Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

This Supporting Information is for the Manuscript:

Title: Kinetic Modeling and Mechanistic Investigations of Transesterification of Propylene Carbonate with Methanol over Fe-Mn Double Metal Cyanide Catalyst

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This Supporting Information has thirteen pages in total and four Tables (Table S1, S2, S3,S4 and S5), eleven Figures (Figure S1, S2, S3, S4, S5, S6, S7, S8, S9, S10 and S11) and seven parts (Part 1: Experimental Setup, Part 2: Detail Information of GC Analysis, Part 3: Concentration-Time Profiles at Different Reaction Conditions, Part 4: Parameter Estimation for Kinetic Studies, Part 5: Evaluation of Internal and External Mass Transfer Limitation, Part 6: Error Analysis of Activation Energy, and Part 7: Criteria and Constraints Used for Model Discrimination).

Supporting Information

Kinetic Modeling and Mechanistic Investigations of Transesterification of Propylene Carbonate with Methanol over Fe-Mn Double Metal Cyanide Catalyst

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Part 1: Experimental Setup

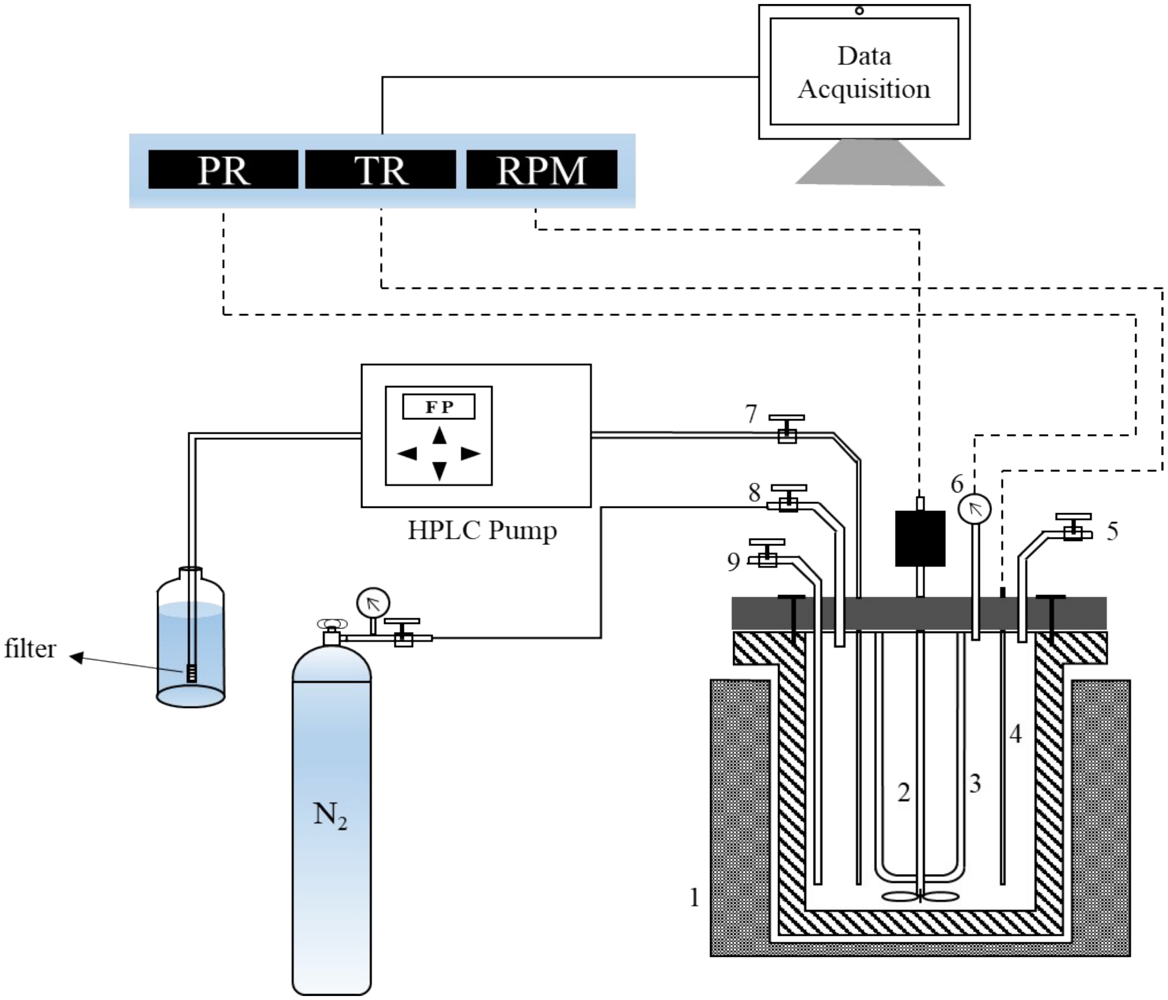


Figure S1. Schematic of experimental unit. 1. Heating jacket; 2. Stirring shaft; 3. Cooling coil; 4. Thermos well; 5. Gas vent; 6. Pressure gauge; 7. Liquid inlet; 8. Gas inlet; 9. Sampling tube. PR: reactor pressure indicator; TR: reactor temperature indicator.

Part 2: Detail Information of GC Analysis

A programmed temperature ramp was needed to separate and analyze the liquid samples. The oven temperature started from 80 °C, which was maintained for 4 min during the analysis. Then a temperature was increased at a rate of 40 °C/min until 250 °C, which was maintained for further 2 min. The liquid samples were separated completely using the above described temperature programming. Mesitylene was used as an internal standard for all samples.

Typical retention times were 3.3 min for methanol, 4.2 min for DMC, 6.4 min for mesitylene, 8.2 min for PG and 9.3 min for PC, respectively. An example of GC result is shown in Figure 4-3. Two intermediates were detected at 8.7 and 8.9 min, which were analyzed to be 1-hydroxypropan-2-yl methyl carbonate and 2-hydroxypropyl methyl carbonate (2-HMC) by GC-MS. Quantitative estimation of the concentrations of reactants and products was done using a calibration method with standards, which was found to give analytical accuracy within ±2.19%.

