REFERENCES

"Acetal." Wikipedia. Wikipedia. 30 Apr. 2010 < http://en.wikipedia.org/wiki/Acetal>

Barrault, J., Clacens, J.-M., and Pouilloux, Y. (2004) Selectivity oligomerization of glycerol over mesoporous catalysts. Topics in Catalysis, 27, 1-4.

Behr, A., Eilting, J., Irawadi, K., Leschinski, J., and Lindner, F. (2008) Improved utilization of renewable resources: New important derivatives of glycerol. Green Chemistry, 10, 13-30.

Boonpokkrong, V. (2005) Homogeneous and Heterogeneous Catalytic Production of Polyglycerols. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

Camila R.B. da Silva., Válter L.C. Goncalves, Elizabeth R.L., and Claudio J.A. Mota. (2009) Etherification of glycerol with benzyl alcohol catalyzed by solid acids. Journal of the Brazilian Chemical Society, 20, 201-204.

Chaimbault, P., Cassel, S., Claude, S., Debaig, C., Benvegnu, T., Plusquellec, D., and Rollin, P., (1999) Direct analysis of industrial oligoglycerols by liquid chromatography with evaporative light-Scattering detection and mass spectrometry. Chromatographia, 50, 239-242.

Chopade, S.P. (1999) Ion-exchange resin-catalyzed ketalization of acetone with 1,4 and 1,2-diols: Use of molecular sieve in reactive distillation. Reactive & Functional Polymers, 42, 201-212.

Clacens, J.-M., Pouilloux, Y., and Barrault, J. (2002) Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. Applied Catalysis A: General, 227, 181-190.

Clarkson J. S., Walker J. A., and Wood M. A., (2001) Continuous reactor technology for ketal formation: An improved synthesis of solketal. Organic Process Research & Development, 5, 630-635.

Claudio J.A. Mota, Carolina X.A. da Silva, Nilton Rosenbach,Jr., Jair Costa, and Flavia da Silva. (2010) Glycerin derivatives as fuel additives: The addition of glycerol/acetone ketal (solketal) in gasolines. Energy & Fuels, 24, 2733-2736.

García, E., Laca, M., Pérez, E., Garrido, A., and Peinado, J. (2008) New class of acetal derived from glycerin as a biodiesel fuel component. Energy & Fuels, 22, 4274-4280.

Greene, W.T. and Wuts, P.G.M. (4Eds). (2007) Greene's Protective Groups On Organic Synthesis. New Jersey: John Wiley & Sons, Inc.

"Glycerol production." AIM-AGI Agri-industry Modeling & Analysis Group. 30 Apr. 2010 <http://beag.ag.utk.edu/pp/biodiesel.pdf>

Jahn, S. and Karpovich, D. (2006) Completing the Cycle: Formation of Cloud Point Depressants from Glycerin Obtained in the Production of Biodiesel. B.S. Thesis, Saginaw Valley State University, Michigan, United state of America.

Kenar, J.A. (2007) Glycerol as a platform chemical: Sweet opportunities on the horizon. Lipid Technology, 19, 249-253.

Krisnandi, Y.K., Eckelt, R., Schneider, M., Martin, A., and Richter, M. (2008) Glycerol upgrading over zeolites by batch-reactor liquid-phase oligomerization: heterogenous versus homogenous reaction. ChemSusChem, 1, 835-844.

Makkam, K. (2010) Synthesis of Fatty Acid Monoglycerides from Palm Oil by Glycerolysis with Protected Glycerol. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

Merino, P., Franco, S., Mates, J.A., Merchan, F.L., Romero, P., Tejero, T., Uriel, S., and Matute, R., (2003) Nucleophilic additions of chiral non-racemic enolates to N-benzyl-C-(alkoxymethyl) nitrones. ARKIVOC (iv), 48-58.

Naveen Kumar, T., Sastry, Y.S.R., and Lakshminarayana, G. (1984) Analysis of polyglycerols by high-performance liquid chromatography. Journal of Chromatography, 298, 360-365.

