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APPENDICES

1.   **Calculation of Vapor Pressure of 1-Hexene**

$\ln(P_{vp}/P_c)$ = $(1-X)^{-1}[(VPA)X + (VPB)X^{1.5} + (VPC)X^3 + (VPD)X^6]$ ..(A-1)[a]

X   = $1-T/T_c$ ....(A-2)[b]

for 1-Hexene[c], Pc = 31.7 bar , Tc = 504 K , VPA = -7.76467 , VPB = 2.29843 ,

VPC = -4.44302 and VPD = 0.89947

From equation A-2 at T = 303.15K (30°C)

X   = $1 - 303.15/504 = 0.3985$

By replacing the X value in Equation A-1

$\ln(P_{vp}/31.7)$ = $(1-0.3985)^{-1}[(-7.76467)(0.3985) + (2.29843)(0.3985)^{1.5} +$

$(-4.44302)(0.3985)^3 + (0.89947)(0.3985)^6] = -4.6445$

Thus P_{vp} =   0.3045 atm

Thus, at the atmospheric pressure of 1 atm and the temperature of 30°C, the 1-hexene

partial pressure of 0.30 atm generates the mixture of 30.45% 1-hexene and the balancing

gas.

[a],[b],[c] = Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. The Properties of Gases and

Liquids Mcgraw-Hill, New York, 1997, p. 181-189.

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2. Calculation of Feed Flow Rate

The catalyst used = 0.3000 g

Packed catalyst into borosilicate reactor which has radius = 0.27 cm

The average height of catalyst bed = 3 cm.

Volume of catalyst bed = $\pi r^2 h$ cm^3

GHSV (Gas Hourly Space Velocity) = 500 h^{-1} at STP

$$\text{GHSV} = \frac{\text{Volumetric flow rate at STP}}{\text{Volume of catalyst}} \quad \text{................(A-3)}$$

Volumetric flow rate(STP) = GHSV x Volume of catalyst

= $500 \times \pi \times (0.27)^2 \times 3$ cm^3/h

= $500 \times \pi \times (0.27)^2 \times (3/60)$ cm^3/min

Thus, volumetric flow rate = 5.72 cm^3/min

At T °C : Volumetric flow rate = $\dfrac{\text{Volumetric flow rate (STP)} \times (273.15 + T)}{273.15}$ ...(A-4)

At 30°C, Volumetric fow rate = $\dfrac{5.72 \times (273.15 + 30)}{273.15}$ = 6.34 cm^3/min

3. Calculation for Weight of Reactant Feed

From ideal gas equation,

$$PV = nRT \qquad \ldots\ldots\ldots\ldots\ldots\ldots(A\text{-}5\}$$

Where

P = Partial pressure of 1-hexene (atm)

V = Volume of gas (L)

n = mole of 1-hexene (mol)

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

T = Temperature of 1-Hexene (K)

From reaction condition, P = 0.3045 atm; V = 0.191 L; T = 303.15 K (30°C)

$$n = \frac{PV}{RT}$$

$$n = \frac{0.3045 \times 0.191}{0.082 \times 303.15}$$

Thus, mol of 1-hexene = 0.0023 mol = 0.1965 g

4. Calculation of Yield to Liquid for 1-Hexene Metathesis

$$\% \text{ yield of liquid product} = \frac{W_{\text{liquid product}}}{W_{\text{1-hexene}}} \times 100 \ldots (A\text{-}6)$$

Where W_{liquid} = Weight of liquid product from cold trap (g)

$W_{\text{1-hexene}}$ = Weight of 1-hexene feed (g)

For example, W_{liquid} = 0.1254 g $\quad W_{\text{1-hexene}}$ = 0.1962 g

Thus, %yield of liquid product = $\frac{0.1254}{0.1962} \times 100 = 63.91\%$

5. Calculation % Coke for 1-Hexene Metathesis

Weight of coke which means the difference between the weight of used catalyst before calcination and the weight of used catalyst after calcination

$$\% \text{ coke} = \frac{W_{coke}}{W_{catalyst}} \times 100 \qquad \text{........(A-7)}$$

Where

W_{coke} = Weight of coke (g)

$W_{catlyst}$ = Weight of catalyst (g)

For example, W_{coke} = 0.0098 g $\qquad W_{catalyst}$ = 0.3682 g

Thus, %yield of coke = $\frac{0.0098}{0.3682} \times 100$ = 2.66%

6.   Calculation of Yield of Gas Product for 1-Hexene Metathesis

% yield of gas product   =   100 – (% liquid + %coke)   (A-8)

Where   %liquid   = %yield of liquid product

               %coke   = %yield of coke

For example,   %liquid   = 63.91, %coke = 2.66

Thus, %yield of gas product =   100-(2.66+63.91) = 33.43%

7. **Calculation of Percent Conversion of 1-Hexene from Peak Area of GC**

Using peak areas obtained from GC analysis,

% Conversion $\qquad = \dfrac{A\ in - A\ out}{A\ in} \times 100$ ....(A-9)

Where   A in   =   Peak area of 1-hexene at the inlet of the catalyst reactor

A out   =   Peak area of 1-hexene at the outlet of the catalyst reactor

8. **Calculation of Percent Selectivity to Gas Product**

$$C_x = \frac{A_x \times C_{std} \times V_{std}}{A_{std} \times V_x} \qquad \text{A-10}$$

$$\% \text{ selectivity} = \frac{C_x \times 100}{C_{total}} \qquad \text{A-11}$$

When C_{std} = Concentration of the component of interest in the standard mixture (% mol)

C_x = Concentration of the component in the sample (% mol)

C_{total} = Concentration of the total component in the sample (% mol)

A_{std} = Peak area of the component in standard mixture (au.)

