

Supporting Information

I Reactor Model Equations

The molar flux, ' J ' of a respective species and their respective net rate of consumption and utilization, ' r ' in different reactions with respect to length of the reactor ' z ' are given by following equations.

$$\frac{dJ_{DMF}}{dz} = -R_1 \quad (S.1.1)$$

$$\frac{dJ_{H_2O}}{dz} = -R_1 - R_8 - R_9 \quad (S.1.2)$$

$$\frac{dJ_{DMA}}{dz} = R_1 - R_3 \quad (S.1.3)$$

$$\frac{dJ_{HCOOH}}{dz} = R_1 - R_2 \quad (S.1.4)$$

$$\frac{dJ_{CO}}{dz} = R_3 - R_8 + R_9 \quad (S.1.5)$$

$$\frac{dJ_{HCHO}}{dz} = R_2 - R_3 \quad (S.1.6)$$

$$\frac{dJ_{H_2}}{dz} = R_3 + R_8 + 3R_9 \quad (S.1.7)$$

$$\frac{dJ_{O_2}}{dz} = 0.5(R_2 - R_{10}) \quad (S.1.8)$$

$$\frac{dJ_{N_2}}{dz} = R_6 \quad (S.1.9)$$

$$\frac{dJ_{CH_4}}{dz} = R_7 - R_9 \quad (S.1.10)$$

$$\frac{dJ_{CO_2}}{dz} = R_8 - R_{10} \quad (S.1.11)$$

By applying quasi steady state approximation to free radicals,

$$C_{(CH_3)_2N\cdot} = \frac{k_4 C_{DMA}}{k_5} \quad (S.1.12)$$

$$C_{CH_3N\cdot} = \sqrt{\frac{k_4 C_{DMA}}{2k_6}} \quad (S.1.13)$$

$$C_{CH_3\cdot} C_{H\cdot} = \frac{k_4 C_{DMA}}{k_7} \quad (S.1.14)$$

II Physical, Thermodynamic and Transport Properties

Based upon the heats of formation at 298 K and the heat capacity data, the heats of reaction were calculated for any temperature by following Equation S.2.

$$\Delta H_{R1} = \Delta H_{1(298K)} + \int_{298}^T \Delta C_{p1} dT \quad (S.2)$$

Wilke's method was utilized to estimate the gas mixture thermal conductivity¹⁷

$$k_m = \frac{\sum y_j k_j (M_j)^{1/3}}{\sum y_j (M_j)^{1/3}} \quad (S.3)$$

In the above equations k_m is the thermal conductivity of the mixture, k_j , y_j , and M_j are the thermal conductivity, mole fraction and molecular weight, respectively, of pure component j . The pure component thermal conductivity was calculated by the following equation (S.4).

Thermal conductivity of single component¹⁷

$$k_j = \mu_j \left(C_{p_j} + \frac{5}{4} \frac{R}{M_j} \right) \quad (S.4)$$

Wilke's method was utilized to estimate the gas mixture viscosity

$$\mu_m = \frac{\sum y_j \mu_j (M_j)^{1/2}}{\sum y_j (M_j)^{1/2}} \quad (S.5)$$

In the above equations μ_m is the viscosity of the mixture, μ_j , y_j , and M_j are the viscosity, mole fraction and molecular weight, respectively, of pure component j . The pure component viscosity was calculated by the following equation.

Viscosity of single component ¹⁶

$$\mu_j = \mu_{rj} \mu_{cj} \quad (S.6)$$

where,

$$\ln(\mu_{rj})^{0.2} = [-0.1208 + 0.1354 \ln(T/T_{cj})] \quad (S.7)$$

and

$$\mu_{cj} = 167.4 \times 10^{-7} M_j^{1/2} P_{cj}^{2/3} T_{cj}^{-1/6} \quad (S.8)$$

