

## REFERENCES

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**APPENDICES**

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### 1. Calculation of Vapor Pressure of 1-Hexene<sup>38</sup>

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

$$X = 1 - T/T_c \dots\dots\dots(A-2)$$

for 1-Hexene,  $P_c = 31.7 \text{ bar}$  ,  $T_c = 504 \text{ K}$  ,  $VPA = -7.76467$  ,  $VPB = 2.29843$ ,

$VPC = -4.44302$  and  $VPD = 0.89947$

From equation A-2 at  $T = 303.15\text{K}$  ( $30^\circ\text{C}$ )

$$X = 1 - 303.15/504 = 0.3985$$

By replacing the X value in Equation A-1

$$\begin{aligned} \ln (P_{vp}/31.7) &= (1-0.3985)^{-1} [(-7.76467)(0.3985) + (2.29843)(0.3985)^{1.5} + \\ &\quad (-4.44302)(0.3985)^3 + (0.89947)(0.3985)^6] = -4.6445 \end{aligned}$$

$$\text{Thus } P_{vp} = 0.3045 \text{ atm}$$

Thus, at the atmospheric pressure of 1 atm and the temperature of  $30^\circ\text{C}$ , the 1-hexene partial pressure of 0.30 atm generates the mixture of 30.45% 1-hexene and the balancing gas.

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## 2. Calculation of Feed Flow Rate

The catalyst used = 0.3500 g

Packed catalyst into borosilicate reactor which has radius = 0.27 cm

The average height of catalyst bed = 3 cm.

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

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

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

$$\begin{aligned} \text{Volumetric flow rate(STP)} &= \text{GHSV} \times \text{Volume of catalyst} \\ &= 500 \times \pi \times (0.27)^2 \times 3 \quad \text{cm}^3/\text{h} \\ &= 500 \times \pi \times (0.27)^2 \times (3 / 60) \quad \text{cm}^3/\text{min} \end{aligned}$$

$$\text{Thus, volumetric flow rate} = 5.72 \quad \text{cm}^3/\text{min}$$

$$\text{At } T \text{ } ^\circ\text{C} : \text{Volumetric flow rate} = \text{Volumetric flow rate (STP)} \times \frac{(273.15 + T)}{273.15} \dots(\text{A-4})$$

$$\text{At } 30^\circ\text{C, Volumetric flow rate} = \frac{5.72 \times (273.15 + 30)}{273.15} = 6.34 \text{ cm}^3/\text{min}$$

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### 3. Calculation for Weight of Reactant Feed

From ideal gas equation,

$$PV = nRT \dots\dots\dots(A-5)$$

Where P = Partial pressure of 1-hexene (atm)

V = Volume of gas (L)

n = mole of 1-hexene (mol)

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

T = Temperature of 1-Hexene (K)

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

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

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

$$\text{Thus, mol of 1-hexene} = 0.0023 \text{ mol} = 0.1965 \text{ g}$$

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

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

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

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

For example,  $W_{\text{liquid}} = 0.1527 \text{ g}$        $W_{\text{1-hexene}} = 0.1962 \text{ g}$

Thus, %yield of liquid product =  $\frac{0.1527}{0.1962} \times 100 = 77.82\%$



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### 5. Calculation % Coke for 1-Hexene Metathesis

Weight of coke which means the difference between the weight of before calcination and the weight of used catalyst after calcinations compared with converted 1-hexene.

$$\% \text{ coke} = \frac{W_{\text{coke}}}{W_{\text{1-hexene}}} \times 100 \quad \dots\dots(A-7)$$

Where  $W_{\text{coke}} = \text{Weight of coke (g)}$

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

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

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

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

$$\% \text{ yield of gas product} = 100 - (\% \text{ liquid} + \% \text{ coke}) \quad (\text{A-8})$$

