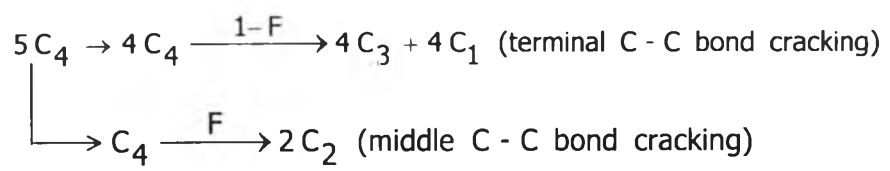# REFERENCES

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APPENDICES

APPENDIX A   F value calculation

For $C_2/C_1 = 1.5$

$$35\,C_4 \rightarrow 20\,C_4 \xrightarrow{\ 1-F\ } 20\,C_3 + 20\,C_1 \quad \text{(terminal C - C bond cracking)}$$

$$\hookrightarrow 15\,C_4 \xrightarrow{\ F\ } 30\,C_2 \quad \text{(middle C - C bond cracking)}$$

$C_2/C_1 = 30/20 = 1.5$
$F = 15/35 = 0.43$

For $C_2/C_1 = 1$

$$3\,C_4 \rightarrow 2\,C_4 \xrightarrow{\ 1-F\ } 2\,C_3 + 2\,C_1 \quad \text{(terminal C - C bond cracking)}$$

$$\hookrightarrow C_4 \xrightarrow{\ F\ } 2\,C_2 \quad \text{(middle C - C bond cracking)}$$

$C_2/C_1 = 2/2 = 1$
$F = 1/3 = 0.33$ (each C-C bonds has the same probability to be broken)

For $C_2/C_1 = 0.6$

$$13\,C_4 \rightarrow 10\,C_4 \xrightarrow{\ 1-F\ } 10\,C_3 + 10\,C_1 \quad \text{(terminal C - C bond cracking)}$$

$$\hookrightarrow 3\,C_4 \xrightarrow{\ F\ } 6\,C_2 \quad \text{(middle C - C bond cracking)}$$

$C_2/C_1 = 6/10 = 0.6$
$F = 3/13 = 0.23$

For $C_2/C_1 = 0.5$

$$5\,C_4 \rightarrow 4\,C_4 \xrightarrow{\ 1-F\ } 4\,C_3 + 4\,C_1 \quad \text{(terminal C - C bond cracking)}$$

$$\hookrightarrow C_4 \xrightarrow{\ F\ } 2\,C_2 \quad \text{(middle C - C bond cracking)}$$

$C_2/C_1 = 2/4 = 0.5$
$F = 1/5 = 0.2$

APPENDIX B   Kinetics calculations

$$A + B \quad \rightarrow \quad C + D + E + F$$

Assign A = n-butane, B = hydrogen, C = methane, D = ethane,

E = propane, and F = isobutane.

$X_A = X$ = n-butane conversion, and X_B = hydrogen conversion.

1. P_A & P_B

$$P_{AO} = \frac{V_{A0}}{V_{T0}} \times P_T$$

$$P_{BO} = \frac{V_{B0}}{V_{T0}} \times P_T$$

$$P_A = P_{A0}(1 - X)$$

$$P_B = P_{B0}(1 - X_B)$$

where:

P_{A0} = initial n-butane partial pressure

P_{B0} = initial hydrogen partial pressure

V_{A0} = initial n-butane volumetric flow rate

V_{B0} = initial hydrogen volumetric flow rate

V_{T0} = initial total volumetric flow rate

P_T = total pressure

P_A = n-butane partial pressure

P_B = hydrogen partial pressure.

From stoichiometry, $X_B = X_A = X$

Hence,

$$P_B = P_{B0}(1 - X)$$

2. Rate of Reaction

$$\text{rate} = \frac{A_{\text{reacted}}}{\text{time} \times \text{g} \cdot \text{cat}} = \frac{A_{\text{react}}}{A_{\text{fed}}} \times \frac{A_{\text{fed}}}{\text{time}} \times \frac{1}{\text{g} \cdot \text{cat}}$$

$$\text{rate} = \frac{\text{conversion} \times \text{molar feed flow rate}}{\text{amount of catalyst}}$$

where:

rate = n-butane consumption rate

A_{react} = mole A reacted

A_{fed} = mole A fed into the reactor.

