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APPENDICES

APPENDIX A

CALCULATION OF CATALYST PREPARATION

Preparation of 8Co/MgO catalyst by the Wet Impregnation Method is shown as follow:

Reagent: - Cobalt acetate tetrahydrate [$Co(CH_3COO)_2 \cdot 4H_2O$]

Molecular weight = 249 g.

Support - Magnesium oxide [MgO]

Molecular weight = 39 g.

Calculation for the preparation of the 8Co/MgO catalyst.

The 8Co/MgO aqueous solution used in catalyst preparation consists of Co 8wt% and MgO 92wt%. The amount of cobalt in 8Co/MgO catalyst is calculated as follows:

Basis: MgO 1 g.

If the weight of catalyst was 100 gram, 8Co/MgO would compose of cobalt 8 g. and MgO 92 g. Therefore, in this system,

the amount of Co = 8/92 × 1

= 0.0869 g.

Cobalt (Co) 0.0869 g. was prepared from $Co(CH_3COO)_2 \cdot 4H_2O$ 99% and molecular weight of Co = 59, then

the $Co(CH_3COO)_2 \cdot 4H_2O$ content = (249×0.0869×100)/(59×99)

= 0.3712 g.

Preparation of 8Co/SiO$_2$ and 8Co/γ-Al$_2$O$_3$ catalysts by the Wet Impregnation Method is shown as follow:

Support - Silica gel (SiO$_2$)

     Pore volume = 1.2 ml./g.

    - Alumina (γ-Al$_2$O$_3$)

     Pore volume = 1 ml./g.

Calculation for the preparation of the 8Co/SiO$_2$ and 8Co/γ-Al$_2$O$_3$ catalysts.

1. 8Co/SiO$_2$ catalyst

The 8Co/SiO$_2$ aqueous solution used in catalyst preparation consists of Co 8wt% and SiO$_2$ 92wt%. The amount of cobalt in 8Co/SiO$_2$ catalyst is calculated as follows:

Basis: SiO$_2$ 2 g.

If the weight of catalyst was 100 gram, 8Co/SiO$_2$ would compose of cobalt 8 g. and SiO$_2$ 92 g. Therefore, in this system,

  the amount of Co   = 8/92 × 2

             = 0.1738 g.

Cobalt (Co) 0.1738 g. was prepared from Co(CH$_3$COO)$_2$·4H$_2$O 99% and molecular weight of Co = 59, then

  the Co(CH$_3$COO)$_2$·4H$_2$O content = (249×0.1738×100)/(59×99)

                = 0.7424 g.

2. 8Co/γ-Al$_2$O$_3$ catalyst

The calculation for the preparation of 8Co/γ-Al$_2$O$_3$ catalyst is the same as the preparation of 8Co/SiO$_2$ catalyst.

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 1-propanal oxidation 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, 8% 1-propanol, 5% O_2 balance with nitrogen was used as the unique reactant in the system. Molecular weight of 1-propanol and air (O_2 5%) are 60 and 28.2, respectively. Thus, the average molecular weight of the gas mixture was calculated as follows:

$$M_{AB} = 0.08 \times 60 + 0.92 \times 28.2$$
$$= 30.744 \text{ g/mol}$$

Calculation of reactant gas density

Consider the 1-propanol oxidation 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.

$$\rho = \frac{PM}{RT} = \frac{1.0 \times 10^5 \times 30.744 \times 10^{-3}}{8.314T}$$

We obtained : $\rho = 0.782$ kg/m^3 at T = 200°C

$\rho = 0.706$ kg/m^3 at T = 250°C

$\rho = 0.645$ kg/m^3 at T = 300°C

$\rho = 0.594$ 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

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

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

M_1, M_2 = molecular weight

Let 1 refer to 1-propanol and 2 to air (O_2 5%)

M_1 = 60 and M_2 = 28.2

From Perry the viscosity of pure 1-propanol at 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C are 0.0124, 0.0135, 0.015 and 0.0162 cP, respectively. The viscosity of pure air at 200°C, 250°C, 300°C and 350°C are 0.0248, 0.0265, 0.0285 and 0.030 cP, respectively.

At 200°C :

$$\phi_{12} = \frac{\left[1 + \left(\frac{0.0124}{0.0248}\right)^{1/2} \left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1 + \frac{60}{28.2}\right)\right]^{1/2}} = 0.502$$

$$\phi_{21} = 0.502\left(\frac{0.0248}{0.0124}\right)\left(\frac{60}{28.2}\right) = 2.14$$

$$\mu_m = \frac{0.08 \times 0.0124}{0.08 + 0.92 \times 0.502} + \frac{0.92 \times 0.0248}{0.92 + 0.08 \times 2.14} = 0.0227 cP = 2.27 \times 10^{-5} kg/m-sec$$

At 250°C :

$$\phi_{12} = \frac{\left[1 + \left(\frac{0.0135}{0.0265}\right)^{1/2} \left(\frac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1 + \frac{60}{28.2}\right)\right]^{1/2}} = 0.506$$

$$\phi_{21} = 0.506\left(\frac{0.0265}{0.0135}\right)\left(\frac{60}{28.2}\right) = 2.113$$

$$\mu_m = \frac{0.08 \times 0.0135}{0.08 + 0.92 \times 0.506} + \frac{0.92 \times 0.0265}{0.92 + 0.08 \times 2.113} = 0.0244 cP = 2.44 \times 10^{-5} kg/m-sec$$

$$\text{At } 300^{\circ}\text{C}: \qquad \phi_{12} = \frac{\left[1 + \left(\dfrac{0.015}{0.0285}\right)^{1/2}\left(\dfrac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1 + \dfrac{60}{28.2}\right)\right]^{1/2}} = 0.512$$

$$\phi_{21} = 0.512\left(\frac{0.0285}{0.015}\right)\left(\frac{60}{28.2}\right) = 2.07$$

$$\mu_m = \frac{0.08 \times 0.015}{0.08 + 0.92 \times 0.512} + \frac{0.92 \times 0.0285}{0.92 + 0.08 \times 2.07} = 0.0263 cP = 2.63 \times 10^{-5} kg/m-\sec$$

$$\text{At } 350^{\circ}\text{C}: \qquad \phi_{12} = \frac{\left[1 + \left(\dfrac{0.0162}{0.030}\right)^{1/2}\left(\dfrac{28.2}{60}\right)^{1/4}\right]^2}{\left[8\left(1 + \dfrac{60}{28.2}\right)\right]^{1/2}} = 0.517$$

$$\phi_{21} = 0.517\left(\frac{0.030}{0.0162}\right)\left(\frac{60}{28.2}\right) = 2.037$$

$$\mu_m = \frac{0.08 \times 0.0162}{0.08 + 0.92 \times 0.517} + \frac{0.92 \times 0.030}{0.92 + 0.08 \times 2.037} = 0.0278 cP = 2.78 \times 10^{-5} kg/m-\sec$$

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

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

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

$\quad$ T $\quad$ = 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,^{0}A

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 $C_3 H_7OH$: σ ($C_3 H_7OH$) = 4.549 ^{0}A, ε /k = 576.7

For air   : σ (air) = 3.711 ^{0}A , ε /k = 78.6

The sample rules are usually employed.

$$\sigma_{AB} = \frac{\sigma_A+\sigma_B}{2} = \frac{4.549+3.711}{2} = 4.13$$

$$\varepsilon_{AB}/k = \left(\frac{\varepsilon_A\varepsilon_B}{k^2}\right)^{1/2} = (576.7\times78.6)^{1/2} = 212.9$$

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

Then $T^* = \dfrac{473}{212.9} = 2.222$ at 200°C

$T^* = \dfrac{523}{212.9} = 2.456$ at 250°C

$T^* = \dfrac{573}{212.9} = 2.691$ at 300°C

$T^* = \dfrac{623}{212.9} = 2.926$ at 350°C

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

$\Omega_D = 1.038$; 200°C

$\Omega_D = 1.006$; 250°C

$\Omega_D = 0.979$; 300°C

$\Omega_D = 0.956$; 350°C

With Equation of D_{AB},

At 200°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})473^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.038}$

$= 3.01 \times 10^{-5}$ m²/s

At 250°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})523^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.006}$

$= 3.62 \times 10^{-5}$ m²/s

At 300°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})573^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.979}$

$= 4.26 \times 10^{-5}$ m²/s

At 350°C : $D(C_3H_7OH\text{-air}) = \dfrac{\left(3.03 - \dfrac{0.98}{30.24^{0.5}}\right)(10^{-3})623^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.956}$

$\qquad\qquad\qquad\qquad = \quad 5.04 \times 10^{-5} \quad m^2/s$

Reactant gas mixture was supplied at 100 ml/min. in tubular microreactor used in the 1-propanol oxidation system at 30°C

1-propanol flow rate through reactor = 100 ml/min. at 30°C

The density of 1-propanol , $\rho = \dfrac{1.0 \times 10^5 \times 30.744 \times 10^{-3}}{8.314(273 + 30)} = 1.236 \ kg/s$

Mass flow rate $= 1.236\left(\dfrac{100 \times 10^{-6}}{60}\right) = 2.06 \times 10^{-6} \ kg/s$

Diameter of quartz tube reactor $= 8$ mm

Cross-sectional area of tube reactor $= \dfrac{\pi(8 \times 10^{-3})^2}{4} = 5.03 \times 10^{-5} \ m^2$

Mass Velocity , $G = \dfrac{2.06 \times 10^{-6}}{5.03 \times 10^{-5}} = 0.04 \ kg/m^2\text{-s}$

Catalysis size = 40-60 mesh = 0.178-0.126 mm

Average catalysis = (0.126+0.178)/2 = 0.152 mm

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

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

We obtained

At 200°C : $Re_p = \dfrac{(0.152 \times 10^{-3} \times 0.04)}{2.27 \times 10^{-5}} = 0.268$

$$\underline{\text{At } 250^{\circ}\text{C}} \; : \; \text{Re}_p = \frac{(0.152 \times 10^{-3} \times 0.04)}{2.44 \times 10^{-5}} = 0.249$$

$$\underline{\text{At } 300^{\circ}\text{C}} \; : \; \text{Re}_p = \frac{(0.152 \times 10^{-3} \times 0.04)}{2.63 \times 10^{-5}} = 0.231$$

$$\underline{\text{At } 350^{\circ}\text{C}} \; : \; \text{Re}_p = \frac{(0.152 \times 10^{-3} \times 0.04)}{2.78 \times 10^{-5}} = 0.219$$

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, $k_m\rho/G$, 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 = uρ)

    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 $\varepsilon_B = 0.5$

<u>At 200°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.268)^{-0.407} = 1.565$

<u>At 250°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.249)^{-0.407} = 1.613$

<u>At 300°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.231)^{-0.407} = 1.663$

<u>At 350°C</u> ; $j_D = \dfrac{0.458}{0.5}(0.219)^{-0.407} = 1.699$

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

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

Where ε is the porosity of the single screen.

