REFERENCES

Aresta, M. (2010). Carbon Dioxide as Chemical Feedstock. John Wiley & Sons, Inc.

Aymes, D., Ballivet-Tkatchenko, D., Jeyalakshmi, K., and Saviot, L. (2009). A comparative study of methanol carbonation on unsupported SnO_2 and ZrO_2. Catalysis Today, 147, 62-67.

Baiker, A. (1999). Supercritical fluid in heterogeneous catalysis. Chemical Review, 99, 453-473.

Beckman, E.J. (2004). Supercritical and near-critical CO_2 in green chemical synthesis and processing. Journal of Supercritical Fluids, 28, 121-191.

"Bioethanol: hydrous and anhydrous." *Fuel4life.eu, go green with biofuels.* 25 May 2010. access on 27 May 2010 <http://www.fuel4life-biofuels.com/bioethanol_hydrous_and_anhydrous.html>.

Briggs, D.N., Lawrence, K.H., and Bell, A.T. (2009). An investigation of carbon supported $CuCl_2/PdCl_2$ catalysts for diethyl carbonate synthesis. Applied Catalysis A: General, 366, 71-83.

Brown, P. and Djerassi, C. (1966). Mass spectrometry in structural and stereochemical problems, CVI, occurrence of alkyl and aryl rearrangements in the fragmentation of some organic carbonates. Journal of the American Chemical Society, 88:11, 2469-2477.

Brusstar, M. (2005). Sustainable technology choices for alternative fuel. (powerpoint). ISAF XV International Symposium on Alcohol Fuels. < www.eri.ucr.edu/ISAFXVCD/ISAFXVPP/SuTCAF.pdf >

"Business report." *MITHR PHOL.* 27 May 2010 <http://www.mitrphol.com/th/o2_business/03_ethanol.php>.

"Chemical products: DIETHYL CARBONATE, PROPYLENE GLYCOL, etc, Detail Description." *Japan External Trade Organization.* 8 Apr. 2004. 2 May 2010 <http://www.jetro.go.jp/ttppoas/anken/0001037000/1037313_e.html>.

Choi, J.C., He, L.N., Yasuda, H., and Sakakura, T. (2002). Selective and high yield synthesis of dimethyl carbonate directly from carbon dioxide and methanol. The Royal Society of Chemistry, 4, 230-234.

Cutrufello, M.G., Ferino, I., Monaci, R., Rombi, E., and Solinas, V. (2002). Acid-base properties of zirconium, cerium and lanthanum oxides by calorimetric and catalytic investigation. Topic in Catalysis, 19, 225-240.

Dai, W.L., Luo, S.L., Yin, S.F., and Au, C.T. (2009). Review: the direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts. Applied Catalysis A: General, 366, 2-12.

"Diethyl Carbonate." *DIETHYLCARBONATE, 99%-GFS-CHEMICALS.* 27 May 2010 <http://www.gfschemicals.com/statics/productdetails/DIETHYCARBONATE_2738.html>.

"Diethyl Carbonate." *Worldwide Chemical Information, Trading & Advertising.* 30 Apr. 2010 <http://chemicalland21.com/industrialchem/solalc/diethyl%20carbonate.htm>.

"Diethyl Carbonate Manufacturers, Suppliers, Wholesale." *Detail Selling Lead Description.* 2008-2012. <http://jintaichem.88chem.com/sell-Other-Organic-Chemicals/301/Diethyl-Carbonate.html>.

"Dimethyl carbonate." *D152927 Dimethyl Carbonate ReagentPlus, 99%.* 27 May 2010 <http://www.sigmaaldrich.com/catalog/ProductDetail.do?D7=0&N5=Product%20No.|BRAND_KEY&N4=D152927|SIAL&N25=0&QS=ON&F=SPEC>.

Diaz, E., De Rivas, B., Lopez-Fonseca, R., Ordonez, S., and Gutierrez-Ortiz, J.I. (2006). Characterization of ceria-zirconia mixed oxides as catalysts for the combustion of volatile organic compounds using inverse gas chromatography. Journal of Chromatography A, 1116, 230-239.