3. Order & Rate Constant

$$r = kP_A^\alpha P_B^\beta$$

Fixed H_2

$$k' = kP_B^\beta$$

hence,

$$r = k' P_A^\alpha$$

$$\ln r = \alpha \ln P_A + \ln k'$$

where:

r = n-butane consumption rate

k = rate constant

α = n-butane order

β = hydrogen order.

Plot $\ln r$ vs. $\ln P_A$

    Slope $= \alpha$

    Y-intercept $= \ln k'$

Fixed HC

$$k^* = kP_A^\alpha$$

hence,

$$r = k * P_B^\beta$$

$$\ln r = \beta \ln P_B + \ln k *$$

Plot $\ln r$ vs. $\ln P_B$

    Slope $= \beta$

    Y-intercept $= \ln k^*$

4. Activation Energy

$$k = Ae^{-E_a/RT}$$

$$r = kP_A^\alpha P_B^\beta = \frac{F_{A0}X}{W}$$

$$X = \frac{Ae^{-Ea/RT} P_A^\alpha P_B^\beta W}{F_{A0}}$$

$$\ln X = \frac{-Ea}{RT} + \ln \frac{AP_A^\alpha P_B^\beta W}{F_{A0}}$$

where:

A = pre-exponential factor

E_a = activation energy

R = gas constant

T = absolute reaction temperature

F_{A0} = n-butane molar feed flow rate

W = the amount of catalyst used for the reaction.

Plot ln X vs. 1/T (Arrhenius plot)

Slope = $-E_a/R$

(Fogler, 1999; Buzzi-Ferraris, 1999)

APPENDIX C   Calculation of chemicals required for IWI & VPI method.

The objective of both preparation methods was to load 1 %wt Pt and 0.15 %wt RE (optional), e.g., Ce, Er, Yb, on the support (zeolite).

For IWI method:

1 %wt Pt/KL 1 gram of catalyst contain 0.01 gram of Pt.

But Pt 1 %wt is extremely insignificant when compared to zeolite weight; hence, catalyst 1 gram ~ zeolite 1 gram, and zeolite 1 gram requires Pt 0.01 gram.

Tetraamineplatinum (II) nitrate 387.09 gram contains Pt 195.09 gram.

So Pt 0.01 gram requires Tetraamineplatinum (II) nitrate

$$\frac{0.01 \times 387.09}{195.09} = 0.0199 \ g$$

Therefore, zeolite 1 gram requires Tetraamineplatinum (II) nitrate 0.0199 gram.

The calculation results of other catalyst samples were shown in Table C1 and Table C2.

Table C1 The amount of chemicals required for catalyst preparation by IWI method.

Chemical	$MW_{chemical}$	MW_{metal}	The amount required per gram of zeolite (gram)
Tetraamineplatinum (II) nitrate	387.09	195.09	0.0199
Cerium (III) nitrate hexahydrate	434.23	140.12	0.0047
Erbium (III) nitrate pentahydrate	443.35	167.26	0.0040
Ytterbium (III) nitrate pentahydrate	449.13	173.04	0.0039

Table C2 The amount of chemicals required for catalyst preparation by VPI method.

Chemical	$MW_{chemical}$	MW_{metal}	The amount required per gram of zeolite (gram)
Platinum (II) acetyl-acetonate	393.31	195.09	0.0202
Cerium (III) acetyl-acetonate	437.45	140.12	0.0047
Erbium (III) acetyl-acetonate	464.26	167.26	0.0042
Ytterbium (III) acetyl-acetonate	470.04	173.04	0.0041

APPENDIX D Langmuir-Hinshelwood kinetics

Set A = n-butane; B = hydrogen

Assume: since n-butane conversion is very low, product coverage can be neglected.