III Statistical analysis of estimated parameters

The estimation procedure is based on a maximum likelihood formulation which provides simultaneous estimation of parameters in the model of steam pyrolysis of dimethyl formamide and the variance model of the measuring sensors. The maximum likelihood goal can be expressed by the objective function

$$\phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta} \left\{ \sum_{i=1}^{N_{exp}} \sum_{j=1}^{N_{var,i}} \sum_{k=1}^{N_{meas,ij}} \left[\ln(\sigma_{ijk}^2) + \frac{(z_{ijk}^{meas} - z_{ijk}^{cal})^2}{\sigma_{ijk}^2} \right] \right\} \quad (S.9)$$

where N is the total number of measurements taken during all experiments, θ are the model parameters to be estimated, constrained between a lower and an upper bound, N_{exp} are the number of experiments performed, $N_{var,i}$ are the number of variables measured in the i^{th} experiment and $N_{meas,ij}$ are the number of measurements of the j^{th} variable in the i^{th}

experiment. σ_{ijk}^2 is the variance of the k^{th} measurement of the variable j in the i^{th} experiment. z_{ijk}^{cal} is the k^{th} measured value of the variable j in the i^{th} experiment.

The data acquisition of the system variables is performed by constant relative variance model. The measurements error are assumed to be statistically independent and normally distributed with zero mean and therefore a constant variance model was used (Eq S.10). For, pressure only heteroscedastic variance model was used (Eq S.11).

$$\sigma^2 = \omega^2(z^2 + \epsilon) \quad (S.10)$$

$$\sigma^2 = \omega^2(z^2 + \epsilon)^\gamma \quad (S.11)$$

where z is the model prediction of the measured quantity, ω is a parameter of the variance model and ϵ is a small but non-zero constant that ensures that the variance is still defined for predicted values that are equal to zero or very small. Table S.1 shows the details of the variance model used. For, composition and temperature variables constant variance model used. For, pressure heteroscedastic variance model was used.

A model with Arrhenius law directly incorporated made the estimation of the parameters very hard because of the high degree of non linearity. Table S.2 shows the result of statistical analysis based on original Arrhenius law. The correlation between pre exponential factors and corresponding activation energy make the problem even worst.

In order to reduce the degree of non-linearity, a re-parameterization of the model was done using reference temperature. Here, Arrhenius law is replaced by the following form.

$$K = k_{ref} \left[\frac{-E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (S.12)$$

This solution proved to be adequate. Table S.3 shows the final results of the overall estimation with the values of pre-exponential parameters reported in the parentheses. Table S.3 shows the

95 %*t* value of each estimated parameter. The test is satisfied when the calculated value is larger than reference *t*-value. The χ^2 –test concerns the goodness of the model fit and is satisfied when the weighted residual value less than the χ^2 value.

List of Figures

Title of Figure

- Figure S.1:** 95 % Confidence ellipsoid between rate at reference temperature (850 K) and activation energy of reaction R1.
- Figure S.2:** 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R2.
- Figure S.3** 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R3.
- Figure S.4** 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R4.
- Figure S.5** 95 % Confidence ellipsoid between rate at reference temperature (850 K) and activation energy of reaction R5.
- Figure S.6:** 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R6.
- Figure S.7** 95 % Confidence ellipsoid between rate constant of reaction R7 at reference temperature (850 K) and activation energy of reaction R4.
- Figure S.8** 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R8 (forward).
- Figure S.9** 95 % Confidence ellipsoid between equilibrium constant at reference temperature (850 K) and activation energy (E_w) of reaction R8.

Figure S.10 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R9.

Figure S.11 95 % Confidence ellipsoid between rate constant at reference temperature (850 K) and activation energy of reaction R10.

Figure S.12(a) Percentage residual for H₂ (◇), N₂ (○), CO₂ (×), dimethyl amine (+) and unconverted DMF (▲) at reactor wall temperature of 973 K.

Figure S.12(b) Percentage residual for O₂ (*), CO(□) , and CH₄ (Δ), at reactor wall temperature of 973 K.

Figure S.12(c) Percentage residual for H₂ (◇), N₂ (○), CO₂ (×), dimethyl amine (+) and unconverted DMF (▲) at reactor wall temperature of 1073 K.

Figure S.12(d) Percentage residual for O₂ (*), CO(□) and CH₄ (Δ) at reactor wall temperature of 1073 K.