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

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

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

At 200°C : $Sc = \dfrac{2.27 * 10^{-5}}{0.782 * 3.01 * 10^{-5}} = 0.964$

At 250°C : $Sc = \dfrac{2.44 * 10^{-5}}{0.706 * 3.62 * 10^{-5}} = 0.955$

At 300°C : $Sc = \dfrac{2.63 * 10^{-5}}{0.645 * 4.26 * 10^{-5}} = 0.957$

At 350°C : $Sc = \dfrac{2.78 * 10^{-5}}{0.594 * 5.04 * 10^{-5}} = 0.928$

Find k_m :   At 200°C, $k_m = \left(\dfrac{1.565 \times 0.04}{0.782} \right)(0.964)^{-2/3} = 0.082 \, m/s$

At 250°C, $k_m = \left(\dfrac{1.613 \times 0.04}{0.706} \right)(0.955)^{-2/3} = 0.094 \, m/s$

At 300°C, $k_m = \left(\dfrac{1.663 \times 0.04}{0.645} \right)(0.957)^{-2/3} = 0.106 \, m/s$

At 350°C, $k_m = \left(\dfrac{1.699 \times 0.04}{0.594} \right)(0.928)^{-2/3} = 0.12 \, m/s$

Properties of catalyst

Density = 0.375 g/ml catalyst

Diameter of 40-60 mesh catalyst particle = 0.152 mm

Weight per catalyst particle $= \dfrac{\pi(0.152\times0^{-1})^{3}\times0.375}{6} = 6.895*10^{-7}$ g/particle

External surface area per particle $= \pi(0.152\times10^{-3})^{2} = 7.26\times10^{-7}$ m²/particle

$a_{m} = \dfrac{7.26\times10^{-7}}{6.895\times10^{-7}} = 1.052\times10^{-2}$ m²/gram catalyst

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

Molar flow rate of gaseous feed stream $= \dfrac{(1\times10^{5})\left(\dfrac{100\times10^{-6}}{60}\right)}{8.314(273+30)} = 6.62\times10^{-5}$ mol/s

1-propanol molar feed rate $= 0.08\times6.62\times10^{-5} = 5.29\times10^{-6}$ mol/s

1-propanol conversion (experimental data): 1.78 % at 200°C

5.73 % at 250°C

28.07 % at 300°C

59.93 % at 350°C

The estimated rate of 1-propanol 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
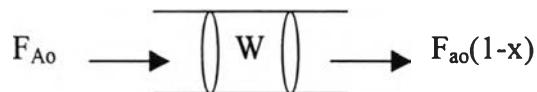
{rate of i into volume element} - {rate of i out of volume element}

+ {rate of production of i within the volume element}

= {rate of accumulation of i within the volume elecment }

$F_{Ao} = F_{Ao}(1-x) + (r_{w}W)$

$$(r_w W) = F_{Ao} - F_{Ao}(1-x) = F_{Ao} = F_{Ao}x$$

$$r_w = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.0178}{0.1} = 4.717 \times 10^{-7} \text{ mol/s-gram catalyst at } 200^{\circ}C$$

$$r_w = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.0573}{0.1} = 1.518 \times 10^{-6} \text{ mol/s-gram catalyst at } 250^{\circ}C$$

$$r_w = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.28}{0.1} = 7.42 \times 10^{-6} \text{ mol/s-gram catalyst at } 300^{\circ}C$$

$$r_w = \frac{F_{Ao}x}{W} = \frac{5.29 \times 10^{-6} \times 0.599}{0.1} = 1.587 \times 10^{-5} \text{ mol/s-gram catalyst at } 350^{\circ}C$$

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:

$$R_{obs} = k_m a_m (C_b - C_s)$$

$$= \frac{1 \text{ - propanol converted (mole)}}{(\text{time})(\text{gram of catalyst})}$$

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

At 200°C. $(C_b - C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{4.717 \times 10^{-7}}{0.082 \times 1.052 \times 10^{-1}} = 5.47 \times 10^{-4} \text{ mol/m}^3$

At 250°C. $(C_b - C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{1.518 \times 10^{-6}}{0.094 \times 1.052 \times 10^{-1}} = 1.53 \times 10^{-4} \text{ mol/m}^3$

At 300°C. $(C_b - C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{7.42 \times 10^{-6}}{0.106 \times 1.052 \times 10^{-1}} = 6.65 \times 10^{-3} \text{ mol/m}^3$

At 350°C. $(C_b - C_s) = \dfrac{r_{obs}}{k_m a_m} = \dfrac{1.587 \times 10^{-5}}{0.12 \times 1.052 \times 10^{-1}} = 1.26 \times 10^{-3} \text{ mol/m}^3$

From C_b (1-propanol) $= 1.59$ 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 1-propanol oxidation reaction rate.

2. Internal diffusion limitation

Next, consider the internal diffusion limitation of the 1-propanol 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

Then, $\qquad r_p = \eta r_s = \eta f(C_s, T_s)$

Suppose that the 1-propanol 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 with in 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,
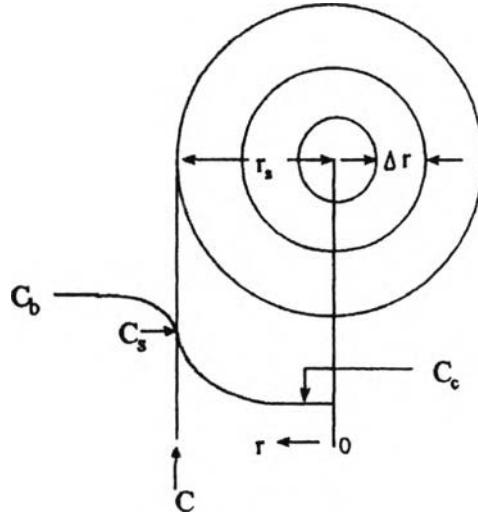
Figure B1. Reactant (A) concentration vs. position for first-order reaction on a spherical catalyst pellet.

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

Take the limit as $\Delta r \to 0$ 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

$C = C_s$ 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, $D_e = (0.5)^2 (3.01 \times 10^{-5}) = 7.53 \times 10^{-6}$

At 250°C, $D_e = (0.5)^2 (3.62 \times 10^{-5}) = 9.04 \times 10^{-6}$

At 300°C, $D_e = (0.5)^2 (4.26 \times 10^{-5}) = 1.06 \times 10^{-5}$

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

$$\phi_s = \frac{0.076 \times 10^{-3} \text{ m}}{3} \sqrt{\frac{k(m^3 / s - kg \text{ cat.}) \times 1000(kg/m^3)}{7.53 \times 10^{-6}(m^2 / s)}} \text{ , at } 200°C$$

$\phi_s = 0.292\sqrt{k}$ (dimensionless) at 200°C

$\phi_s = 0.266\sqrt{k}$ (dimensionless) at 250°C

$\phi_s = 0.246\sqrt{k}$ (dimensionless) at 300°C

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

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

where $r_w = kC_A$

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

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

$$W = \frac{F_{Ao}}{kC_{Ao}} \int_0^{0.1} \frac{1}{1-x}\ dx$$

$$W = \frac{F_{Ao}}{kC_{Ao}} \left[-\ln(1-x) \right]_0^{0.1} = \frac{\overline{F_{Ao}}}{kC_{Ao}}(-\ln(0.9))$$

$$k = \frac{F_{Ao}}{WC_{Ao}}(-\ln(0.9822))$$

$$k = \frac{5.29\times10^{-6}\ (mol/s)}{0.1\times10^{-3}\ (kg)\times1.03(mol/m^3)}(-\ln(0.9822))$$

$$= 0.92 \times 10^{-4}\ m^3/s\text{-kg catalyst}$$

Calculate ϕ_s : $\phi_s = 0.292\ \sqrt{0.92\times10^{-4}}\ = 0.0028$ at 200°C

$$\phi_s = 0.266\ \sqrt{3.03\times10^{-3}}\ = 0.015\ \text{at 250°C}$$

$$\phi_s = 0.246\ \sqrt{1.68\times10^{-2}}\ = 0.032\ \text{at 300°C}$$

For such small values of ϕ_s it was concluded that the internal mass transport has no effect on the rate of 1-propanol oxidation reaction.

APPENDIX C
CALIBRATION CURVE

Flame ionization detector gas chromatographs, model 14A and 14B, were used to analyze the concentrations of oxygenated compounds and light hydrocarbons, respectively. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, formaldehyde, acetaldehyde, and propionaldehyde were analyzed by GC model 14A while methane, ethylene, propane, and propylene were analyzed by GC model 14B.

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO_2 and CO by using Porapak-Q and Molecular Sieve 5-A column, respectively.

The calibration curves of methane, ethylene, propane, propylene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, CO_2, formaldehyde, acetaldehyde, and propionaldehyde are illustrated in the following figures.