"Ethanol Reference Prices." *Retail Oil Prices.* 31 May 2010. access on 2 May 2010 < http://www.eppo.go.th/retail_prices.html >.

"Ethanol." *Welcome to Mitr Phol Sugar Group.* access on 27 May 2010

<http://www.mitrphol.com/eng/02_business/03_ethanol.php>.

"Ethanol." *Wikipedia, the free encyclopedia.* 28 May 2010. access on 28 May 2010 <http://en.wikipedia.org/wiki/Ethanol>.

"Ethanol (data page)." *Wikipedia, the free encyclopedia.* 12 Feb. 2010. access on 28 May 2010 <http://en.wikipedia.org/wiki/Ethanol_%28data_page%29>.

Energizer Holding, Inc. (2009). Energizer rechargeable ACCU battery. Product Safety Data Sheet.

"Fenghua Lithium Battery limited." Fenghua Lithium Battery limited. 27 May 2010 <http://th.list-of-companies.org/Details/10206525/China/Fenghua_Lithium_Battery_Co_Ltd_/>.

Fogler, H.S. (2005). Elements of Chemical Reaction Engineering (4th Edition). New Jercy: Pearson Education, Inc.

"Fuels With High Octane Number 89." *HubPages.* 27 May 2010 <http://hubpages.com/hub/Fuels-With-High-Octane-Number>.

"Genghua Lithium Battery Co. Ltd." Genghua Lithium Battery Co. Ltd. 27 May 2010 <http://th.list-of-companies.org/Details/10206525/China/Fenghua_Lithium_Battery_Co_Ltd_/>.

Kim, W.B., and Lee, J.S. (1999). A new process for the synthesis of diphenyl carbonate from dimethyl carbonate and phenol over heterogeneous catalysts. Catalysis Letters, 59, 83-88.

Ikeda, Y., Sakaihori, T., Tomishige, K., and Fujimoto, K. (2000). Promoting effect of phosphoric acid on zirconia catalysts in selective synthesis of dimethyl carbonate from mathanol and carbon dioxide. Catalysis Today, 66, 59-62.

Liu, C.J., Mallinson, R.G., and Aresta, M. (2003). Utilization of Greenhouse Gases. Oxford University Press.

Methanex Corporation. (2005). Methanol. Material Safety Data Sheet, CAS 67-56-1.

"Methanol." *Wikipedia the free encyclopedia.* 12 May 2010. access on 27 May 2010 <http://en.wikipedia.org/wiki/Methanol>.

"Methanol-An Alternative Fuel." *Methanol- An Alternative Fuel.* access on 27 May 2010 <http://dnr.louisiana.gov/sec/execdiv/techasmt/ecep/auto/m/m.htm>.

"Methanol (data page)." *Wikipedia, the free encyclopedia.* 12 May 2010. access on 27 May 53 2010 <http://en.wikipedia.org/wiki/Methanol_%28data_page%29>.

Niessen, H.G. and Woelk, K. (2007). Investigations in supercritical fluids. Top Current Chemistry, 276, 69-110.

Ono, Y. (1997). Review: Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block. Applied Catalysis A: General, 155, 133-166.

Pacheco, M.A., and Marshall, C.L. (1997). Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive. Energy & Fuels, 11, 2-29.

"Phenobarbital." *Wikipedia, the free encyclopedia.* 21 May 2010. access on 27 May 2010 <http://en.wikipedia.org/wiki/Phenobarbital>.

Qiu, P., Yang, B., and Yi, C. (2010). Characterization of KF/γ-Al_2O_3 catalyst for the synthesis of diethyl carbonate by transesterification of ethylene carbonate. Catalysis Letters, DOI 10.1007/s10562-010-0354-8.

Rodriguez, A., Canosa, J., Dominguez, A., and Tojo, J. (2004). Viscosities of dimethyl carbonate with alcohols at several temperatures UNIFAC-VISCO interaction parameters (-OCOO-/alcohol). Fluid Phase Equilibria, 216, 167-174.

Sakakura, T., Choi, J.C., Saito, Y., and Sako, T. (1999). Synthesis of dimethyl carbonate from carbon dioxide: catalysis and mechanism. Polyhedron, 19, 573-576.