Ruppert, A.M., Meeldijk, J.D., Kuiper, B.W.M., Erne B.H., and Weckhuysen, B.M. (2008) Glycerol etherification over highly active CaO-based materials: new mechanistic aspects and related colloidal particle formation. Chemistry: A European Journal, 14, 2016-2024.

Richter, M., Krisnandi, Y.K., Eckelt, R., Schneider, M., and Martin, A. (2008) Homogeneously catalyzed batch reactor glycerol etherification by $CsHCO_3$. Catalysis Communications, 9, 2112-2116.

Sigma-Aldrich. (1997) The Aldrich Library of FT-IR Spectra Edition II. Milwaukee, Wisconsin: Sigma-Aldrich Co.

Thanasanvisut, D. (2008) Synthesis of Diglycerol from Glycerol by Heterogeneous Base Catalysts. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

Yu, C.C., Lee, Youn-Sik, Cheon, B. S., and Lee, S.H. (2003) Synthesis of glycerol monostearate with high purity, Bulletin of the Korean Chemical Society, 24(8), 1229-1231.

Zhou, C.H., Beltramini, J.N., Fan, Y.X., and Lu, G.Q. (2008). Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. Chemical Society Reviews, 37, 527-549.

APPENDICES

Appendix A Gas Chromatography Calculation

Preparation of GC sample

The calculation is based on the calibration curve. Isopropanol is the solvent for external standard. The volume of isopropanol is fixed at 0.5 ml. The assumption of this calculation is the constant isopropanol volume. The reference area of isopropanol is 500000. In addition, the injection of sample in gas chromatography is 1 µl. For the preparation of GC sample, the product sample was collected for 0.5 ml. and then collected the product sample weight (grams) of 0.5 ml (sample product). After that, isopropanol was added for external standard for 0.5 ml. The combination of produce sample and isopropanol made the GC sample for 1 ml (concentration g/ml). Table A2 showed the product sample weights at different time.

Calculation of GC sample (Part I)

In this case, the 1:6 glycerol to acetone molar ratio sample at 4 hours was selected for calculation. The area of isopropanol was 910381.8 and the area of solketal was 161580 (Table A3). The area of solketal converted to the reference area of isopropanol at 500000 by Equation 1.

$$Solketal\ area\ at\ ref. = \frac{Solketal\ area}{Isopropanol\ area} \times isopropanol\ area\ at\ ref. \quad (1)$$

So the solketal area at ref. was 88742. Then, the solketal area was converted to concentration by using the solketal calibration curve (Figure A1 and Equation 2).

$$Concentration\left(\frac{g}{ml}\right) = \frac{Solketal\ area\ at\ ref.}{Slope\ of\ product\ calibration\ curve\frac{ml}{g}} \times 10^{-6} \quad (2)$$

The concentration was 0.0854 g/ml. after that, the concentration was scaled up to the total product mixture weight by Equation 3. In this case, total product weight was 96.92 g (glycerol 20.75 g, acetone, 75.5 g and catalyst 0.67 g).

$$Solketal\ weight\ (g) = \frac{Concentration\frac{g}{ml}}{product\ sample\frac{g}{ml}} \times total\ product\ weight(g) \quad (3)$$

The last step calculated the conversion which based on limiting reactant (glycerol) by Equation 4. The conversion of glycerol was 73.92%

$$\%Conversion = \frac{Solketal\ weight(g)}{Solketal\ M.W.}(mol) \times \frac{Glycerol\ M.W.}{Glycerol\ weight(g)}\left(\frac{1}{mol}\right) \times 100 \quad (4)$$

Table A1 Solketal calibration curve

Solketal	Concentration(μg/ml)	Area
5%Vol.	67400	39895.16
10%Vol.	120800	104762.24
50%Vol.	545100	574981.74

