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**APPENDICES**

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## Appendix

### A-1 Calculation for Vapor Pressure of Methanol

Antoine's equation

$$\ln (P \times (V_p/P_c)) = (1-X)^{-1}[(V_pA)X + (V_pB)X^{1.5} + (V_pC)X^3 + (V_pD)X^6] \quad (A-1)$$

Where P = Total pressure

V<sub>p</sub> = Vapor pressure

P<sub>c</sub> = Critical pressure

X = 1 - (T/T<sub>c</sub>) ; T<sub>c</sub> = critical temperature, T = trial temperature (K)

V<sub>pA</sub>, V<sub>pB</sub>, V<sub>pC</sub>, V<sub>pD</sub> = constant

Example: Determination of vapor pressure of methanol at 30°C

For methanol; T<sub>c</sub> = 512.6 K, P<sub>c</sub> = 80.9 atm P = 1 atm

V<sub>pA</sub> = -8.54796, V<sub>pB</sub> = 0.76982, V<sub>pC</sub> = -3.10850,

V<sub>pD</sub> = 1.54481, T = 30°C = 301.15 K

X = 1 - (301.15/512.6) = 0.40860

$$\ln (1 \times (V_p/80.9)) = (1-0.40860)^{-1}[(-8.54796)(0.40860) + (0.76982)(0.40860)^{1.5} + (-3.10850)(0.40860)^3 + (1.54481)(0.40860)^6]$$

$$\ln (V_p/80.9) = -5.9123$$

$$V_p/80.9 = \exp(-5.9123) = 2.706 \times 10^{-3}$$

$$V_p = 0.2189 \text{ atm}$$

**A-2 Calculation for Feed Flow Rate**

The used catalyst = 0.3 g

Packed catalyst into borosilicate reactor (inside diameter = 0.54 cm)

Determine the average height of catalyst bed = 1.6 cm, so that,

$$\begin{aligned}\text{Volume of bed} &= \pi r^2 h = (22/7) \times (0.27)^2 \times 1.6 \\ &= 0.3666 \text{ cm}^3\text{-cat.}\end{aligned}$$

Use Gas Hourly Space Velocity (GHSV) = 2000 h<sup>-1</sup>

$$\text{GHSV} = \frac{\text{Volumetric flow rate}}{\text{Volume of bed}} \quad \text{at STP condition}$$

$$\begin{aligned}\text{Volumetric flow rate} &= 2000 \times 0.3666 = 733.16 \text{ cm}^3/\text{h} \\ &= 733.16/60 = 12.22 \text{ cm}^3/\text{min}\end{aligned}$$

At room temperature

$$\text{Volumetric flow rate} = 12.22 \frac{(273.15 + T)}{273.15}$$

Where T = measured temperature of methanol saturator (°C)

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### A-3 Calculation for Conversion of Methanol in MTO reaction

Methanol conversion activity was evaluated in term of conversion of methanol into other hydrocarbons.

$$\text{Methanol conversion (\%)} = \frac{(A_{\text{in}} - A_{\text{out}})}{A_{\text{in}}} \times 100 \quad (\text{A-2})$$

Where A = GC peak area of methanol

If  $A_{\text{in}} = 8620$  ;  $A_{\text{out}} = 66$

$$\begin{aligned} \text{Methanol conversion (\%)} &= \frac{(8620 - 66)}{8620} \times 100 \\ &= 99.23\% \end{aligned}$$



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#### A-4 Calculation of GC Peak Area to Concentration

$$C_x = \frac{A_x \times C_{\text{std}} \times V_{\text{std}}}{A_{\text{std}} \times V_x} \quad (\text{A-3})$$

$$\% \text{ selectivity} = \frac{C_x \times 100}{C_{\text{total}}} \quad (\text{A-4})$$

When  $C_{\text{std}}$  = Concentration of the component of interest in the standard mixture, % mol

$C_x$  = Concentration of the component in the sample, % mol.

