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Adiabatic Correction for the Esterification of Acetic Anhydride by Methanol via Accurate Kinetics

Ze Dong[a,b], Li-ping Chen[a], Ying-ying Ma[b], Hao-liang Peng[b], Wang-hua Chen[a]*

a) Nanjing University of Science & Technology, School of Chemical Engineering, 200 Xiao ling wei street, NanJing, China, 210000

b) Solvay (China) Co.,Ltd, jindu road 3966, ShangHai, China, 201108

Abstract:

In the field of adiabatic correction for complex reactions, a simple one-stage kinetic model was used to estimate the real reaction kinetics. However, this assumption simplified the real process, inevitably generated inaccurate or even unsafe results. Therefore, it was necessary to find a new correction method for complex reactions. In this work, esterification of acetic anhydride by methanol was chosen as an object reaction of study. The reaction was studied under different conditions by Reaction Calorimeter (RC1). Then, Thermal Safety Software (TSS) was used to establish the kinetic model and estimate the parameters, where, activation energies for three stages were 67.09, 81.02, 73.77 kJ·mol^{-1} respectively, and corresponding frequency factors in logarithmic form were 16.05, 19.59, 15.72 s^{-1}. In addition, two adiabatic tests were performed by Vent Sizing Package2 (VSP2). For accurate correction of VSP2 tests, a new correction method based on Enhanced Fisher method was proposed. Combined with kinetics, adiabatic correction of esterification reaction was achieved. Through this research, accurate kinetic parameters for a three-step kinetic model of the esterification reaction were acquired. Furthermore, the correlation coefficients between simulated curves and corrected curves were 0.976 and 0.968, which proved the accuracy of proposed new adiabatic correction method. Based on this new method, conservative corrected results were able to be acquired and be applied in safety assessment.

Key words: adiabatic correction, kinetics, new method, complex reaction, esterification, model reaction

1 Introduction

Design of emergency relief systems to accommodate runaway reactions often requires using bench-scale adiabatic calorimeters to evaluate thermokinetic data of a full-scale reactor (Fauske, 2006, Westerterp and Molga, 2006). Besides, adiabatic calorimeters are also applied in the safe manufacturing, transporting, storage, and processing of chemicals, accurate adiabatic data is extremely important. However, in adiabatic calorimeter, part of the heat released from decomposition or reaction is always used to heat the vessel. Thus, the measured

data cannot be used to simulate industry-scale production directly. This phenomenon can be described as "thermal inertia," or the Phi factor, which usually equals to one for industrial scale and larger than one for bench-scale (Fisher, 2010, Wilcock and Rogers, 1997). Based on "thermal inertia," two well-known methods were proposed many years ago to correct bench-scale experimental data, i.e. Fisher method and Townsend method (Townsend and Tou, 1980, Leung and Fauske, 1987). Contrast to Townsend method, Fisher method is more intuitive because it can obtain corrected curves directly, instead of several specific points like maximum temperature rate, temperature rate at maximum temperature, etc.

Although more intuitive, data corrected by Fisher method is not accurate enough because of two issues. Firstly, under adiabatic conditions, reaction heat generation always results in the increasing of temperature rate when compared to real condition. Consequently, the reaction is accelerated by this increasing rate, the reaction time is inevitably shorter, which is not taken into account in the Fisher method. Hence, Enhanced Fisher method was proposed (Kossoy, et al., 2015), in which time correction was supplemented. The second issue is the assumption in Fisher method that the reaction kinetics is replaced with single Nth-order kinetics, which is commonly used for simple reactions but less accurate in complex reaction. In order to avoid these problems, a new correction method is presented in this paper, which is explained in detail in section 4.1.

The reaction chosen for investigation was the esterification of acetic anhydride by methanol. This is a typical complex reaction with three stages (Widell and Karlsson, 2006, Steensma and Westerterp, 1991). In this paper, reaction kinetics was estimated based on four RC1 tests under different conditions by Thermal Safety Software (TSS). Data from two VSP2 experiments are corrected by the new method based on kinetic parameters measured before. The proposed method was validated by comparing the simulated curves and the corrected reaction curves.

2   Experiment

2.1   Equipment

A Mettler RC1 (Reisen and Grob, 1985) with 1L glass reactor was used. It was equipped with a Pt100 temperature probe, an electrical calibration heater, a stirring system (anchor type) and one dosing system consisting of two pumps. Working temperature range of heating–cooling system is from −15 °C to 200 °C, which used a single heat transfer fluid.

The VSP2 (Vent Sizing Package 2) (Askonas, et al., 2000), which was commercialized by Fauske, used 115 mL stainless steel test cells. The advantage of VSP2 was low thermal inertia, the thin wall of the test cell is the reason. VSP2 was equipped with two temperature probes, two heaters and two pressure transducers in and out of the test cell, a magnetic stirring system and an inlet system (two dosing pumps). Working temperature range was ambient temperature to 500°C. A pressure compensation system was used to track pressure inside the cell from 0 to 100 bar. The sensitivity of temperature measurements was 0.1°C/min.