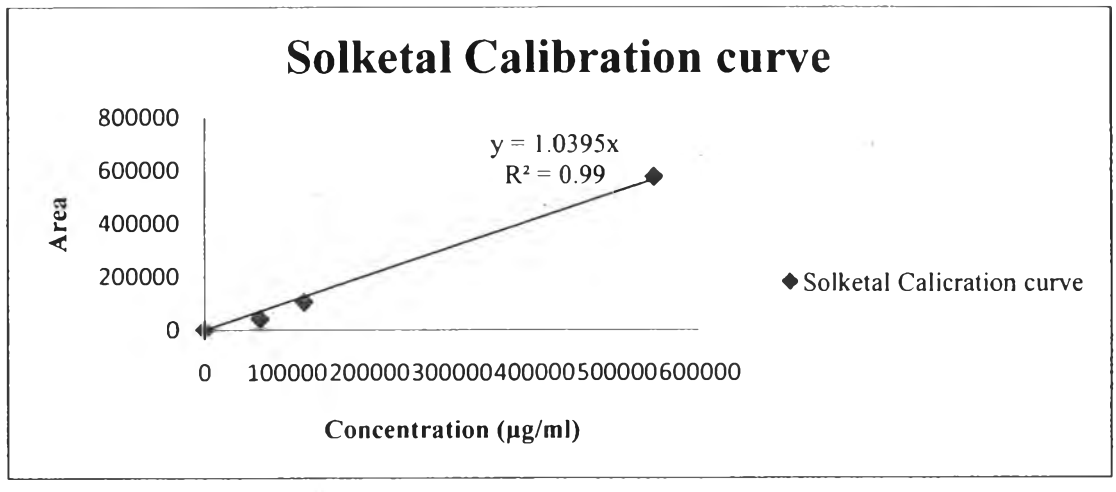

Figure A1 Solketal Calibration curve.

Table A2 Sample weight of 1:6 glycerol to acetone molar ratio at different time

	Expend drop weight(g)	Drop + sample weight(g)	Sample weight(g)
2hr	1.0275	1.389	0.3615
4hr	0.973	1.3487	0.3757
6hr	0.979	1.342	0.363
8hr	1.0027	1.3635	0.3608
10hr	0.9927	1.3603	0.3676
12hr	0.9637	1.3394	0.3757

Table A3 Area solketal of 1:6 glycerol to acetone molar ratio at different time

	Isopropanol area	Solketal area	%Conversion
2hr	1201743	195150	70.29
4hr	910381.8	161580	73.92
6hr	1112272.7	225207.1	76.81
8hr	1166015.4	216628	80.57
10hr	1218259.4	226200.7	79.04
12hr	959250.9	189475	82.27

Calculation of GC sample (Part II)

In this part, there are two main assumptions. This calculation is based on benzyl alcohol conversion only. For this assumption, the selectivity of products that concerned in this calculation are benzyl solketal ether, benzyl glycerol ether and dibenzyl ether. For the second assumption, the mass ratio of benzyl solketal ether to benzyl glycerol ether equals to area ratio of benzyl solketal ether to benzyl glycerol because of without compared standards as shown in Equation 5.

$$Area\ ratio = mass\ ratio = \frac{The\ weights\ of\ benzyl\ solketal\ ether}{The\ weight\ of\ benzyl\ glycerol\ ether} \quad (5)$$

In this case, the 1:1 is the model for calculation the selectivity of the products mixture. The benzyl alcohol calculation is following Part I (Equations 1 to 4) by changing solketal to benzyl alcohol as shown in Table A7. Dibenzyl ether is also calculated by Equation 1 to 3 by changing solketal to dibenzyl ether. The result of dibenzyl ether is shown in Table A8. Equation (6) shows the overall mole balance based on benzyl alcohol conversion. In this case, the initial mole of benzyl alcohol is fixed at 0.152 moles. There are two variable parameters which are Mol_{BS} and Mol_{BG}. The combination of Equation 6 and 7 can solve these parameters. The results are reported in Table A9.

$$Mol_{BA,S} - Mol_{BA,R} = Mol_{BS} + 2Mol_{BG} + Mol_{DB} \quad (6)$$

$Mol_{BA,S}$ = Moles of starting benzyl alcohol

$Mol_{BA,R}$ = Moles of remaining benzyl alcohol

Mol_{BS} = Moles of benzyl solketal ether

Mol_{BG} = Moles of benzyl glycerol ether

Mol_{DB} = Moles of dibenzyl ether

$$Molar\ ratio = area\ ratio \times \frac{Benzyl\ glycerol\ ether\ M.W.}{Benzyl\ solketal\ ether\ M.W.} \quad (7)$$

