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APPENDICES

APPENDIX A

CALCULATION OF CATALYST PREPARATION

A.1 Calculation for the preparation of the 10V2MgTi catalyst.

The aqueous solution used for catalyst preparation consists of 0.4 wt% NH_4VO_3 . The volume of this solution is designed to be 50 ml., hence NH_4VO_3 and H_2O are weighted for 0.2 and 49.8 gram, respectively.

$$\text{The amount of V in 0.2 g of } \text{NH}_4\text{VO}_3 = \frac{0.2 \times 50.9414}{116.98}$$

$$\approx 0.0871$$

$$\text{Therefore, mole of V} = \frac{0.0871}{50.9414}$$

$$\approx 0.0017 \text{ mole}$$

$$\text{The amount of V calculated as } \text{V}_2\text{O}_5 = \frac{0.0871 \times 181.8828}{101.8828}$$

$$\approx 0.1555 \text{ g}$$

If the weight of catalyst is 100 gram, 10Vti would compose of 10 g of V_2O_5 and 90 g of TiO_2 . Thus, in this system,

$$\text{The amount of } \text{TiO}_2 = \frac{90 \times 0.1555}{10}$$

$$\approx 1.3995 \text{ g}$$

Then 2 wt% of Mg is added to the 10Vti catalyst (when the weight of V_2O_5 plus TiO_2 is calculated as 100%).

$$\text{The amount of Mg in 10V2MgTi} = 0.02 \times (0.1555 + 1.3995)$$

$$\approx 0.0311 \text{ g}$$

$$\text{The amount of } \text{Mg}(\text{NO}_3)_2 \text{ used} = \frac{0.0311 \times 256.41}{24.305}$$

$$\approx 0.3286 \text{ g}$$

APPENDIX B

CALCULATION OF DIFFUSIONAL LIMITATION EFFECT

In the present work there are doubt whether the external and internal diffusion limitations interfere with the propane reaction. Hence, the kinetic parameters were calculated based on the experimental data so as to prove the controlled system. The calculation is divided into two parts; one of which is the external diffusion limitation, and the other is the internal diffusion limitation.

1. External diffusion limitation

The phthalic anhydride combustion reaction is considered to be an irreversible first order reaction occurred on the interior pore surface of catalyst particles in a fixed bed reactor. Assume isothermal operation for the reaction.

In the experiment, 0.05% phthalic anhydride, 21% O₂ was used as the unique reactant in the system. Because percentage of phthalic anhydride was rather small compared to the oxygen that it can be neglected. Molecular weight of nitrogen and oxygen are 28.02 and 31.98, respectively. Thus, the average molecular weight of the gas mixture was calculated as follows:

$$\begin{aligned}M_{AB} &= 0.72 \times 28.02 + 0.21 \times 31.98 \\ &= 26.890 \text{ g/mol}\end{aligned}$$

Calculation of reactant gas density

Consider the phthalic anhydride combustion is operated at low pressure and high temperature. We assume that the gases are respect to ideal gas law. The density of such gas mixture reactant at various temperatures is calculated in the following.

$$\rho = \frac{PM}{RT} = \frac{1.0 \times 10^5 \times 26.890 \times 10^{-3}}{8.314T}$$

We obtained :

$\rho = 0.684 \text{ kg/m}^3$	at T = 200°C
$\rho = 0.618 \text{ kg/m}^3$	at T = 250°C
$\rho = 0.564 \text{ kg/m}^3$	at T = 300°C
$\rho = 0.519 \text{ kg/m}^3$	at T = 350°C

Calculation of the gas mixture viscosity

The simplified methods for determining the viscosity of low pressure binary are described anywhere (Reid, 1988). The method of Wilke is chosen to estimate the gas mixture viscosity.

For a binary system of 1 and 2,

$$\mu_m = \frac{y_1 \mu_1}{y_1 + y_2 \Phi_{12}} + \frac{y_2 \mu_2}{y_2 + y_1 \Phi_{21}}$$

where μ_m = viscosity of the mixture
 μ_1, μ_2 = pure component viscosity
 y_1, y_2 = mole fractions

$$\phi_{12} = \frac{\left[1 + \left(\frac{\mu_1}{\mu_2} \right)^{1/2} \left(\frac{M_1}{M_2} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{M_1}{M_2} \right) \right]^{1/2}}$$

$$\phi_{21} = \phi_{12} \left(\frac{\mu_2}{\mu_1} \right) \left(\frac{M_1}{M_2} \right)$$

M_1, M_2 = molecular weight

Let 1 refer to nitrogen and 2 to oxygen

$$M_1 = 28.02 \text{ and } M_2 = 31.98$$

From Perry the viscosity of nitrogen at 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C are 0.0248, 0.027, 0.0286, 0.0305, 0.032, 0.0338, and 0.0368 cP, respectively. The viscosity of oxygen at 200°C, 250°C, 300°C and 350°C are 0.0281, 0.03, 0.032 and 0.034 cP, respectively.

$$\text{At } 200^\circ\text{C} : \quad \phi_{12} = \frac{\left[1 + \left(\frac{0.0248}{0.0281} \right)^{1/2} \left(\frac{28.02}{31.98} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{28.02}{31.98} \right) \right]^{1/2}} = 0.940$$

$$\phi_{21} = 0.940 \left(\frac{0.0281}{0.0248} \right) \left(\frac{28.02}{31.98} \right) = 0.933$$

$$\mu_m = \frac{0.79 \times 0.0248}{0.79 + 0.02 \times 0.940} + \frac{0.21 \times 0.0281}{0.21 + 0.79 \times 0.933} = 0.0260 \text{cP} = 2.60 \times 10^{-5} \text{ kg/m-sec}$$

$$\text{At } 250^\circ\text{C} : \quad \phi_{12} = \frac{\left[1 + \left(\frac{0.027}{0.03} \right)^{1/2} \left(\frac{28.02}{31.98} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{28.02}{31.98} \right) \right]^{1/2}} = 0.949$$

$$\phi_{21} = 0.949 \left(\frac{0.03}{0.027} \right) \left(\frac{28.02}{31.98} \right) = 0.924$$

$$\mu_m = \frac{0.79 \times 0.027}{0.79 + 0.21 \times 0.949} + \frac{0.21 \times 0.03}{0.21 + 0.79 \times 0.924} = 0.0283 \text{cP} = 2.83 \times 10^{-5} \text{ kg/m-sec}$$