Sakakura, T., Saito, Y., Okano, M., Choi, J.C., and Sako, T. (1998). Selective conversion of carbon dioxide to dimethyl carbonate by molecular catalysis. Journal of Organic Chemistry, 63, 7095-7096.

Science Lab.com, Chemical & Laboratory Equipment. (2005). Dimethyl carbonate. Material Safety Data Sheet, CAS 616-38-6.

"Shell Unleaded E10." Shell Fuels. 27 May 2010 <http://www.colesexpress.com.au/shell-fuels.aspx>.

Song, C. (2006). Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing. Catalysis Today, 115, 2-32.

Supple, D., MIT Energy Club. Unit & conversions fact sheet. Massachusetts Institute of Technology.

Thammachart, M. (2000). CO Oxidation on CeO_2-ZrO_2 Solid Solution Prepared by Sol-Gel Technique under Oxidizing and Reducing Conditions. M.S. Thesis, the Petroleum and Petrochemical College, Chulalongkorn University.

Tomishige, K., Ikeda, Y., Sakaihori, T., and Fujimoto, K. (2000). Catalytic properties and structure of zirconia catalysts for direct synthesis of dimethyl carbonate from methanol and carbon dioxide. Journal of Catalysis, 192, 355-362.

Tomishige, K., and Kunimori, K. (2002). Catalytic and direct synthesis of dimethyl carbonate starting from carbon dioxide using CeO_2-ZrO_2 solid solution heterogeneous catalyst: effect of H_2O removal from the reaction system. Applied Catalysis A: General, 237, 103-109.

Tundo, P., and Selva, M. (2002). The chemistry of dimethyl carbonate. Accounts of Chemical Research, 35(9), 706-716.

United States Patent. (1981). US4,307,032.

United States Patent. (1982). US4,335,051.

United States Patent Office. (1963). US3,114,762.

Vatani, A., Mehrpooya, M., and Gharagheizi, F. (2007). Prediction of standard enthalpy of formation by a QSPR model. International Journal of Molecular Sciences, 8, 407-432.

VEE GEE Scientific, Inc. (2004). Ethanol, absolute. Material Safety Data Sheet, MSDS number: M1004.

Wang, D., Yang, B., Zhai, X., and Zhou, L. (2007). Synthesis of diethyl carbonate by catalytic alcoholysis of urea. Fuel Processing Technology, 88, 807-812.

Wang, W., Wang, S., Ma, X., and Gong, J. (2009). Crystal structures, acid-base properties, and reactivities of $Ce_xZr_{1-x}O_2$ catalysts. Catalysis Today, 148, 323-328.

Wu, X.L., Xiao, M., Meng, Y.Z., and Lu, Y.X. (2005). Direct synthesis of dimethyl carbonate on H_3PO_4 modified V_2O_5. Journal of Molecular Catalysis A: Chemical, 238, 158-162.

Wu, X.L., Meng, Y.Z., and Lu, Y.X. (2006). Direct synthesis of dimethyl carbonate (DMC) using Cu-Ni/VSO as catalyst. Journal of Molecular Catalysis A: Chemical, 249, 93-97.

