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APPENDICES

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APPENDIX

1. Calculation of Vapor Pressure of 1-Hexene

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

$$X = 1 - T/T_c \dots\dots\dots(A-2)^{(b)}$$

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

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

From equation A-2 at $T = 303.15 \text{ K}$ (30°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°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.

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 = $\pi r^2 h$ cm³

GHSV (Gas Hourly Space Velocity) = 500 h⁻¹ at STP

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

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

$$= 500 \times \pi \times (0.27)^2 \times 3 \quad \text{cm}^3/\text{h}$$

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

Thus, volumetric flow rate = 5.72 cm³/min

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

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

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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, $P = 0.3045 \text{ atm}$; $V = 0.191 \text{ L}$; $T = 303.15 \text{ K}$ (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

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

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

For example, $W_{\text{liquid}} = 0.0039 \text{ g}$ $W_{\text{1-hexene}} = 0.1962 \text{ g}$

Thus, %yield of liquid product = $\frac{0.0039}{0.1962} \times 100 = 1.99\%$

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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

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

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

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

For example, $W_{\text{coke}} = 0.0581 \text{ g}$ $W_{\text{1-hexene}} = 0.1962 \text{ g}$

Thus, %yield of liquid product = $\frac{0.0581}{0.1962} \times 100 = 18.57\%$

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

$$\% \text{ yield of gas product} = \frac{W_{\text{hexene}} - (W_{\text{liquid}} + W_{\text{coke}})}{W_{\text{hexene}}} \times 100 \text{ .. (A-8)}$$

Where W_{hexene} = Weight of 1-hexene feed

W_{liquid} = Weight of liquid product from cold trap

W_{coke} = Weight of coke

For example, $W_{\text{coke}} = 0.0581 \text{ g}$, $W_{\text{liquid}} = 0.0039 \text{ g}$, $W_{\text{1-hexene}} = 0.1962 \text{ g}$

Thus, %yield of gas product = $\frac{0.1962 - (0.0039 + 0.0581)}{0.1962} \times 100 = 68.40\%$

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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_{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



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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 (μl)

V_x = Injected Volume of the sample (μl)

From GC data of ethylene product,

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

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

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

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

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

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

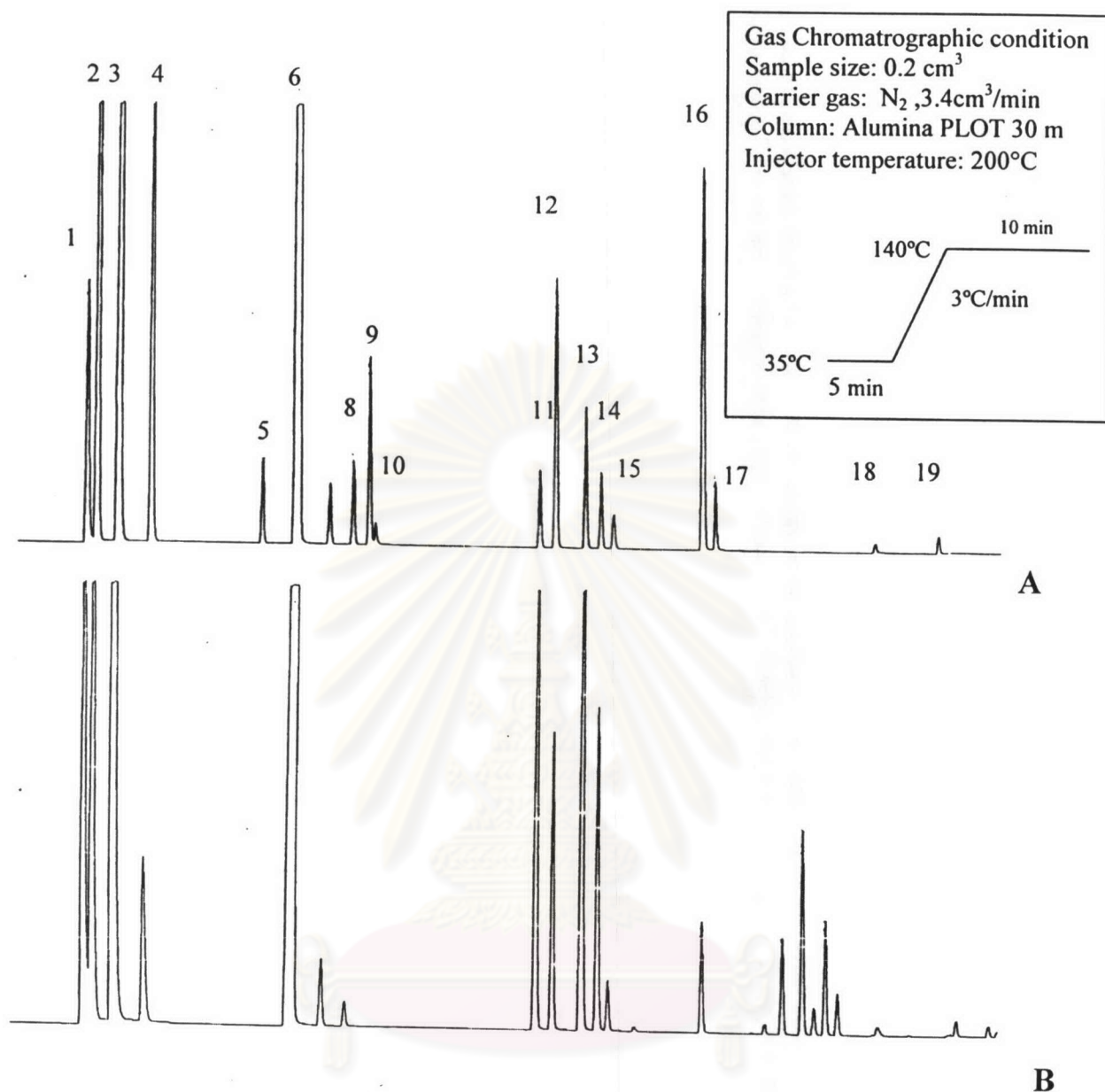


Figure A-1 The comparison of gas chromatogram of gas standards (A) with gas products (B)

Where	1 = Methane	8 = n-butane	15 = iso-petane
	2 = Ethane	9 = propadiene	16 = methyl acetylene
	3 = Ethylene	10 = acetylene	17 = 1,3-butadiene
	4 = Propane	11 = trans-2-butene	18 = ethyl acetylene
	5 = Cyclopropane	12 = 1-butene	19 = vinyl acetylene
	6 = Propylene	13 = iso-butene	
	7 = Iso-butane	14 = cis-2-butene	

VITAE



Miss Piyasuda Sawangkam was born on January 18, 1978 in Saraburi, Thailand. She received a Bachelor's Degree of Science in Chemistry from Kasetsart University in 1998. She continued her Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated with her Master Degree of Science in 2003. She was awarded by research grants from Graduate School at Chulalongkorn University and Ministry of University Affairs, Thailand.



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