After solved all parameters, the selecitivity of products are calculated by Equation 8A to 8C. In addition, the results of the selectivity of products from benzyl alcohol are represented in Table A10.

$$\%Selectivity\ of\ benzyl\ solketal\ ether = \left(\frac{Mol_{BS}}{(Mol_{BS}+Mol_{BG}+Mol_{DB})}\right) \times 100 \quad (8A)$$

$$\%Selectivity\ of\ benzyl\ glycerol\ ether = \left(\frac{Mol_{BG}}{(Mol_{BS}+Mol_{BG}+Mol_{DB})}\right) \times 100 \quad (8B)$$

$$\%Selectivity\ of\ dibenzyl\ ether = \left(\frac{Mol_{DB}}{(Mol_{BS}+Mol_{BG}+Mol_{DB})}\right) \times 100 \quad (8C)$$

Table A4 Benzyl alcohol calibration curve

Benzyl alcohol	Concentration(µg/ml)	Area
0%Vol.	0	0
10%Vol.	115400	187558.3841
30%Vol.	321500	616686.8329

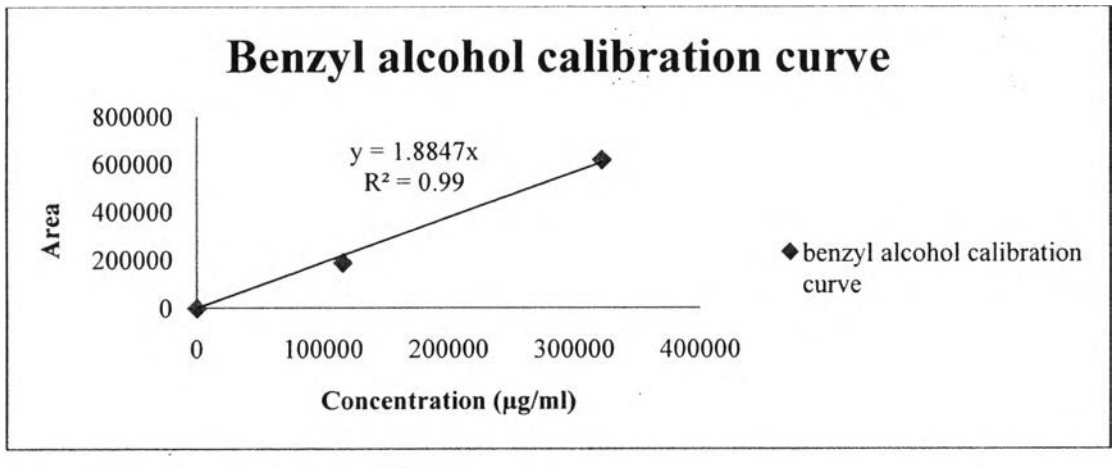

Figure A2 Benzyl alcohol calibration curve.

Table A5 Dibenzyl ether calibration curve

Dibenzyl ether (%wt)	Concentration(µg/ml)	Area
54.63239	272614.37	759070.2345
76.7007	379432.247	982482.6254