A_x = Peak area of the component in the sample (au.)

V_{std} = Injected volume of the standard mixture (μl)

V_x = Injected Volume of the sample (μl)

From GC data of ethylene product,

$A_{ethylene}$ = 219681; $A_{std\ of\ ethylene}$ = 119958; Cstd = 24.88 % molar,

V_{std} = 5 μl; $V_{ethylene}$ = 200 μl, C_{total} = 3.47 % molar

$$C_{ethylene} = \frac{219681 \times 24.88 \times 5}{119958 \times 200}$$

Thus, $C_{ethylene}$ = 1.1392 % molar

$$\% \text{ selectivity} = \frac{1.1392 \times 100}{3.4729}$$

Thus, % selectivity to ethylene = 32.80%

methane (2.68)
ethane (3.05)
ethylene (3.90)
propane (5.15)

cyclopropane (9.76)

propylene (10.95)

iso-butane (12.10)

n-butane (13.02)

propadiene (13.94)

acetylene(14.51)

trans-2-butylene (20.49)

1-butylene (21.08)

iso-butylene (22.24)

cis-2-butylene (22.82)

iso-pantane (23.01)

methyl acetylene (26.80)

1,3-butadiene(27.66)

ethyl acetylene (33.73)

vinyl acetylene (36.27)

Gas Chromatographic condition

140°C

3°C/min

35°C, 5 min

Sample size : 2.0 μl

Carrier gas : N_2, 3.4 cm^3/min at 26 °C

Column : Alumina PLOT 30 m
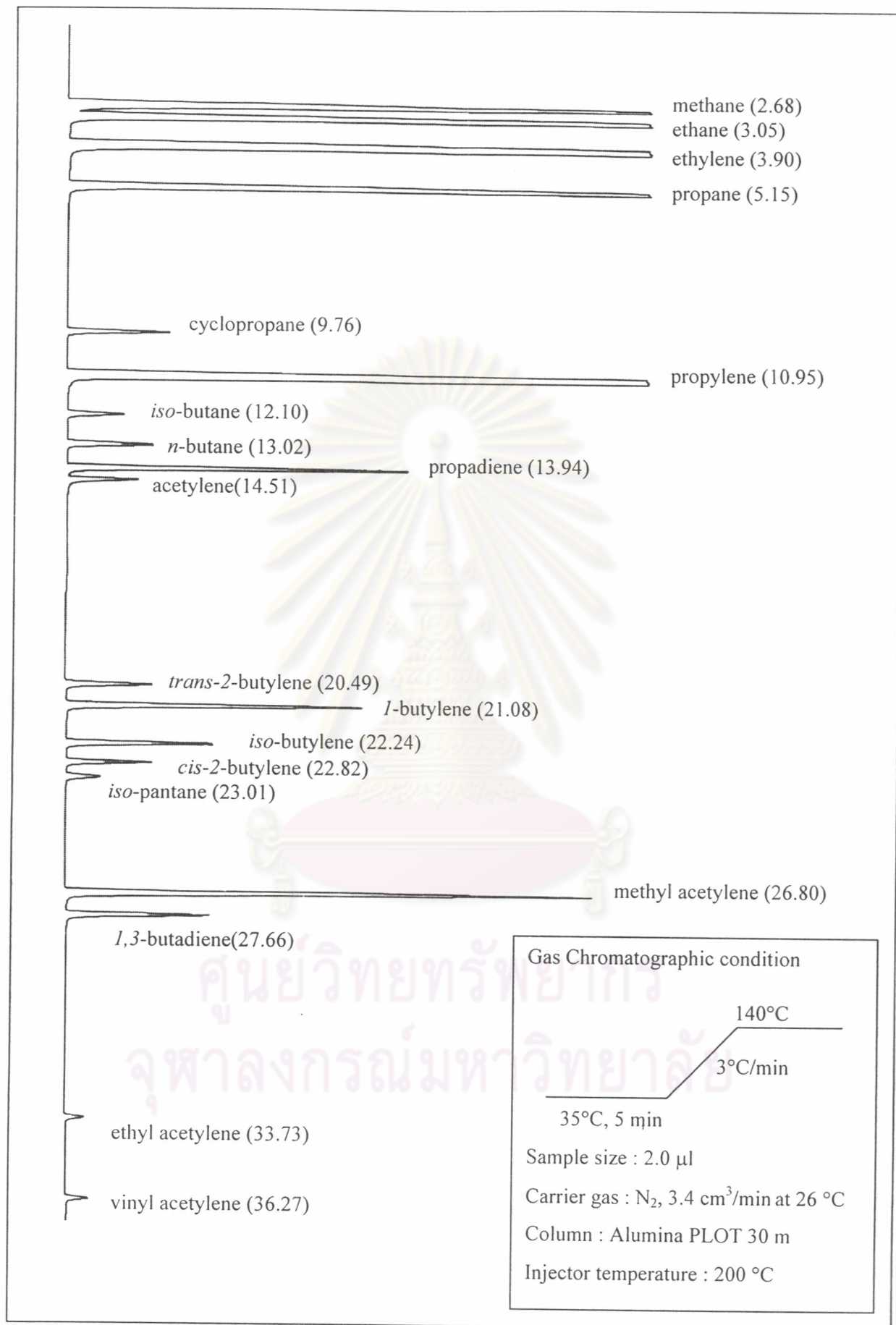
Injector temperature : 200 °C