Where  $\% \text{ liquid} = \% \text{ yield of liquid product}$

$\% \text{ coke} = \% \text{ yield of coke}$

For example,  $\% \text{ liquid} = 63.91$ ,  $\% \text{ coke} = 2.66$

Thus,  $\% \text{ yield of gas product} = 100 - (2.66 + 63.91) = 33.43\%$



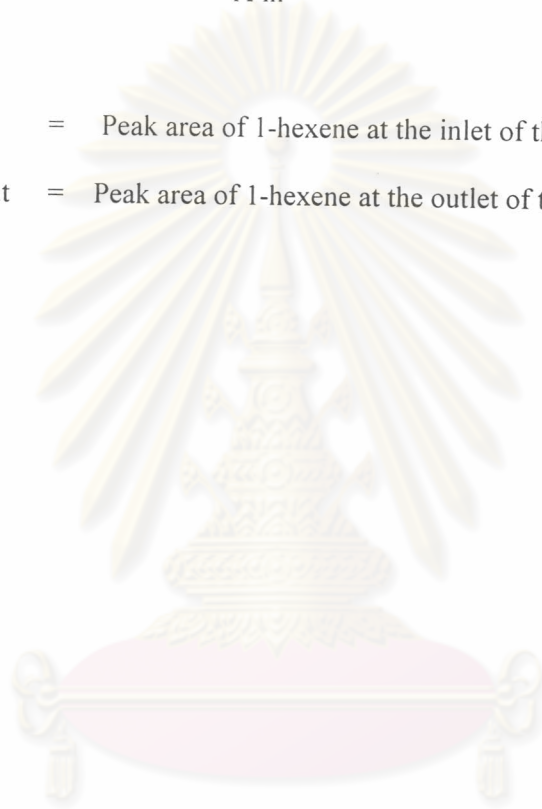
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### 7. Calculation of Percent Conversion of 1-Hexene from Peak Area of GC

Using peak areas obtained from GC analysis,

$$\% \text{ Conversion} = \frac{A_{\text{in}} - A_{\text{out}}}{A_{\text{in}}} \times 100 \dots\dots\dots(\text{A-9})$$

Where  $A_{\text{in}}$  = Peak area of 1-hexene at the inlet of the catalyst reactor  
 $A_{\text{out}}$  = Peak area of 1-hexene at the outlet of the catalyst reactor



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

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

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

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 ( $\mu\text{l}$ )

$V_x$  = Injected Volume of the sample ( $\mu\text{l}$ )

From GC data of ethylene product,

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

$V_{\text{std}} = 5$   $\mu\text{l}$ ;  $V_{\text{ethylene}} = 200$   $\mu\text{l}$ ,  $C_{\text{total}} = 3.47$  % molar

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

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

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

$$\text{Thus, \% selectivity to ethylene} = 32.80\%$$

### 9. Calculation of Percent Selectivity to Liquid Product

$$C_y = \frac{A_y \times C_{b_{std}} \times C_{std}}{A_{std} \times C_{b_y}}$$

$$\% \text{ selectivity} = \frac{C_x \times 100}{C_{total}}$$

$$C_{std} = \frac{D \times V \times 1000}{MW}$$

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

$C_y$  = Concentration of the component in the sample (mol)

$C_{std}$  = Concentration of the internal the sample (mol)

$C_{b_{std}}$  = Carbon effective number of the internal stadard

$C_{b_y}$  = Carbon effective number of the component in the sample

$A_{std}$  = Peak area of the internal standard mixture (au.)

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

$D$  = Density of ethyl benzene ( 0.86 g/cm<sup>3</sup>)

$V$  = Volume of ethyl benzene (L)