Table S.1 Measurements Parameter for estimation

Measurements variable	Parameter, ω	Variance model	Initial Guess	Lower Bound	Upper Bound
DMF,DMA	0.00118	Constant Variance	0.01	0.001	1
Hydrogen, Nitrogen, Carbon dioxide	0.00158	Constant Variance	0.01	0.001	1
Methane, Carbon Monoxide, Oxygen	0.00142	Constant Variance	0.01	0.001	3
Pressure	$\omega = 0.01305$	Heteroscedastic variance	0.01	0.01	1
	$\gamma = 0.28210$		0.5	0	1
Temperature	0.00028	Constant Variance	0.1	0.0001	3

Table S.1 Results of parameter estimation based on the original Arrhenius equation

Parameter	Optimal Estimate	Lower Bound	Upper Bound	95% Confidence Interval	95% t-value	Standard Deviation	Reference t-value (95%)	Weighted Residual	χ^2 value
E ₁	38822	37050	40950	242.36	160.18	123.38	1.647	361.12	602.5
E ₂	1.88×10 ⁵	1.78×10 ⁵	1.97×10 ⁵	945.96	198.46	481.56			
E ₃	1.80×10 ⁵	1.71×10 ⁵	1.89×10 ⁵	1219.02	147.56	620.57			
E ₄	2.73×10 ⁵	2.53×10 ⁵	2.79×10 ⁵	665.53	410.06	338.80			
E ₅	2.75×10 ⁵	2.61×10 ⁵	2.89×10 ⁵	1964.23	139.94	999.93			
E ₆	30021	28500	31500	1456.83	20.61	741.63			
E ₈	53079	50312	55608	928.31	57.18	472.58			
E _w	59933	57000	63000	1061.59	56.46	540.43			
E ₉	124510	118475	130946	3317.96	37.53	1689.08			
E ₁₀	99685	94780	104756	1043.42	95.54	531.18			
k ₀₁	235	221	245	7.61	30.87	3.88			
k ₀₂	6.49×10 ¹⁴	6.18×10 ¹⁴	6.83×10 ¹⁴	8.17×10 ¹³	7.94	4.16×10 ¹³			
k ₀₃	1.20×10 ¹⁵	1.14×10 ¹⁵	1.26×10 ¹⁵	1.96×10 ¹⁴	6.14	9.96×10 ¹³			
k ₀₄	9.54×10 ¹⁶	9.03×10 ¹⁶	9.98×10 ¹⁶	8.39×10 ¹⁵	11.36	4.27×10 ¹⁵			
k ₀₅	7.00×10 ²¹	6.65×10 ²¹	7.35×10 ²¹	1.85×10 ²¹	3.79	9.40×10 ²⁰			
k ₀₆	1.00×10 ⁹	9.50×10 ⁸	1.05×10 ⁹	1.94×10 ⁸	5.16	9.89×10 ⁷			
k ₀₇	1.95×10 ¹¹	1.90×10 ¹¹	2.10×10 ¹¹	1.38×10 ⁹	141.64	7.00×10 ⁸			
k ₀₈	1.01×10 ⁶	9.50×10 ⁵	1.05×10 ⁶	1.27×10 ⁵	7.94	6.46×10 ⁴			
k _{0w}	518	494	546	72.72	7.13	37.02			
k ₀₉	2.98×10 ⁵	2.85×10 ⁵	3.15×10 ⁵	1.21×10 ⁵	2.47	6.15×10 ⁴			
k ₀₁₀	8.81×10 ¹⁰	8.41×10 ¹⁰	9.29×10 ¹⁰	1.23×10 ¹⁰	7.17	6.26×10 ⁹			

E_i , k_{oi} are activation energy and pre-exponential factor for i^{th} reaction.