Calibration curve
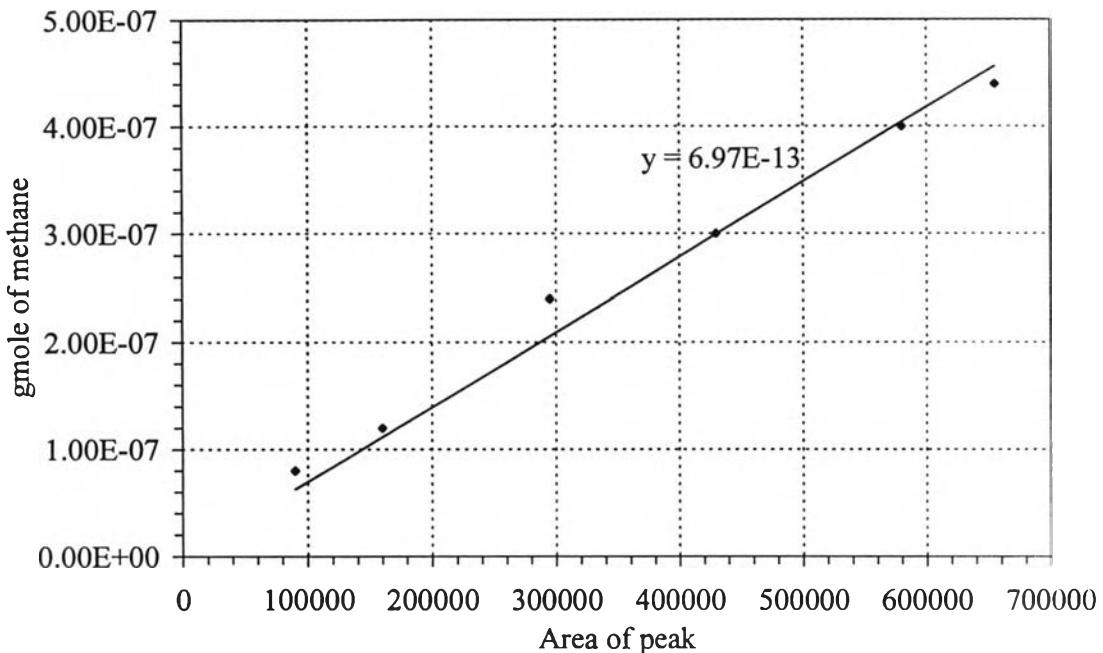
Figure C1 The calibration curve of methane
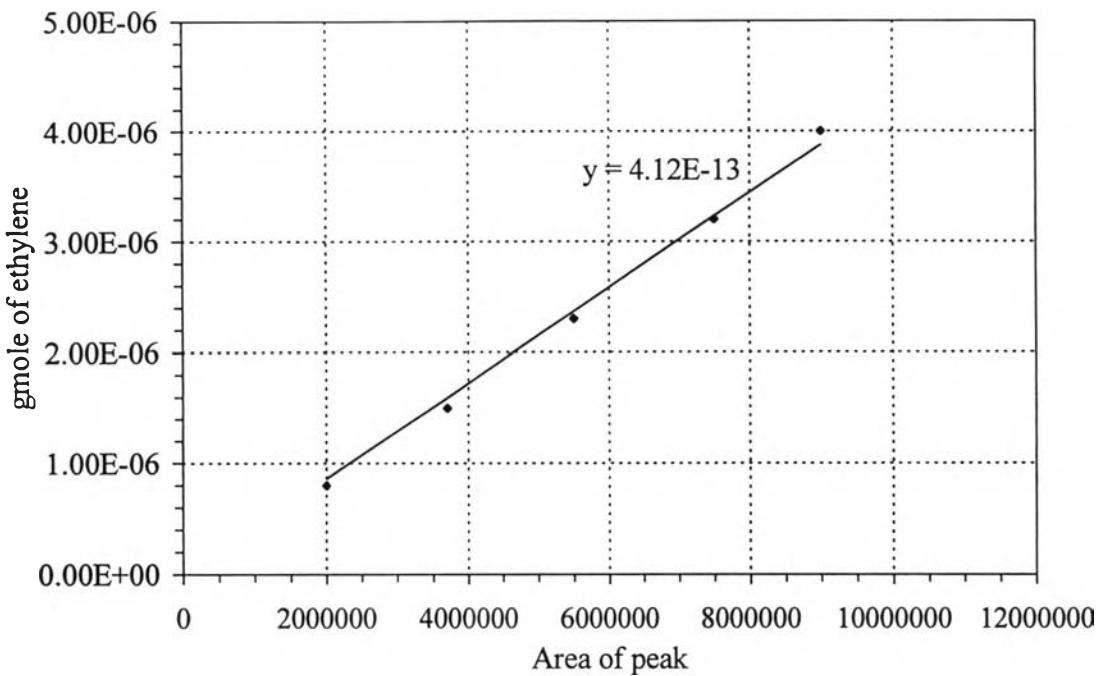
Figure C2 The calibration curve of ethylene
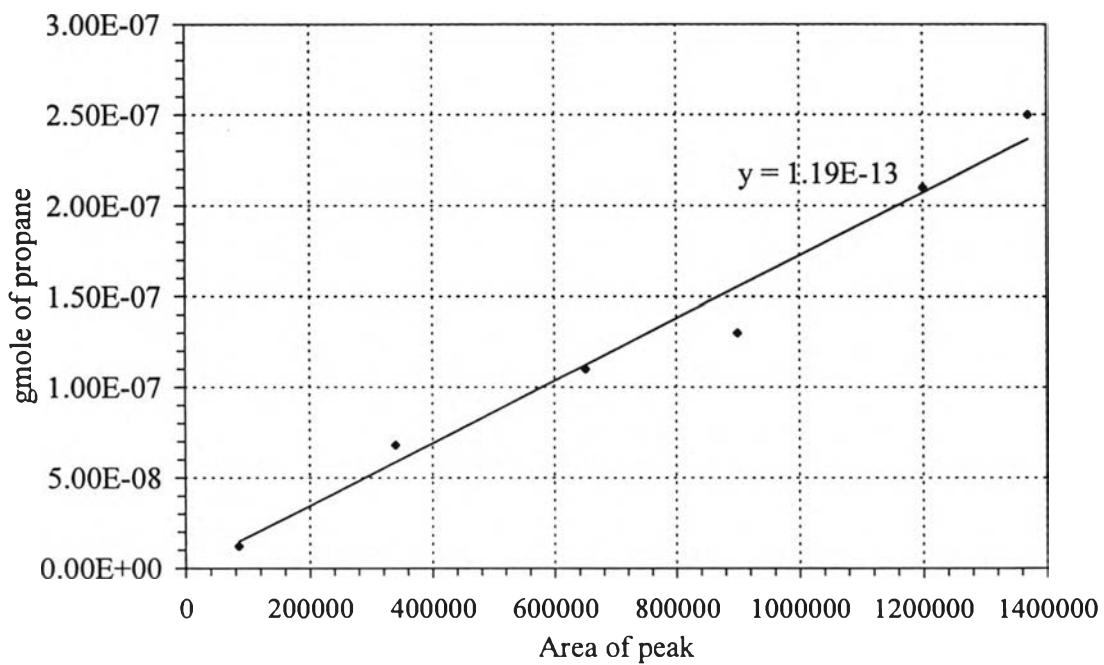
Figure C3 The calibration curve of propane
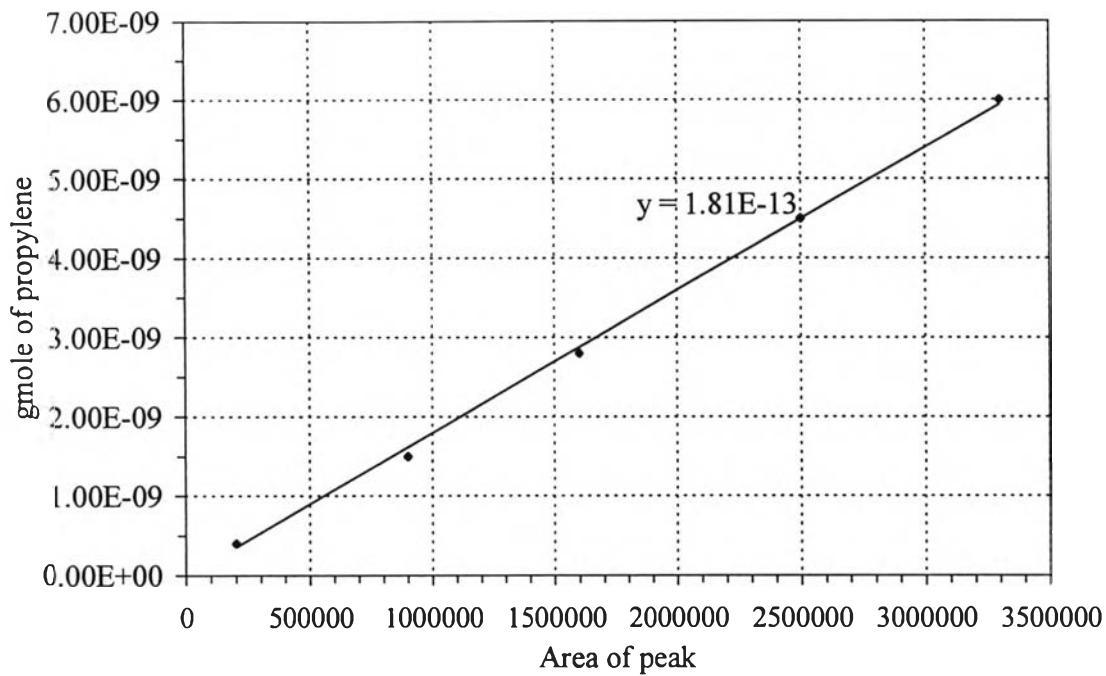
Figure C4 The calibration curve of propylene
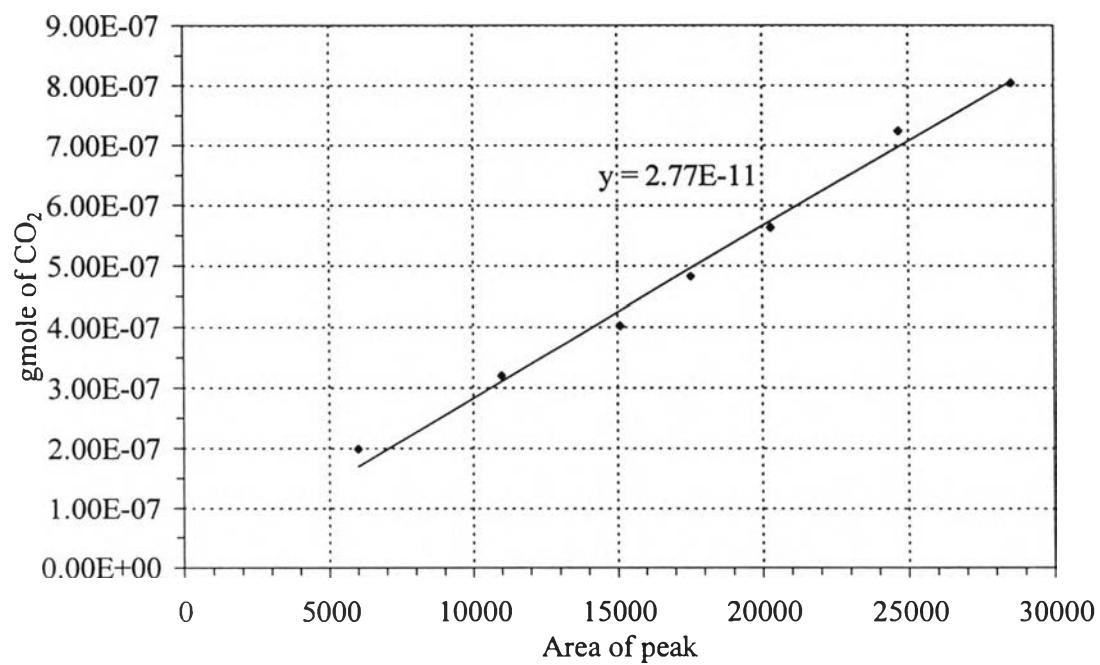