$$\text{At } 300^\circ\text{C} : \quad \phi_{12} = \frac{\left[1 + \left(\frac{0.0286}{0.032} \right)^{1/2} \left(\frac{28.02}{31.98} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{28.02}{31.98} \right) \right]^{1/2}} = 0.948$$

$$\phi_{21} = 0.948 \left(\frac{0.032}{0.0286} \right) \left(\frac{28.02}{31.98} \right) = 0.929$$

$$\mu_m = \frac{0.79 \times 0.0286}{0.79 + 0.21 \times 0.948} + \frac{0.21 \times 0.032}{0.21 + 0.79 \times 0.929} = 0.0299 \text{cP} = 2.99 \times 10^{-5} \text{kg/m-sec}$$

$$\text{At } 350^\circ\text{C:} \quad \phi_{12} = \frac{\left[1 + \left(\frac{0.0305}{0.034} \right)^{1/2} \left(\frac{28.02}{31.98} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{28.02}{31.98} \right) \right]^{1/2}} = 0.945$$

$$\phi_{21} = 0.945 \left(\frac{0.034}{0.0305} \right) \left(\frac{28.02}{31.98} \right) = 0.923$$

$$\mu_m = \frac{0.79 \times 0.0305}{0.79 + 0.21 \times 0.945} + \frac{0.21 \times 0.034}{0.21 + 0.79 \times 0.923} = 0.0320 \text{cP} = 3.20 \times 10^{-5} \text{kg/m-sec}$$

Calculation of diffusion coefficients

Diffusion coefficients for binary gas system at low pressure calculated by empirical correlation are proposed by Reid (1988). Wilke and Lee method is chosen to estimate the value of D_{AB} due to the general and reliable method. The empirical correlation is

$$D_{AB} = \frac{\left(3.03 - \frac{0.98}{M_{AB}^{1/2}} \right) (10^{-3}) T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}$$

where D_{AB} = binary diffusion coefficient, cm^2/s

T = temperature, K

M_A, M_B = molecular weights of A and B, g/mol

$$M_{AB} = 2 \left[\left(\frac{1}{M_A} \right) + \left(\frac{1}{M_B} \right) \right]^{-1}$$

P = pressure, bar

σ = characteristic length, \AA

Ω_D = diffusion collision integral, dimensionless

The characteristic Lennard-Jones energy and Length, ε and σ , of nitrogen and propane are as follows: (Reid,1988)

For O_2 : $\sigma = 3.467 \text{ \AA}$, $\varepsilon/k = 106.7$

For N_2 : $\sigma = 3.798 \text{ \AA}$, $\varepsilon/k = 71.4$

The sample rules are usually employed.

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{3.798 + 3.467}{2} = 3.63$$

$$\varepsilon_{AB}/k = \left(\frac{\varepsilon_A \varepsilon_B}{k^2} \right)^{1/2} = (71.4 \times 106.7)^{1/2} = 87.28$$

Ω_D is tabulated as a function of kT/ε for the Lennard-Jones potential. The accurate relation is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

where $T^* = \frac{kT}{\varepsilon_{AB}}$, $A = 1.06036$, $B = 0.15610$, $C = 0.19300$, $D = 0.47635$, $E = 1.03587$, $F = 1.52996$, $G = 1.76474$, $H = 3.89411$

$$\text{Then } T^* = \frac{473}{87.28} = 5.419 \text{ at } 200^\circ\text{C}$$

$$T^* = \frac{523}{87.28} = 5.992 \text{ at } 250^\circ\text{C}$$

$$T^* = \frac{573}{87.28} = 6.565 \text{ at } 300^\circ\text{C}$$

$$T^* = \frac{623}{87.28} = 7.138 \text{ at } 350^\circ\text{C}$$

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

$$\Omega_D = 0.928 ; 200^\circ\text{C}$$

$$\Omega_D = 0.813 ; 250^\circ\text{C}$$

$$\Omega_D = 0.799 ; 300^\circ\text{C}$$

$$\Omega_D = 0.787 ; 350^\circ\text{C}$$

With Equation of D_{AB} ,

$$\begin{aligned} \text{At } 200^\circ\text{C} : D(\text{N}_2\text{-O}_2) &= \frac{\left(3.03 - \frac{0.98}{29.869^{0.5}}\right)(10^{-3})473^{3/2}}{1 \times 29.869^{0.5} \times 3.63^2 \times 0.829} \\ &= 0.491 \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} \text{At } 250^\circ\text{C} : D(\text{N}_2\text{-O}_2) &= \frac{\left(3.03 - \frac{0.98}{29.869^{0.5}}\right)(10^{-3})523^{3/2}}{1 \times 29.869^{0.5} \times 3.63^2 \times 0.813} \\ &= 0.582 \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} \text{At } 300^\circ\text{C} : D(\text{N}_2\text{-O}_2) &= \frac{\left(3.03 - \frac{0.98}{29.869^{0.5}}\right)(10^{-3})573^{3/2}}{1 \times 29.869^{0.5} \times 3.63^2 \times 0.799} \\ &= 0.679 \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} \text{At } 350^\circ\text{C} : D(\text{N}_2\text{-O}_2) &= \frac{\left(3.03 - \frac{0.98}{29.869^{0.5}}\right)(10^{-3})623^{3/2}}{1 \times 29.869^{0.5} \times 3.63^2 \times 0.799} \\ &= 0.899 \text{ m}^2/\text{s} \end{aligned}$$

Reactant gas mixture was supplied at 100 ml/min. in tubular microreactor used in the phthalic anhydride oxidation system at 30°C

oxygen flow rate through reactor = 100 ml/min. at 30°C

$$\text{The density of oxygen, } \rho = \frac{1.0 \times 10^5 \times 26.890 \times 10^{-3}}{8.314(273 + 30)} = 1.067 \text{ kg/s}$$

$$\text{Mass flow rate} = 1.067 \left(\frac{100 \times 10^{-6}}{60} \right) = 1.78 \times 10^{-6} \text{ kg/s}$$

$$\text{Diameter of stainless steel tube reactor} = 9.5 \text{ mm}$$

$$\text{Cross-sectional area of tube reactor} = \frac{\pi(9.5 \times 10^{-3})^2}{4} = 7.09 \times 10^{-5} \text{ m}^2$$

$$\text{Mass Velocity, } G = \frac{1.78 \times 10^{-6}}{7.09 \times 10^{-5}} = 0.025 \text{ kg/m}^2\text{-s}$$

