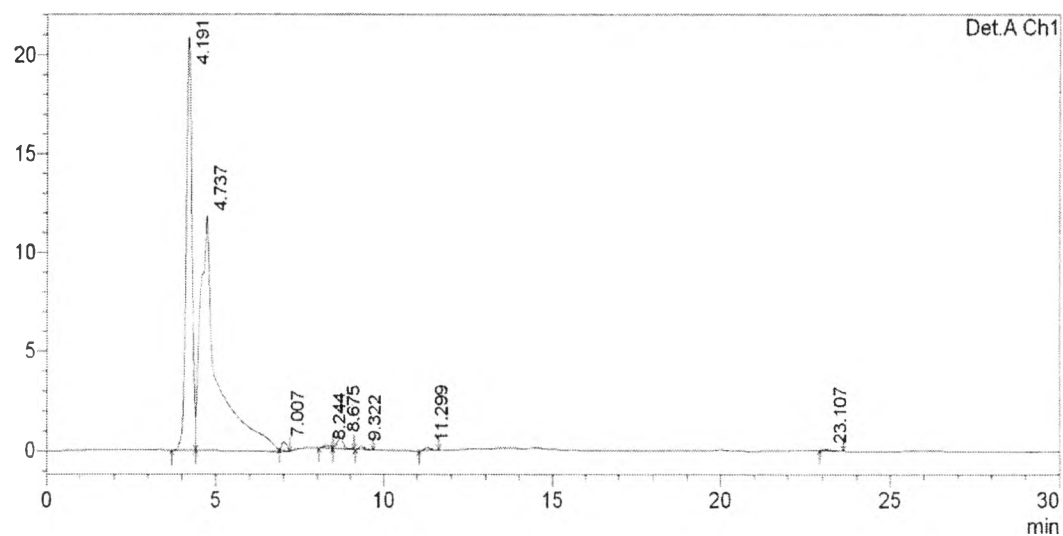
**Figure C3** Chromatogram of 0.5 % w/v piperazine-2-carboxylic acid standard.



**Figure C4** Chromatogram of 0.7 % w/v piperazine-2-carboxylic acid standard.



**Figure C5** Chromatogram of 0.9 % w/v piperazine-2-carboxylic acid standard.



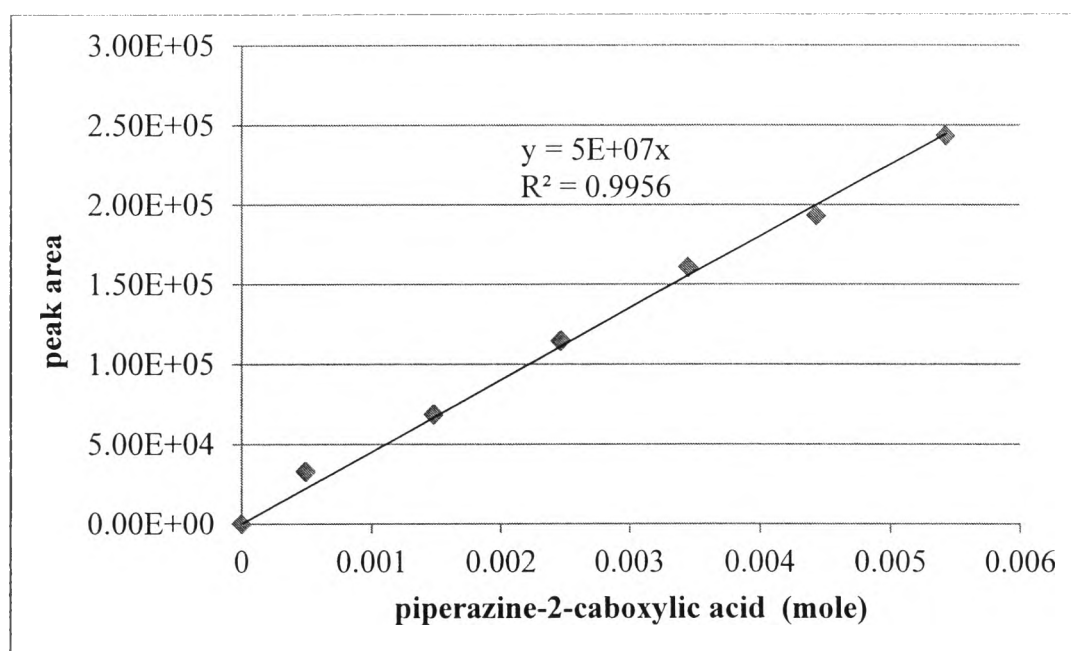
**Figure C6** Chromatogram of 0.9 % w/v piperazine-2-carboxylic acid standard.