Table S.2 Results of parameter estimation based on the re-parameterization of Arrhenius equation

Parameter	Optimal Estimate	Lower Bound	Upper Bound	95% Confidence Interval	95% t-value	Standard Deviation	Reference t-value (95%)	Weighted Residual	χ^2 value
E ₁	39106	37050	40950	293	133	149	1.6479	467.14	498.34
E ₂	185551	178458	197243	3899	48	1985			
E ₃	180309	171000	189000	1001	180	510			
E ₄	267067	252700	279300	2105	126	1071			
E ₅	275035	261250	288750	23361	117	1188			
E ₆	29476	28234	31206	1246	24	634			
E ₈	53036	50312	55608	929	57	473			
E _{W8}	59614	57000	63000	594	100	302			
E ₉	125149	118475	130946	664	188	338			
E ₁₀	122919	117800	130200	1523	81	775			
k _{1,Tref}	0.951(240)	0.9120	1.0080	0.0024	383	0.00126			
k _{2,Tref}	1975(4.99×10 ¹⁴)	1787	1975	86.40	22.86	43.99			
k _{3,Tref}	10373(1.2×10 ¹⁵)	9886	10927	147.70	70.23	75.19			
k _{4,Tref}	4.35(1.12×10 ¹⁷)	4.056	4.483	0.086	72.37	0.030585			
k _{5,Tref}	89583(7.15×10 ²¹)	83708	92519	1893	47.93	950			
k _{6,Tref}	1.4×10 ⁷ (9.3×10 ⁸)	1.36×10 ⁷	1.51×10 ⁵	162549	88.90	82749			
k ₇	1.97×10 ¹¹	1.90×10 ¹¹	2.10×10 ¹¹	1.5×10 ⁹	127	7.87×10 ⁸			
k _{8,Tref}	551(1×10 ⁶)	529	584	3.96	139	2.016			
k _{w,Tref}	0.1066(491)	0.1010	0.1120	0.000826	129	4.20×10 ⁻⁴			
k _{9,Tref}	0.0065(3.1×10 ⁵)	0.0061	0.0068	6.21×10 ⁻⁵	104	3.16×10 ⁻⁵			
k _{10,Tref}	14.82(5.31×10 ⁸)	13.75	15.25	0.251	58	0.128			

E_i , k_{iTref} are activation energy and rate constant for i^{th} reaction at reference temperature 850 K respectively. A value in the parentheses represents the pre-exponential factor of i^{th} reaction.