Figure C5 The calibration curve of CO_2
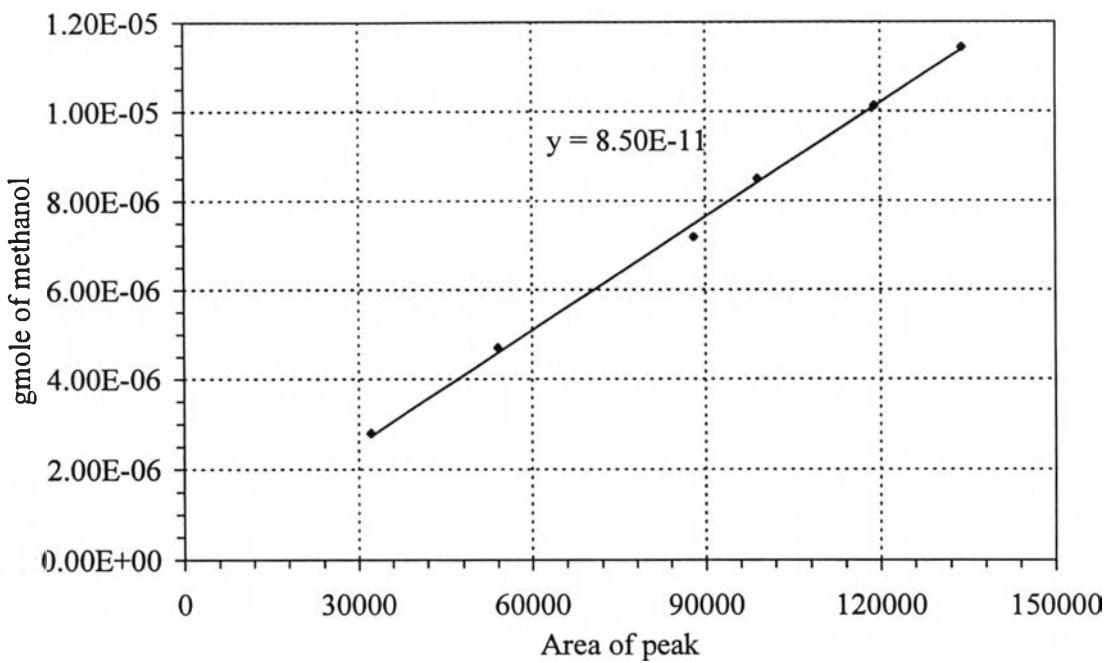
Figure C6 The calibration curve of methanol
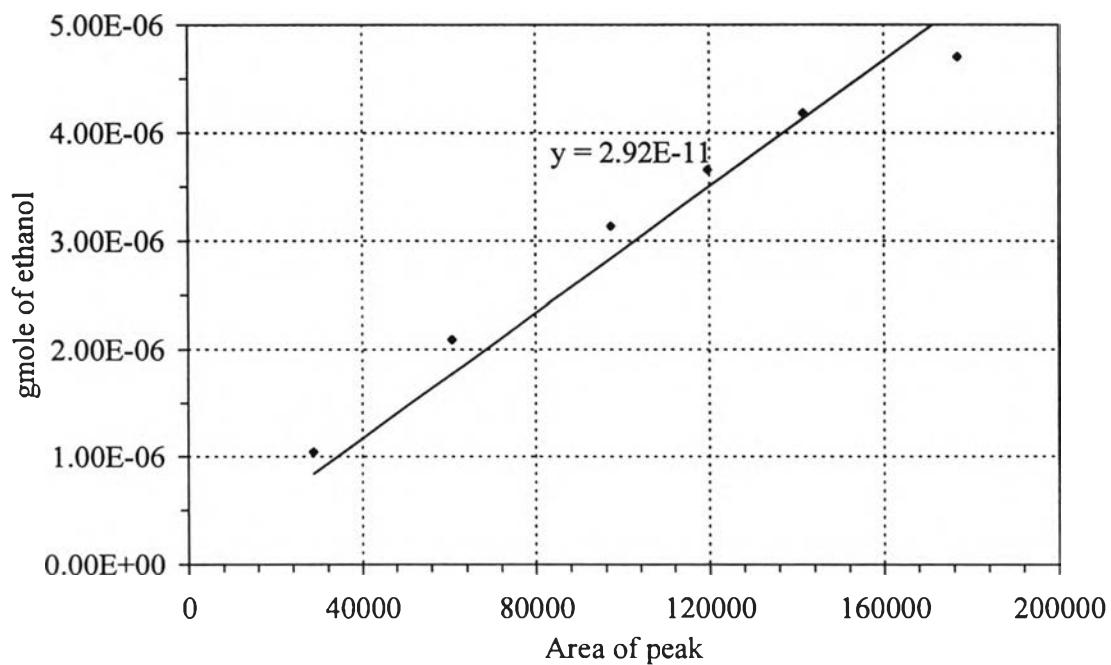
Figure C7 The calibration curve of ethanol
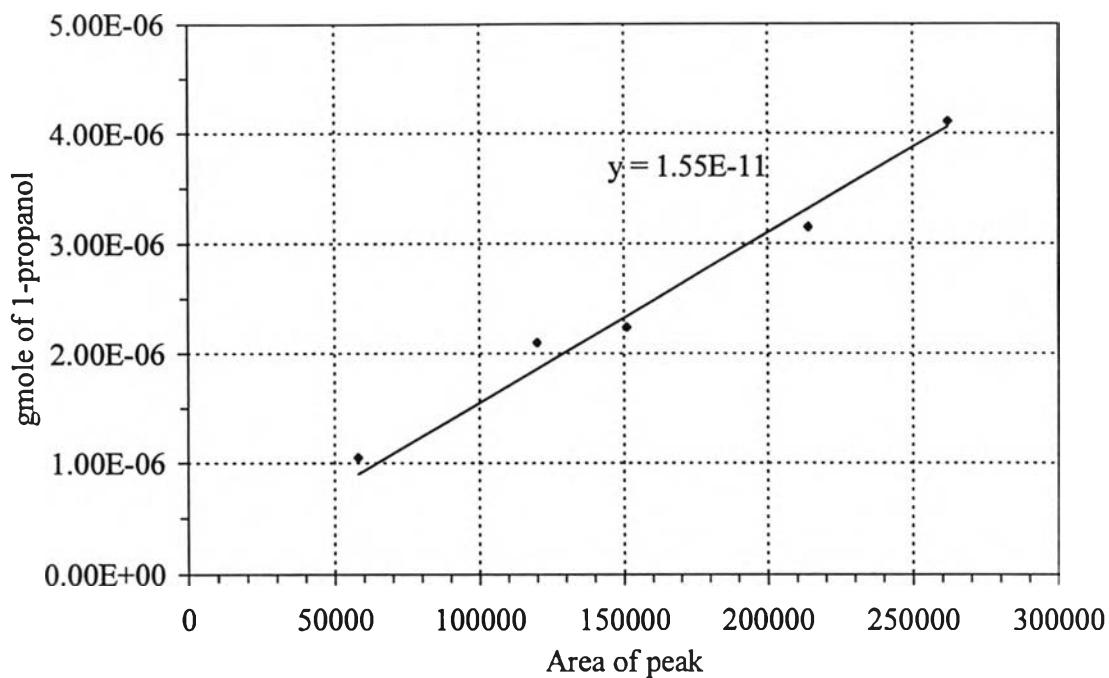
Figure C8 The calibration curve of 1-propanol
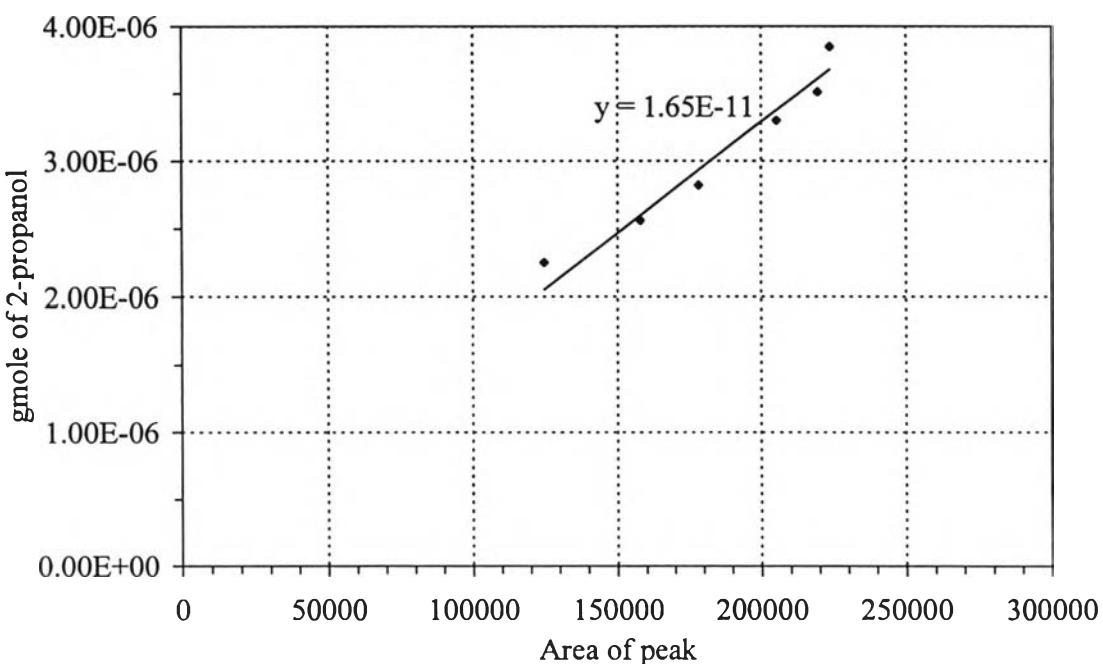
Figure C9 The calibration curve of 2-propanol