$C_{\text{total}}$  = Concentration of the total component in the sample, % mol.

$A_{\text{std}}$  = Peak area of the component in standard mixture, au.

$A_x$  = Peak area of the component in the sample, au.

$V_{\text{std}}$  = injected volume of the standard mixture,  $\mu\text{l}$ .

$V_x$  = injected volume of the sample,  $\mu\text{l}$ .

If data of propylene,  $A_{\text{propylene}} = 105380$ ;  $A_{\text{std}} = 190640$ ;  $C_{\text{std}} = 15.0$  % molar;

$V_{\text{std}} = 2.0$   $\mu\text{l}$ ;  $V_{\text{propylene}} = 10$   $\mu\text{l}$ ,  $C_{\text{total}} = 3.097$  % molar

$$C_{\text{propylene}} = \frac{105380 \times 15.0 \times 2.0}{190640 \times 10}$$

$$= 1.66\% \text{ molar}$$

$$\% \text{ selectivity to propylene} = \frac{1.66 \times 100}{3.097}$$

$$= 53.54$$



### A-5 Calculation for Initial Weight of Feed Methanol

$$P V = n R T \quad (A-5)$$

When  $P$  = partial pressure of methanol, atm

$V$  = volume of gas, L

$n$  = mole of methanol, mol

$R$  = constant =  $0.082 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$T$  = temperature of methanol, K

If  $P = 0.2189 \text{ atm}$ ,  $V = 0.5381 \text{ L}$ ,  $T = 30^\circ\text{C} = 303.15 \text{ K}$

$$\begin{aligned} n &= \frac{P V}{R T} \\ &= \frac{0.2189 \times 0.5381}{0.082 \times 303.15} \\ &= 0.004739 \text{ mol} = 0.1579 \text{ g} \end{aligned}$$

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### A-6 Calculation for Yield of Gas Product and Liquid Product

$$(A-6) \quad \% \text{ Yield of liquid product} = \frac{\text{wt. liquid product} \times \% \text{conversion}}{\text{wt. MeOH}}$$

$$(A-7) \quad \% \text{ Yield of gas product} = \frac{\text{wt. gas product} \times \% \text{conversion}}{\text{wt. MeOH}}$$

When wt. gas product = wt.MeOH – wt. liquid product – wt. coke

If wt. MeOH = 0.1517 g, wt. liquid product = 0.1199 g, wt. coke = 0.0022 g

$$\begin{aligned} \% \text{ Yield of liquid product} &= \frac{0.1199 \times 99}{0.1517} \\ &= 78.24 \end{aligned}$$

$$\begin{aligned} \% \text{ Yield of gas product} &= \frac{0.1517 - 0.1199 - 0.0022 \times 99}{0.1517} \\ &= 19.32 \end{aligned}$$