**Table C1** The peak area of piperazine-2-carboxylic acid at various concentrations

Concentration of piperazine-2-carboxylic acid	Mole of piperazine-2-carboxylic acid in 100 mL solution( $\times 10^4$ )	Peak area at 4.1 min	Average Peak Area
0	0	0	0 $\pm$ 0.000
		0	
		0	
0.1	4.9261	32,936	32,933 $\pm$ 4.359
		32,935	
		32,928	
0.3	14.7783	68,715	68,713 $\pm$ 6.245
		68,706	
		68,718	
0.5	24.6305	114,623	114,621 $\pm$ 5.291
		114,625	
		114,615	

**Table C2** The peak area of piperazine-2-carboxylic acid at various concentration (continue)

Concentration of piperazine-2-carboxylic acid	Mole of piperazine-2-carboxylic acid in 100 mL solution( $\times 10^4$ )	Peak area at 4.1 min	Average Peak Area
0.7	34.4828	160,763	160,769.50 $\pm$ 6.264
		160,770	
		160,776	
0.9	44.3349	193,094	193,094.50 $\pm$ 6.763
		193,088	
		193,102	
1.1	54.1872	243,287	243,292 $\pm$ 6.244
		243,299	
		243,290	



**Figure C7** The calibration curve of piperazine-2-carboxylic acid.



According to Figure C1, the regression equation of piperazine-2-carboxylic acid and peak area is expressed in equation (C1)

$$Y = 5 \times 10^7 X \quad (C1)$$

Where y is peak area of piperazine-2-carboxylic acid (retention time of 4.1 min) and X is mole of piperazine-2-carboxylic acid.

Hence the unreacted piperazine-2-carboxylic acid was evaluated using equation (C2), then the reacted piperazine-2-carboxylic acid was calculated using equation (C3). Finally, the degree of substitution which is the ratio of mole of reacted of piperazine-2-carboxylic acid and mole of glucosamine group of purified biopolymer was calculated using equation (C4).

The unreacted piperazine-2-carboxylic acid (mole)

$$= \frac{\text{peak area of piperazine-2-carboxylic acid}}{5 \times 10^7} \quad (C2)$$

The reacted piperazine-2-carboxylic acid (mole)

$$= \text{The initial piperazine-2-carboxylic acid (mole)} - \text{The unreacted piperazine-2-carboxylic acid (mole)} \quad (C3)$$

The degree of substitution (%DS) =

$$\frac{\text{The reacted piperazine-2-carboxylic acid (mole)}}{\text{The initial purified biopolymer (mole)} \times \%DD} \times 100 \quad (C4)$$

Example of calculation the modified biopolymer at the ratio of 1:1

$$\text{The unreacted piperazine-2-carboxylic acid} = \frac{29231.50}{5 \times 10^7} \text{ mole}$$

$$\text{So, The unreacted piperazine-2-carboxylic acid} = 5.85 \times 10^{-4} \text{ mole}$$

$$\text{The reacted piperazine-2-carboxylic acid} = (10.22 \times 10^{-4}) - (5.85 \times 10^{-4})$$

$$\text{So, The reacted piperazine-2-carboxylic acid} = 3.92 \times 10^{-4} \text{ mole}$$

$$\text{The degree of substitution (\%DS)} = \frac{3.92 \times 10^{-4}}{10.22 \times 10^{-4}} \times 100$$