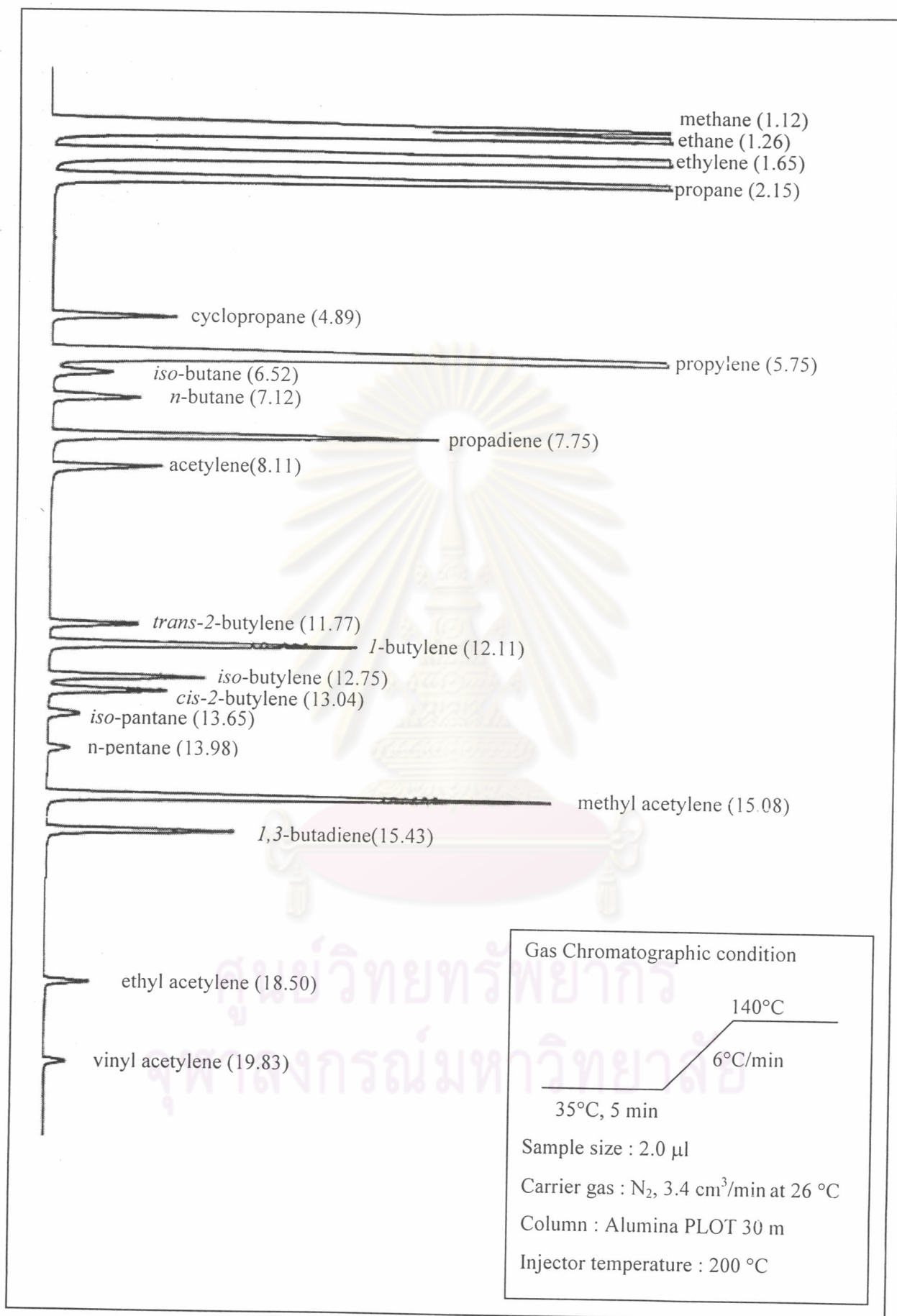
$MW$  = Molecular weight of ethyl benzene ( 106.16 g/mol)

From GC data of C<sub>6</sub> alkene product,

$$A_y = 291862; A_{std} = 44504; C_{b_y} = 6; C_{b_{std}} = 8; C_{std} = 0.0000162 \text{ mol}$$