88.3845	435817.3911	996660.0063
94.43643	466280.5153	961815.5346

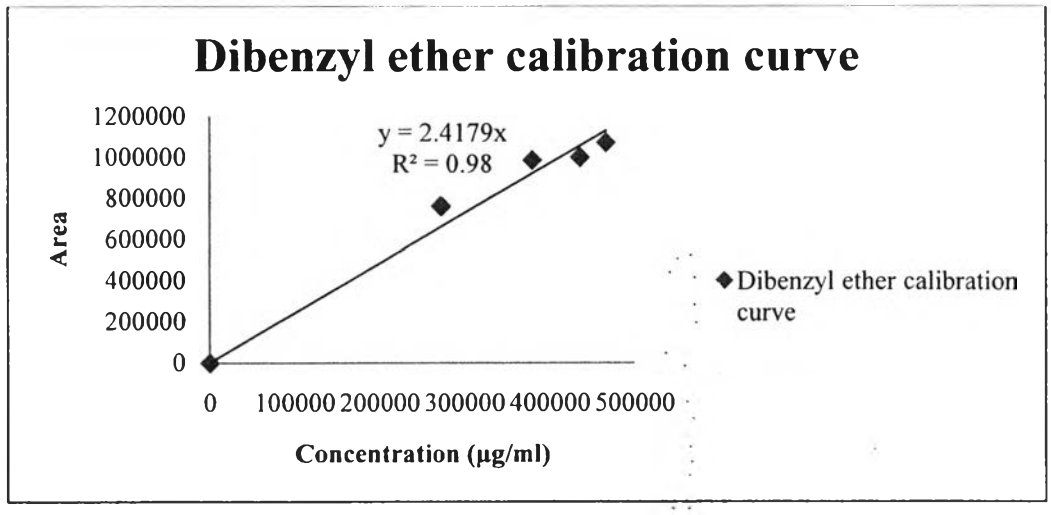

Figure A3 Dibenzyl ether calibration curve.

Table A6 Sample weight of 1:1 solketal to benzyl alcohol at different time

	Expend drop weight(g)	Drop + sample weight(g)	Sample weight(g)
2hr	0.95	1.4878	0.5378
4hr	0.9484	1.5018	0.5534
6hr	0.9933	1.5487	0.5554
8hr	0.9632	1.4726	0.5094
10hr	1.0183	1.589	0.5707
12hr	1.0037	1.592	0.5883
12hr	0.9787	1.5276	0.5489

Table A7 Benzyl alcohol conversion

	Isopropanol area	Benzyl alcohol area	Benzyl alcohol (mol)	%Conversion
2hr	820428.5	312597.85	0.064640635	57.53534911
4hr	769935.45	167155.65	0.035822323	76.46708722
6hr	727210.05	101851.3	0.023032579	84.86910884
8hr	911229.05	75735.6	0.014888003	90.21956009
10hr	725277.15	59586.8	0.013149608	91.36157109

12hr	846859.6	58693.2	0.010856297	92.86812598

Table A8 Dibenzyl ether calculation

	Isopropanol area	Dibenzyl ether area	Dibenzyl ether (mol)
2hr	820428.5	269075.5	0.026028572
4hr	769935.45	274619.45	0.0275131
6hr	727210.05	277134.5	0.029281022
8hr	911229.05	278253.35	0.025544552
10hr	725277.15	279121.5	0.028734741
12hr	846859.6	287350.5	0.025069063

Table A9 Benzyl solketal ether and benzyl glycerol ether calculation

	Mol_{BS} and Mol_{BG}	Mass ratio(BS/BG)	Molar ratio (BS/BG)	Benzyl glycerol ether (mol)	Benzyl solketal ether (mol)
2hr	0.0355	1.1390	0.9338	0.0184	0.0172
4hr	0.0614	0.7111	0.5830	0.0388	0.0226
6hr	0.0706	0.5189	0.4254	0.0496	0.0211
8hr	0.0862	0.4159	0.3410	0.0643	0.0219
10hr	0.0816	0.2992	0.2453	0.0655	0.0161
12hr	0.0912	0.4002	0.3281	0.0687	0.0225

Table A10 The selectivity of benzyl solketal ether, benzyl glycerol ether and dibenzyl ether

	%Selectivity BS	%Selectivity BG	%Selectivity DB
2hr	19.5863	20.9753	59.4385
4hr	19.4175	33.3091	47.2734
6hr	16.3149	38.3548	45.3303
8hr	15.9675	46.8319	37.2006
10hr	11.5588	47.1179	41.3234
12hr	15.9435	48.5896	35.4669