$$\text{Catalysis size} = 40\text{-}60 \text{ mesh} = 0.178\text{-}0.126 \text{ mm}$$

$$\text{Average catalysis} = (0.126 + 0.178) / 2 = 0.152 \text{ mm}$$

Find Reynolds number, Re_p , which is well known as follows:

$$Re_p = \frac{d_p G}{\mu}$$

We obtained

$$\text{At } 200^\circ\text{C} : Re_p = \frac{(0.152 \times 10^{-3} \times 0.025)}{2.60 \times 10^{-5}} = 0.146$$

$$\text{At } 250^\circ\text{C} : Re_p = \frac{(0.152 \times 10^{-3} \times 0.0025)}{2.83 \times 10^{-5}} = 0.134$$

$$\text{At } 300^\circ\text{C} : Re_p = \frac{(0.152 \times 10^{-3} \times 0.025)}{2.99 \times 10^{-5}} = 0.127$$

$$\text{At } 350^\circ\text{C} : Re_p = \frac{(0.152 \times 10^{-3} \times 0.025)}{3.20 \times 10^{-5}} = 0.119$$

Average transport coefficient between the bulk stream and particles surface could be correlated in terms of dimensionless groups, which characterize the flow conditions. For mass transfer the Sherwood number, kmp/G , is an empirical function of the Reynolds number, $d_p G/\mu$, and the Schmit number, $\mu/\rho D$. The j-factors are defined as the following functions of the Schmidt number and Sherwood numbers:

$$j_D = \frac{k_m \rho}{G} \left(\frac{a_m}{a_t} \right) (\mu / \rho D)^{2/3}$$

The ratio (a_m/a_t) allows for the possibility that the effective mass-transfer area a_m , may be less than the total external area, a_t , of the particles. For Reynolds number greater than 10, the following relationship between j_D and the Reynolds number well represents available data.

$$j_D = \frac{0.458}{\varepsilon_B} \left(\frac{d_p G}{\mu} \right)^{-0.407}$$

where G = mass velocity(superficial) based upon cross-sectional area of empty reactor

$$(G = u\rho)$$

d_p = diameter of catalyst particle for spheres

μ = viscosity of fluid

ρ = density of fluid

ε_B = void fraction of the interparticle space (void fraction of the bed)

D = molecular diffusivity of component being transferred

Assume $\varepsilon_B = 0.5$

$$\text{At } 200^\circ\text{C} : j_D = \frac{0.458}{0.5} (0.146)^{-0.407} = 2.004$$

$$\text{At } 250^\circ\text{C} : j_D = \frac{0.458}{0.5} (0.134)^{-0.407} = 2.076$$

$$\text{At } 300^\circ\text{C} : j_D = \frac{0.458}{0.5} (0.127)^{-0.407} = 2.122$$

$$\text{At } 350^\circ\text{C} : j_D = \frac{0.458}{0.5} (0.119)^{-0.407} = 2.178$$

A variation of the fixed bed reactor is an assembly of screens or gauze of catalytic solid over which the reacting fluid flows. Data on mass transfer from single screens has been reported by Gay and Maughan. Their correlation is of the form

$$j_D = \left(\frac{j_D G}{\mu} \right) (\mu / \rho D)^{2/3}$$

Where ε is the porosity of the single screen.

$$\text{Hence, } k_m = \left(\frac{j_D G}{\mu} \right) (\mu / \rho D)^{2/3}$$

$$k_m = \left(\frac{0.458G}{\varepsilon_B \rho} \right) \text{Re}^{-0.407} \text{Sc}^{-2/3}$$

Find Schmidt number, Sc : $\text{Sc} = \frac{\mu}{\rho D}$

$$\text{At } 200^\circ\text{C} : \text{Sc} = \frac{2.60 \times 10^{-5}}{0.684 \times 0.491} = 7.74 \times 10^{-5}$$

$$\text{At } 250^\circ\text{C} : \text{Sc} = \frac{2.83 \times 10^{-5}}{0.618 \times 0.582} = 7.87 \times 10^{-5}$$

$$\text{At } 300^\circ\text{C} : \text{Sc} = \frac{2.99 \times 10^{-5}}{0.564 \times 0.679} = 7.81 \times 10^{-5}$$

$$\text{At } 350^\circ\text{C} : \text{Sc} = \frac{3.20 \times 10^{-5}}{0.519 \times 0.899} = 6.86 \times 10^{-5}$$

$$\text{Find } k_m : \quad \text{At } 200^\circ\text{C, } k_m = \left(\frac{2.004 \times 0.025}{0.684} \right) (7.74 \times 10^{-5})^{-2/3} = 42.57 \text{ m/s}$$

$$\text{At } 250^\circ\text{C, } k_m = \left(\frac{2.076 \times 0.025}{0.618} \right) (7.87 \times 10^{-5})^{-2/3} = 45.73 \text{ m/s}$$

$$\text{At } 300^{\circ}\text{C, } k_m = \left(\frac{2.122 \times 0.025}{0.564} \right) (7.81 \times 10^{-5})^{-2/3} = 51.48 \text{ m/s}$$

$$\text{At } 350^{\circ}\text{C, } k_m = \left(\frac{2.178 \times 0.025}{0.519} \right) (6.86 \times 10^{-5})^{-2/3} = 62.61 \text{ m/s}$$

Properties of catalyst

Density = 0.375 g/ml catalyst

Diameter of 40-60 mesh catalyst particle = 0.152 mm

$$\text{Weight per catalyst particle} = \frac{\pi(0.152 \times 10^{-1})^3 \times 0.375}{6} = 6.895 \times 10^{-7} \text{ g/particle}$$

$$\text{External surface area per particle} = \pi(0.152 \times 10^{-3})^2 = 7.26 \times 10^{-7} \text{ m}^2/\text{particle}$$

$$a_m = \frac{7.26 \times 10^{-7}}{6.895 \times 10^{-7}} = 1.052 \text{ m}^2/\text{gram catalyst}$$

Volumetric flow rate of gaseous feed stream = 100 ml/min

$$\text{Molar flow rate of gaseous feed stream} = \frac{(1 \times 10^5) \left(\frac{100 \times 10^{-6}}{60} \right)}{8.314(273 + 30)} = 6.62 \times 10^{-5} \text{ mol/s}$$

$$\text{oxygen molar feed rate} = 0.21 \times 6.62 \times 10^{-5} = 1.39 \times 10^{-5} \text{ mol/s}$$