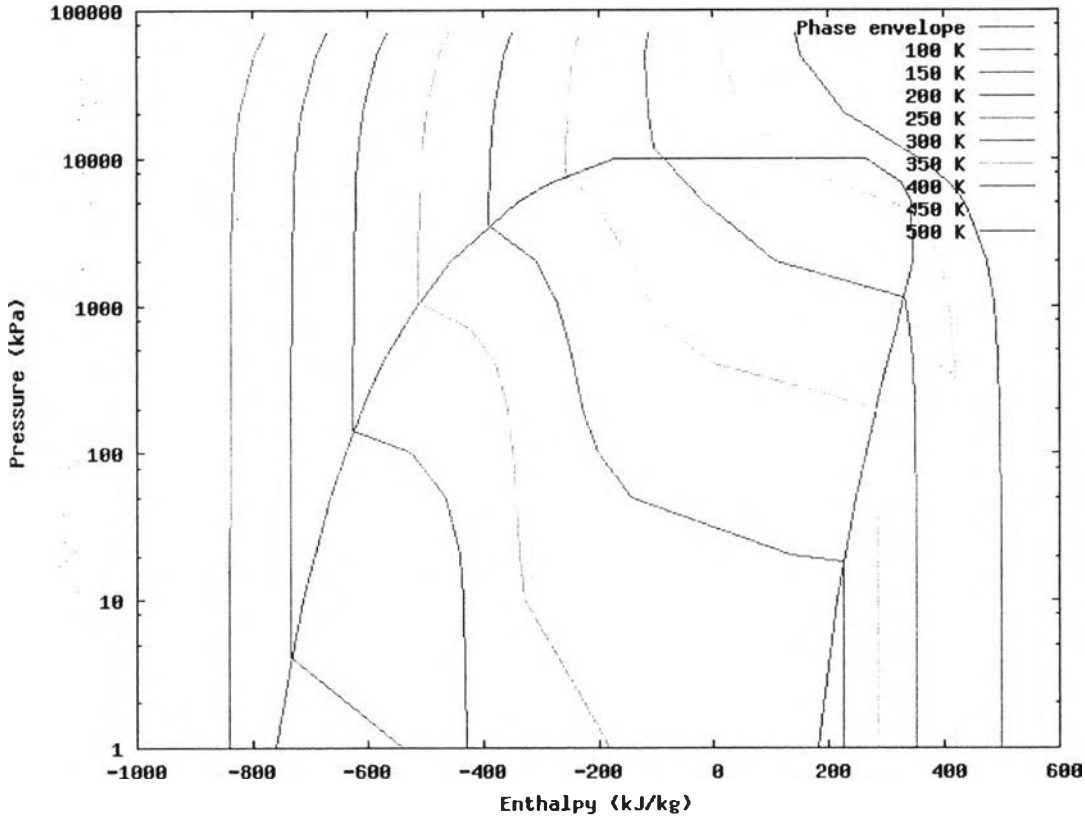
Yang, C., Lai, H., Liu, Z., and Ma, P. (2006). Density and viscosity of binary mixtures of diethyl carbonate with alcohols at (293.15 to 363.15) K and predictive results by UNIFAC-VISCO group contribution method. Journal of Chemical Engineering Data, 51, 1345-1351.

Zhao, T., Han, Y., and Sun, Y. (2000). Novel reaction route for dimethyl carbonate synthesis from CO_2 and methanol. Fuel Processing Technology, 62, 187-194.

"1.2.3 Oxygenates in gasoline." 1.2-MTBE in gasoline: European Fuel Oxygenates Association: the reference for MTBE and fuel oxygenates. 27 May 2010 <http://www.efoa.org/mtbegasoline.html>.

APPENDICES

Appendix A Carbon Dioxide: Pressure-Enthalpy Diagram of CO_2 Mixture (CO_2 mol fraction at 0.5 and EtOH mol fraction at 0.5) (http://www2.questconsult.com/cgi-bin/jrm_enthpres)



Appendix B Calculations for Catalyst Preparation

First of all, the desired molar ratios of the catalyst were calculated from Equation B.1. The unknowns parameters are A and B. Therefore, another equation must be used to solve the equation simultaneously.

$$\frac{A}{B} = \text{ratio} \times \frac{a}{b} \tag{B.1}$$

where A = Weight of $Ce(NO_3)_3 \bullet 6H_2O$, g

B = Weight of $ZrO(NO_3)_2 \bullet 8H_2O$, g

ratio = molar ratio of Ce/Zr

a = Molecular weight of $Ce(NO_3)_3 \bullet 6H_2O$, 434.22 g/mol (Acros)

b = Molecular weight of $ZrO(NO_3)_2 \bullet 8H_2O$, 231.23 g/mol (Acros)

Equation B.2 is represented the amount of CeO_2-ZrO_2 catalyst at desired molar ratio.

$$C + D = E \tag{B.2}$$

where C = Weight of CeO_2, g

D = Weight of ZrO_2, g

E = Weight of CeO_2-ZrO_2 catalyst at desired molar ratio, g

The mole of Ce in CeO_2 and $Ce(NO_3)_3 \bullet 6H_2O$, and the mole of Zr in ZrO_2 and $ZrO(NO_3)_2 \bullet 8H_2O$ are equal (1 mol) as written in Equations B.3 and B.4.