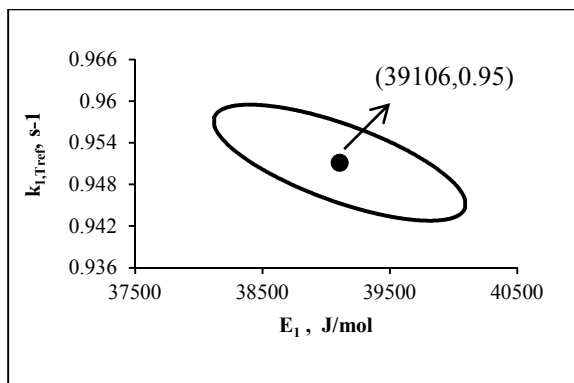


Figure S.1

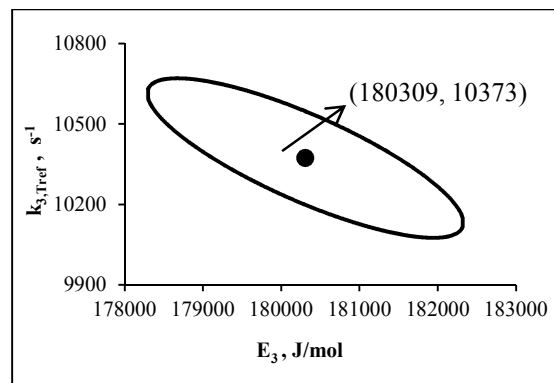


Figure S.3

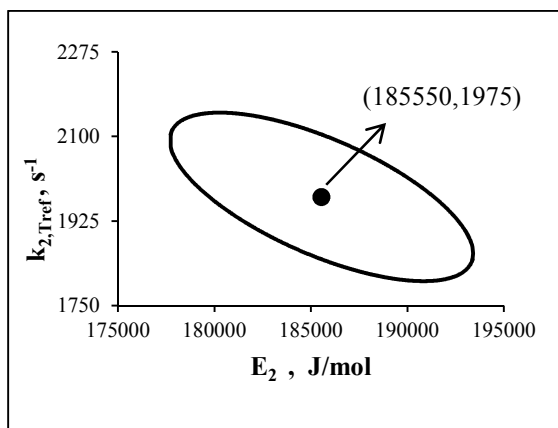


Figure S.2

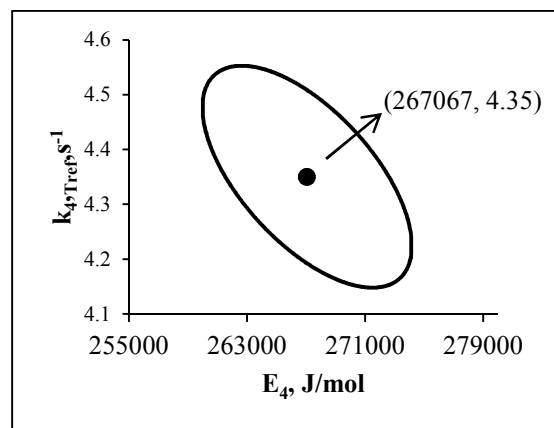


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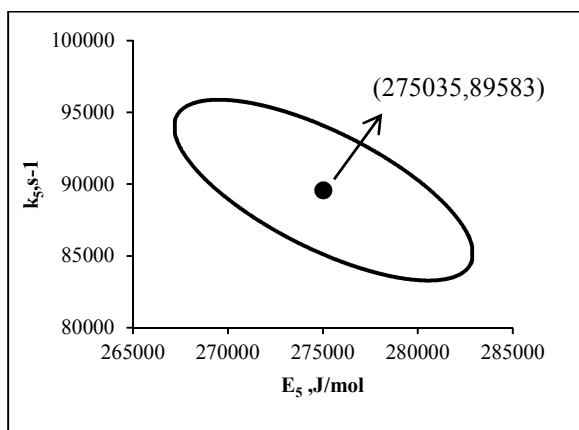


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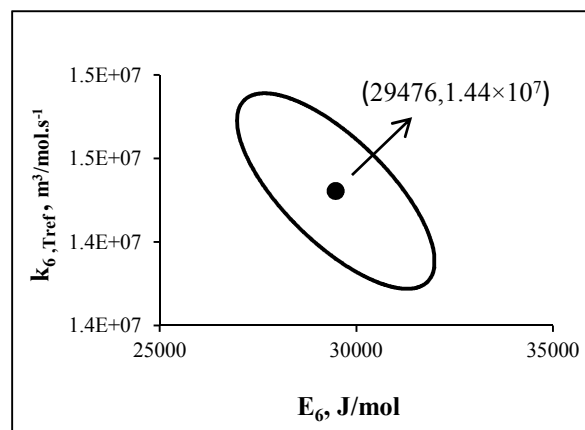


Figure S.6

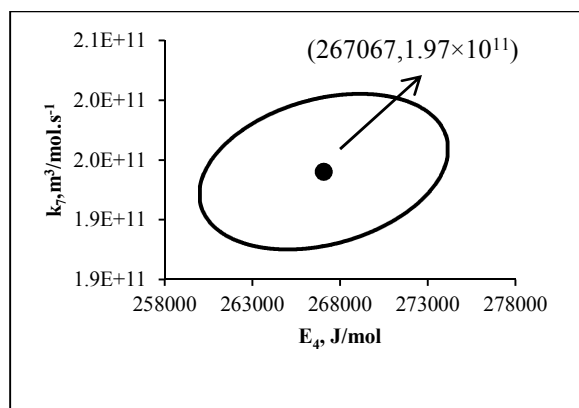


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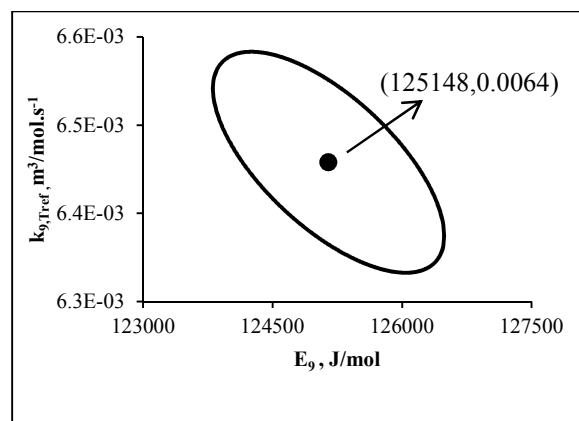