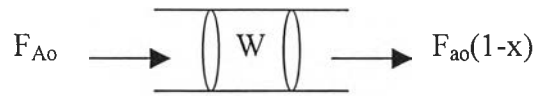
phthalic anhydride conversion (experimental data): 5 % at 200°C

20 % at 250°C

45 % at 300°C

72 % at 350°C

The estimated rate of phthalic anhydride oxidation reaction is based on the ideal plug flow reactor which there is no mixing in the direction of flow and complete mixing perpendicular to the direction of flow (i.e., in the radial direction). The rate of reaction will vary with reaction length. Plug flow reactors are normally operated at steady state so that properties at any position are constant with respect to time. The mass balance around plug flow reactor becomes



$$\begin{aligned} & \{\text{rate of } i \text{ into volume element}\} - \{\text{rate of } i \text{ out of volume element}\} \\ & + \{\text{rate of production of } i \text{ within the volume element}\} \\ & = \{\text{rate of accumulation of } i \text{ within the volume element}\} \end{aligned}$$

$$F_{A_0} = F_{A_0}(1-x) + (r_W W)$$

$$(r_W W) = F_{A_0} - F_{A_0}(1-x) = F_{A_0} x = F_{A_0} X$$

$$r_W = \frac{F_{A_0} X}{W} = \frac{1.39 \times 10^{-5} \times 0.291}{0.1} = 4.045 \times 10^{-5} \text{ mol/s-gram catalyst at } 200^\circ\text{C}$$

$$r_W = \frac{F_{A_0} X}{W} = \frac{1.39 \times 10^{-5} \times 0.515}{0.1} = 7.159 \times 10^{-5} \text{ mol/s-gram catalyst at } 250^\circ\text{C}$$

$$r_W = \frac{F_{A_0} X}{W} = \frac{1.39 \times 10^{-5} \times 0.845}{0.1} = 1.175 \times 10^{-5} \text{ mol/s-gram catalyst at } 300^\circ\text{C}$$

$$r_W = \frac{F_{A_0} X}{W} = \frac{1.39 \times 10^{-5} \times 0.85}{0.1} = 1.582 \times 10^{-4} \text{ mol/s-gram catalyst at } 350^\circ\text{C}$$

At steady state the external transport rate may be written in terms of the diffusion rate from the bulk gas to the surface. The expression is:

$$\begin{aligned} R_{\text{obs}} &= k_m a_m (C_b - C_s) \\ &= \frac{\text{phthalic anhydride converted (mole)}}{(\text{time})(\text{gram of catalyst})} \end{aligned}$$

where C_b and C_s are the concentrations in the bulk gas and at the surface, respectively.

$$\text{At } 200^\circ\text{C, } (C_b - C_s) = \frac{r_{\text{obs}}}{k_m a_m} = \frac{4.045 \times 10^{-5}}{42.57 \times 1.052} = 9.03 \times 10^{-7} \text{ mol/m}^3$$

$$\text{At } 250^{\circ}\text{C, } (C_b - C_s) = \frac{r_{\text{obs}}}{k_m a_m} = \frac{7.459 \times 10^{-5}}{45.73 \times 1.052} = 1.49 \times 10^{-6} \text{ mol/m}^3$$

$$\text{At } 300^{\circ}\text{C, } (C_b - C_s) = \frac{r_{\text{obs}}}{k_m a_m} = \frac{1.175 \times 10^{-4}}{51.48 \times 1.052} = 2.17 \times 10^{-6} \text{ mol/m}^3$$

$$\text{At } 350^{\circ}\text{C, } (C_b - C_s) = \frac{r_{\text{obs}}}{k_m a_m} = \frac{1.182 \times 10^{-4}}{62.61 \times 1.052} = 1.79 \times 10^{-6} \text{ mol/m}^3$$

Consider the difference of the bulk and surface concentration is small. It means that the external mass transport has no effect on the phthalic anhydride oxidation reaction rate.

2. Internal diffusion limitation

Next, consider the internal diffusion limitation of the phthalic anhydride reaction. An effectiveness factor, η , was defined in order to express the rate of reaction for the whole catalyst pellet, r_p , in terms of the temperature and concentrations existing at the outer surface as follows:

$$\eta = \frac{\text{actual rate of whole pellet}}{\text{rate evaluated at outer surface conditions}} = \frac{r_p}{r_s}$$

The equation for the local rate (per unit mass of catalyst) may be expected functionally as $r = f(C, T)$.

Where C represents, symbolically, the concentrations of all the involved components

$$\text{Then, } r_p = \eta r_s = \eta f(C_s, T_s)$$

Suppose that the phthalic anhydride oxidation is an irreversible reaction $A \rightarrow B$ and first order reaction, so that for isothermal conditions $r = f(C_A) = k_1 C_A$. Then $r_p = \eta k_1 (C_A)_s$.

For a spherical pellet, a mass balance over the spherical-shell volume of thickness Δr . At steady state the rate of diffusion into the element less the rate of diffusion out will equal the rate of disappearance of reactant within the element. This rate will be $\rho_p k_1 C_A$ per unit volume, where ρ_p is the density of the pellet. Hence, the balance may be written, omitting subscript A on C,

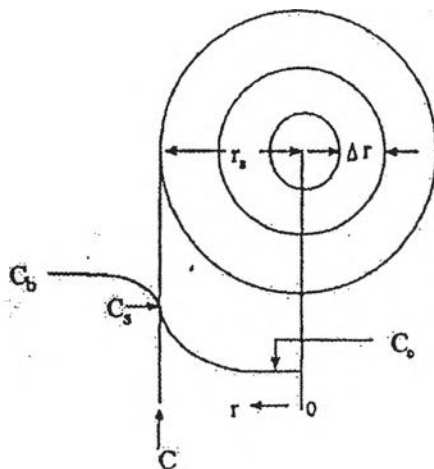


Figure B1. Reactant (A) concentration vs. position for first-order reaction on a spherical catalyst pellet.

$$\left(-4\pi r^2 D_e \frac{dC}{dr} \right)_r - \left(-4\pi r^2 D_e \frac{dC}{dr} \right)_{r+\Delta r} = -4\pi r^2 \Delta r_p k_1 C$$