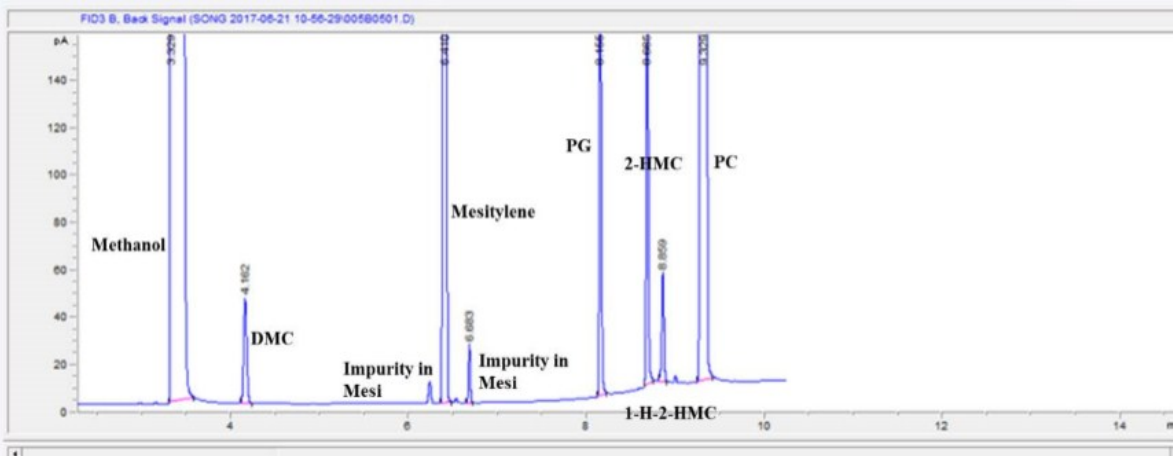


Figure S2. Typical GC graph

Part 3: Concentration-Time Profiles at Different Reaction Conditions

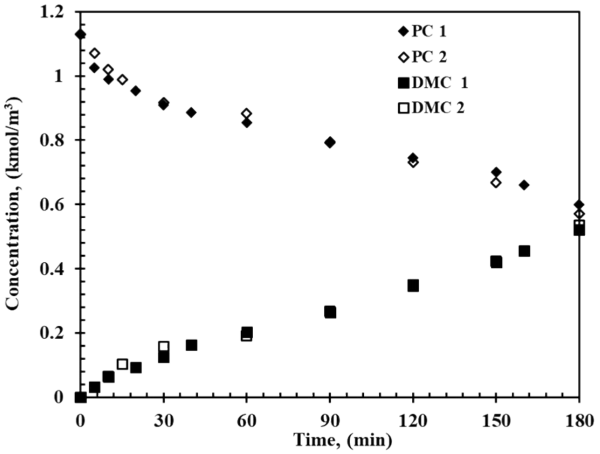


Figure S3. Repeatability of experiment.

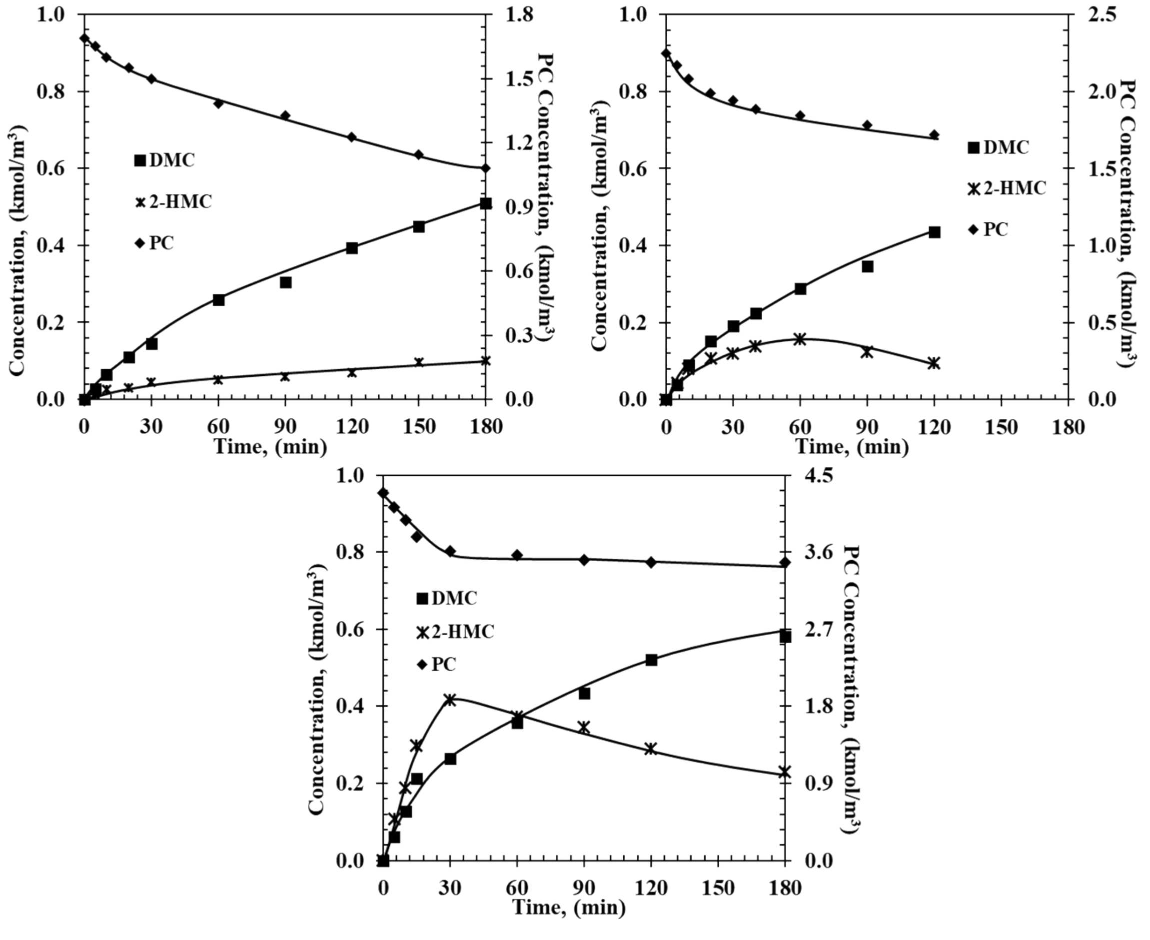


Figure S4. Concentration-time profiles on Fe-Mn catalyst at 140 °C with different initial PC and methanol concentration