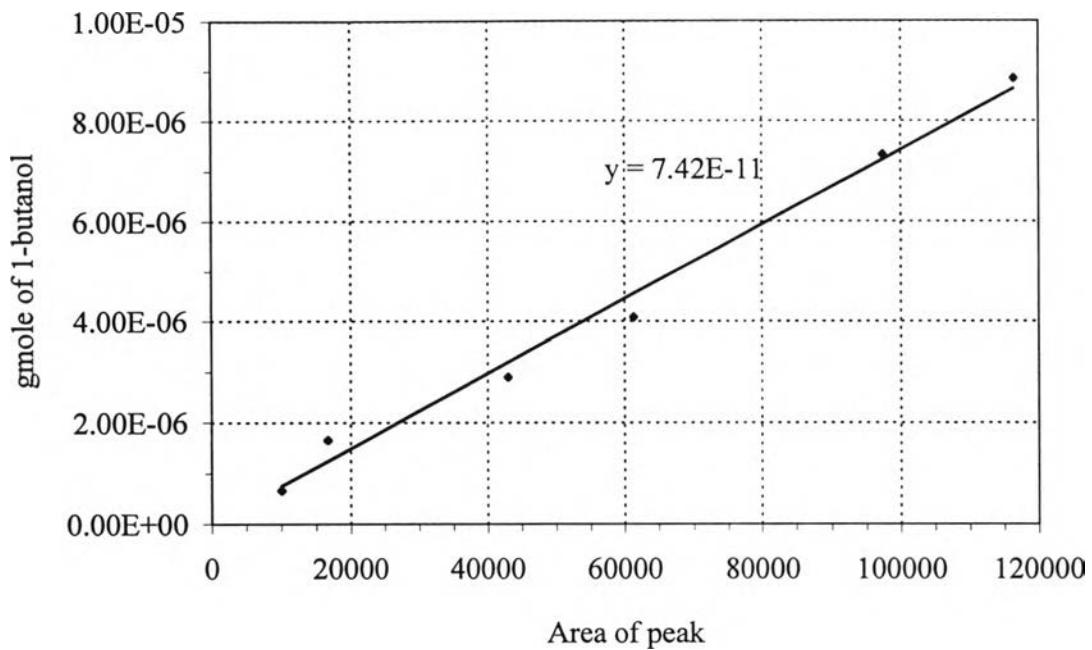
Figure C10 The calibration curve of 1-butanol
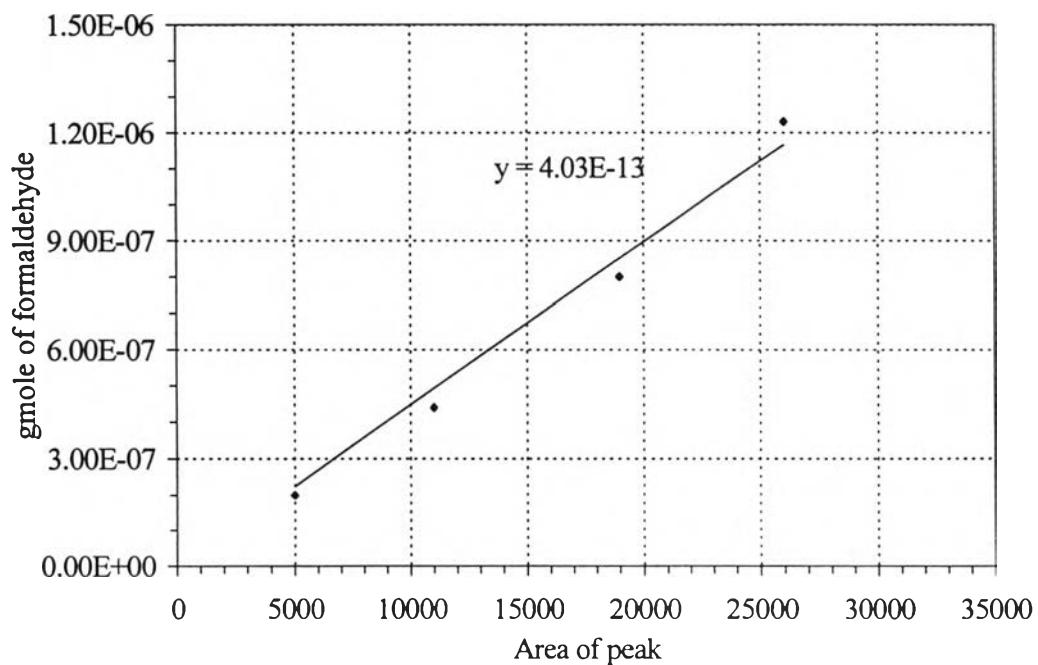
**Figure C11** The calibration curve of formaldehyde
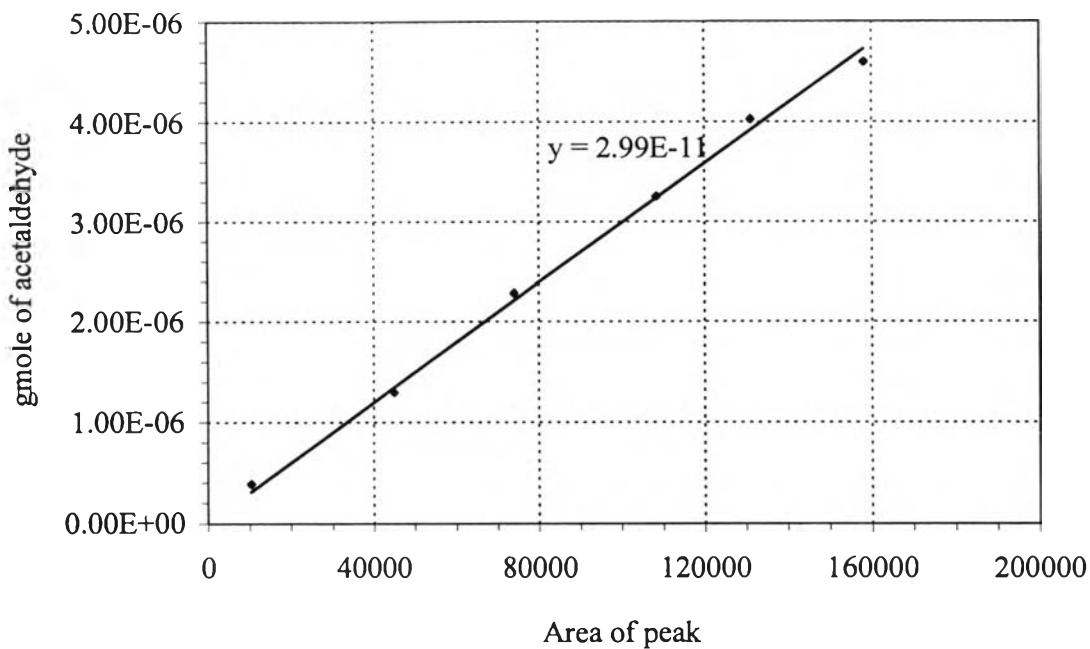
Figure C12 The calibration curve of acetaldehyde
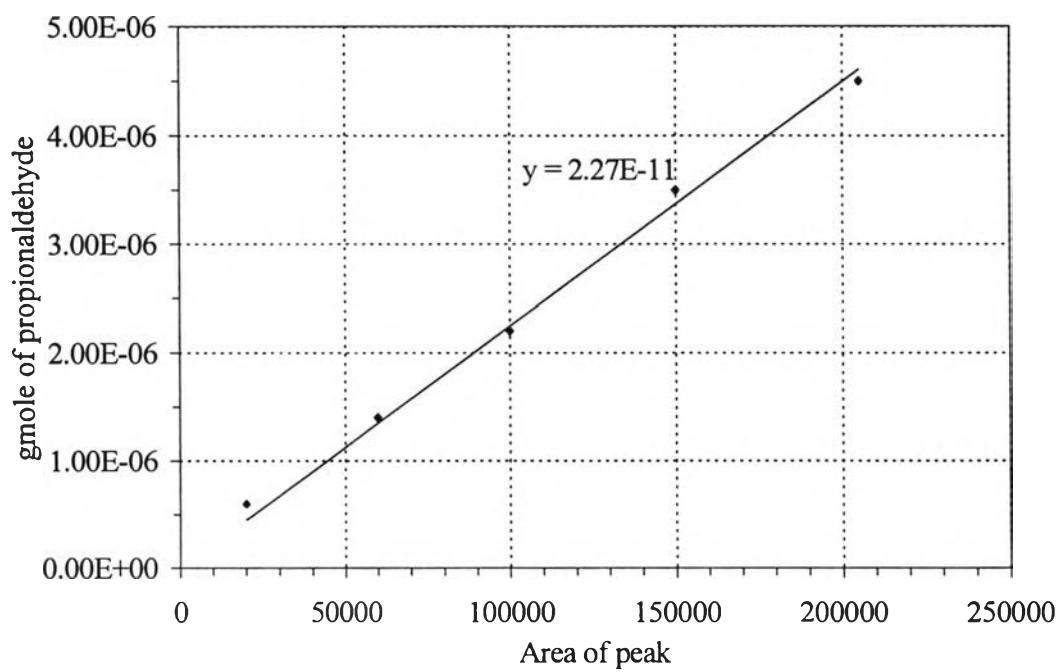
Figure C13 The calibration curve of propionaldehyde