Take the limit as $\Delta r \rightarrow 0$ and assume that the effective diffusivity is independent of the concentration of reactant, this difference equation becomes

$$\frac{d^2 C}{dr^2} + 2 \frac{dC}{dr} - \frac{k_1 \rho_p C}{D_e} = 0$$

At the center of the pellet symmetry requires

$$\frac{dC}{dr} = 0 \text{ at } r = 0$$

and at outer surface

$$C = C_s \text{ at } r = r_s$$

Solve linear differential equation by conventional methods to yield

$$\frac{C}{C_s} = \frac{r_s \sinh\left(3\phi_s \frac{r}{r_s}\right)}{r \sinh 3\phi_s}$$

where ϕ_s is Thiele modulus for a spherical pellet defined by $\phi_s = \frac{r_s}{3} \sqrt{\frac{k_1 \rho_p}{D_e}}$

Both D_e and k_1 are necessary to use $r_p = \eta k_1 (C_A)_s$. D_e could be obtained from the reduced pore volume equation in case of no tortuosity factor.

$$D_e = (\varepsilon_s)^2 D_{AB}$$

At 200°C, $D_e = (0.5)^2 (0.491) = 0.123$

At 250°C, $D_e = (0.5)^2 (0.582) = 0.146$

At 300°C, $D_e = (0.5)^2 (0.679) = 0.169$

Substitute radius of catalyst pellet, $r_s = 0.107 \times 10^{-3}$ m with ϕ_s equation

$$\phi_s = \frac{0.107 \times 10^{-3} \text{ m}}{3} \sqrt{\frac{k(\text{m}^3/\text{s} \cdot \text{kg cat.}) \times 3.75 \times 10^{-4} (\text{kg}/\text{m}^3)}{0.123 (\text{m}^2/\text{s})}}, \text{ at } 200^\circ\text{C}$$

$$\phi_s = 1.97 \times 10^{-6} \sqrt{k} \text{ (dimensionless) at } 200^\circ\text{C}$$

$$\phi_s = 1.81 \times 10^{-6} \sqrt{k} \text{ (dimensionless) at } 250^\circ\text{C}$$

$$\phi_s = 1.68 \times 10^{-6} \sqrt{k} \text{ (dimensionless) at } 300^\circ\text{C}$$

Find k (at 200°C) from the mass balance equation around plug-flow reactor.

$$r_w = \frac{F_{A0} dx}{dW}$$

where $r_w = kC_A$

Thus, $kC_A = \frac{F_{A_0} dx}{dW}$

$$kC_{A_0}(1-x) = \frac{F_{A_0} dx}{dW}$$

$$W = \frac{F_{A_0}}{kC_{A_0}} \int_0^{0.3} \frac{1}{1-x} dx$$

$$W = \frac{F_{A_0}}{kC_{A_0}} [-\ln(1-x)]_0^{0.3} = \frac{F_{A_0}}{kC_{A_0}} (-\ln(0.7))$$

$$k = \frac{F_{A_0}}{WC_{A_0}} (-\ln(0.7))$$

$$k = \frac{1.39 \times 10^{-5} \text{ (mol/s)}}{0.1 \times 10^{-3} \text{ (kg)} \times 6.05 \text{ (mol/m}^3)} (-\ln(0.7))$$

$$= 8.19 \times 10^{-3} \text{ m}^3/\text{s-kg catalyst}$$

Calculate ϕ_s : $\phi_s = 1.97 \times 10^{-6} \sqrt{0.92 \times 10^{-4}} = 1.78 \times 10^{-7}$ at 200°C

$$\phi_s = 1.81 \times 10^{-6} \sqrt{0.92 \times 10^{-4}} = 2.28 \times 10^{-7} \text{ at } 250^\circ\text{C}$$

$$\phi_s = 1.68 \times 10^{-6} \sqrt{0.92 \times 10^{-4}} = 1.02 \times 10^{-6} \text{ at } 300^\circ\text{C}$$

For such small values of ϕ_s it was concluded that the internal mass transport has no effect on the rate of phthalic anhydride oxidation reaction.

APPENDIX C

CALCULATION OF SPECIFIC SURFACE AREA

From Brunauer-Emmett-Teller (BET) equation [Anderson J. R. and co-worker (1985)]

$$\frac{p}{n(1-p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C} \quad (C1)$$

Where, p = Relative partial pressure of adsorbed gas, P/P_0
 P_0 = Saturated vapor pressure of adsorbed gas in the condensed state at the experimental temperature, atm
 P = Equilibrium vapor pressure of adsorbed gas, atm
 n = Gas adsorbed at pressure P , ml. at the NTP/g of sample
 n_m = Gas adsorbed at monolayer, ml. at the NTP/g of sample
 C = $\text{Exp} [(H_C - H_1)/RT]$
 H_C = Heat of condensation of adsorbed gas on all other layers
 H_1 = Heat of adsorption into the first layer

Assume $C \gg 1$, then

$$\frac{p}{n(1-p)} = \frac{p}{n_m} \quad (C2)$$
$$n_m = n(1-p)$$

The surface area, S , of the catalyst is given by

$$S = S_b n_m \quad (C3)$$

From the gas law

$$\frac{P_b V}{T_b} = \frac{P_t V}{T_t} \quad (C4)$$

Where, P_b = Pressure at 0°C
 P_t = Pressure at $t^\circ\text{C}$
 T_b = Temperature at $0^\circ\text{C} = 273.15 \text{ K}$
 T_t = Temperature at $t^\circ\text{C} = 273.15 + t \text{ K}$

$V = \text{Constant volume}$

Then, $P_b = (273.15/T_t) \times P_t = 1 \text{ atm}$

Partial pressure

$$P = \frac{[\text{Flow of (He + N}_2\text{)} - \text{Flow of He}]}{\text{Flow of (He + N}_2\text{)}} \quad (\text{C5})$$

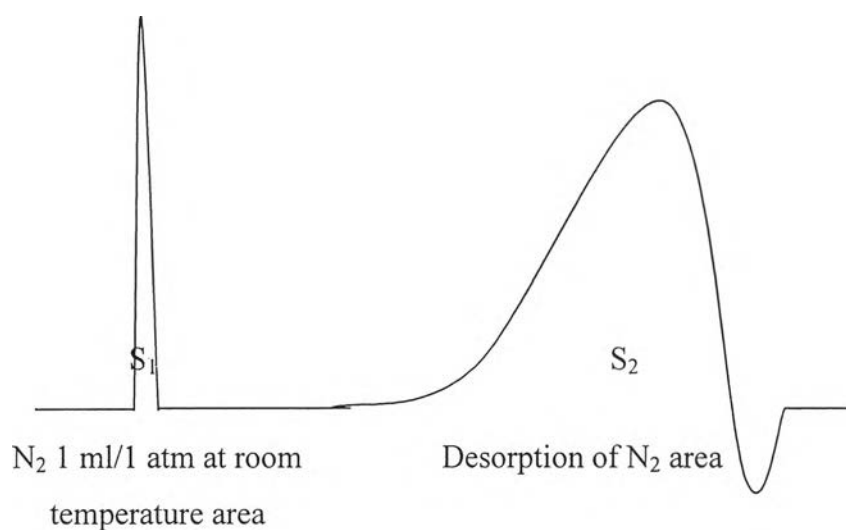
$$= 0.3 \text{ atm}$$

For nitrogen gas, the saturated vapor pressure equals to

$$P_0 = 1.1 \text{ atm}$$

then, $p = P/P_0 = 0.3/1.1 = 0.2727$

To measure the volume of nitrogen adsorbed, n



$$n = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml. /g of catalyst} \quad (\text{C6})$$