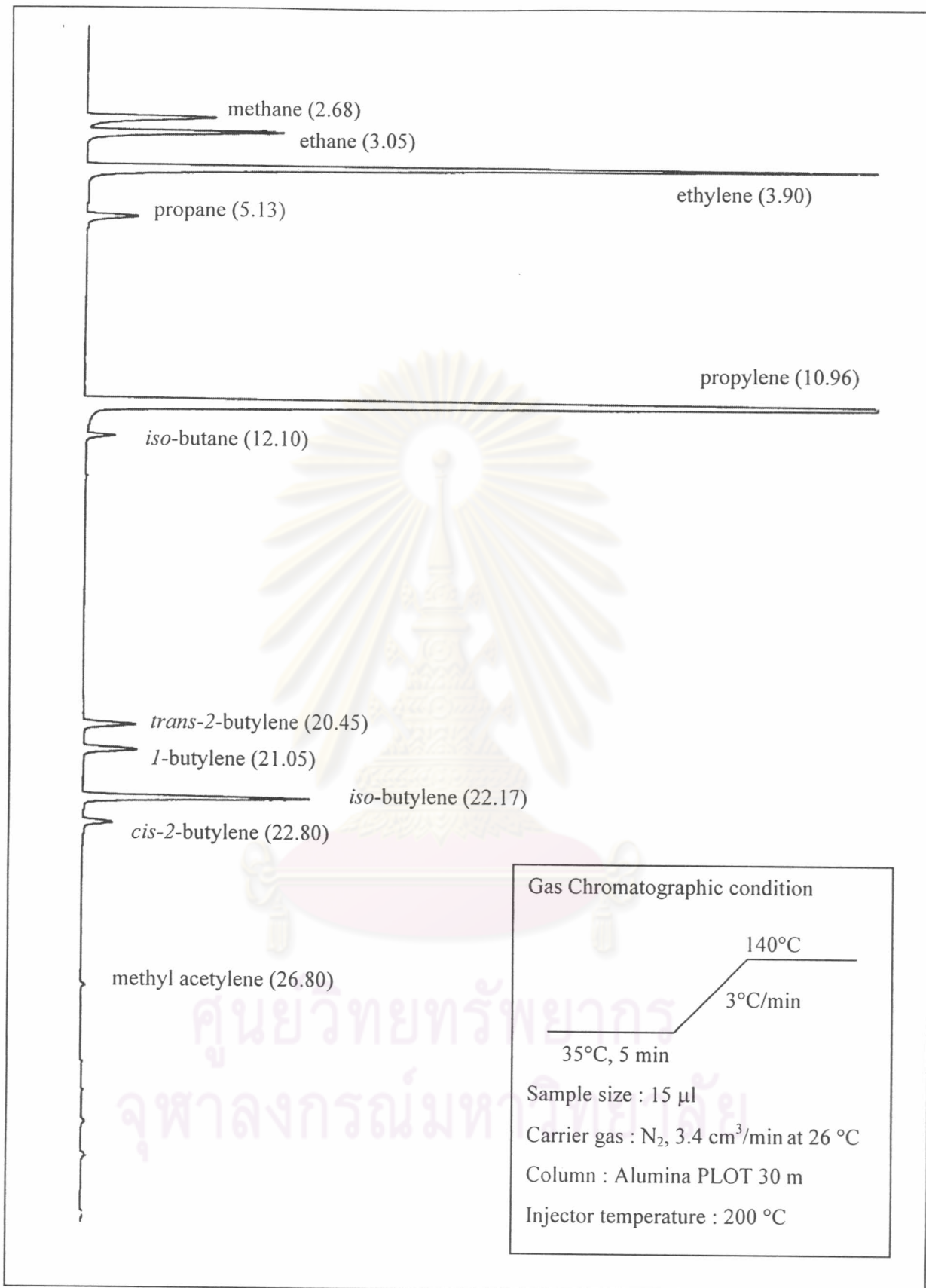**Figure A-1**   Gas chromatogram of standard mixture C_4 gas.

Figure A-2 Gas chromatogram of gas product from 1-hexene on 9% WO₃/HMS at

500°C (Condition: 0.35 g of catalyst, feed at GHSV of 500 h⁻¹, time on

stream 30 min.).

VITAE

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