This calculation also applied to other ratios of the modified biopolymer and the results are shown in table C2. The degree of substitution of modified biopolymer in the purified biopolymer to piperazine derivative ratio of 1:1, 1:2 and 1:5 are 39.76%, 72.63% and 71.60 %

**Table C2** The degree of substitution of the modified biopolymer

Mole ratio		Peak area at 4.1 min	Average peak area	The unreacted piperazine-2- carboxylic acid ( $\times 10^{-4}$ mole)	The initial piperazine-2- carboxylic acid ( $\times 10^{-4}$ mole)	The reacted piperazine-2- carboxylic acid ( $\times 10^{-4}$ mole)	The initial biopolymer ( $\times 10^{-4}$ mole)	%DS
Biopolymer	piperazine- 2-carboxylic acid							
1	1	29,236	29,231.50 $\pm 5.408$	5.85	9.77	3.92	10.22	39.76
		29,233						
		29,226						
1	2	61,791	61,796.50 $\pm 4.769$	12.36	19.54	7.18	10.27	72.16
		61,799						
		61,799						
1	5	208,883	208,882.50 $\pm 3.279$	41.78	44.82	7.05	10.22	71.08
		208,879						
		208,886						

## Appendix D Modification of Purified Biopolymer (Preparation Method in Section 3.2.3 in Chapter III)

### *D1 Preparation of reactant for modification*

The purified biopolymer was modified with piperazine-2-carboxylic acid in the mixture solution of isopropyl alcohol, 1% w/v glacial acetic acid and water. A mole ratio of biopolymer to piperazine-2-carboxylic acid which was 1:1 for 1A, 1:2 for 2A and 1:5 for 3A were prepared.

For example, the calculation for batch # 1 of the modified biopolymer at ratio of 1:1, 0.2667 g of modified biopolymer was needed for characterizations. the quantities of the reactants were calculated following equation (D1), (D2) and (D3).

*The initial glucosamine group in purified biopolymer*

$$\begin{aligned}
 &= \frac{\text{Needed modified biopolymer (g)}}{273} \times 161 & (D1) \\
 &= \frac{0.2667 \times 161}{273} \\
 &= 0.1573 \text{ g}
 \end{aligned}$$

Where 273 is molecular weight of 1 repeating unit of modified biopolymer and 161 is molecular weight of 1 repeating unit of glucosamine group in purified biopolymer.

Since the degree of deacetylation of biopolymer was 96.43% , so the 1 gram of purified biopolymer has only 0.9554 gram of glucosamine group. The initial purified biopolymer and the piperazine-2-carboxylic acid were calculated using question (D2) and (D3).

*The initial purified biopolymer*

$$\begin{aligned}
 &= \frac{1}{0.9554} \times \text{The initial glucosamine group} \\
 (D2)
 \end{aligned}$$

$$\text{The initial purified biopolymer} = \frac{1}{0.9554} \times 0.1573$$

$$\text{The initial purified biopolymer} = 0.1646 \text{ g}$$

*The initial piperazine – 2 – carboxylic acid dihydrochloride*

$$= \frac{\text{The initial glucosamine group in purified biopolymer (g)}}{161} \times 203 \quad (\text{D3})$$

Where 203 is molecular weight of piperazine-2-carboxylic acid and 161 is molecular weight of 1 repeating unit of glucosamine group in purified biopolymer.

The initial piperazine – 2 – carboxylic acid dihydrochloride

$$\begin{aligned} &= \frac{0.1573}{161} \times 203 \\ &= 0.1983 \text{ g} \end{aligned}$$

The calculations also apply to other batch of the modified biopolymer and the results are shown in Table D1.