Therefore, $\Theta_T = \Theta_A + \Theta_B + \Theta_V = 1$

Consider A:

$$r_{adsorb} = kP_A\Theta_V$$

$$r_{desorb} = k'\Theta_A$$

At equilibrium

$$r_{adsorb} = r_{desorb}$$

$$kP_A\Theta_V = k'\Theta_V$$

$$\Theta_A = \frac{k}{k'}P_A\Theta_V = K_AP_A\Theta_V = K_AP_A(1-\Sigma\Theta)$$

let

$$\Sigma\Theta = \Theta_A + \Theta_B = (1-\Sigma\Theta)(K_AP_A + K_BP_B)$$

$$\Sigma\Theta = K_AP_A + K_BP_B - K_AP_A\Sigma\Theta - K_BP_B\Sigma\Theta$$

$$\Sigma\Theta(1 + K_AP_A + K_BP_B) = K_AP_A + K_BP_B$$

$$\Sigma\Theta = \frac{K_AP_A + K_BP_B}{1 + K_AP_A + K_BP_B}$$

$$1-\Sigma\Theta = 1 - \frac{K_AP_A + K_BP_B}{1 + K_AP_A + K_BP_B} = \frac{1}{1 + K_AP_A + K_BP_B}$$

Therefore;

$$\Theta_A = \frac{K_AP_A}{1 + K_AP_A + K_BP_B}$$
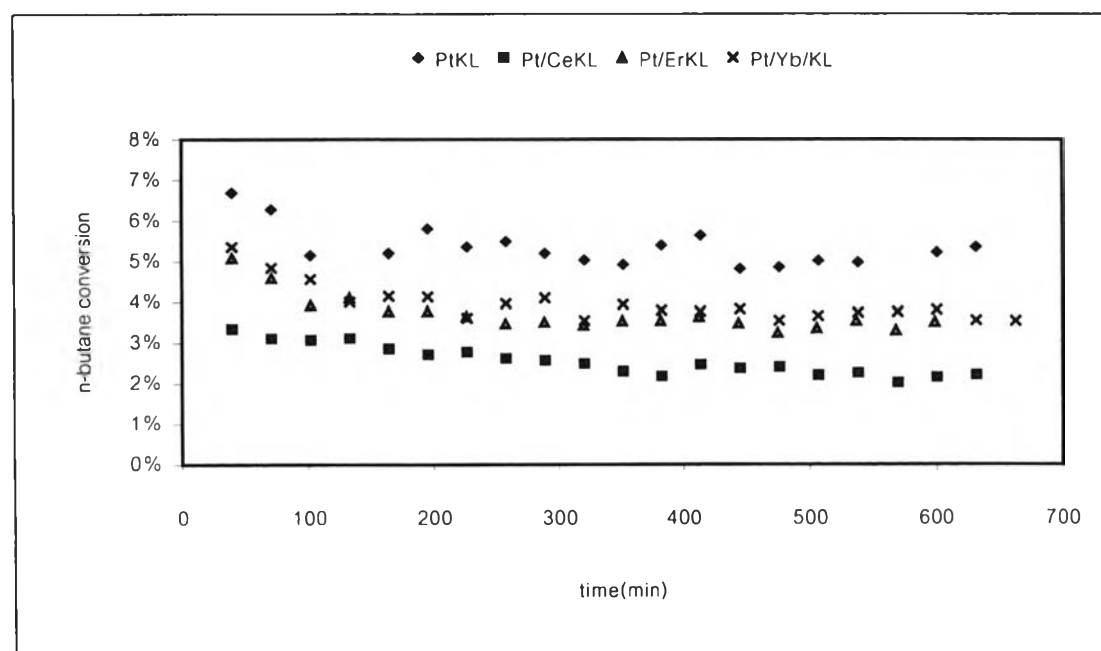
$$\Theta_B = \frac{K_BP_B}{1 + K_AP_A + K_BP_B}$$

let

$$r = k\Theta_A \Theta_B = \frac{kK_A P_A K_B P_B}{\left(1 + K_A P_A + K_B P_B\right)^2}$$