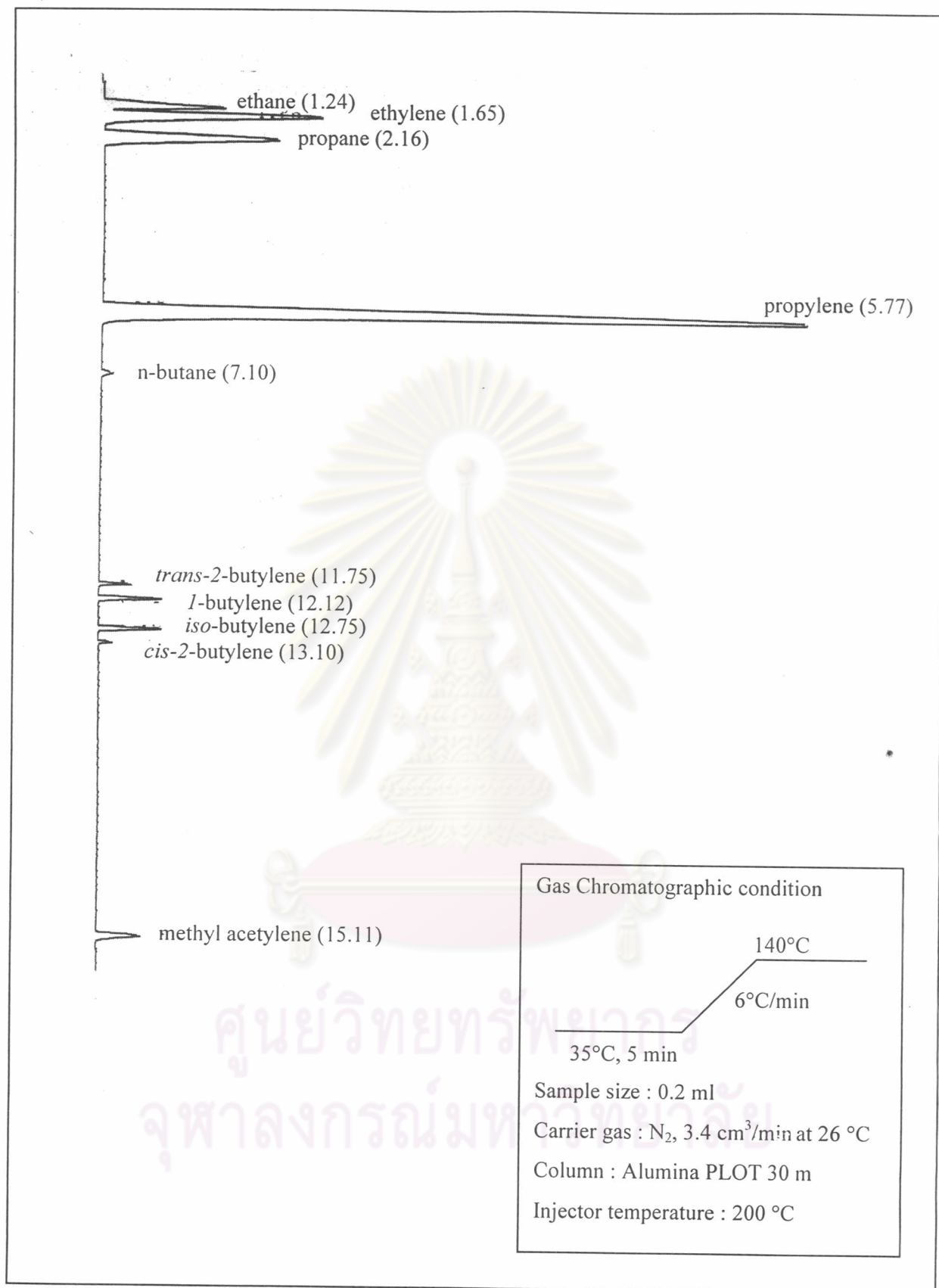
$$C_y = \frac{291862 \times 8 \times 0.0000162}{44504 \times 6}$$

$$= 0.000142 \text{ mol}$$



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





**Figure A-2** Gas chromatogram of gas product from 1-hexene on 5%WO<sub>3</sub>/SBA-15 at 500°C (condition: 0.35 g of catalyst, feed at GHSV of 500 h<sup>-1</sup>, time on stream 30 min.).

## VITAE

Mr. Worapong Pangma was born on June 4, 1979 in Phare, Thailand. He received the Bachelor's Degree of Science in Chemistry from Chiang Mai University in 2000. Since then, he has been a Master's Degree student in the program of Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University. During his graduate study, he received a teaching assistantship from the Petrochemical and Polymer Science program, Faculty of Science in 2001-2002.



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