**Table D1** Quantity of theoretical reactant in the modified biopolymer.

Mole ratio		BP(g)	PZ2CH <sup>c</sup> (g)	Isopropyl alcohol (mL)	1% w/v glacial acetic acid (mL)	Water (mL)
BP <sup>a</sup>	PZ2C <sup>b</sup>					
1	1	0.1646	0.1983	52.42	26.21	10.48
1	2	0.1646	0.3969	52.42	26.21	10.48
1	5	0.1646	0.9915	52.42	26.21	10.48

Note : <sup>a</sup> PZ2C is piperazine-2-carboxylic acid

<sup>b</sup> BP is purified biopolymer

<sup>c</sup> PZ2CH is piperazine-2-carboxylic acid dihydrochloride

#### D2 Determination of Yield of The Modified Biopolymer

Reaction of purified biopolymer (Average degree of deacetylation (%DD) of 96.43% which is calculated from %DD of FTIR method (96.80%) and pH-metric (96.05%) ) with piperazine-2-carboxylic acid was prepared to produce the modified biopolymer. Yield of the modified biopolymer was calculated using equation (D4).

% Yield of the modified biopolymer

$$= \frac{\text{Weight of the modified biopolymer} \times \frac{\%DS}{100}}{\text{Weight of the purified biopolymer}} \times 100 \quad (D4)$$

Where %DS is % degree of substitution shown in Appendix C which is 39.76%, 72.63% and 71.60 % in the purified biopolymer/ piperazine derivative ratios of 1:1 , 1:2 and 1:5 , respectively

Example of calculation for batch # 1 of the modified biopolymer in% yield in the purified biopolymer to piperazine derivative ratios of 1:1,

$$\% \text{ Yield of the modified biopolymer} = \frac{0.1740 \times \left(\frac{39.76}{100}\right)}{0.1661} * 100$$

$$\% \text{ Yield of the modified biopolymer} = 41.65 \%$$

The calculations also apply to other batch of the modified biopolymer and the results are shown in Table D1. The average of yield of modified biopolymer in the purified biopolymer to piperazine derivative ratio of 1:1, 1:2 and 1:5 are 42.50 %, 76.84% and 75.10%, respectively.

**Table D2** Yield of the modified biopolymer

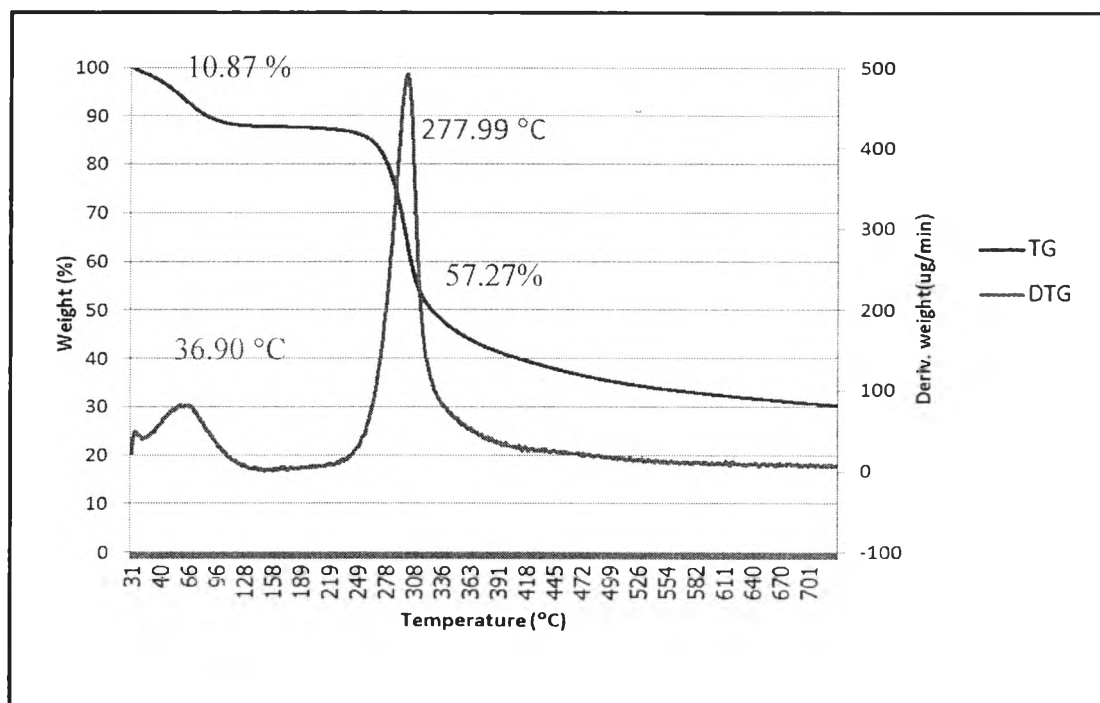
Mole ratio		Modified biopolymer	BP(g)	PZ2CH(g)	Modified biopolymer (g)	%Yield of the modified biopolymer
BP <sup>a</sup>	PZ2C <sup>b</sup>					
1	1	Batch #1	0.1661	0.1983	0.1740	41.65
		Batch #2	0.1653	0.1982	0.1778	42.77
		Batch #3	0.1670	0.1985	0.1809	43.07
		Average				
1	2	Batch #1	0.1667	0.3969	0.1789	77.95
		Batch #2	0.1656	0.3977	0.1625	71.27
		Batch #3	0.1677	0.396	0.1877	81.29
		Average				
1	5	Batch #1	0.1659	0.9915	0.1688	72.85
		Batch #2	0.1677	0.9920	0.1803	76.85
		Batch #3	0.1644	0.9910	0.1733	75.48
		Average				