$$C' = A' \tag{B.3}$$

$$D' = B' \tag{B.4}$$

where A' = Mole of $Ce(NO_3)_3 \bullet 6H_2O$, mol

B' = Mole of $ZrO(NO_3)_2 \bullet 8H_2O$, mol

C' = Mole of CeO_2, mol

D' = Mole of ZrO_2, mol

Therefore, parameters C and D are rearranged and expressed as Equation B.5.

$$c \times \left(\frac{A}{a}\right) + d \times \left(\frac{B}{b}\right) = E \qquad (B.5)$$

where c = Molecular weight of CeO_2, 172.12 g/mol
(http://en.wikipedia.org/wiki/CeO2)

d = Molecular weight of ZrO_2, 123.22 g/mol
(http://en.wikipedia.org/wiki/Zirconium_dioxide)

Equations B.1 and B.2 are solved simultaneously to find the weight of the precursors for the desired molar ratio of the catalyst.

Appendix C Equilibrium Conversion Calculations

In this work, the reactions as shown in Equations C.1 to C.3 were occurred.

$$2CH_3CH_2OH(l) + CO_2(l) \longrightarrow (CH_3CH_2O)_2CO(l) + H_2O(l) \quad (C.1)$$

$$CH_3CH_2OH(l) \longrightarrow CH_3COH(l) + H_2(g) \quad (C.2)$$

$$CH_3COH(l) + 2CH_3CH_2OH(l) \longrightarrow (CH_3CH_2O)_2CCH_3(l) + H_2O(l) \quad (C.3)$$

To determine the equilibrium conversion of the reactions, the first step is to calculation Gibb's free energy at the reaction temperature. The reference state is 298.15 K and 1 atm. Equations C.4 and C.5 show the relationship equation between enthalpy equation and Gibb's free energy equation, respectively.

$$\Delta H_T = J + (\Delta a)T + (\Delta b/2)T^2 + (\Delta c/3)T^3 + (\Delta d/4)T^4 \quad C.4[1]$$

$$\Delta G_T/RT = J/RT - (\Delta a/R)\ln T - (\Delta b/2R)T - (\Delta c/6R)T^2 - (\Delta d/12R)T^3 + I \quad C.5[1]$$

where ΔH_T = the change of heat of formation at T K (kJ/kmol);

J = the constant value found by using a known numerical value;

T = temperature (K);

ΔG_T = the change of Gibb's free energy at T K (kJ/kmol);

I = the constant value;

R = gas constant (8.314 kJ/kmole-K);

Δa, Δb, Δc, and Δd = the change of the heat capacity coefficient (kJ/kmole-K).

The thermodynamic properties required for the calculation are shown in Tables C.1 and C.2.

Table C.1 Basic chemical properties[2]

Components	Molecular Weight	V_c	T_c	P_c	Z_c	Liquid density at 298.15 K	Specific volume of liquid at 298.15 K	Vapor pressure at 298.15 K
Unit		**m^3/kmol**	**K**	**kPa**	**-**	**kmol/m^3**	**m^3/kmol**	**Pa**
Ethanol	46.07	0.167	513.92	6148	0.24	17.05969827	0.058617684	7927.721194
CO_2	44.01	0.094	304.21	7383	0.274	16.21319281	0.061678166	6447890.526
DEC	118.13	0.356	576	3390	0.252	8.215115755	0.12172683	1443.546677
Acetaldehyde	44.05	0.154	466	5550	0.221	17.5784734	0.056887761	116643.0291
Acetal	118.17	0.402	541	2980	0.266	6.951278998	0.143858418	4498.034707
H_2	2.02	0.064147	33.19	1313	0.305	-	-	-
H_2O	18.01	0.055948	647.13	22055	0.229	55.2272548	0.018107002	3170.385775

Table C.2 Enthalpy, Gibbs free energy, and heat capacity coefficient of the chemicals[2]