APPENDIX D

DATA OF EXPERIMENTS

The data of oxidation reaction test

- *Methanol oxidation*

Table D1 Data of figure 5.13

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
% Methanol (C)	2.03	8.33	21.56	62.21	93.76	98.71	99.69
% Methane (S)	4.13	5.32	7.6	15.79	16.72	17.87	17.8
% CO_2 (S)	94.53	93.17	91.46	82.87	80.69	79.8	79.23

Table D2 Data of figure 5.14

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
% Methanol (C)	5.43	13.78	28.83	71.52	98.64	99.36	100
% Methane (S)	2.06	2.41	4.78	8.1	12.82	14.44	13.89
% CO_2 (S)	97.45	96.74	94.31	90.59	86.05	84.42	84.9

Table D3 Data of figure 5.15

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
% Methanol (C)	9.74	18.28	63.91	91.41	98.79	100	100
% Methane (S)	0.24	0.67	1.76	2.27	3.11	4.2	5.58
% CO_2 (S)	99.61	99.03	97.01	96.23	95.94	95.12	93.53

- *Ethanol oxidation*

Table D4 Data of figure 5.16

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% Ethanol (C)	3.5	10.07	20.36	56.9	75.13	80.21	82.72
% Methane (S)	0.29	0.41	0.55	0.89	3.17	4.2	5.06
% Ethylene (S)	0	1.37	2.19	4.26	5.67	6.19	7.08
% Propylene (S)	0	0.01	0.03	0.05	0.11	0.37	0.92
% Acetaldehyde (S)	98.06	96.16	92.33	86.12	77.32	70.64	67.68
% CO_2 (S)	1.43	2.45	5.13	9.15	15.62	16.33	18.35
% Acetaldehyde (Y)	3.43	9.68	18.8	49	58.09	56.66	55.99

Table D5 Data of figure 5.17

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% Ethanol (C)	6.97	10.13	21.65	60.66	84.27	94.09	95.31
% Methane (S)	0	0	0.01	0.03	0.33	1.7	2.04
% Ethylene (S)	2.2	3.16	5.98	9.56	14.13	17.49	18.56
% Propylene (S)	0	0	0	0	0.04	0.22	0.76
% Acetaldehyde (S)	91.56	90.46	82.56	58.17	51.54	43.26	39.08
% CO_2 (S)	4.15	5.61	10.15	29.84	32.96	36.54	39.58
% Acetaldehyde (Y)	6.39	9.16	17.87	35.29	43.43	40.7	37.25

Table D6 Data of figure 5.18

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% Ethanol (C)	9.88	11.62	39.66	73.82	85.67	93.46	93.95
% Methane (S)	0.56	0.46	0.21	0.83	2.03	2.96	4.16
% Ethylene (S)	3.14	7.15	26.59	32.64	36.26	40.17	41.47
% Propylene (S)	0	0.25	0.14	0.26	0.72	1.78	1.3
% Acetaldehyde (S)	95.29	88.97	65.05	50.02	36.19	28.33	25.12
% CO_2 (S)	0.92	3.21	7.49	15.26	23.58	26.36	28.15
% Acetaldehyde (Y)	9.41	10.33	25.8	36.93	31	26.48	23.6

- *1-Propanol oxidation*

Table D7 Data of figure 5.19

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% 1-Propanol (C)	1.78	5.73	28.07	59.93	73.8	75.26	76.39
% Methane (S)	0.09	0.03	0.02	0.04	0.1	0.27	0.26
% Ethylene (S)	1.24	0.64	0.27	0.6	1.32	1.23	1.42
% Propylene (S)	1.26	0.74	1.67	2.1	2.32	2.39	1.27
% Propane (S)	0	0	0	0	0.01	0.03	0.04
% Formaldehyde (S)	0	3.18	3.83	4.51	4.01	3.69	3.59
% Propionaldehyde (S)	91.19	89.85	87.13	77.59	71.98	69.01	68.25
% CO2 (S)	5.17	4.26	5.6	13.02	18	18.57	20.07
% Propionaldehyde (Y)	1.63	5.14	24.46	46.5	53.12	51.94	52.14

Table D8 Data of figure 5.20

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% 1-Propanol (C)	6.28	12.4	29.86	57.82	70.42	74.58	76.64
% Methane (S)	0.02	0.01	0.03	0.04	0.08	0.38	0.46
% Ethylene (S)	0.47	0.5	0.91	0.81	1.09	1.93	3.61
% Propylene (S)	2.15	2.5	7.48	15.32	20.16	24.46	26.51
% Propane (S)	0	0	0	0	0.01	0.08	0.01
% Formaldehyde (S)	0	1	3.42	3.43	3.22	3.09	2.92
% Propionaldehyde (S)	90.52	89.48	75.83	58.76	52.46	44.15	41.27
% CO2 (S)	5.21	8.61	10.45	13.72	20.43	23.91	25.77
% Propionaldehyde (Y)	5.68	11.1	22.64	33.98	36.94	32.93	31.63

Table D9 Data of figure 5.21

Component	Temperature (^{o}C)						
	200	250	300	350	400	450	500
% 1-Propanol (C)	7.65	12.42	37.78	68.62	80.15	83.44	85.1
% Methane (S)	0	0.03	0.04	0.04	0.13	0.38	0.46
% Ethylene (S)	0.02	0.1	0.18	0.62	1.34	1.93	2.48
% Propylene (S)	5.36	7.41	18.75	26.52	34.61	38.98	41.2
% Propane (S)	0	0	0	0.01	0.03	0.08	0.08
% Formaldehyde (S)	0.1	1	2.12	3.41	3.16	3.11	2.95
% Propionaldehyde (S)	87.46	86.36	74.49	49.41	36.13	31.51	29.86
% CO2 (S)	1.89	5.78	8.65	15.31	19.78	22.46	24.71
% Propionaldehyde (Y)	6.69	10.73	28.14	33.91	28.96	26.29	25.41

- *2-Propanol oxidation*

Table D10 Data of figure 5.22

Component	Temperature ($^{\circ}$C)						
	200	250	300	350	400	450	500
% 2-Propanol (C)	14.92	32.08	43.12	50.52	60.79	57.78	58.23
% Methane (S)	0	0	0.06	0.08	0.11	0.36	0.98
% Ethylene (S)	0	0.04	0.07	0.1	0.16	0.31	0.49
% Propylene (S)	92.12	90.15	83.02	67.23	62.41	60.57	54.2
% Propane (S)	0	0	0	0	0.03	0.05	0.05
% CO2 (S)	7.7	9.23	16.12	27.87	32.64	35.63	41.62

Table D11 Data of figure 5.23

Component	Temperature ($^{\circ}$C)						
	200	250	300	350	400	450	500
% 2-Propanol (C)	14.11	18.13	26.54	49.47	66.13	69.02	68.87
% Methane (S)	0.02	0.08	0.14	0.26	0.34	0.67	1.26
% Ethylene (S)	0	0.01	0.03	0.06	0.17	0.12	0.6
% Propylene (S)	95.1	94.16	91.86	80.04	71.61	66.23	56.53
% Propane (S)	0	0	0.02	0.03	0.01	0.02	0.02
% CO2 (S)	4.05	4.5	6.45	18.24	25.28	32.41	39.9

Table D12 Data of figure 5.24

Component	Temperature ($^{\circ}$C)						
	200	250	300	350	400	450	500
% 2-Propanol (C)	27.96	52.18	67.41	76.56	77.78	79.2	77.98
% Methane (S)	0	0.01	0.02	0.06	0.21	0.69	0.71
% Ethylene (S)	0	0	0.02	0.12	0.3	0.36	0.24
% Propylene (S)	99.6	98.32	96.65	90.45	86.89	78.46	58.15
% Propane (S)	0	0.01	0.01	0	0.03	0.06	0.06
% CO2 (S)	0	0.17	3.05	9.67	12.13	19.56	40.46

- *1-Butanol oxidation*

Table D13 Data of figure 5.25

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% 1-Butanol (C)	1.76	9.79	45.78	71.44	90.43	94.35	96.53
% Methane (S)	7.02	3.82	0.35	0.65	0.25	1.47	1.99
% Ethylene (S)	2.75	2.39	1.15	1.44	1.2	2.81	3.12
% Propylene (S)	11.38	7.51	6.86	6.49	3.09	5.06	5.11
% Propane (S)	0	0.06	0.45	0.11	0.32	0.3	0.38
% Formaldehyde (S)	5.74	6.46	4.13	3.04	0.94	0.16	0
% CO2 (S)	73	76.43	83.36	87.19	90.09	88.73	86.84