Note : <sup>a</sup> PZ2CH is piperazine-2-carboxylic acid dihydrochloride

<sup>b</sup> BP is purified biopolymer

## Appendix E Thermogravimetric Analysis

The thermogravimetric analysis was studied thermal stability of the modified biopolymer. The thermogram of the biopolymer, piperazine-2-carboxylic acid and modified biopolymer show two curves including thermogravimetric curve and derivative thermogravimetric curve. Both of graphs was used to evaluated the decomposition temperature, weight loss and quantity of char residue. Figure E1, E2, E3, E4 and E5 shows the thermogram of biopolymer, piperazine-2-carboxylic acid and modified biopolymer at the ratio of 1:1, 1:2 and 1:5.



**Figure E1** Thermogram of the purified biopolymer.

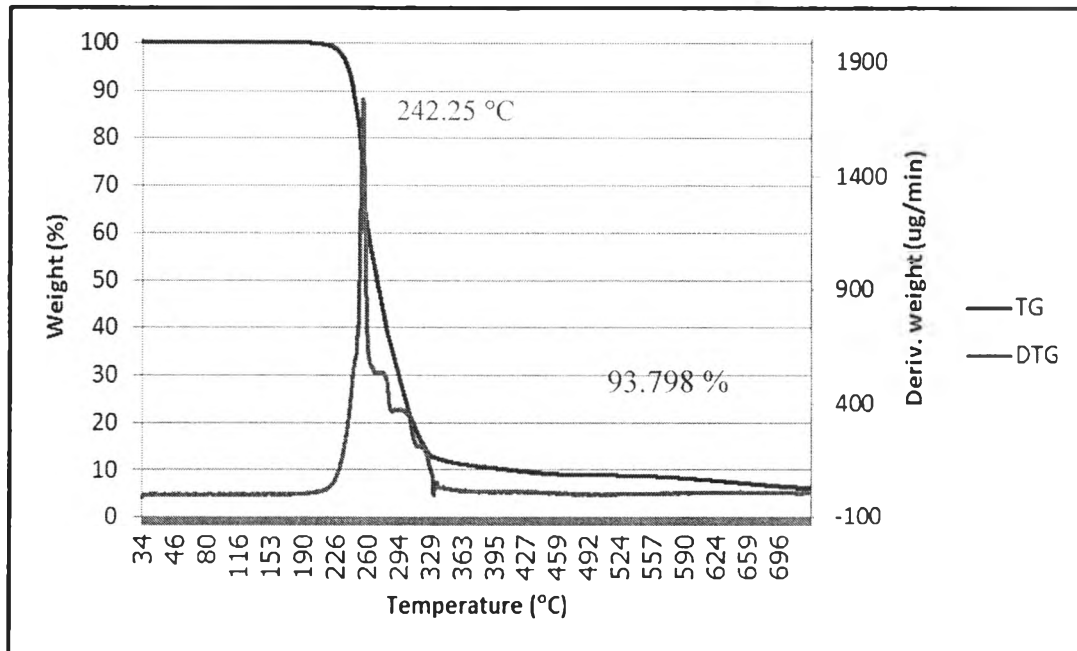


Figure E2 Thermogram of the piperazine-2-carboxylic acid.