Components	**△H at 298.15 K and 1 atm**	**△G at 298.15 K and 1 atm**	a	b	c	d
Unit	**kJ/kmol**	**kJ/kmol**				
Ethanol	-277501.87	-174161	-26.165	0.30889	-0.0010075	0.000001
CO_2	-403923.212	-384466	0.26663	0.002976	-0.0000041	0.000000002
DEC	-684104.177	-475177	-21.42	0.17472	-0.0004269	0.0000003
Acetaldehyde	-192037.488	-132752	0.92311	-0.00071	0.0000087	-0.000000008
Acetal	-491707.188	-252707	-53.176	0.4455	-0.0011838	0.000001
H_2	0	0	11.812	0.014655	-0.0000259	0.00000001
H_2O	-285682.886	-237176	-214.555	1.7934	-0.0048142	0.0000042

After the calculations to find I and J constant are precede, Gibbs free energy in each reaction and reaction temperature can be found. Gibbs free energy of the reaction at the reaction temperature is used to calculate the equilibrium constant as shown in Equation C.6.

$$-\Delta G_T/RT = \ln(K) \qquad C.6^{[1]}$$

where K = equilibrium constant.

To find the chemical compositions at the operating condition, the relation of equilibrium constant to composition in gas and liquid phase reactions are shown in Equations C.7 and C.8, respectively.

$$\Pi(y_i\phi_i)^{\nu_i} = (P/P^\circ)^{-\nu}K \qquad C.7^{[3]}$$

$$\Pi(x_i\gamma_i)^{\nu_i} = K\exp[[(P^\circ-P)/RT]\Sigma(\nu_i V_i)] \qquad C.8^{[3]}$$

where y_i = fraction of component in gas phase;
ϕ_i = fugacity coefficient;
P° = standard pressure (1 atm);
ν_i = stoichiometric number;
x_i = fraction of component in liquid phase;
γ_i = activity coefficient;
V_i = specific volume of liquid (m^3/mol).

In this calculation, ideal solution is assumed, so, activity coefficient is unity. Next, to evaluate the chemical composition at equilibrium, mole balances of the multiple reactions as shown in Table C.3 are converted to the fraction of each component.

Table C.3 Mole balances of the multiple reactions

Component	Mole input	Mole output
EtOH	A	A-2X-Y-2Z
CO_2	B	B-X
DEC	-	X
Acetaldehyde	-	Y-Z
Acetal	-	Z
H_2	-	Y
H_2O	-	X+Z
Total	**A+B**	**A+B-X+Y-Z**

where A = an initial mole of ethanol (1 mole);

B = an initial mole of CO_2 (1 mole);

X = reaction coordinate of the Equation C.1;

Y = reaction coordinate of the Equation C.2;

Z = reaction coordinate of the Equation C.3.

Finally, when all parameters are found, using the Solver in Microsoft Excel 2007 to find the values of X, Y, and Z simultaneously in each reaction temperature.

---

[1]Eilliott, J.R., and Lira, C.T. Introductory Chemical Engineering Thermodynamics, Chapter 14, Prentice Hall, 1999.

[2]ProII simulation softwere.

[3]Smith, J.M., Van Vess, H.C., and Abbott, M.M. Introduction to Chemical Engineering Thermodynamics, 7th edition, Chapter 13, McGraw Hill, 2005.

Appendix D Calculations for Chemical Compositions from Experimental Data

After obtain the area of DEC, acetaldehyde, and acetal from the GC, the area is converted to the amount of the component by the calibration curve in each component as shown in Appendix E. This amount converted from area is an amount in 1 μL. The amount of ethanol can be calculated as shown in Equation D.1.

$$1\ \mu L = V_l - aA - bB - cC - d(\delta D) \quad (D.1)$$

where V_l = volume of ethanol in a syringe (μL);

A = mass of DEC converted from its area (g);

B = mass of acetaldehyde converted from its area (g);

C = mass of acetal converted from its area (g);

D = mass of water based on the mole of water equilibrium in each reaction temperature (2.7, 8.27, and 10.2 times of DEC mole at 110, 140, 170 °C, respectively);

a = density of DEC at 298.15 K (0.975 g/mL);

b = density of acetaldehyde at 298.15 K (0.788 g/mL);

c = density of acetal at 298.15 K (0.828 g/mL);

d = density of water at 298.15 K (0.997 g/mL)

After the amount of ethanol inside the syringe is known, the conversion of ethanol can be calculated as shown in Equation D.2. Next, the real amount of ethanol inside the autoclave can be found as shown in Equation D.3. Finally, the amount of DEC, acetaldehyde, and acetal inside the autoclave are calculated in Equation D.4.

$$\text{EtOH conv. (\%)} = 100\times[I - R]/I \quad (D.2)$$

where I = initial mass of EtOH in 1 μL;

R = mass of EtOH calculated from the above.