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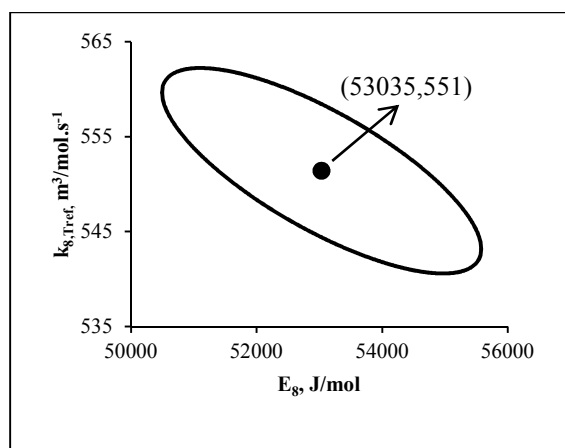


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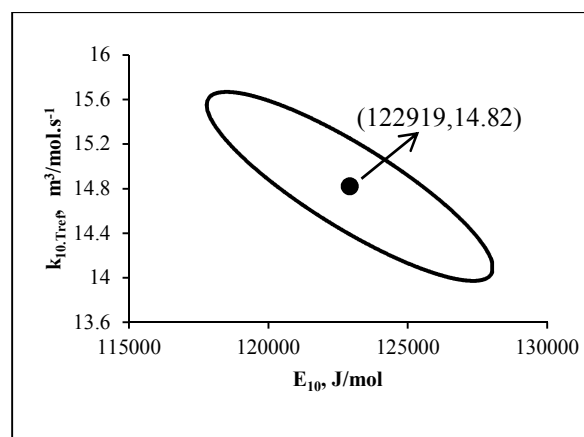


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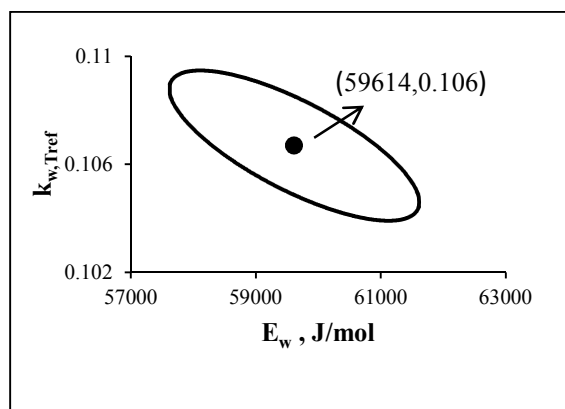
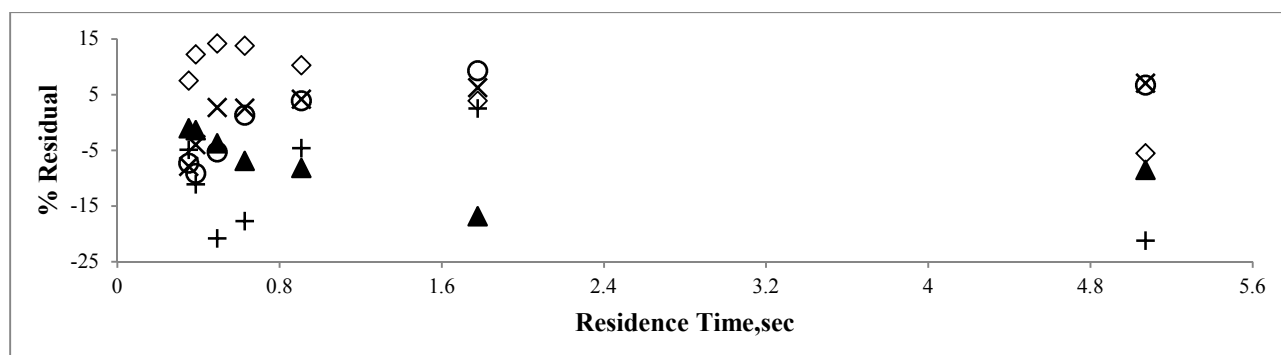
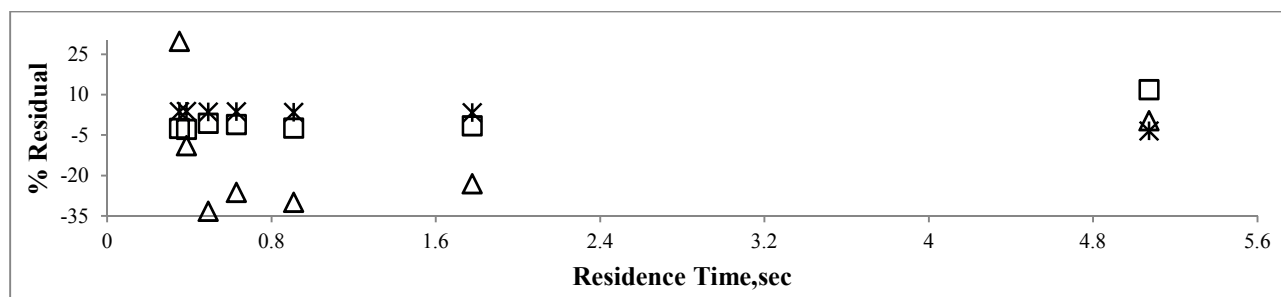