$$r = \frac{k_0 e^{-E/RT} K_{A0} e^{\Delta H_A/RT} K_{B0} e^{\Delta H_B/RT} P_A P_B}{\left(1 + K_{A0} e^{\Delta H_A/RT} P_A + K_{B0} e^{\Delta H_B/RT} P_B\right)^2}$$
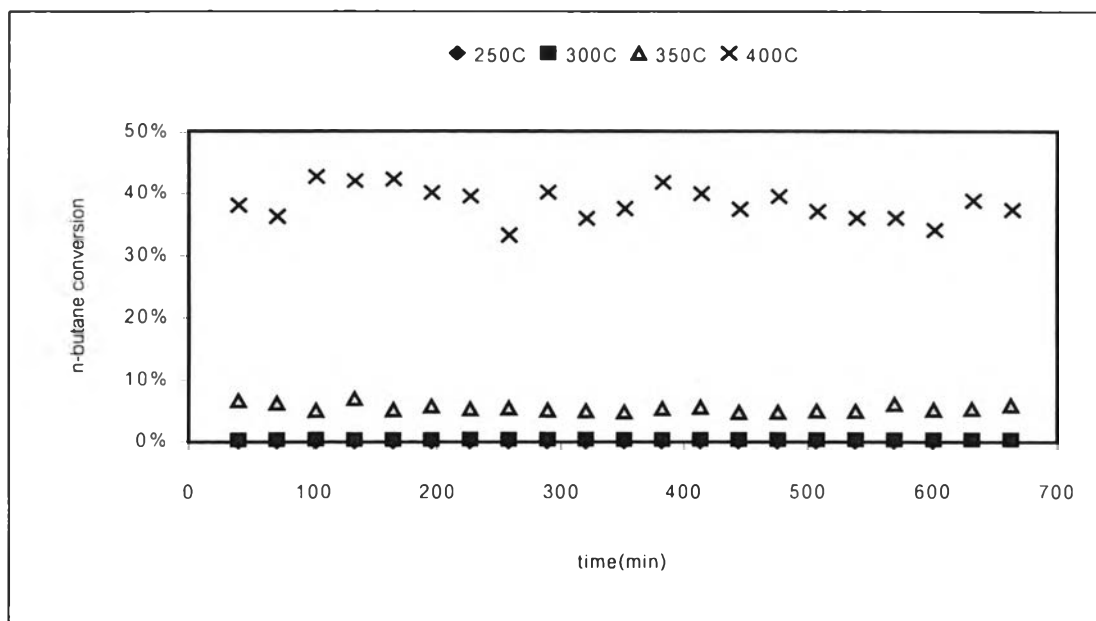
## APPENDIX E   n-Butane conversion results
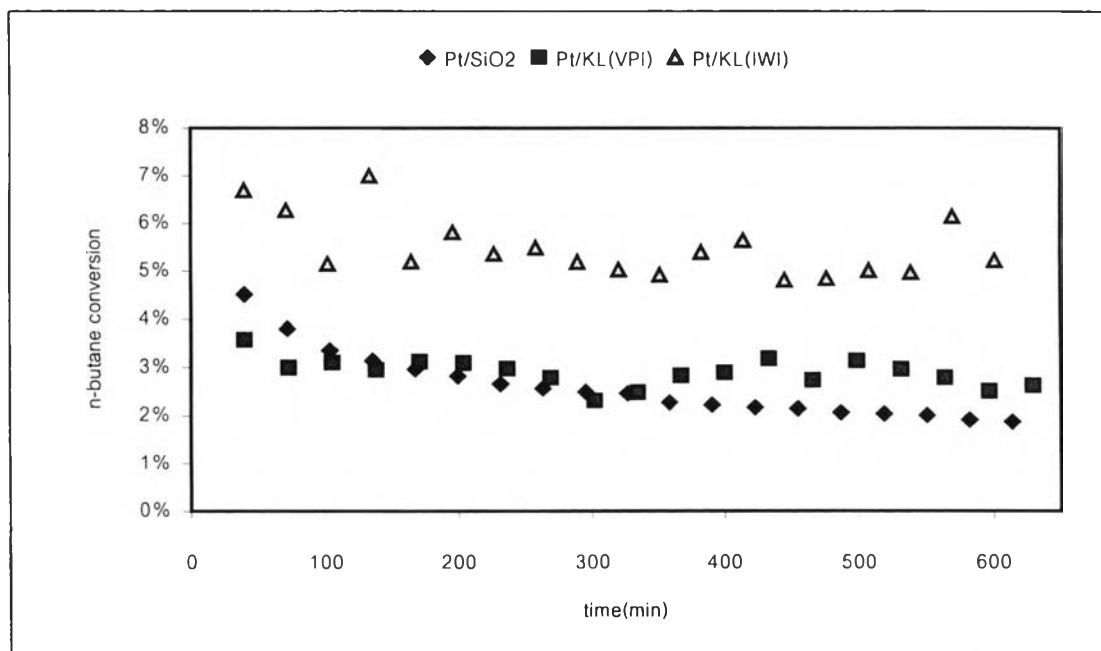
Figure E1 Relationship between n-butane conversion and reaction time of different catalyst types and preparation methods carried out at 350°C, HC : H$_2$ ~ 1 : 10.