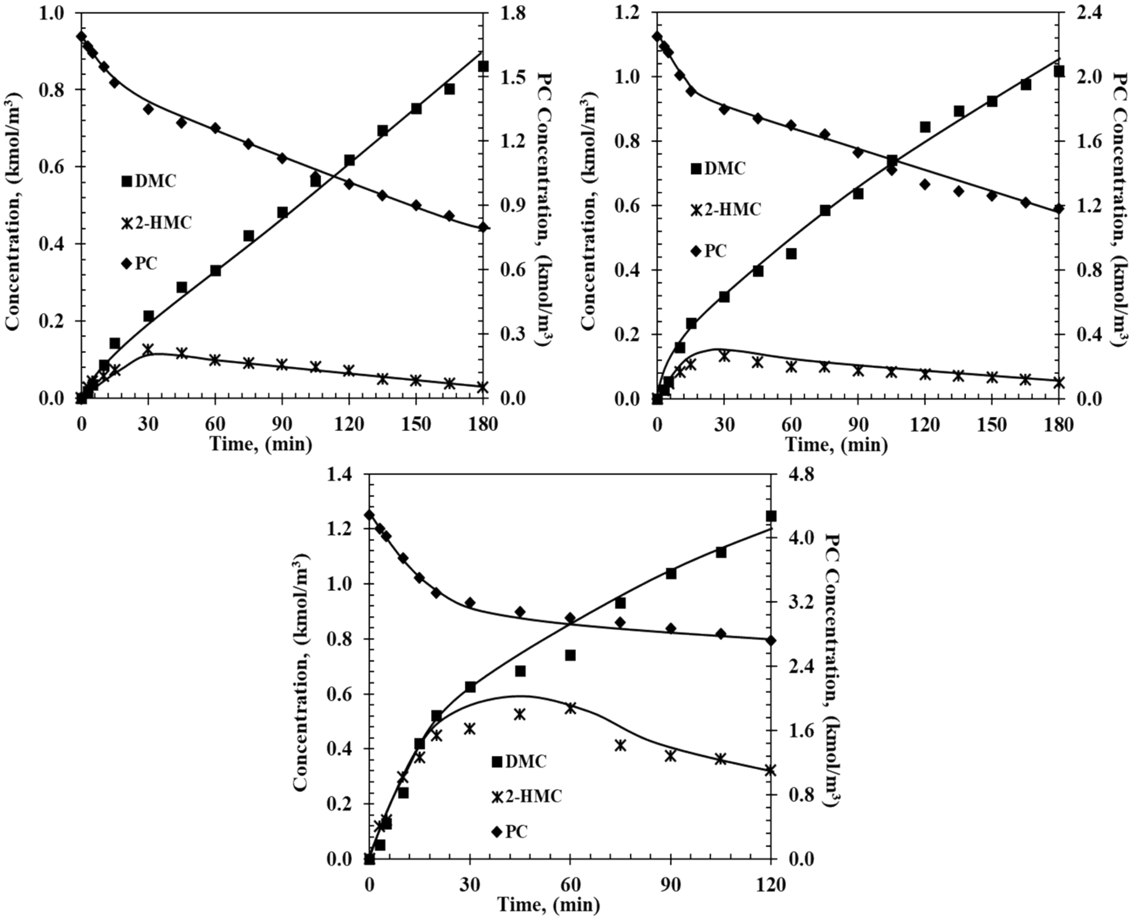
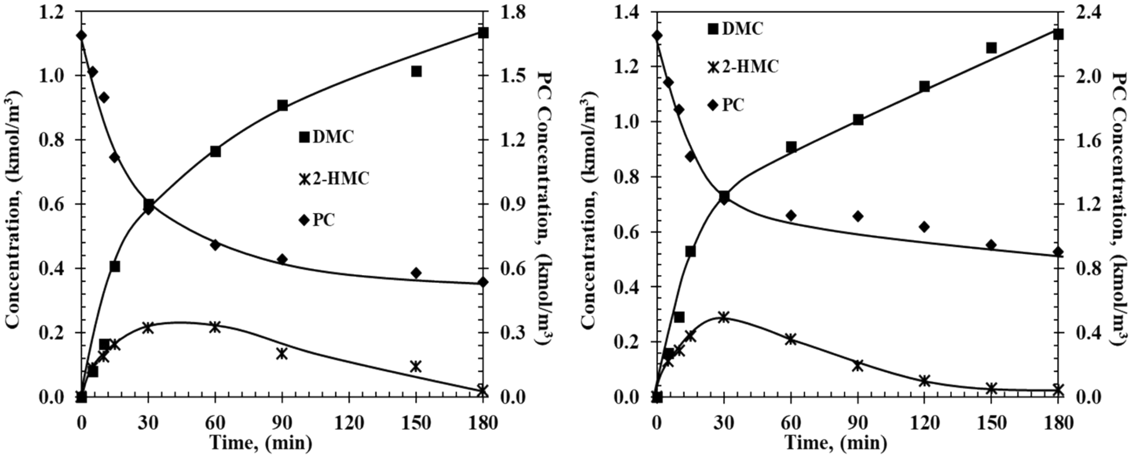


Figure S5. Concentration-time profiles on Fe-Mn catalyst at 160 °C with different initial PC and methanol concentration



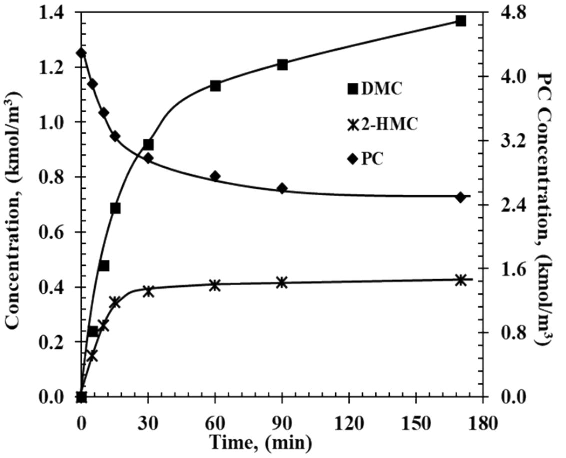


Figure S6. Concentration-time profiles on Fe-Mn catalyst at 180 °C with different initial PC and methanol concentration