Table D14 Data of figure 5.26

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% 1-Butanol (C)	16.72	52.26	72.51	97.74	100	100	100
% Methane (S)	4.13	3.76	2.28	2.09	0.97	1.24	1.55
% Ethylene (S)	2.16	2.45	1.89	1.53	1.12	0.75	1.06
% Propylene (S)	8.81	6.35	5.98	5.61	5.04	4.49	3.26
% Propane (S)	0	0.01	0.05	0.04	0.66	0.43	0.29
% Formaldehyde (S)	4.66	3.83	2.86	1.64	0	0	0
% CO2 (S)	80.16	83.67	86.87	89.31	90.04	92.42	92.36

Table D15 Data of figure 5.27

Component	Temperature (°C)						
	200	250	300	350	400	450	500
% 1-Butanol (C)	14.48	48.32	73.73	97.39	98.65	100	99.64
% Methane (S)	5.16	2.67	1.91	0.89	0.86	1.86	2.05
% Ethylene (S)	3.46	3.19	2.27	2.03	2.68	2.13	1.98
% Propylene (S)	12.43	10.89	9.45	9.31	5.73	4.16	4.34
% Propane (S)	0	0.03	0.16	0.09	0.24	0.15	0.06
% Formaldehyde (S)	0.96	1.34	0.38	0.07	0	0	0
% CO2 (S)	76.83	79.11	82.99	85.25	88.76	88.13	90.46