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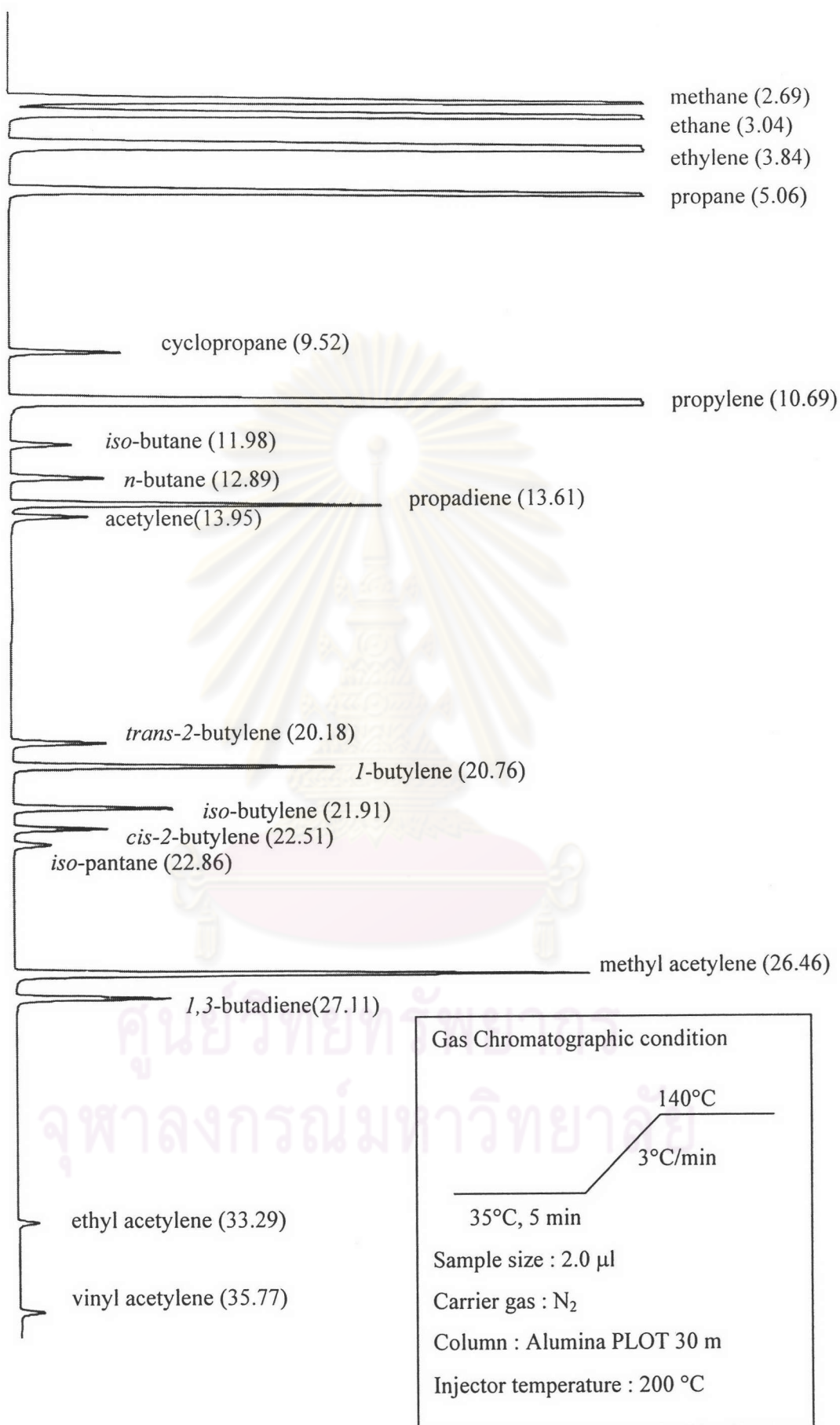
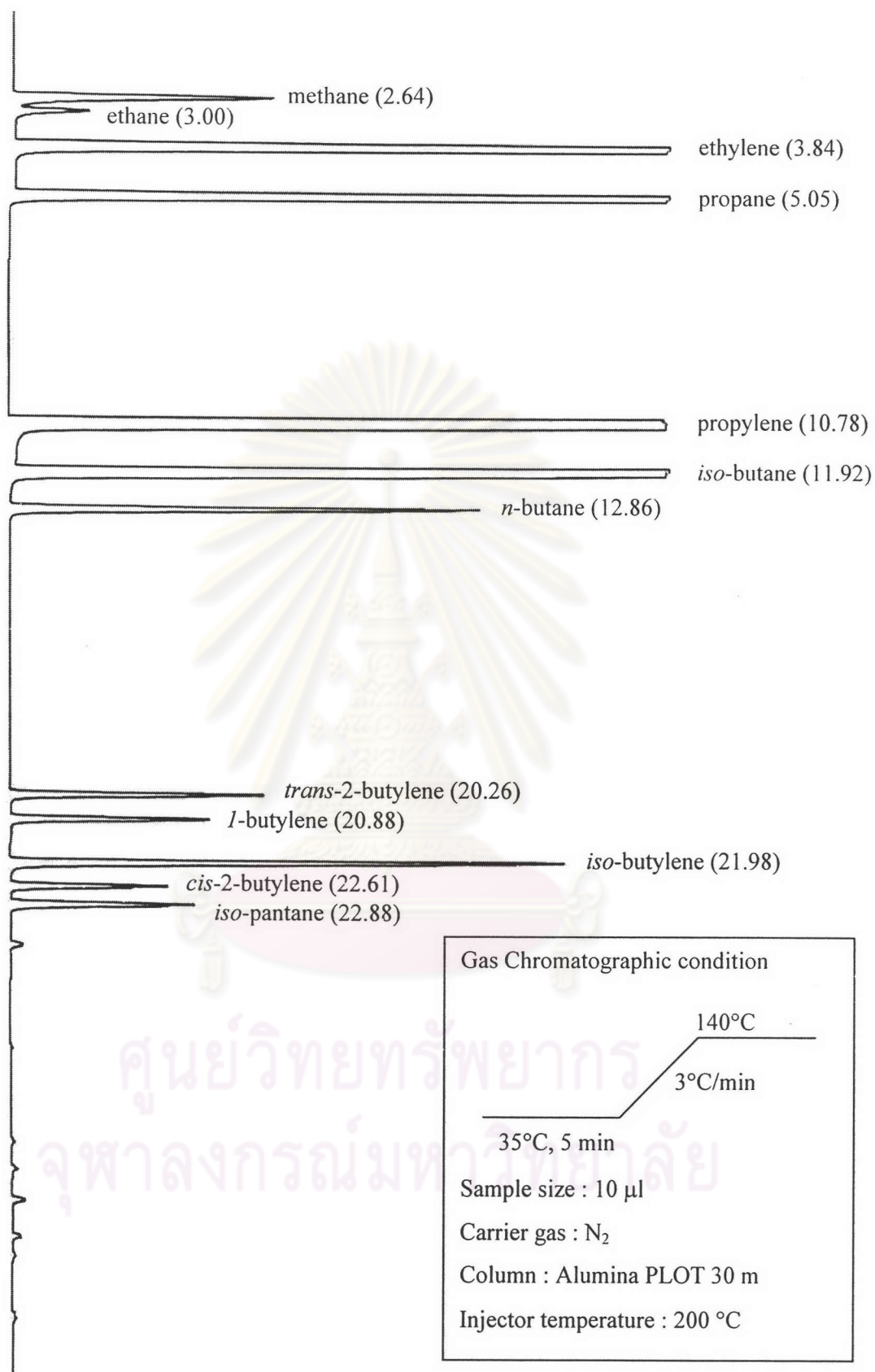


Figure A-1 Gas chromatogram of standard mixture C<sub>4</sub> gas.



**Figure A-2** Gas chromatogram of gas product from methanol conversion reaction on H-Fe-MFI (Si/Fe ratio = 90) at 400°C (Condition: 0.3 g of catalyst, feed at GHSV of 2000 h<sup>-1</sup>, T<sub>MeOH</sub> = 30°C, time on stream 40 min.).

## VITAE

Miss Intira Sangvaraporn was born on May 17, 1977 in Chanthaburi, Thailand. She received a Bachelor Degree of Science in Chemistry from Burapha University in 2000. Since then, she has been a graduate student studying Inorganic Chemistry in Faculty of Science, Chulalongkorn University. During her graduate studies towards her Master's degree, she also received a teaching assistant scholarship by the Faculty of Science in 2001 and a research grant from the Graduate School, Chulalongkorn University. She was invited to present her thesis work at the Student and Young Scientists Forum on Green & Sustainable Chemistry at Waseda University, Japan in March 2003 sponsored by IUPAC chemrawn XIV Committee.



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