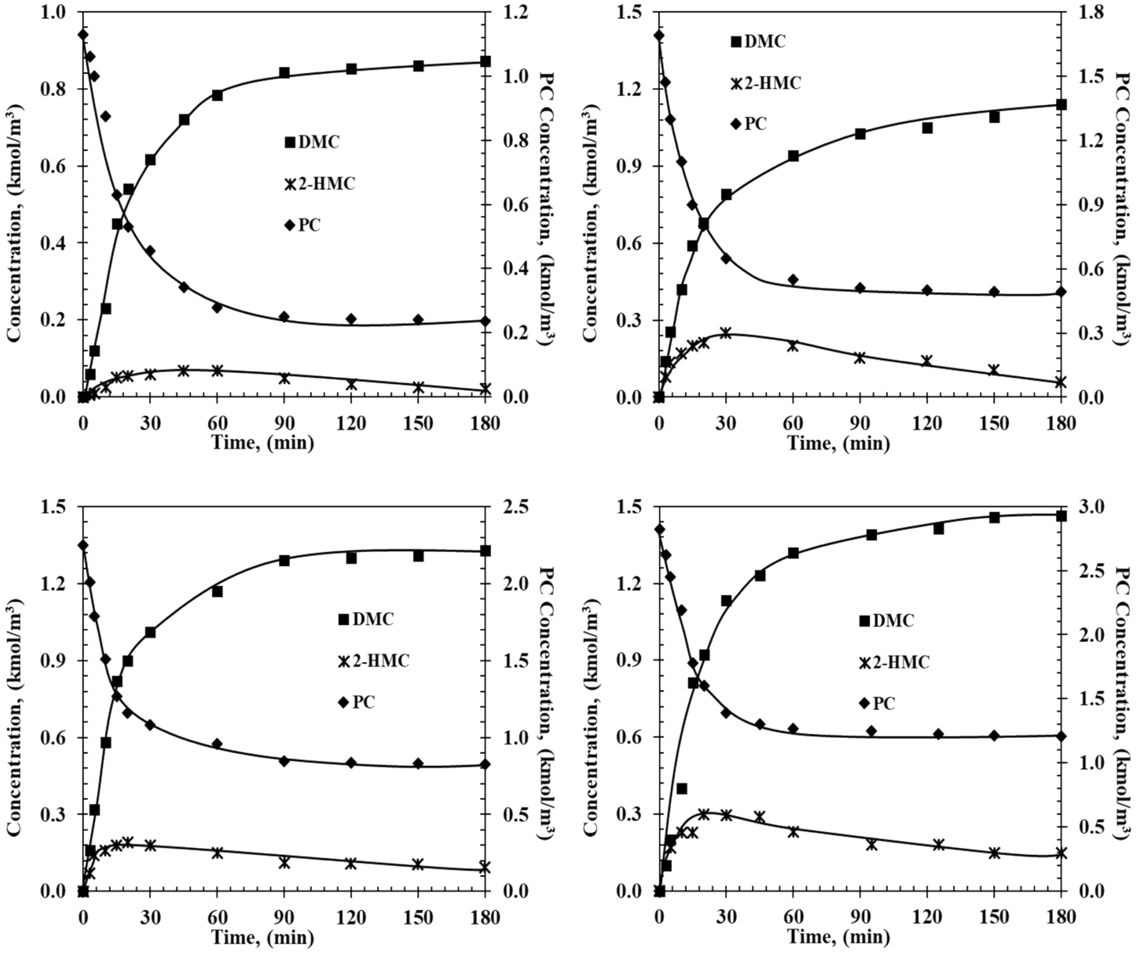


Figure S7. Concentration-time profiles on Fe-Mn catalyst at 200 °C with different initial PC and methanol concentration

Part 4: Parameter Estimation for Kinetic Studies

(1). Estimation of initial reaction rate

For the estimation of initial reaction rate, a set of experimental data from 200 °C was taken as an example. For the consumption of PC, a trend line was added to fit the experimental data points. A mathematical equation was fitted for the trend line. The slope at t=0 is the initial reaction rate, in this case, at t=0, the slope is -0.0315. Therefore, the initial reaction rate is 0.0315 kmol/(m^3·min).

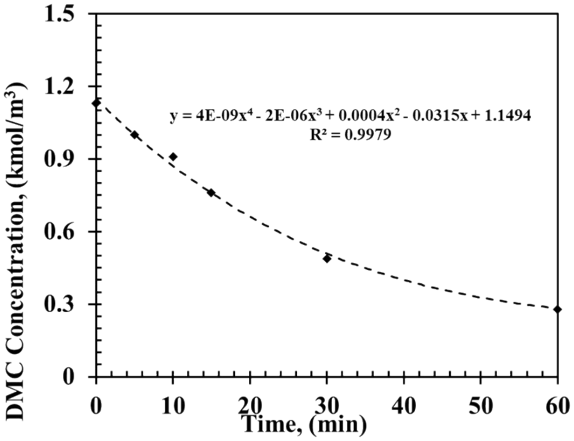


Figure S8. Estimation of initial reaction rate. Markers are the experimental data points of PC, the dot line is the added trend line.

