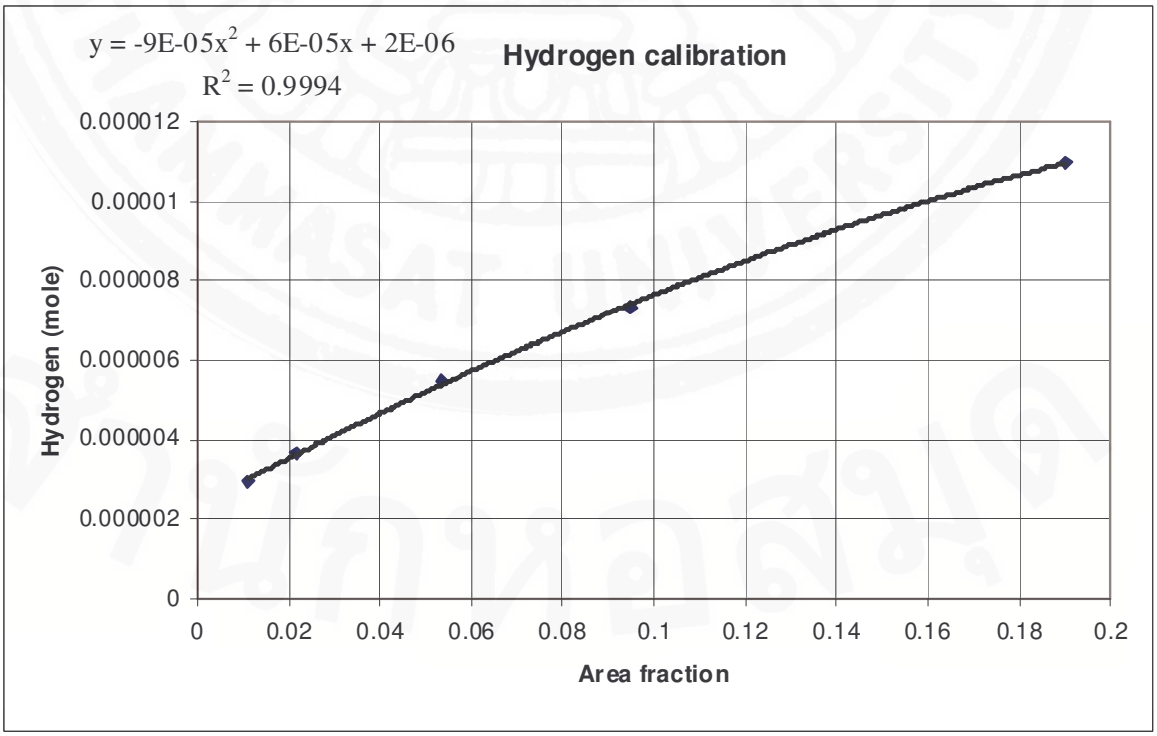
Appendix 1

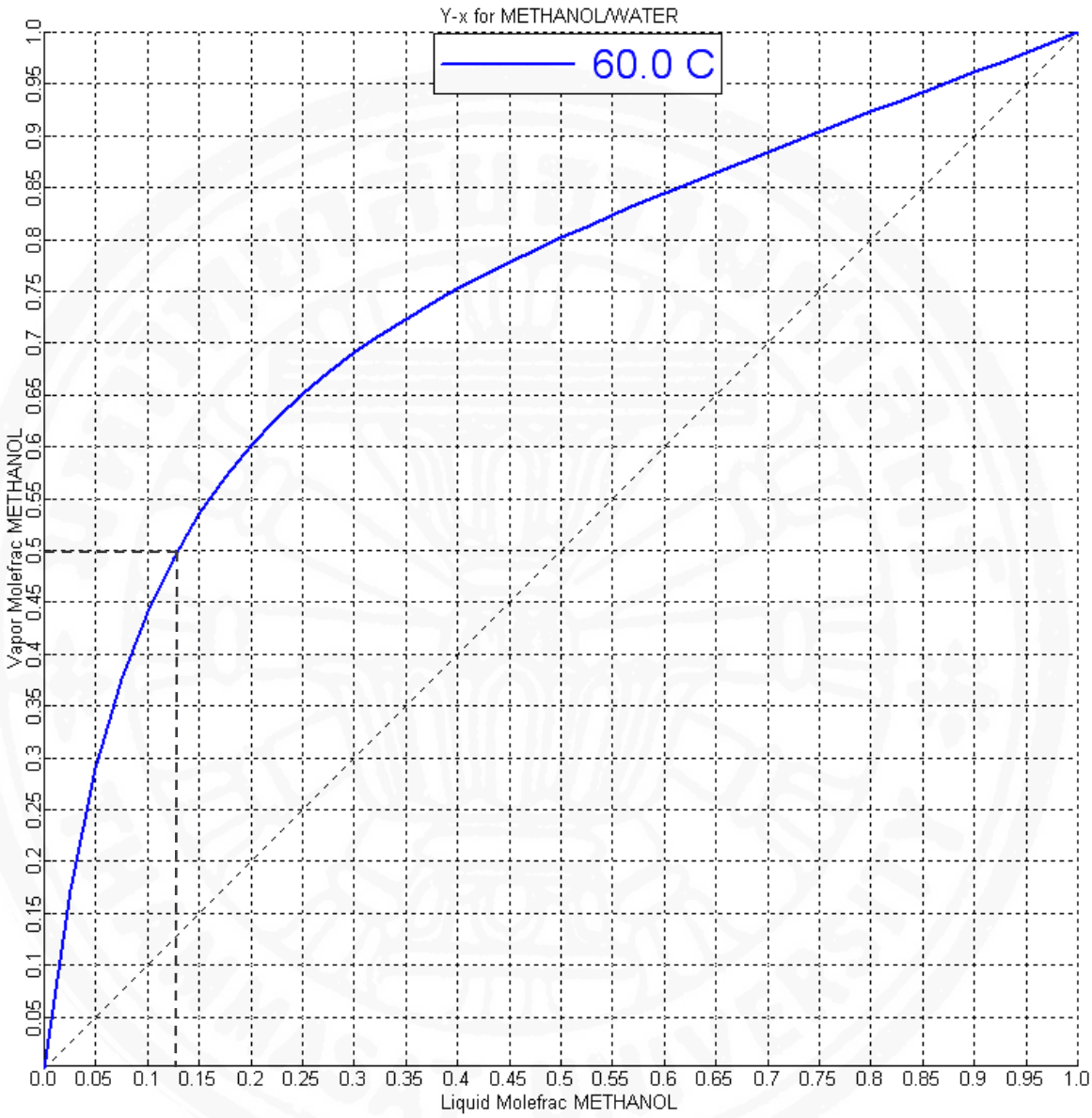
Calibration curve for Gas Chromatograph

H_2 (vol%)	H_2 (mole)	Area	Average area	Area fraction
8	2.92769E-06	4984	5036	0.0111021
		4827		
		5296		
10	3.65962E-06	9880	9805	0.0216171
		9912		
		9623		
15	5.48943E-06	23539	24306	0.0535881
		24955		
		24425		
20	7.31923E-06	42528	42955	0.0947035
		43928		
		42410		
30	1.09789E-05	86230	86291	0.1902463
		85172		
		87472		
100	0.000365962	458533	453577	1
		468485		
		433713		



Appendix 2

Vapor-liquid equilibrium of methanol and water



The composition of methanol and water in liquid phase was calculated by Aspen plus simulation program using the Non-Random Two Liquid model (NRTL) and Modified Raoult's Law. From the graph, the mixture of methanol and water was mixed at 0.125:0.875 mole fraction in order to obtain the composition of methanol and water in vapor phase at 1:1 mole fraction.