Appendix B FT-IR Spectra for Characteriazation of Reactants

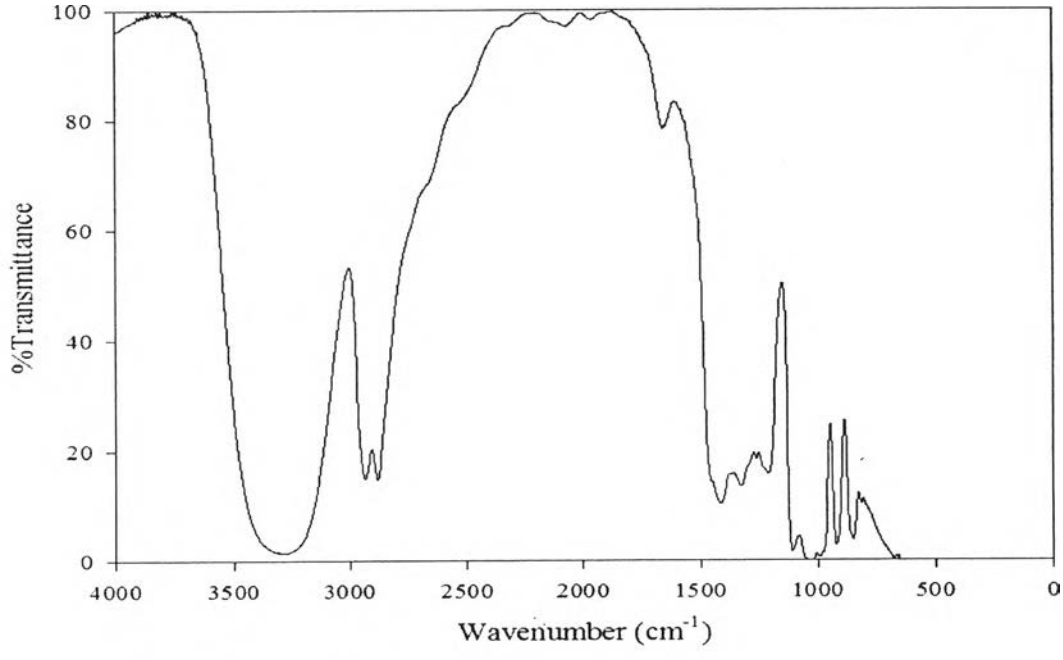

Figure B1 FT-IR spectra of glycerol.

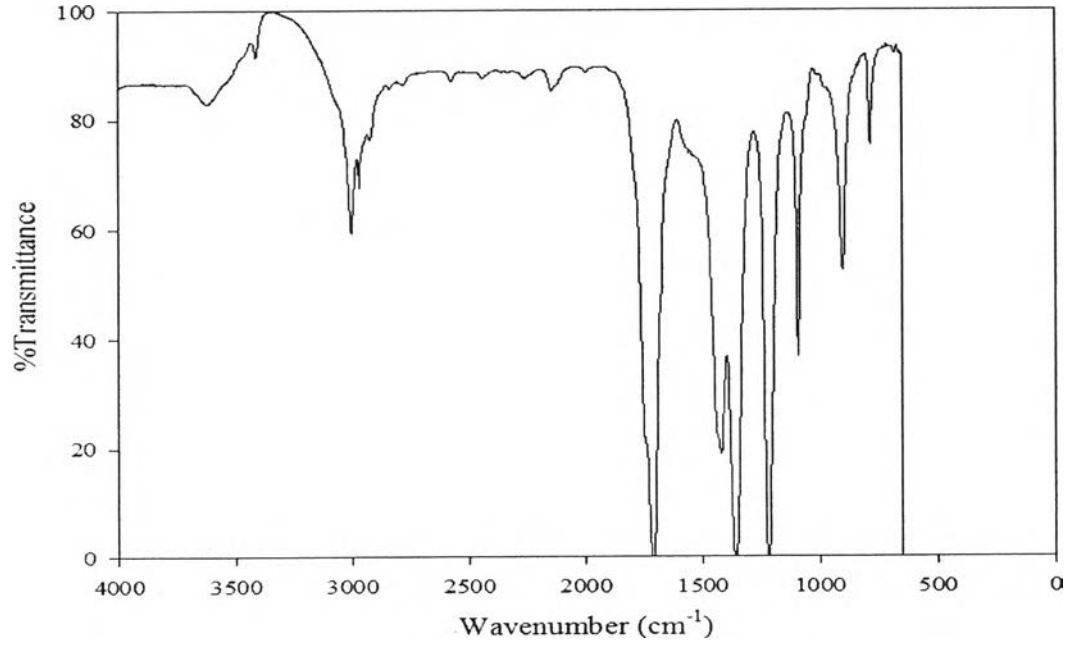

Figure B2 FT-IR spectra of acetone.