(2). Arrhenius plot for reaction kinetics

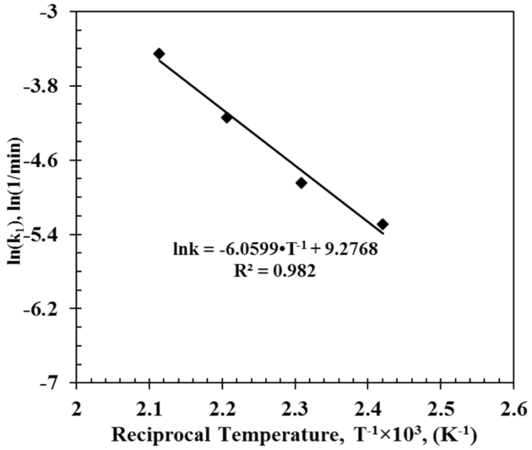


Figure S9. Arrhenius plot from initial reaction rate

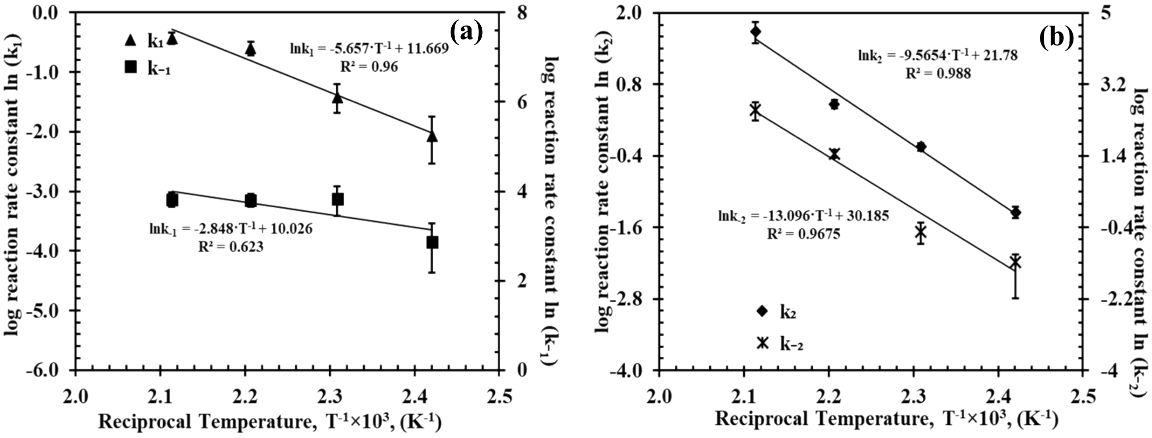
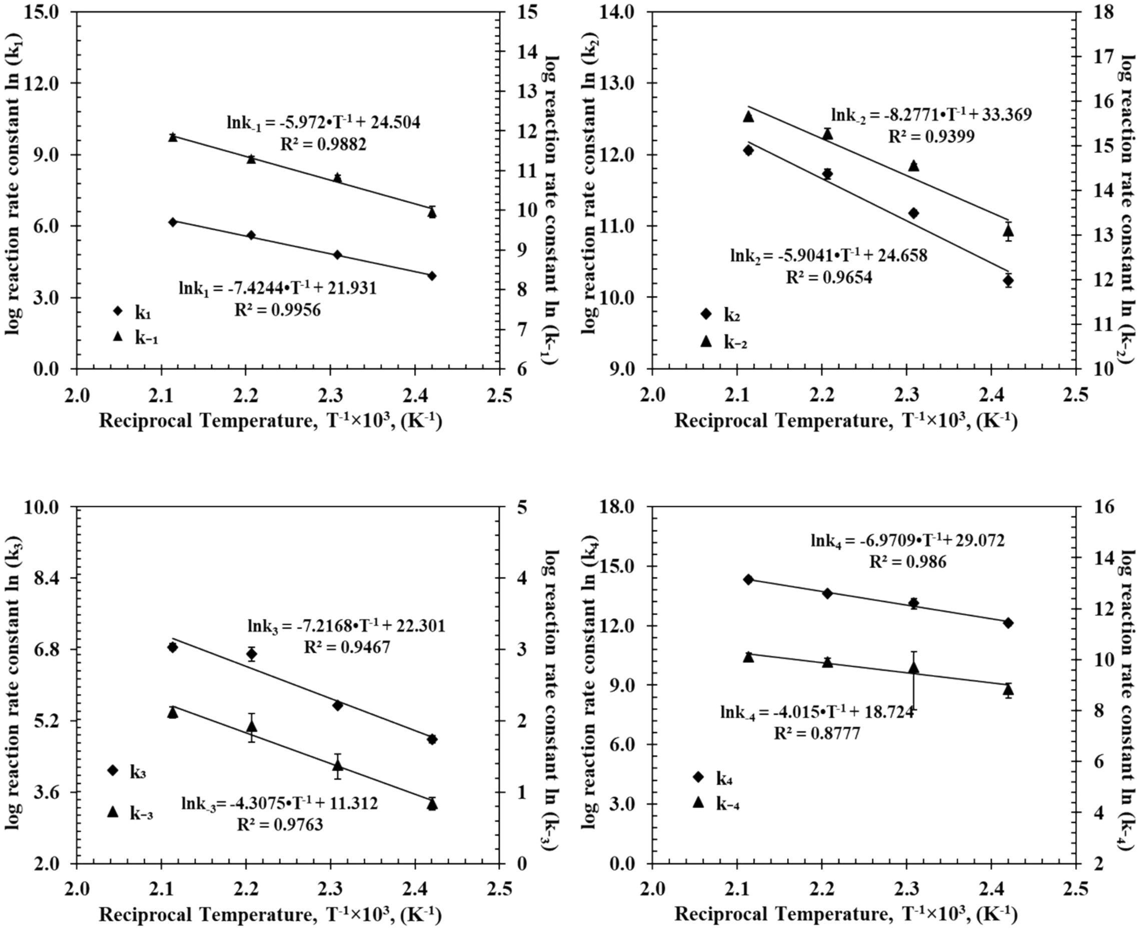


Figure S10. Arrhenius plot. Parameters estimation from modelling with two-step power law for (a) first step, (b) second step



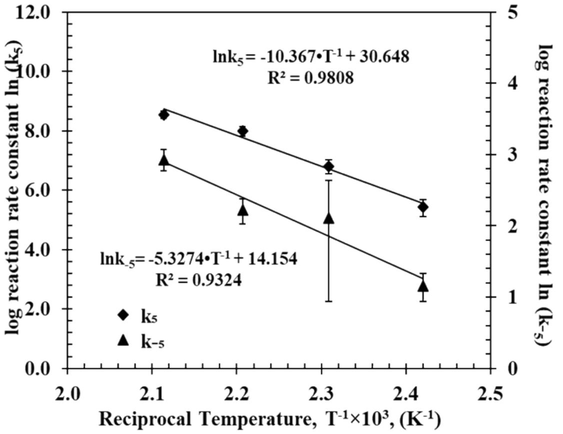


Figure S11. Arrhenius plot. Parameters estimation from microkinetic modelling for (a) first step, (b) second step, (c) third step, (4) fourth step, (5) fifth step