Where, $S_1 = \text{N}_2 \text{ 1 ml/1 atm at room temperature area}$

$S_2 = \text{Desorption of N}_2 \text{ area}$

$W = \text{Sample weight, g}$

$T = \text{Room temperature, K}$

Therefore,

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1 - p)$$

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \quad (C2.1)$$

Whereas, the surface area of nitrogen gas from literature equal to

$$S_b = 4.373 \text{ m}^2/\text{ml of nitrogen gas}$$

Then,

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \times 4.343$$

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 3.1582 \text{ m}^2/\text{g} \quad (C7)$$

APPENDIX D

CALIBRATION CURVES

Flame ionization detector gas chromatographs; using Chromosorb WAW column used model 9A to analyze the concentrations of phthalic anhydride, maleic anhydride, acetic acid, ethylbenzene, toluene, and benzene.

Using Porapak-Q and Molecular Sieve 5-A column, respectively, used gas chromatograph with the thermal conductivity detector, model 8A, to analyze the concentration of CO₂ AND CO.

The calibration curves of phthalic anhydride, maleic anhydride, acetic acid, ethylbenzene, toluene, and benzene are illustrated in the following figures.

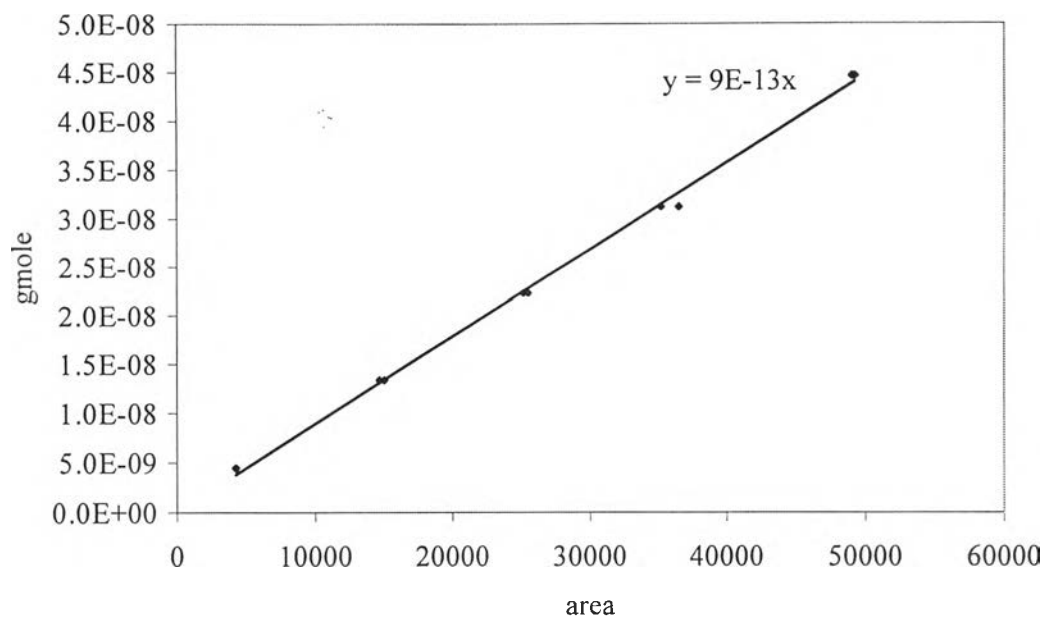


Figure D1 The calibration curve of phthalic anhydride

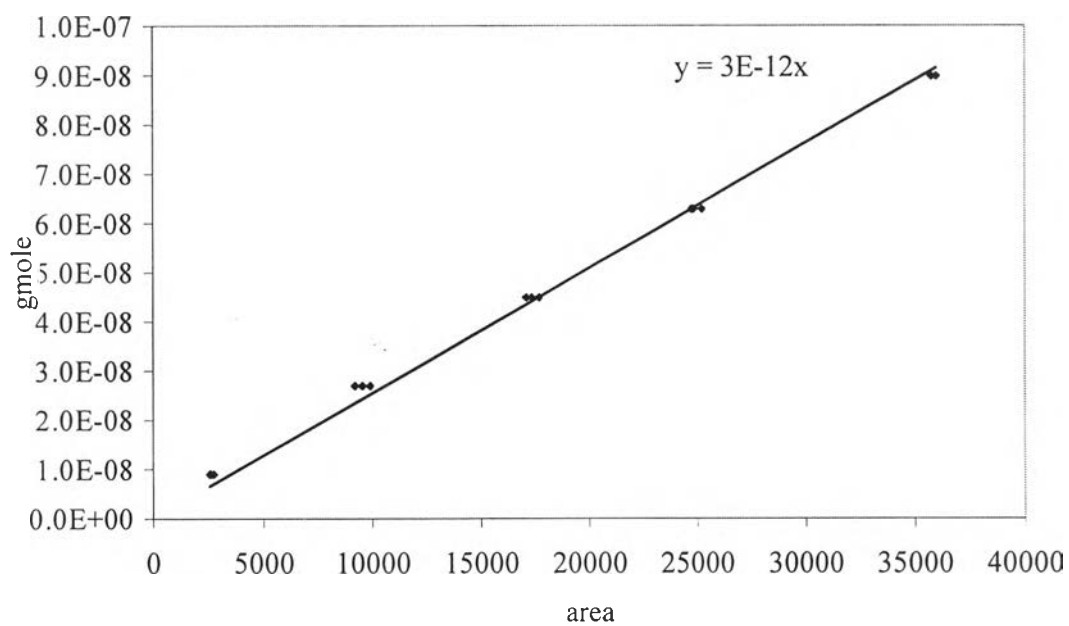