R_l = [EtOH conv×Inital mass of EtOH in the autoclave]/100 (D.3)

where R_l = mass of ethanol inside the autoclave during the experiment.

$Z = (R_l \times A \text{ or } B \text{ or } C)/V_l$ (D.4)

where Z = the mass of DEC or acetaldehyde or acetal in the autoclave.

Appendix E The Calibration Curves of DEC, Acetaldehyde, and Acetal

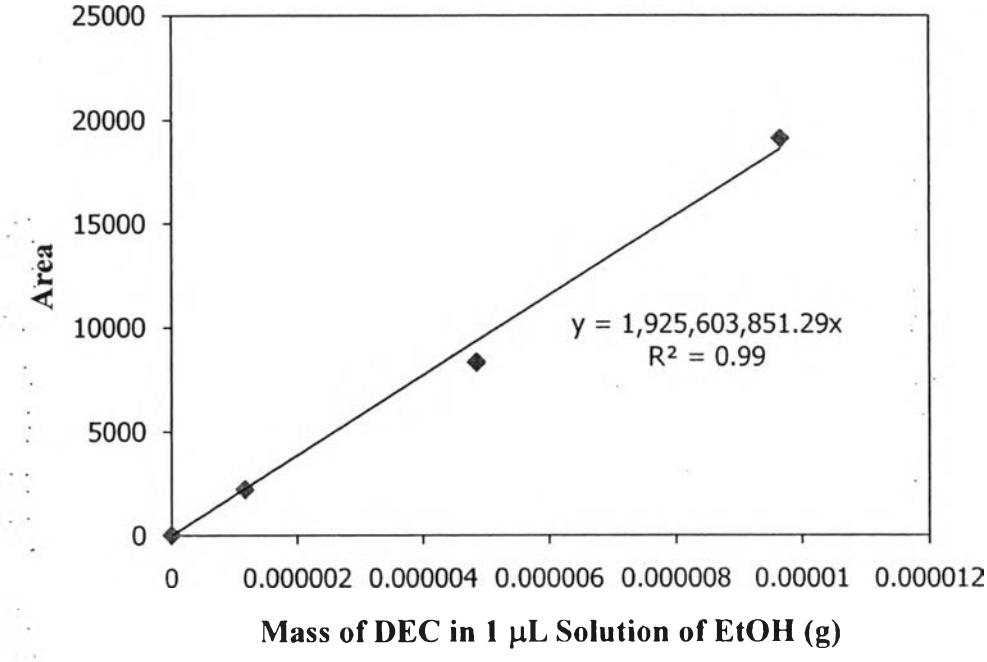


Figure E.1 The calibration curve of DEC.