Table S1. Batch Reactor Equations

Models	Batch reactor equations
Model i	$\frac{d[PC]}{dt} = -r_2$ $\frac{d[MeOH]}{dt} = -r_1$ $\frac{d[C_{2-HMC}]}{dt} = r_3$ $\frac{d[DMC]}{dt} = \frac{d[PG]}{dt} = r_5$ $\frac{d[S]}{dt} = -r_1 + r_3 + r_4 + r_5$ $\frac{d[I]}{dt} = r_1 - r_2 - r_4$ $\frac{d[II]}{dt} = r_2 - r_3 - r_4$ $\frac{d[III]}{dt} = r_4 - r_5$
Model ii	$\frac{d[PC]}{dt} = -r_2$ $\frac{d[MeOH]}{dt} = -r_1$ $\frac{d[C_{2-HMC}]}{dt} = r_3 - r_4$ $\frac{d[DMC]}{dt} = \frac{d[PG]}{dt} = r_5$ $\frac{d[S]}{dt} = -r_1 + r_3 + r_5$ $\frac{d[I]}{dt} = r_1 - r_2 - r_4$ $\frac{d[II]}{dt} = r_2 - r_3$ $\frac{d[III]}{dt} = r_4 - r_5$
Model iii	$\frac{d[PC]}{dt} = -r_2$ $\frac{d[MeOH]}{dt} = -r_1$ $\frac{d[C_{2-HMC}]}{dt} = r_4$ $\frac{d[DMC]}{dt} = \frac{d[PG]}{dt} = r_6$ $\frac{d[S]}{dt} = -r_1 - r_2 + r_3 + r_4 +$ $\frac{d[I]}{dt} = r_1 - r_3 - r_5$ $\frac{d[II]}{dt} = r_2 - r_3$ $\frac{d[III]}{dt} = r_3 - r_4 - r_5$ $\frac{d[IV]}{dt} = r_5 - r_6$
Model iv	$\frac{d[PC]}{dt} = -r_2$ $\frac{d[MeOH]}{dt} = -r_1$ $\frac{d[C_{2-HMC}]}{dt} = r_4 - r_5$ $\frac{d[DMC]}{dt} = \frac{d[PG]}{dt} = r_6$ $\frac{d[S]}{dt} == -r_1 - r_2 + r_3 + r_4$ $\frac{d[I]}{dt} = r_1 - r_3 + r_5$ $\frac{d[II]}{dt} = r_2 - r_3$ $\frac{d[III]}{dt} = r_3 - r_4$ $\frac{d[IV]}{dt} = r_5 - r_6$

Parameter estimation for Model (ii)–Model (iv):

Table S2. Parameter estimation for Model *ii*

Rate Constants	140 °C	160 °C	180 °C	200 °C
k_1, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	3.05±1.51	4.46±0.43	11.49±2.14	22.70±1.88
$k_{-1} \times 10^{-4}$, (min^{-1})	1.13±0.15	2.27±0.59	6.61±0.84	8.87±6.64
$k_2 \times 10^{-3}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	0.37±0.35	1.18±1.02	2.95±3.81	4.54±0.15
$k_{-2} \times 10^{-3}$, (min^{-1})	1.31±0.09	7.88±7.56	9.36±12.91	27.06±33.92
$k_3 \times 10^{-3}$, (min^{-1})	1.34±0.09	2.02±0.06	3.23±0.20	4.54±0.16
$k_{-3} \times 10^{-1}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	2.07±1.22	0.86±0.17	3.24±0.19	1.36±0.24
$k_4 \times 10^{-3}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	0.48±0.31	3.38±0.94	3.04±0.88	7.05±1.82
$k_{-4} \times 10^{-2}$, (min^{-1})	3.93±1.03	1.52±0.58	1.71±0.36	1.80±0.44
$k_5 \times 10^{-5}$, (min^{-1})	0.26±0.05	1.00±0.17	5.93±0.65	10.31±0.08
$k_{-5} \times 10^{-3}$, ($m^6 \cdot min^{-1} \cdot kmol^{-2}$)	1.30±0.34	9.53±3.62	9.08±1.87	31.67±7.80

Table S3. Parameter estimation for Model *iii*

Rate Constants	140 °C	160 °C	180 °C	200 °C
k_1, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	4.18±0.30	11.57±4.92	256.64±78.21	11.48±3.01
$k_{-1} \times 10^{-2}$, (min^{-1})	2.36±2.02	Negative	1.28±0.34	1.64±0.53
$k_2 \times 10^{-3}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	2.26±0.68	2.39±5.36	0.17±0.91	0.31±0.09
$k_{-2} \times 10^{-4}$, (min^{-1})	1.60±0.22	7.44±0.25	1.06±0.89	0.50±0.47
$k_3 \times 10^{-6}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	2.61±2.76	1.33±3.11	5.23±0.16	19.30±19.58
$k_{-3} \times 10^{-7}$, ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	2.09±0.14	2.84±0.48	2.12±0.56	4.78±0.15

$k_4 \times 10^{-2}$, (min^{-1})	1.05±0.14	4.98±1.09	11.20±2.82	0.77±0.15
k_{-4}, (m^3·min^{-1}·kmol^{-1})	4.88±1.07	1362.9±705.9	584.76±315.2	10.42±2.32
$k_5 \times 10^{-4}$, (m^3·min^{-1}·kmol^{-1})	1.95±0.94	2.48±1.16	4.60±0.91	2.46±0.23
$k_{-5} \times 10^{-4}$, (m^3·min^{-1}·kmol^{-1})	0.08±0.01	1.76±5.94	0.46±0.36	1.04±0.28
$k_6 \times 10^{-4}$, (min^{-1})	7.86±0.88	1.74±0.46	2.27±0.78	8.64±0.76
$k_{-6} \times 10^{-4}$, (m^6·min^{-1}·kmol^{-2})	1.24±0.53	3.43±7.79	6.04±4.56	0.43±0.18