Figure D2 The calibration curve of maleic anhydride

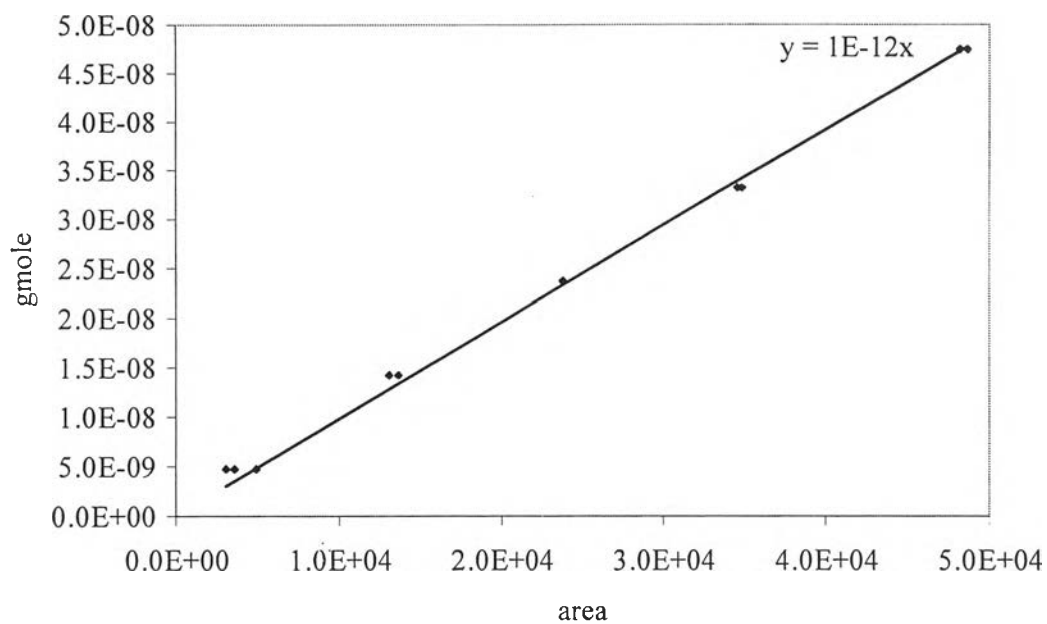


Figure D3 The calibration curve of acetic acid

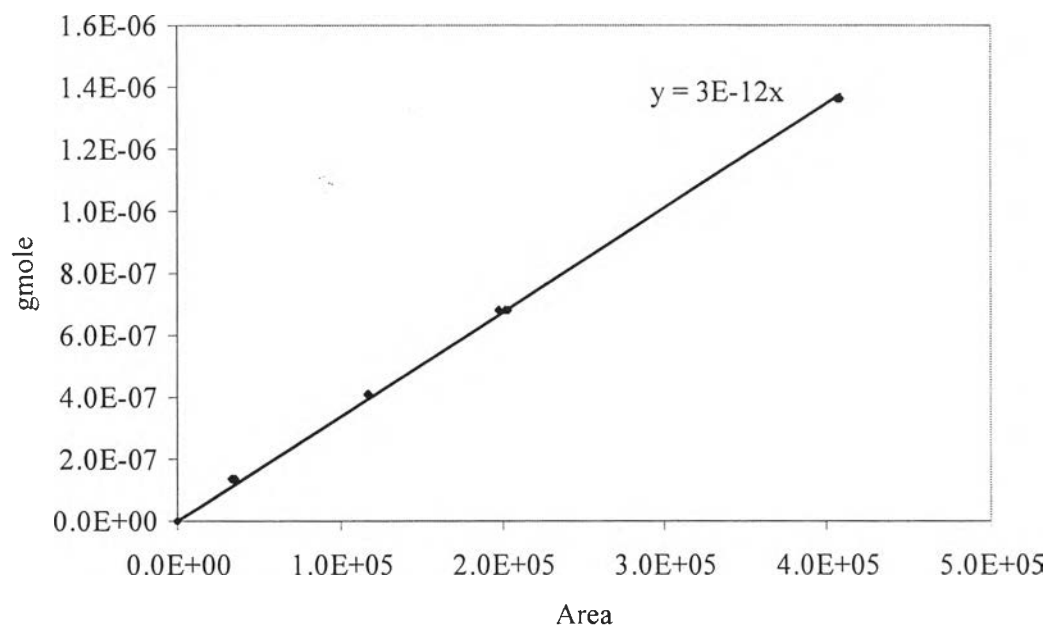


Figure D4 The calibration curve of ethyl-benzene

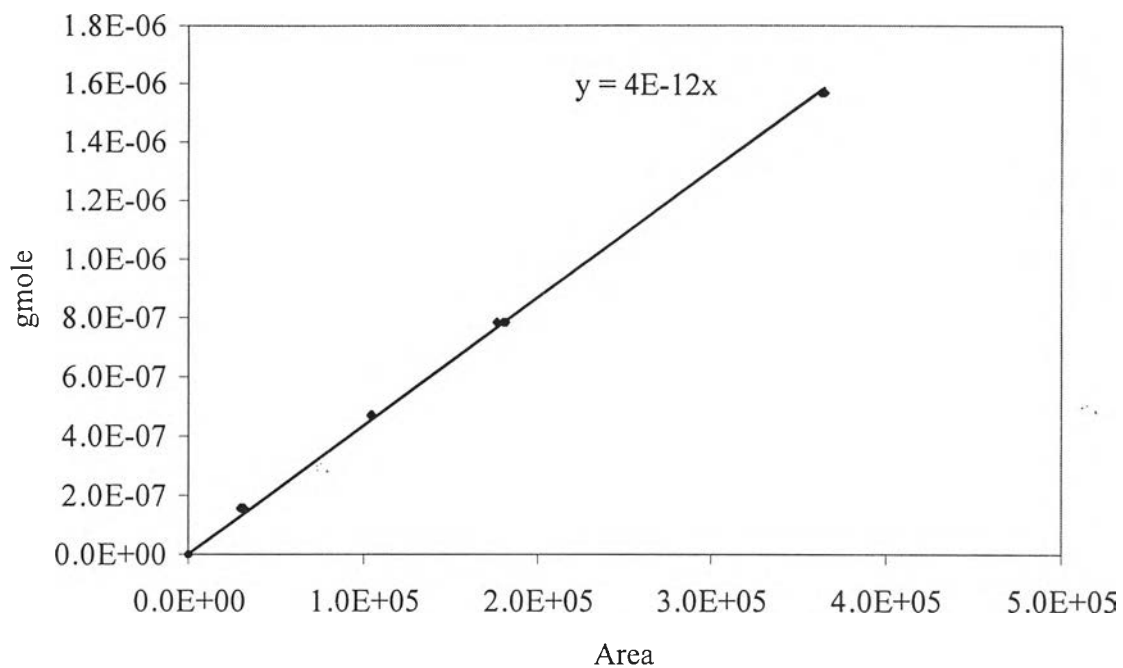


Figure D5 The calibration curve of toluene

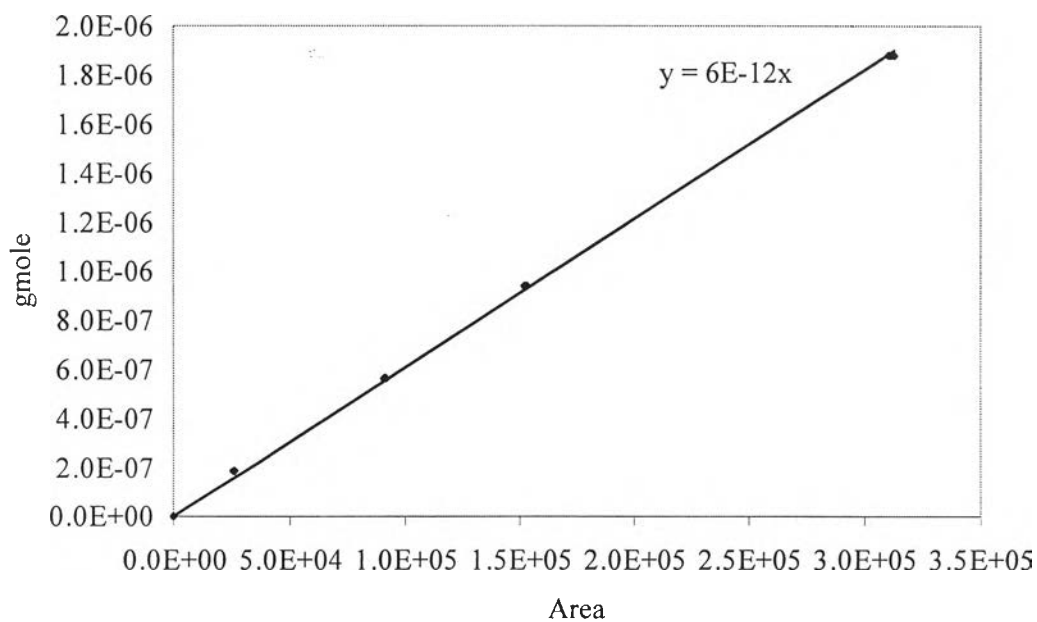


Figure D6 The calibration curve of benzene

APPENDIX E

DATA OF EXPERIMENTS

Table D1 Data of figure 5.3

Temp (°C)	Phthalic anhydride conversion (%)				
	10V2MgOTi	10VTi	MgTi	TiO ₂	blank
200	5	4	3	4	2
250	20	13	9	17	3
300	45	22	14	35	6
350	72	43	34	50	16
400	81	60	57	61	22
450	86	67	65	69	28
500	87	74	72	75	34
550	89	81	78	82	44

Table D2 Data of figure 5.4

Temp (°C)	Phthalic anhydride conversion (%)		
	10V2MgOTi	10V4MgOTi	10V8MgOTi
200	3	2	2
250	4	4	3
300	16	15	7
350	48	63	44
400	84	88	66
450	85	91	70
500	86	92	73
550	90	95	78

Table D3 Data of figure 5.5

Temp (°C)	Phthalic anhydride conversion (%)					
	6V4MgOTi	8V4MgOTi	10V4MgOTi	12V4MgOTi	14V4MgOTi	16V4MgOTi
200	2	2	2	2	3	2
250	3	4	4	3	4	3
300	13	12	15	12	19	7
350	38	41	63	44	40	38
400	61	59	88	80	75	47
450	70	74	91	83	86	65
500	71	78	92	84	88	70
550	74	80	95	85	90	71

Table D4 Data of figure 5.6

Temp (°C)	Maleic anhydride conversion (%)				
	10V2MgOTi	10VTi	MgTi	TiO ₂	blank
200	3	2	2	3	1
250	6	5	4	5	2