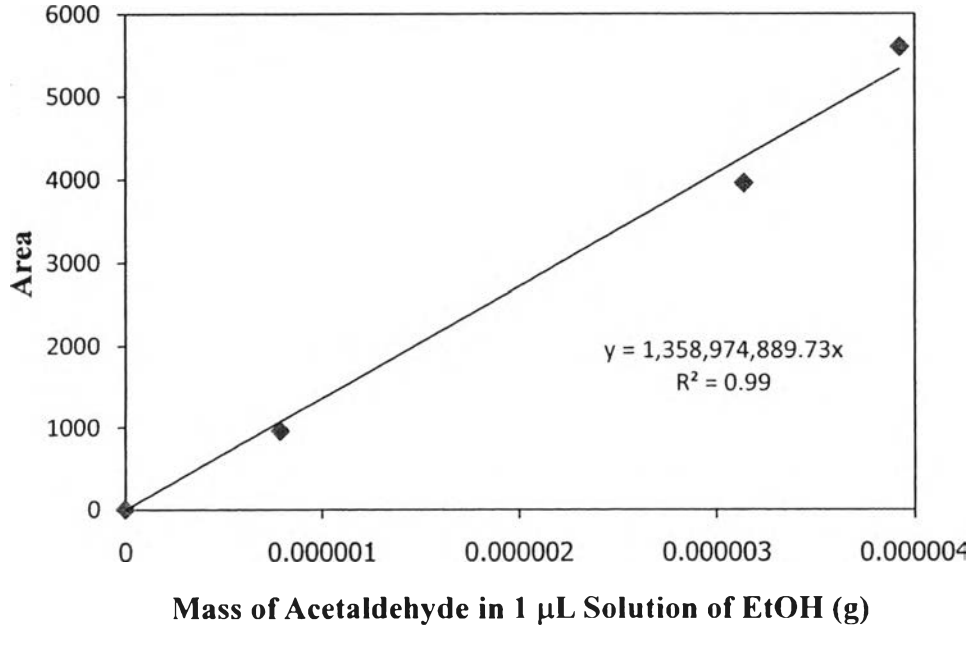


Figure E.2 The calibration curve of acetaldehyde.

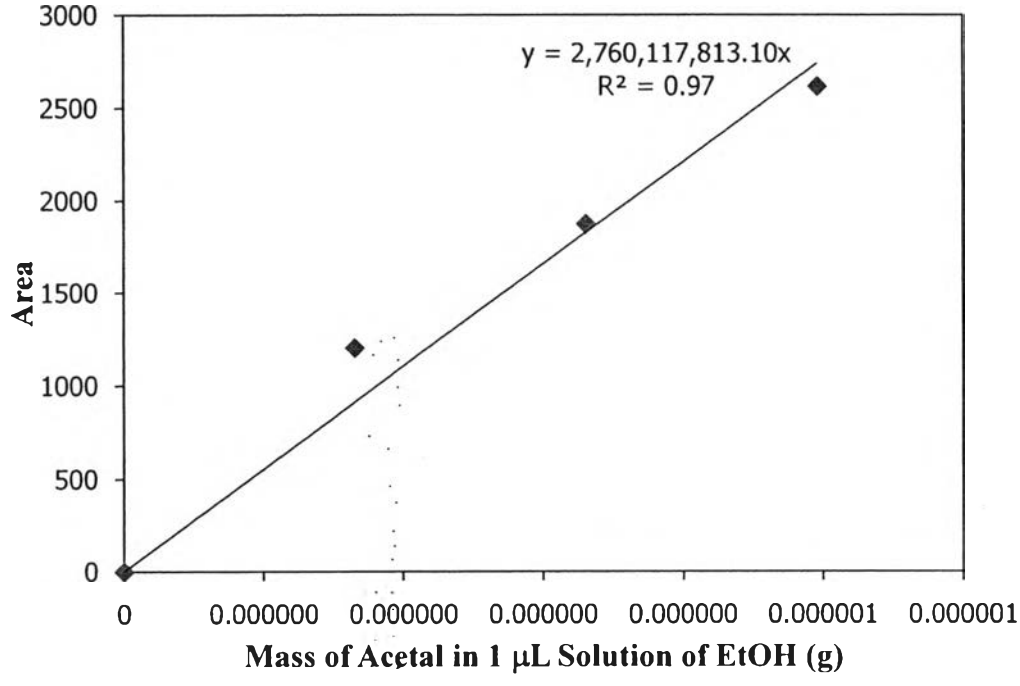


Figure E.3 The calibration curve of acetal.

CURRICULUM VITAE

Name: Mr. Danuwat Bunstapornpipat

Date of Birth: January 31, 1987

Nationality: Thai

University Education:

2005–2008 Bachelor Degree of Science in Chemical Engineering (Fuel Technology), Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

Work Experience:

April 2008 Position: Student Internship

Company name: PTT Chemical Public Company Limited

Proceedings:

1. Bunstapornpipat, D., Rirksomboon, T., Jongpatiwut, S., and Sreethawong, T. (2011, April 26) Diethyl Carbonate Synthesis from Ethanol and Supercritical Carbon Dioxide over CeO_2-ZrO_2 Catalysts. Proceedings of the 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and the 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.