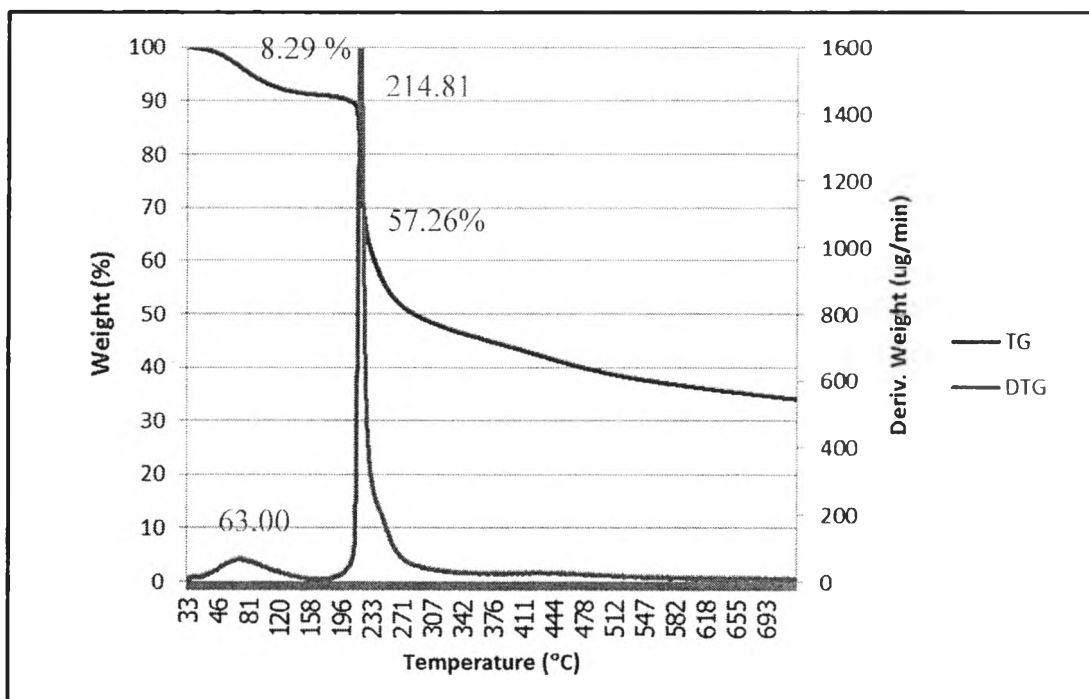
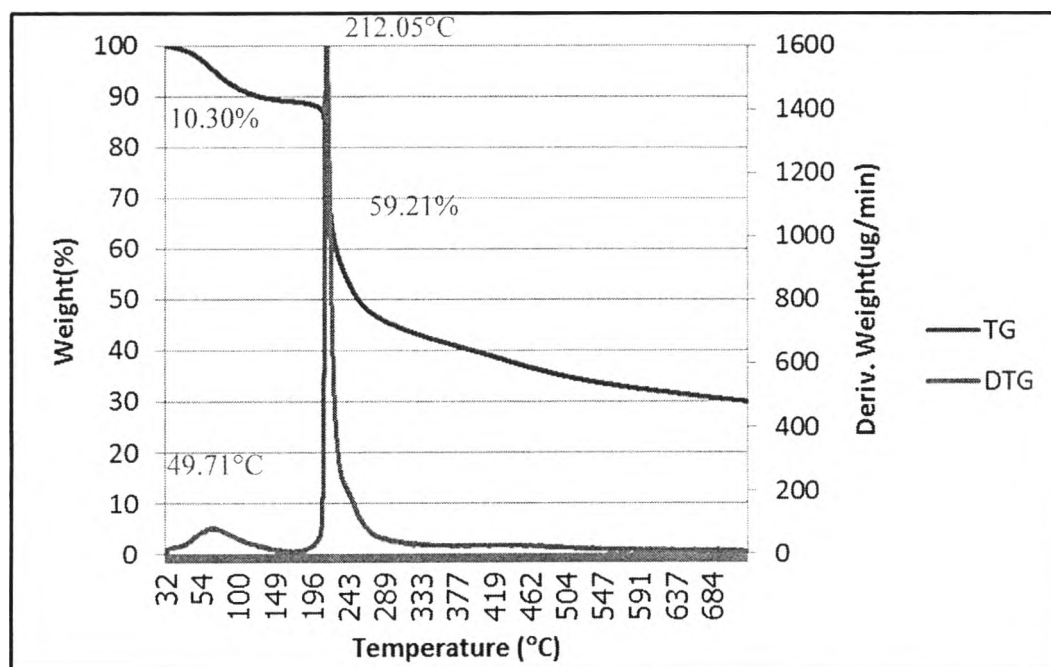
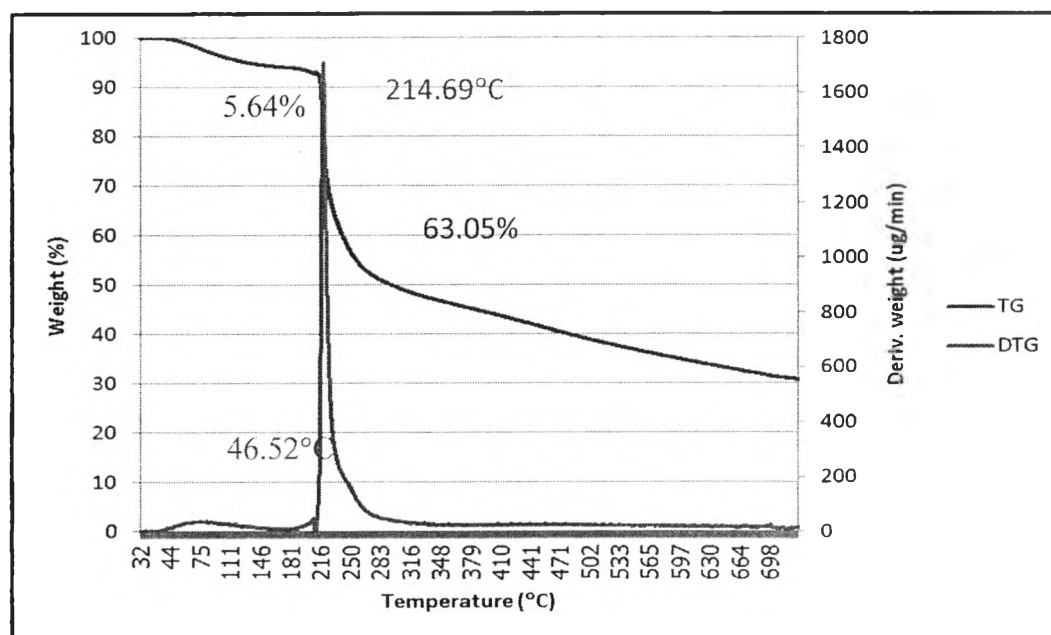


Figure E3 Thermogram of the modified biopolymer at ratio 1:1.





**Figure E4** Thermogram of the modified biopolymer at ratio 1:2.



**Figure E5** Thermogram of the modified biopolymer at ratio 1:5.

## CURRICULUM VITAE

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1. Srisuwanvichien, S., Saiwan, C., Tontiwachwuthikul, P., (2012, April 24). Biopolymer modified with piperazine derivative for CO<sub>2</sub> adsorption. Proceedings of the 3<sup>rd</sup> Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and the 18<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

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