

## REFERENCES

- Babayan, V.K. and Lehman, H. (1972). U.S. Patent 3 637 774.
- Barrault, J., Pouilloux, Y., Vanhove, C., Cottin, K., Abro, S., and Clacens, J.M. (1998). Catalysis in Organic Reactions. New Orleans, LA, USA: Marcel Dekker.
- Barrault, J., Clacens, J.M., and Pouilloux, Y. (2004). Selective oligomerization of glycerol over mesoporous catalysts. Topics in Catalysis, 27, 137-141.
- Barrault, J., Pouilloux, Y., Clacens, J.M., Vanhove, C., and Bancquart, S. (2002). Catalysis and fine chemistry. Catalysis Today, 75, 177-181.
- Chai, S-H., Wang, H-P., Liang, Y., and Xu B-Q. (2009). Sustainable production of acrolein: Preparation and characterization of zirconia-supported 12-tungstophosphoric acid catalyst for gas-phase dehydration of glycerol. Applied Catalysis A, 353, 213-222.
- Clacens, J.M., Pouilloux, Y., and Barrault, J. (2002). Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalyst. Applied Catalysis A, 227, 181-190.
- Clacens, J.M., Pouilloux, Y., Barrault, J., Linares, C., and Goldwasser, M., (1998). Mesoporous basic catalysts: comparison with alkaline exchange zeolites (basicity and porosity). Application to the selective etherification of glycerol to polyglycerols. Studies in Surface Science and Catalysis, 118, 895-902.
- Corma, A., Iborra, S., and Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. Chemical Reviews, 107, 2411-2502.
- Engu'ídanos, M., Soria, A., Kavalov, B., and Jensen, P. (2002). Techno-economic analysis of Bio-diesel production in the EU: a short summary for decision-makers 4. European Commission Joint Research Centre Report, EUR 20279 EN.
- Foglia, T.A., Ashby, R.D., Wyatt, V.T., Solaiman, D. (2006). Industrial Products from Biodiesel Glycerol [abstract]. International Symposium on Biocatalysis and Bioenergy, 36.

- Garti, N., Arserin, A., and Zaidman, B. (1981). Polyglycerol esters: optimization and techno-economic evaluation. Journal of the American Oil Chemists' Society, 58, 878-883.
- Handa, H., Fu, Y., Baba, T., and Ono, Y., (1999). Characterization of strong solid bases by test reactions. Catalysis Letters, 59, 195–200.
- Harris, E. G., Hees, U., Bunte, R., Hachgenei, J., and Kuhm, P. U.S. Patent 5 349 094.
- Hattori, H. (1995). Heterogenous basic catalysis. Chemical Reviews, 95, 537-558.
- Henard, M.C. (2007). Impacts on oilseed industry following biofuel boom. Global Agriculture Information Network Report, FR7009.
- Hoek, I., Nijhuis, T.A., Stankiewicz, A.I., and Moulijn, J.A. (2004). Kinetics of solid acid catalysed etherification of symmetrical primary alcohols: zeolite BEA catalysed etherification of 1-octanol. Applied Catalysis A, 266, 109–116.
- Jakobsen, G., Linke., H., and Siemanowsky, W. (1990). U.S. Patent 4 973 763.
- Jakobsen, G. and Siemanowski, W. (1990). U.S. Patent 4 960 053.
- Jakobsen, G. and Siemanowski, W. (1991). U.S. Patent 4 992 594.
- Jakobsen, G. and Siemanowski, W., and Dillenburg, H. (1993). U.S. Patent 5 243 086.
- Kumar, T.N., Sastry, Y.S.R., and Lakshminarayana, G. (1984). Analysis of Polyglycerols by High-Performance Liquid Chromatography. The journal of chromatography, 298, 360–365.
- Lafosse, M., Chaimbault, P., Cassel, S., and Claude, S., (1999). Direct analysis of industrial oligoglycerols by liquid chromatography with evaporative light-scattering detection and mass spectrometry. Chromatographia, 50(3/4), 239–242.
- Lemke, D.W. (2002). U.S. Patent 6 620 904 B2.
- Li, Q., Zhang W., Zhao N., Wei W., and Sun, Y., (2006). Synthesis of cyclic carbonates from urea and diols over metal oxides. Catalysis Today, 115, 111–116.