Table S4. Parameter estimation for Model *iv*

Rate Constants	140 °C	160 °C	180 °C	200 °C
k_1, (m^3·min^{-1}·kmol^{-1})	0.25±0.024	0.37±0.28	3.42±0.38	6.93±0.73
$k_{-1} \times 10^{2}$, (min^{-1})	1.24±0.36	9.24±1.87	6.08±0.82	9.04±0.95
$k_2 \times 10^{-1}$, (m^3·min^{-1}·kmol^{-1})	1.24±0.99	2.47±1.98	3.86±0.39	10.42±6.89
$k_{-2} \times 10^{-2}$, (min^{-1})	3.12±3.52	1.32±3.92	2.91±1.64	5.95±0.48
$k_3 \times 10^{-5}$, (m^3·min^{-1}·kmol^{-1})	0.72±0.05	4.58±0.23	6.39±1.28	43.60±3.49
$k_{-3} \times 10^{-8}$, (m^3·min^{-1}·kmol^{-1})	0.30±0.022	1.35±0.044	2.86±0.57	5.67±0.45
$k_4 \times 10^{-3}$, (min^{-1})	1.24±0.009	14.94±43.80	19.05±0.69	19.30±0.64
$k_{-4} \times 10^{-3}$, (m^3·min^{-1}·kmol^{-1})	0.12±0.005	6.01±0.19	12.13±6.85	108.64±3.62
$k_5 \times 10^{-3}$, (m^3·min^{-1}·kmol^{-1})	1.10±0.002	0.23±0.45	7.29±1.14	38.42±5.34
$k_{-5} \times 10^{-6}$, (min^{-1})	0.89±0.04	0.85±0.13	7.24±1.13	70.23±6.22
$k_6 \times 10^{-7}$, (min^{-1})	0.21±0.009	0.89±1.72	1.50±0.23	5.43±0.48

$k_{-6}\times10^{-6}$, ($m^6\cdot min^{-1}\cdot kmol^{-2}$)	0.52±0.02	2.46±2.09	4.67±1.18	7.01±0.62

Part 5: Evaluation of Internal and External Mass Transfer Limitation

Intraparticle transfer limitation of PC:

$$\varphi = \frac{d_p}{6}\left[\frac{(m+1)\cdot\rho_p\cdot R_{Initial}}{2\cdot D_e\cdot\omega_{cat}\cdot C_{PC}}\right]^{0.5}$$

$d_p \leq$ 0.000125 m (catalyst particle diameter)

$\rho_p \approx$ 744 kg/m^3 (density of catalyst))

$R_{Initial} =$ 0.00011–0.00122 kmol/(m$^3\cdot$s) (initial reaction rate)

$D_e = \frac{D_M\varepsilon}{\tau}$ m^2/s (effective diffusivity)

$D_M = \frac{7.8\times10^{-8}\cdot T\cdot(XM_W)^{0.5}}{\mu_l V_m^{0.6}}$ ≈ 3.11×10^{-5} cm^2/s (molecular diffusivity) = 3.11×10^{-9} m^2/s

ω_{cat} = 5 kg/m^3 (catalyst loading)

C_{PC} = 1.1–4.2 kmol/m^3

$\varphi \approx$ 4.52×10^{-2}– 7.77×10^{-2}

Which is much lower than 0.2, therefore, there is no intraparticle transfer limitation existing during the reaction.

Liquid-solid mass transfer limitation:

$$\alpha = \frac{R_{Initial}}{k_{l-s}\cdot a_p\cdot C_{PC}}$$

$R_{Initial} =$ 0.00011–0.00122 kmol/(m$^3\cdot$s) (initial reaction rate)

$k_{l-s} = D_M F_C(2 + 0.4\left[\frac{e(d_p)^4 {\rho_l}^3}{{\mu_l}^3}\right]^{0.25}\left[\frac{\mu_l}{\rho_l D_M}\right]^{0.333})/d_p$ $\approx$ 0.498 m/s (liquid-solid mass transfer coefficient)

$a_p = \frac{6\omega_{cat}}{\rho_p \cdot d_p} \approx$ 322.6 (m^{-1}) (specific surface area)

$\rho_p \approx$ 744 kg/m^3 (density of catalyst)

$d_p \leq$ 0.000125 m (catalyst particle diameter)

ω_{cat} = 5 kg/m^3 (catalyst loading)

C_{PC} = 1.1–4.2 kmol/m^3

α $\approx$ 6.13×10^{-7}– 1.81×10^{-6}

Even if the error of parameter is 10000%, the external liquid-solid mass transfer limitation (6.13×10^{-5}– 1.81×10^{-4}) is still much lower than 0.1.

Part 6: Error Analysis of Activation Energy

(1) Uncertainty of activation energy from uncertainty of reaction rate constant

The activation energy was estimated based on estimated reaction rate constants from experimental data at each temperature, therefore, the uncertainty of activation energy relies on the uncertainty of reaction rate constants. The procedure for estimation of uncertainty of activation energy is summarized as follows.

The relationship between activation energy and reaction rate constant is $k=k_o\times e^{(-Ea/RT)}$

(a) Functions for error propagation are listed in Table S2, which will be used to calculate uncertainty of activation energy.

Table S5. Functions for propagation of error

Function	Propagated error

$z = a + b$	$\Delta z = \left[(\Delta a)^2 + (\Delta b)^2\right]^{1/2}$
$z = ca$	$\Delta z = \lvert c \rvert \Delta a$
$z = a \times b$	$\frac{\Delta z}{z} = \left[\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta b}{b}\right)^2\right]^{1/2}$
$z = lna$	$\Delta z = \frac{\Delta a}{a}$

c is known exactly as constant, Δa is the uncertainty of a.

(b) The uncertainty for activation energy is determined by the following equation:

$$\ln(k_T) = \ln(k_0) - {}^{E_a}\!/_{RT}$$

After rearrangement,

$$E_a = RT\left[\ln(k_0) - \ln(k_T)\right]$$

Therefore, the uncertainty for activation energy can be expressed as,

$$\frac{\Delta E_a}{E_a} = \left[\left(\frac{\Delta T}{T}\right)^2 + \frac{\left[\frac{\Delta k_o}{k_0}\right]^2 + \left[\frac{\Delta k_T}{k_T}\right]^2}{\left[\ln(k_0) - \ln(k_T)\right]^2}\right]^{1/2}$$

(c) Take E_{a1} from power law for example,

The error from k_1 at 140 °C (413 K) is expressed in the following equation:

$$\Delta E_{a1T1} = E_{a1}\left[\left(\frac{\Delta T}{T_1}\right)^2 + \frac{\left[\frac{\Delta k_0}{k_0}\right]^2 + \left[\frac{\Delta k_{T_1}}{k_{T_1}}\right]^2}{\left[\ln(k_0) - \ln\left(k_{T_1}\right)\right]^2}\right]^{1/2}$$

$$= 47.03\frac{kJ}{mol} \times \left[\left(\frac{1\,K}{413\,K}\right)^2 + \frac{(1 - 0.96) + \left(\frac{0.047}{0.126}\right)^2}{\left[11.669 - \ln(0.126)\right]^2}\right]^{\frac{1}{2}} = 1.45\ kJ/mol$$

(d) Similarly, error from 160 °C, 180 °C and 200 °C is 1.12 kJ/mol, 0.88 kJ/mol and 0.86 kJ/mol respectively.