2.2 Experiments

In the RC1 experiments, acetic anhydride was added to the reactor and heated up to target temperature. After measuring specific heat capacity, methanol was fed into the reactor with a constant rate, after stabilization of temperature, specific heat capacity was measured again. Then, cool down the mixture and finished the experiment. Detailed experimental conditions, such as target temperature, dosing rate and molar ratio, are listed in Table 1.

For VSP2 experiments, acetic anhydride and methanol were mixed at ambient temperature and charged into the test cell. The cell was sealed, when the experiment was implemented with a heat-wait-search (HWS) mode. The reaction was considered as completed when temperature started to decrease. The experiment was stopped when temperature inside is close to ambient temperature. The specific experimental information is listed in Table 2.

Methanol and acetic anhydride (>99%) were purchased from Aladdin (Shanghai, China). It is important to note that the catalyst (sulfuric acid) was not used in this reaction.

2.3 Experimental results

The values of overall heat transfer coefficient (U) need to be measured before and after the esterification to calculate the values of U within the dosing period. In addition, assumptions that the values of U increase linearly within the dosing period and remain constant after the dosing period must be made. Then, specific heat capacity (C_p) before and after reaction are possible to be calculated by standard calibration. The total heat effect (Q) is able to be determined by integration of reaction heat release rate (q_r), where q_r equals the sum of heat accumulation (q_{accu}) by the reaction mass and inserts, heat flow (q_{flow}) though the reactor wall and heat input (q_{dos}) due to dosing. Here are some relevant literatures for well understanding the calculation method for these parameters (Crevatin et al., 1999, Leveneur et al., 2012).

Figure 1 shows heat flow curves of four RC1 experiments, in which the inflection points of peaks existed at the end of dosing. From these four experiments, several parameters were obtained directly, such as specific heat capacity before and after reaction (C_p), overall heat transfer coefficient (U), total heat effect (Q), etc., which are listed in Table 3. Figure 2 shows the measured temperature curves from VSP2 (only exothermic phase). In both two curves, temperature ushered in a burst point after a stable temperature rise phase.

From table 3, the specific heat capacity is very similar in four experiments, which illustrates that the products and their ratios are almost same. The maximum reaction heat release rate increases with the increasing of reaction temperature. Besides, compared test 2 and test 4, the extra dosing results in the more heat production, which demonstrates the extra methanol is able to be reacted, in other words, three-stage kinetic model is more suitable to describe this esterification.
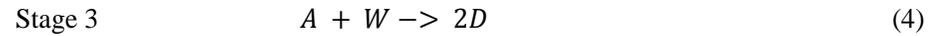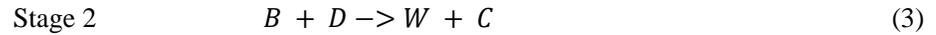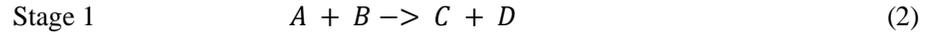
3 Mathematical model and simulation

3.1 Reaction description

Some scholars (Friedel and Wehmeier, 1991, Wright and Rogers, 1986, Duh et al., 1996, Casson et al., 2012) modeled the esterification of acetic anhydride by methanol using second order kinetics to calculate the kinetic parameters:

$$A + B \rightarrow C + D \tag{1}$$
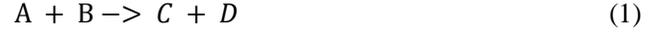
Where A is acetic anhydride, B is methanol, C is methyl acetate and D is acetic acid. But in reality, the reaction mechanism is much more complex, and several stages may be involved. Someone (Balland et al., 2002) proposed the following reaction stages, which were more suitable for this esterification:

$$\text{Stage 1} \qquad A + B \rightarrow C + D \tag{2}$$

$$\text{Stage 2} \qquad B + D \rightarrow W + C \tag{3}$$

$$\text{Stage 3} \qquad A + W \rightarrow 2D \tag{4}$$

Where W is water. In attention, this model is not considered of reversible reactions. Besides, this model is applied in kinetics study successfully in recent study (Guo Z C et al., 2016).

3.2 Mathematical derivation

For example of stage 1, with two reactants in reaction 1, the reaction rate is expressed as (Pollak and Talkner, 2005):

$$r_1 = k_1 C_A{}^{n_1} C_B{}^{m_1} \tag{5}$$

Where k_1 is the rate constant of reaction stage 1, C_A is the concentration of acetic anhydride, C_B is concentration of methanol and $n_1 + m_1$ is the order of the reaction stage 1.

The reaction rate constant is a function of the activation energy E_1 and temperature T according to Arrhenius equation (Laidler, 1984):

$$k_1 = A_1 e^{-E_1/RT} \tag{6}$$

Where A_1 is the frequency factor of reaction 1.