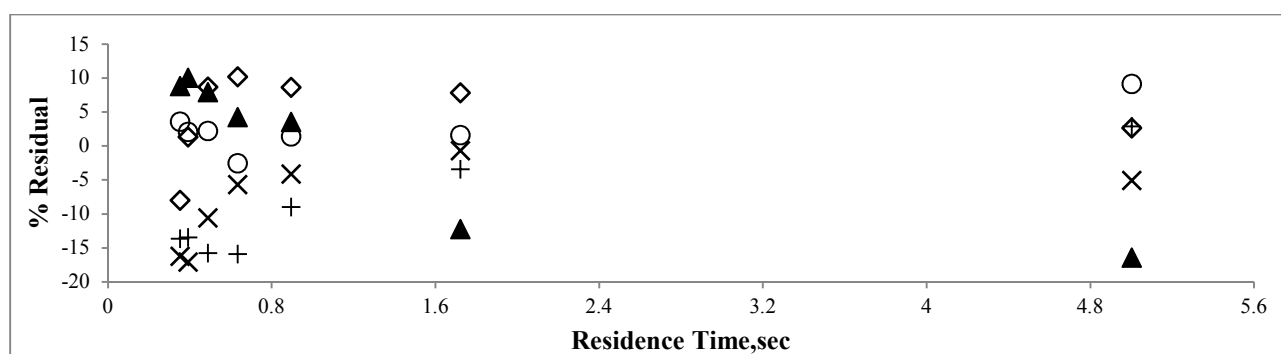
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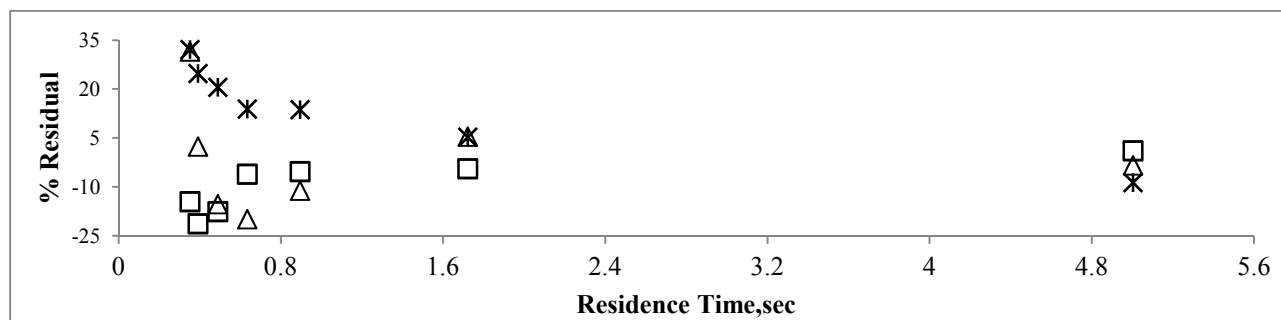
(a)



(b)



(c)



(d)

Figure S.12