300	16	7	6	10	4
350	48	40	45	45	36
400	84	75	73	76	43
450	85	77	75	83	62
500	86	80	78	84	68
550	90	81	77	85	69

Table D5 Data of figure 5.7

Temp (°C)	Maleic anhydride conversion (%)		
	10V2MgOTi	10V4MgOTi	10V8MgOTi
200	3	2	2
250	4	4	3
300	16	15	7
350	48	63	44
400	84	88	66
450	85	91	70
500	86	92	73
550	90	95	78

Table D6 Data of figure 5.8

Temp (°C)	Maleic anhydride conversion (%)					
	6V4MgOTi	8V4MgOTi	10V4MgOTi	12V4MgOTi	14V4MgOTi	16V4MgOTi
200	2	2	2	2	3	2
250	3	4	4	3	4	3
300	13	12	15	12	19	7
350	38	41	63	44	40	38
400	61	59	88	80	75	47
450	70	74	91	83	86	65
500	71	78	92	84	88	70
550	74	80	95	85	90	71

Table D7 Data of figures 5.9, 5.10, 5.11

Temp (°C)	Benzene		Toluene		EthylBenzene	
	Blank	VMgOTi	Blank	VMgOTi	Blank	VMgOTi
200	0	0	0	0	0	0
250	0	0	0	0	0	0
300	0	0	0	0	0	10
350	0	0	0	0	0	18
400	0	3	5	6	10	20
450	33	37	30	34	38	40
500	43	42	43	44	48	50
550	55	58	56.1	59	62	66

Table D8 Data of figure 5.12

Temp (°C)	acetic acid		
	Blank	VMgOTi	TiO2
200	8	13	12
250	12	27	19
300	15	46	30
350	89	93	93
400	93	95	95
450	94	96	95
500	95	98	96
550	96	99	96

VITA

Mr. Pongsakorn Tongsang was born in Ubonrajchatanee on April 28, 1977. He graduated high school from Benjamamaharaj School, Ubonrajchatanee on 1993 and received his Bachelor degree of Chemical Engineering from the Faculty of Engineering, Khonkean University in 1997.