Figure E2 Relationship between n-butane conversion and reaction time with and without promoters carried out at 350°C, HC : H$_2$ ~ 1 : 10.
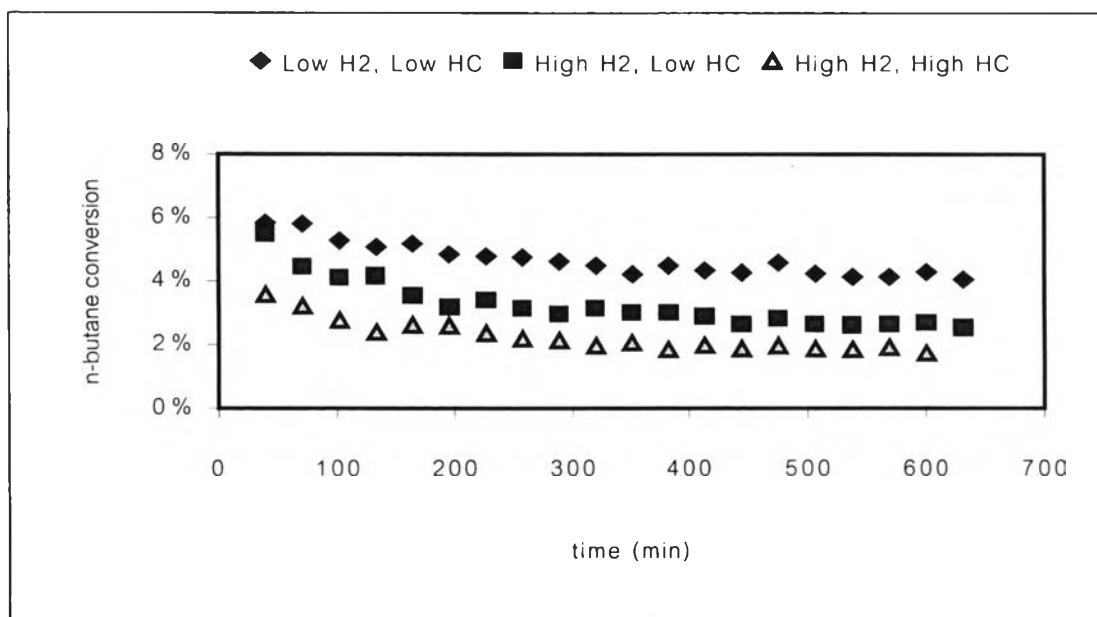
Figure E3 Relationship between n-butane conversion and reaction time carried out on Pt/KL (IWI) catalyst at different temperatures, HC : $H_2 \sim 1 : 10$.
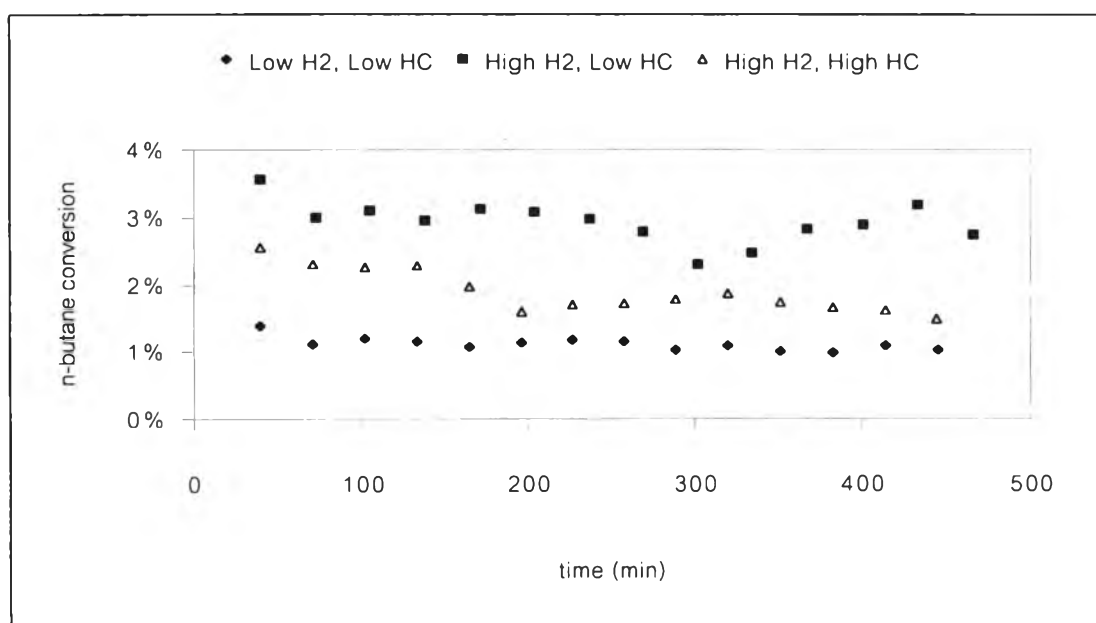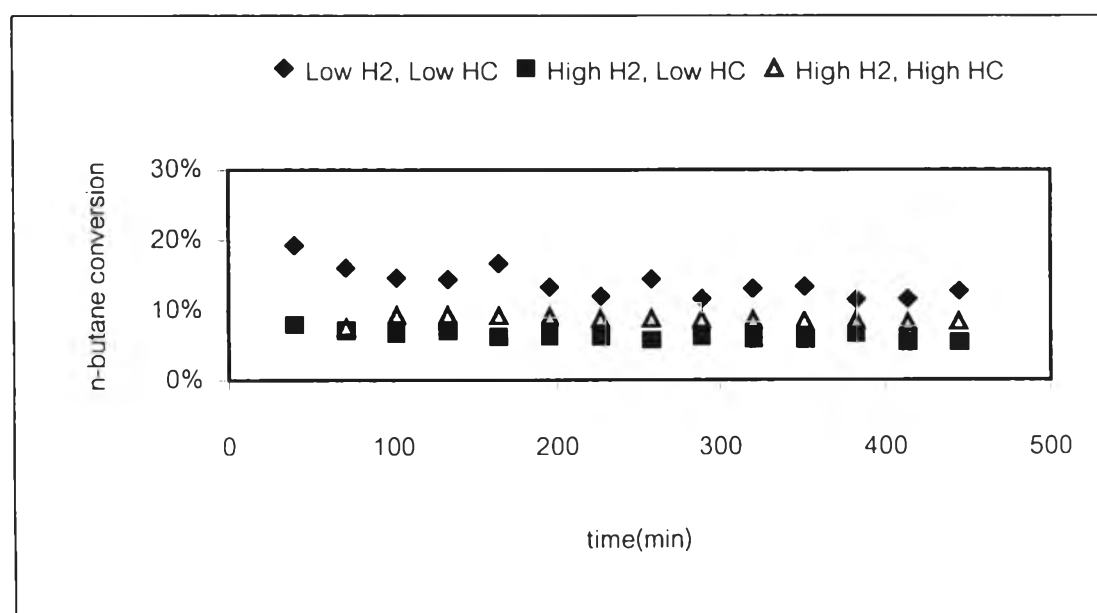

Figure E4 Relationship between n-butane conversion and reaction time carried out on Pt/KL (VPI) catalyst at $350°C$, with different hydrogen and hydrocarbon flow rates*.

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* High H_2 flow rate refer to 30 cm^3 min^{-1}, Low H2 flow rate refer to 17.5 cm^3/min.
  High HC flow rate refer to 4.5 cm^3 min^{-1}, Low HC flow rate refer to 3 cm^3/min.

Figure E5 Relationship between n-butane conversion and reaction time carried out on Pt/KL (VPI) catalyst at 375°C, with different hydrogen and hydrocarbon flow rates.

Figure E6 Relationship between n-butane conversion and reaction time carried out on Pt/KL (VPI) catalyst at 400°C, with different hydrogen and hydrocarbon flow rates.

CURRICULUM VITAE

Name: Titipong Issariyakul

Date of Birth: 24 February 1978

Nationality: Thai

University Education:

1995-1998   Bachelor Degree of Engineering in Chemical Engineering, Thammasat University, Bangkok, Thailand.