APPENDIX E
BLANK TEST OF OXIDATION REACTION

The oxidation reaction of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol at the same reaction condition but have no catalyst (blank test) are shown as follow:
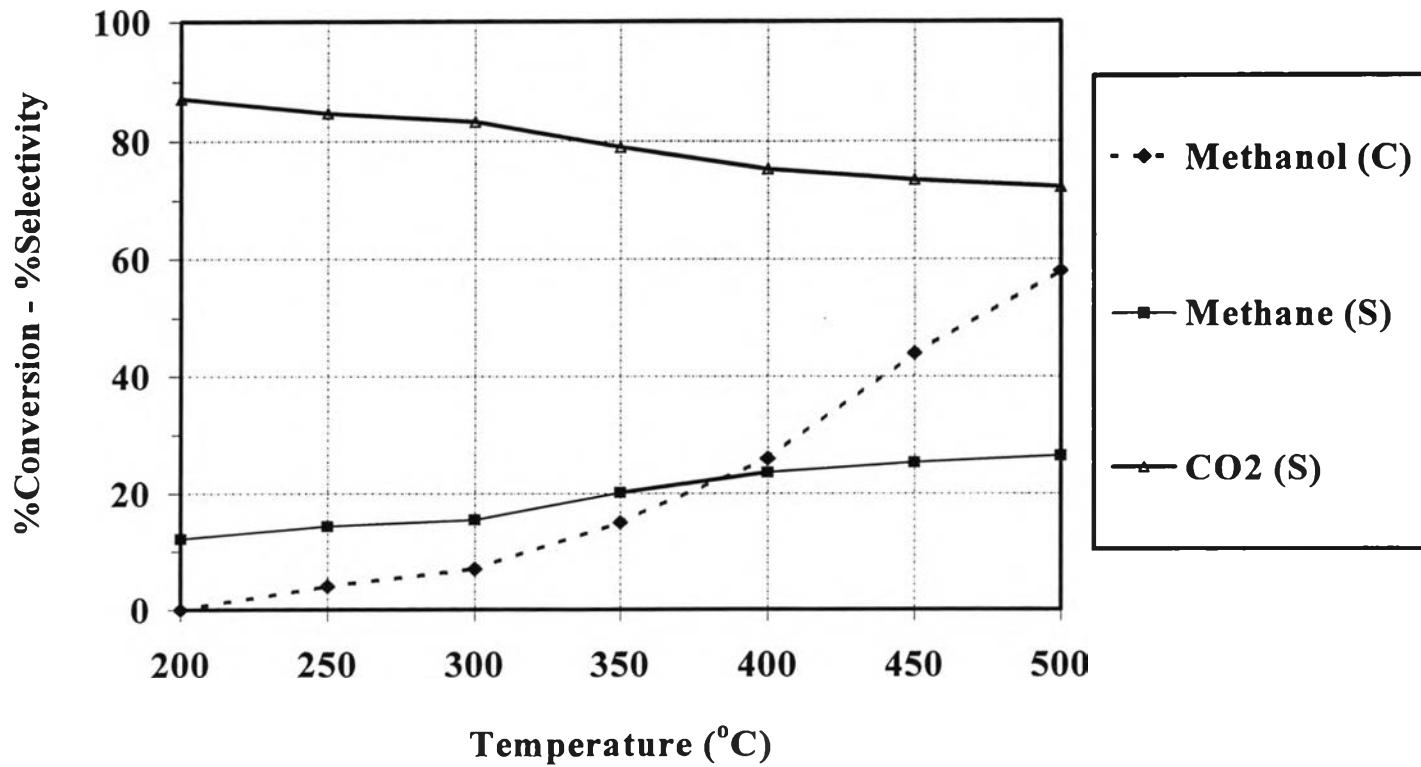
Figure E1 Conversion (C) of methanol and product selectivities (S) in the methanol oxidation.
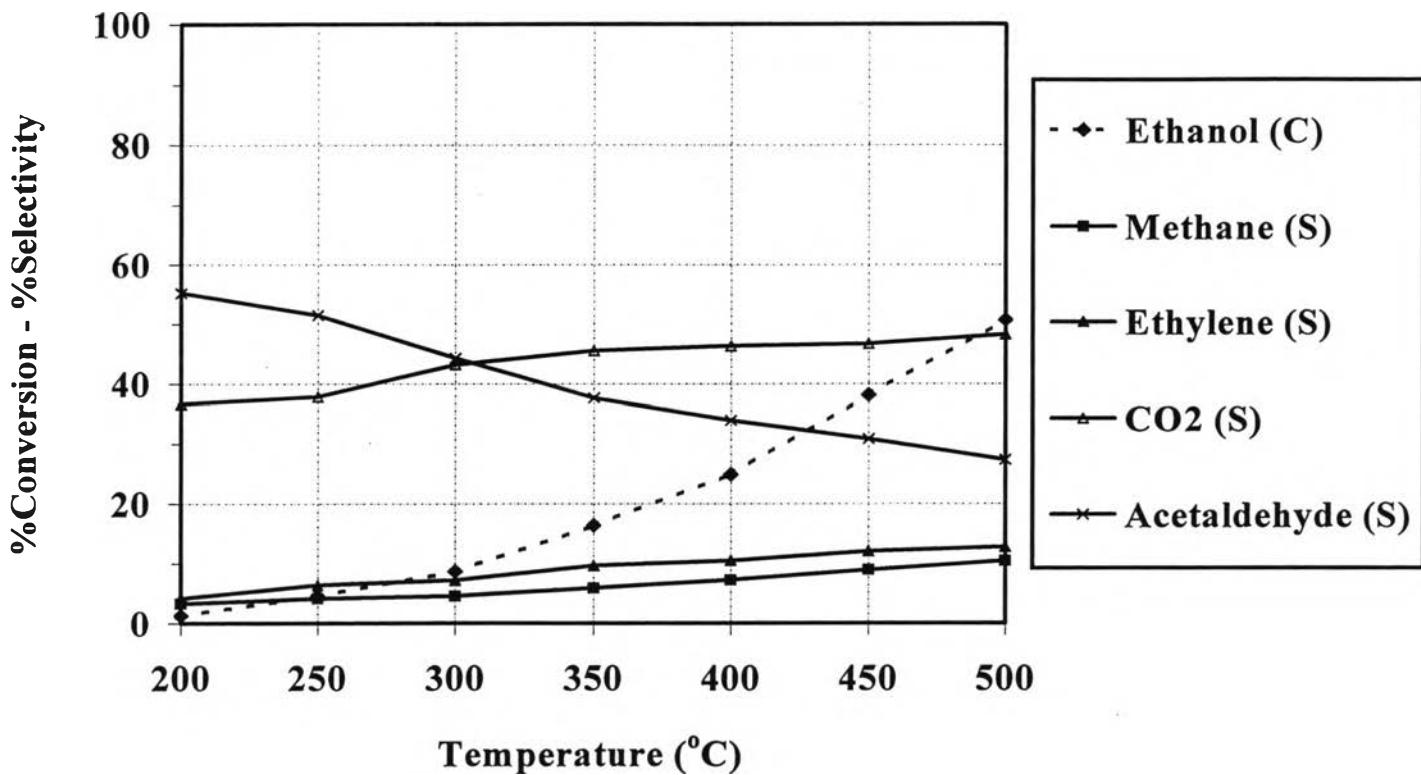
Figure E2 Conversion (C) of ethanol and product selectivities (S) in the ethanol oxidation.
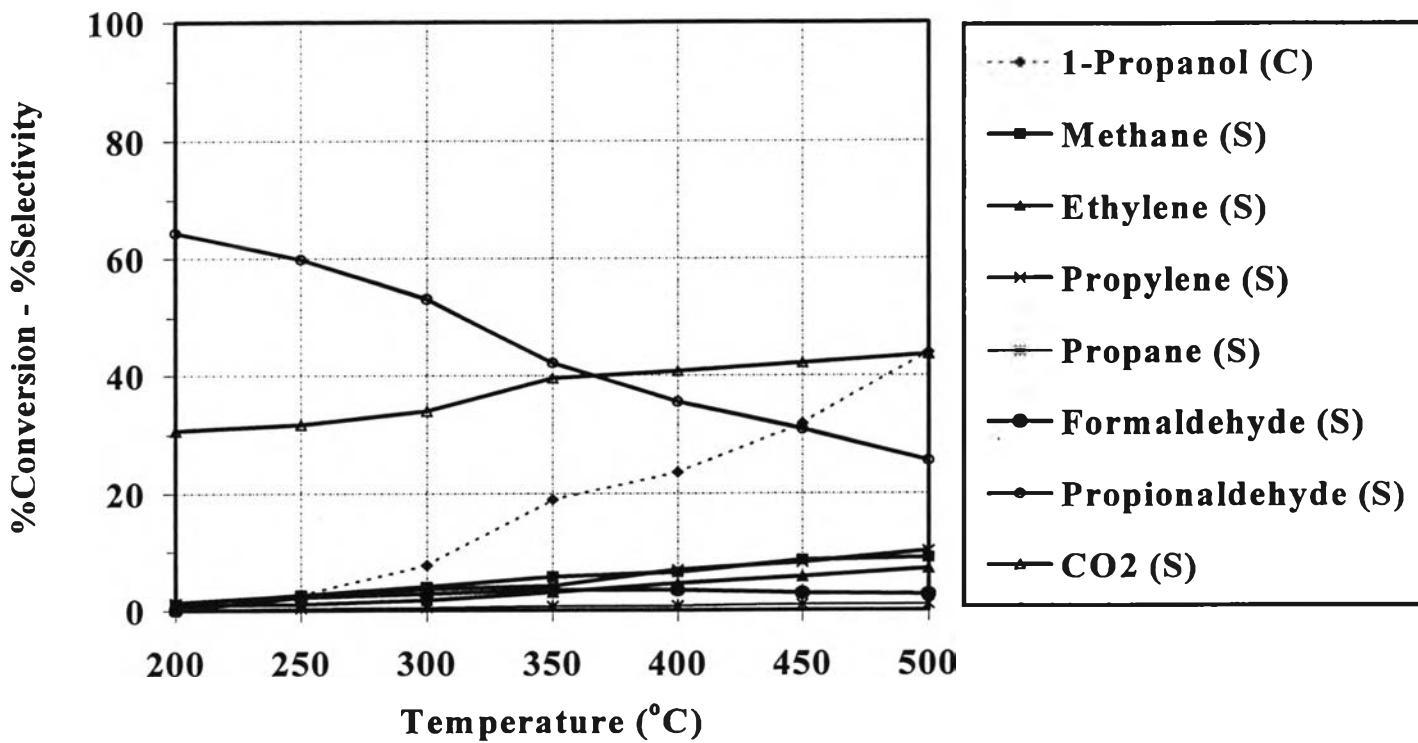
Figure E3 Conversion (C) of 1-propanol and product selectivities (S) in the 1-propanol oxidation.
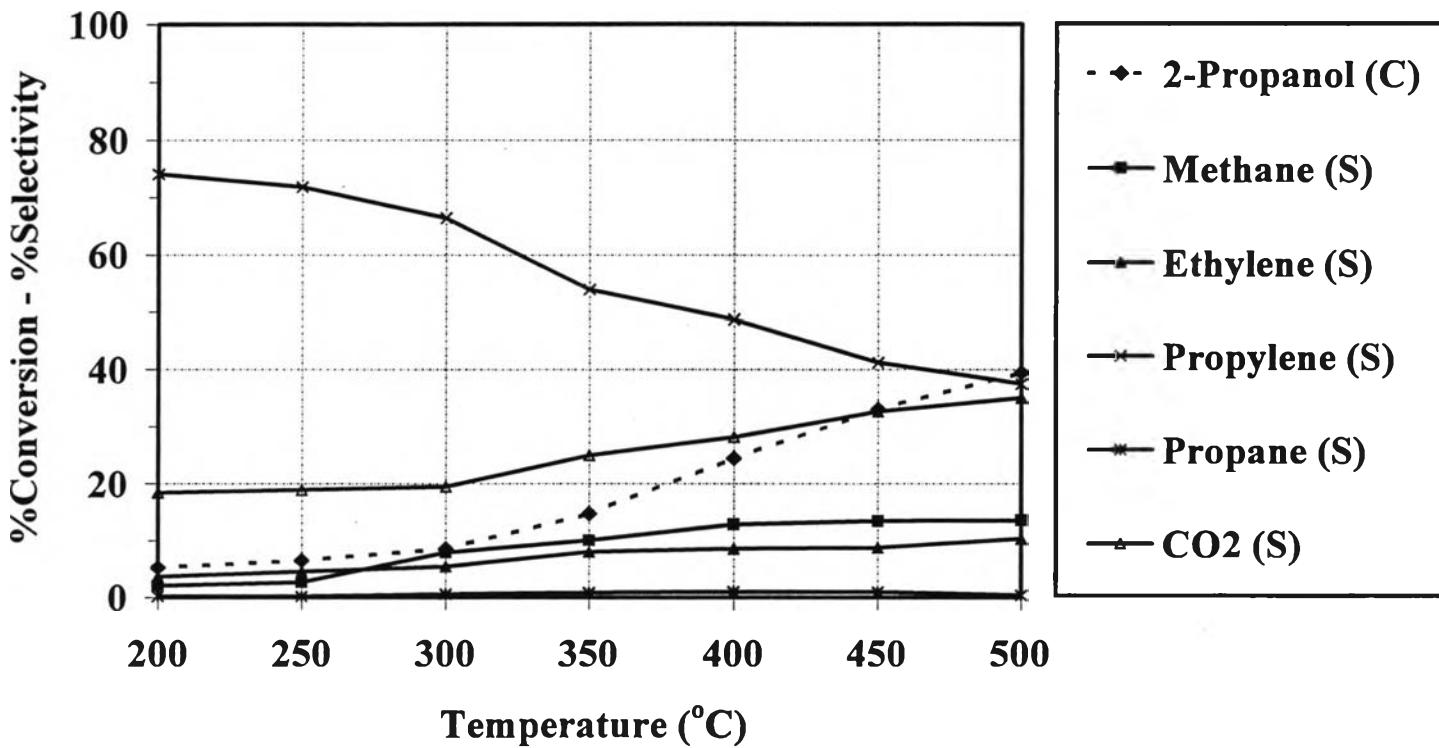
Figure E4 Conversion (C) of 2-propanol and product selectivities (S) in the 2-propanol oxidation.
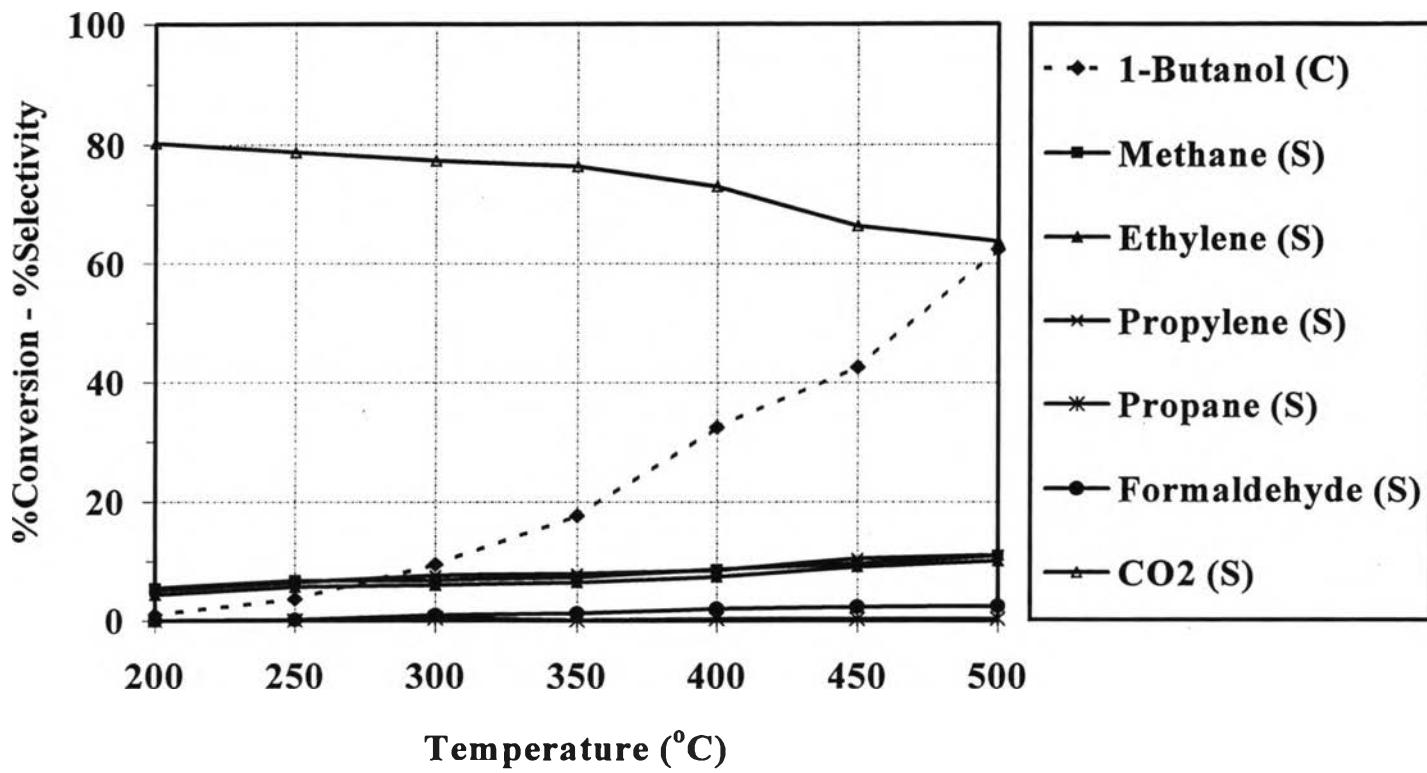
Figure E5 Conversion (C) of 1-butanol and product selectivities (S) in the 1-butanol oxidation.

VITA

Mr. Sakchai Kittikerdkulchai was born on September 28, 1977 in Bangkok, Thailand. He received the Bachelor Degree of Chemical Engineering from Faculty of Engineering, Chulalongkorn University in 1998. He continued his Master's Study at Chulalongkorn University in June, 1998.