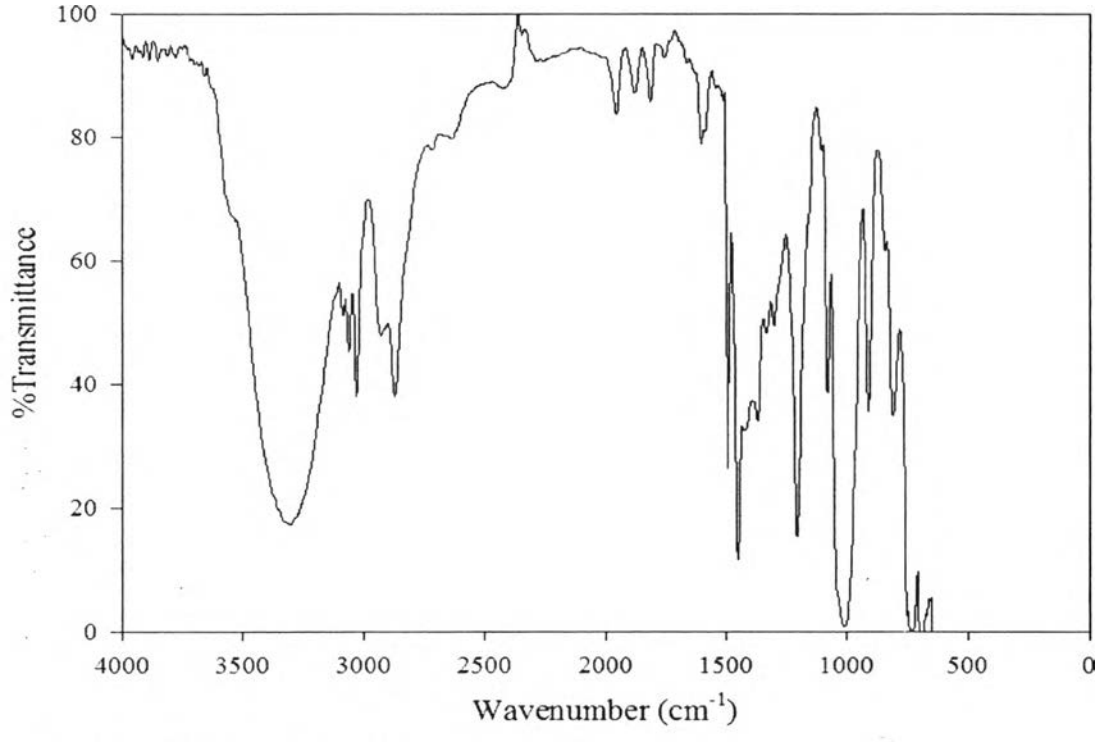

Figure B3 FT-IR spectra of benzyl alcohol.

CURRICULUM VITAE

Name: Mr. Narinthorn Suriyaprapadilok

Date of Birth: December 10, 1986

Nationality: Thai

University Education:

2005-2009 Bachelor Degree of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

Work Experience:

2008	Position:	Trainee (2 months)
	Company name:	Unilever Thai Holding Ltd.

Proceedings:

1. Suriyaprapadilok, N. and Kitiyanan, B. (2011, April 26) Production of solketal from glycerol: Effect of water removal and its use in preparation of benzyl solketal ether. Proceeding of the 2nd Research Symposium on Petroleum, Petrochemical, and Advanced Materials and 17th PPC Symposium on Petroleum, Petrochemical, and Polymers, Bangkok, Thailand.

Presentations:

1. Suriyaprapadilok, N. and Kitiyanan, B. (2011, March 31) Production of solketal from glycerol: Effect of water removal and its use in preparation of benzyl solketal ether. Paper presented at the TRF-MASTER Research Congress V, Chonburi, Thailand.