(e) Therefore, the average activation energy uncertainty ΔE_{a1} is:

$$\Delta E_{a1} = \frac{\Delta E_{aT1} + \Delta E_{aT2} + \Delta E_{aT3} + \Delta E_{aT4}}{4} = 1.08\ kJ/mol$$

(2) Error of activation energy from temperature

The sensitivity of activation energy to temperature is calculated based on the temperature range and the maximum error of reaction constants within this temperature range. the following equation was used for the calculation:

$$\Delta E_{a2} = \frac{2 \times R \times T_1 \times T_2}{|T_1 - T_2|} \times err_{max}\%$$

Where ΔE_{a2} is maximum error (sensitivity) of activation energy, R is the gas constant, T_1 and $T_2$are investigated temperature (K) and $err_{max}\%$ is the maximum error in reaction constants.

Take k_1 from power law for example, the maximum error for k_1 in the temperature range is 37.3%, while the temperature range is 473 K (200 °C)-413 K (140 °C) = 60 K. Therefore, the sensitivity of E_a for k_1 is

$$\Delta E_{a2} = \frac{2 \times 8.314 \times 473 \times 413}{1000 \times 60} \times 0.373 = 20.2\ kJ/mol$$

Therefore, the total uncertainty of activation energy is:

$$\Delta E_a = \sqrt{\Delta E_{a1}{}^2 + \Delta E_{a1}{}^2} = 20.22\ kJ/mol$$

Part 7: Criteria and Constraints Used for Model Discrimination

Estimation of kinetic parameters was performed through Athena Visual Studio software. During the parameter estimation and model discrimination, the following several criteria need to be satisfied, the priority of the five criteria are in the order of (1) to (5):

(1). All reaction/adsorption constants must be positive.

(2). Uncertainty (95% confidence level) of rates should not increase or decrease significantly with changing reaction conditions.

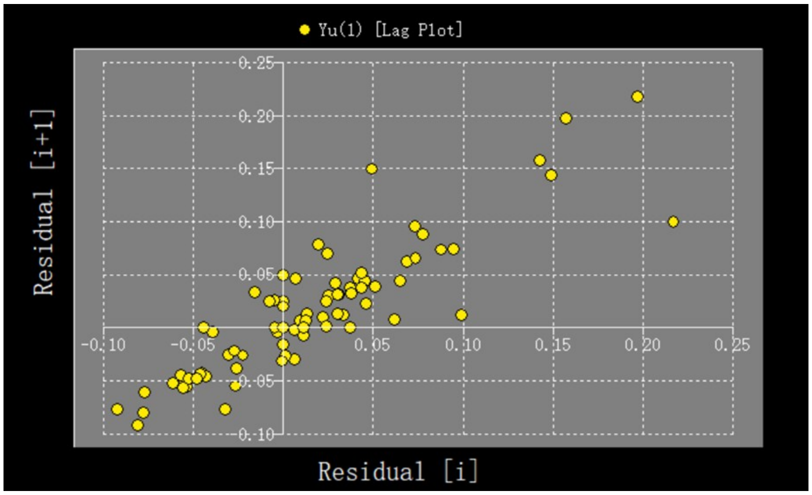
(3). Reaction rate constants must follow Arrhenius relationship.

(4). The error in experimental and predicted functions should not indicate systematic trends.

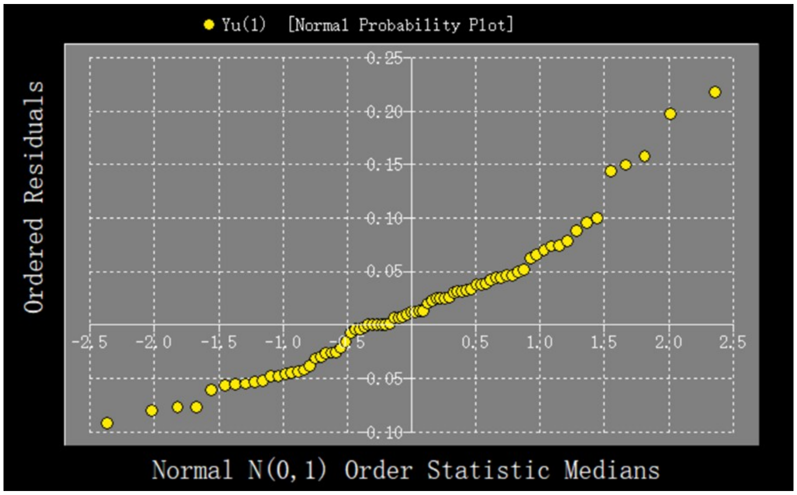
(such as in Lag Plot and Normal Probability Plot)

The experimental data sets from 200 ^{o}C are used to illustrate the criteria (4) and (5).

Lag Plot: A lag plot checks whether a data set or time series is random or not. Random data should not exhibit any identifiable structure in the lag plot. The lag plot derived from experimental data sets is shown as in following figure. The pattern in this lag plot is between Total random and weak autocorrection, which can be accepted for kinetic simulation.



Normal Probability Plot: The normal probability plot is a graphical technique for assessing whether or not a data set is approximately normally distributed (Chambers, Cleveland, Kleiner, & Tukey, 1983). The data are plotted against a theoretical normal distribution in such a way that the points should form an approximate straight line. Departures from this straight line indicate departures from normality. The following figure is derived from the experimental data sets, which is nearly straight line, indicating the data set is approximately normally distributed.



(5). Has minimum S_j.

$$S_j = \sum_{1}^{N} (C_{j,E} - C_{j,P})^2$$

Where S_j is the sum of squares of (concentration) residuals of component j. $C_{j,E}$ and $C_{j,P}$ are the experimental (E) and predicted (P) concentrations, respectively.

The data set includes 385 data points, the sum of squares of residuals is 1.47.

Chambers, J. M., Cleveland, W. S., Kleiner, B., & Tukey, P. A. (1983). Graphical methods for data analysis. Wadsworth & Brooks. Cole Statistics/Probability Series.