- Richardson, J. T. (1989). Principles of Catalyst Development. Fundamental and applied catalysis. Plenum Press.
- Richter, M., Krisnandi, Y.K., Eckelt, R., and Martin, A. (2008), Homogeneously catalyzed batch reactor glycerol etherification by  $\text{CsHCO}_3$ . Catalysis Communications, 9, 2112–2116.
- Roberts, G., Minihan, A.R., Laan, J.M., and Eshuis, J.W. (1998). U.S. Patent 5 723 696.
- Ruppert, A.M., Meeldijk, J. D., Kuipers, B.W. M., Ern, 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.
- Seiden, P. and Martin, J.B. (1976). U.S. Patent 3 968 169.
- Silva, G.P., Mack, M., and Contiero, J. (2009). Glycerol: A promising and abundant carbon source for industrial microbiology. Biotechnology Advances, 27, 30–39.
- Snchez, N., Martnez, M., and Aracil, J. (1997). Selective esterification of glycerine to 1-glycerol monooleate. 1. Kinetic modeling. Industrial and Engineering Chemistry Research, 36 (5), 1524-1528.
- Tanabe, K., Misono, M., Ono, Y., and Hattori, H. (1989). New solid acids and bases. Studies in Surface Science and Catalysis, 51, 26.
- Thanasanvisut, D., Kitiyanan, B., and Abe, M. (2008, April 23) Synthesis of Diglycerol from Glycerol by Heterogeneous Base Catalysts. Proceedings of 14<sup>th</sup> PPC Symposium on Petroleum, Petrochems, and Polymers, Bangkok, Thailand.
- Thomas, J. M., and Robert J. P. Williams. (2005). Catalysis: principles, progress, prospects. Philosophical Transactions of the Royal Society A, 363, 765–791.

## APPENDICES

### Appendix A The glycerol conversion, diglycerol selectivity and diglycerol yield of the studied catalysts

In this study, the catalytic activities of some heterogeneous catalysts were compared with homogeneous catalyst in terms of total glycerol conversion, diglycerol selectivity, and diglycerol yield. The representative of homogeneous catalysts was NaOH and Na<sub>2</sub>CO<sub>3</sub>, while the heterogeneous catalysts were BaO, CaO, and MgO. The reaction temperature was fixed at 240°C and 2.0 wt% of catalyst.

**Table A1** The glycerol conversion, diglycerol selectivity and diglycerol yield when studied the effect of catalyst types

Time (h)	NaOH		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	13	95	12
2	32	75	24
3	53	57	30
4	68	40	27
5	80	27	21
6	81	24	20

Time (h)	Na <sub>2</sub> CO <sub>3</sub>		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	22	100	22
2	37	83	30
3	46	75	35
4	54	74	40
5	65	55	36
6	76	41	31

Time (h)	BaO		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	20	80	16
2	37	73	27
3	50	60	30
4	59	58	34
5	66	52	34
6	72	42	30

Time (h)	CaO		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	8	100	8
2	23	100	23
3	34	81	28
4	50	62	31
5	55	53	29
6	68	40	27

Time (h)	MgO		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	2	100	2
2	7	100	7
3	10	100	10
4	17	73	12
5	22	75	16
6	30	51	15

**Table A2** The glycerol conversion, diglycerol selectivity and diglycerol yield when studied the effect of reaction temperature

Time (h)	BaO 220 °C		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	7	100	7
2	12	58	7
3	18	55	10
4	22	79	18
5	28	70	20
6	32	85	27

Time (h)	BaO 230 °C		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	15	100	15
2	21	100	21
3	31	84	25
4	36	84	30
5	39	86	34
6	47	71	33

Time (h)	BaO 240 °C		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	20	80	16
2	37	73	27
3	50	60	30
4	59	58	34
5	66	52	34
6	72	42	30

Time (h)	BaO 250 °C		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	40	60	27
2	62	45	30
3	78	28	23
4	85	27	22
5	88	24	20
6	93	10	10

**Appendix B The glycerol conversion, diglycerol selectivity and diglycerol yield of the pilot scale studied**

**Table B** The glycerol conversion, diglycerol selectivity and diglycerol yield when studied the effect of reaction temperature

Time (h)	CaO 240 °C		
	% Glycerol Conversion	% Diglycerol Selectivity	% Diglycerol Yield
1	4	100	4
2	8	100	8
3	20	94	19
4	26	92	24
5	35	80	28
6	39	78	30

## CURRICULUM VITAE

**Name:** Mr. Chaloeimpan Petsriprasit

**Date of Birth:** July 23, 1985

**Nationality:** Thai

**University Education:**

2002-2006 Bachelor Degree of Chemical Technology, Faculty of Science,  
Chulalongkorn University, Bangkok, Thailand

**Working Experience:**

2006 Position: Internship Student  
Company name: Asahi Thai Alloy Co., Ltd.

**Proceedings:**

Petsriprasit, C., and Kitiyanan, B. (2009, April 22) Etherification of Glycerol by Alkaline Earth Oxides as Solid Catalysts: Kinetics and Pilot Scale Study. Proceedings of 15<sup>th</sup> PPC Symposium on Petroleum, Petrochems, and Polymers, Bangkok, Thailand.

**Presentations:**

1. Petsriprasit, C., and Kitiyanan, B. (2009, April 22) Etherification of Glycerol by Alkaline Earth Oxides as Solid Catalysts: Kinetics and Pilot Scale Study. Poster presented at the 15<sup>th</sup> PPC Symposium on Petroleum, Petrochems, and Polymers, Bangkok, Thailand.