The Non-Random Two Liquid model (NRTL)

The Non-Random Two Liquid model is an activity coefficient model that correlates the activity coefficients γ with the composition of a mixture of chemical compounds, expressed by mole fractions x. The concept is based on the hypothesis of Wilson that the local concentration around a molecule will be different from the bulk concentration when there is a difference between the interaction energy of the central molecule with the molecules of its own kind and that with the molecules of the other kind. This difference introduces a non-randomness at the molecular level.

Modified Raoult's Law

The modified Raoult's law is used to calculation for VLE when the pressure of system is high so, the second major Raoult's law assumption is abandoned, and the system is deviated from solution ideality in the liquid phase. The parameter "activity coefficient" is added into the Raoult's law.

Modified Raoult's law;

$$y_i P = x_i \gamma_i P_i^{sat} \qquad \text{(i = 1, 2,.....,N)} \qquad (2)$$

The factor γ_i is called an activity coefficient. The activity coefficients are functions of temperature and liquid-phase composition. The pressure of system could be calculation by;

$$P = \sum x_i \gamma_i P_i^{Sat} \qquad \text{(i = 1, 2,.....,N)} \qquad (3)$$

Saturated pressure, P^{sat}, could be calculated by Antoine equation;

$$\ln P^{Sat} = A - \frac{B}{t + C} \qquad (4)$$

Where P^{sat} is saturated pressure [kPa].

t is temperature [°C].

A, B and C are parameters for the Antoine equation shown as follow

Parameters for the Antoine equation

	A	B	C
Methanol	16.5938	3,644.30	239.76
Water	16.2620	3,799.89	226.35

Appendix 3

Hydrogen production from methanol steam reforming

Cu-Zn-Al_2O_3 Catalysts (Cu/Zn/Al_2O_3) %wt		Temperature (K)	% H_2 yield
10CZ	(5/5/90)	453	< 10
10CZU1	(5/5/90)		< 10
10CZU2	(5/5/90)		14
20CZ	(10/10/80)		13
20CZNa	(10/10/80)		13
20CZU1	(10/10/80)		15
20CZU2	(10/10/80)		19
Commercial	(40/30/30)		27
10CZ	(5/5/90)	523	14
10CZU1	(5/5/90)		20
10CZU2	(5/5/90)		23
20CZ	(10/10/80)		28
20CZNa	(10/10/80)		28
20CZU1	(10/10/80)		35
20CZU2	(10/10/80)		42
Commercial	(40/30/30)		43

Appendix 4

Estimated crystallize size of CuO

Sample	Estimated crystallize size of CuO [a] (nm)
10CZ	28
10CZU1	21
10CZU2	14
20CZ	29
20CZNa	24
20CZU1	22
20CZU2	14
Commercial	10

[a] determined by XRD using peak at 2-theta equal to 38.8°

Appendix 5

Properties of substances

Methanol

Chemical formula:	CH_3OH
Brand:	Carlo Erba
Purity:	≥ 99 %
Molar mass:	32.05 g/mol
Density:	0.7918 g/cm^3
Boiling point:	64.7 °C

Copper nitrate trihydrate

Chemical formula:	$Cu(NO_3)_2 \cdot 3H_2O$
Brand:	Fluka
Purity:	≥ 99 %
Molar mass:	241.6 g/mol
Density:	2.32 g/cm^3
Melting point:	114 °C
Boiling point:	170 °C

Zinc nitrate hexahydrate

Chemical formula:	$Zn(NO_3)_2 \cdot 6H_2O$
Brand:	Fluka
Purity:	≥ 99 %
Molar mass:	297.49 g/mol
Density:	2.065 g/cm^3
Melting point:	45.5 °C
Boiling point:	125 °C

Alumina

Chemical formula:	Al_2O_3
Brand:	Riedel-de Haen
Purity:	≥ 98 %
Molar mass:	101.96 g/mol
Density:	3.95-4.1 g/cm^3
Melting point:	2072 °C
Boiling point:	2980 °C

Urea

Chemical formula:	CH_4N_2O
Brand:	Carlo Erba
Purity:	≥ 99 %
Molar mass:	60.07 g/mol
Density:	1.32 g/cm^3
Melting point:	132.7-135 °C