The rate of variation of species concentration are established after determining the kinetic model, the equations are as follows:

$$\frac{dC_A}{dt} = (-r_1 - r_3) \tag{7}$$

$$\frac{dC_B}{dt} = C_{B,in} v/(V_0 + vt) + (-r_1 - r_2) \tag{8}$$

$$\frac{dC_C}{dt} = (r_1 + r_2) \tag{9}$$

$$\frac{dC_D}{dt} = (r_1 - r_2 + 2r_3) \tag{10}$$

$$\frac{dC_W}{dt} = (r_2 - r_3) \tag{11}$$

Where C is concentration of species, V_0 is initial volume of mixture, v is flow rate of dosing, $C_{B,in}$ is molar concentration of dosing methanol. Therefore, concentrations of reagents and products are able to be obtained by integration of equation 7-11.

The heat generation Q is related to the heat release rate q_r. Accordingly, it is proportional to the reaction enthalpy ΔH_{r1} and to the reaction rate r_1 (Stoessel, 2008):

$$q_{r1} = r_1 V (-\Delta H_{r1}) \tag{12}$$

So, the heat generation of reaction stage 1, Q_1, could be expressed as the integration of q_{r1}:

$$Q_1 = \int_0^t q_{r1}\, dt \tag{13}$$

The same derivation for reaction stages 2 and 3 acquires similar equations of heat production rate and heat generation. Therefore, the total heat generation and the total heat rate of the whole reaction were calculated as:

$$Q = Q_1 + Q_2 + Q_3 \tag{14}$$

$$q = q_{r1} + q_{r2} + q_{r3} \tag{15}$$

3.3   Estimation of kinetic parameters

According to the equations 5~15, the kinetic parameters were estimated by the Desk module in TSS under the standard of Least Squares Method (LSM) (Anderson, et al., 1996, Flammersheim and Opfermann, 2002, Mehrvar, et al., 2000, Himmelblau, 1972, Vyazovkin, 2011). The software simulated reaction heat release rate and reaction heat generation by kinetics and surroundings (heat exchange condition, well stirred assumption etc.). During solution of best results, kinetic parameters were given initial values at the beginning of the simulation and these parameters could be changed during simulation until the correlation coefficient reached the maximum, i.e. simulation curves of reaction heat release rate and reaction heat generation matched the experimental results best. This correlation coefficient was calculated for experimental and simulated results. The correlation coefficients of four tests were 0.978, 0.987, 0.969 and 0.973, respectively, which illustrated the suitability of the model and parameters for this complex reaction. The simulated curves are showed in the Figures 3 and 4.

And the concrete values of parameters for every stage are listed in Table 4. Then, compared activation energy and frequency factor with literatures' (table 5), the comparison indicated that first stage kinetics was close to the non-catalytic reaction kinetics, while the last two stages were a little larger. These large activation energies and frequency factors leaded to the variation of reaction rate, which affected adiabatic correction. So, as long as kinetic parameters fitted experimental results well, the correction effects can be eliminated and this kinetics can be accepted in application of adiabatic correction.

4   Adiabatic correction

4.1   Correction method

For the Enhanced Fisher method, following equations were used:

$$\frac{1}{T_{A0}} = \frac{1}{T_{M0}} + \frac{R}{E} ln\emptyset \tag{16}$$

$$T_A = T_{A0} + \emptyset(T_M - T_{M0}) \tag{17}$$

$$\frac{dT}{dt}_{A(\emptyset=1)} = \emptyset exp\left[\frac{E}{R}\left(\frac{1}{T_M} - \frac{1}{T_A}\right)\right]\frac{dT}{dt}_{M(\emptyset>1)} \tag{18}$$

$$t = \int_{T_{A0}}^{T_A} \frac{dT}{\left(\frac{dT}{dt}\right)_{A(\emptyset=1)}} \tag{19}$$

Where, T_{M0} is initial measured onset temperature, T_{A0} is adjusted onset temperature, T_M is measured temperature, T_A is adjusted temperature, $\frac{dT}{dt}_{A(\emptyset=1)}$ is adjusted heat rate, $\frac{dT}{dt}_{M(\emptyset>1)}$ is measured heat rate.

And kinetic parameters (E) from Widell's research was chosen in this correction.

As mentioned in section 1, the Fisher method has two problems: one is the lack of time correction and the other is assumption, which supposes the reaction obeys single stage Nth-order reaction mechanism. These two problems result in inaccurate and unsafe corrected data. In order to avoid these problems, the following correction method was proposed.

Due to similar expressions of heat production (Q), temperature (T), corrected temperature (T_{cor}) and corrected temperature rate ($\frac{dT}{dt}_{cor(\emptyset=1)}$) for the three stages, only the expressions of stage 1 are listed as an example in following four correction steps.

Step 1 is separating the temperature curve for each stage from the total temperature curve. The following equations are used:

$$Q_r = Q_{r1} + Q_{r2} + Q_{r3} \tag{20}$$

$$Q_{r1} = mC_p(T_{r1} - T_0) \tag{21}$$

$$T_{r1} = Q_{r1}/mC_p + T_0 \tag{22}$$

Step 2 is correction of onset temperature. Assumption that, the measured onset T is always T_0, the corrected onset T is always T_{r0} in three stages. T_{r0} is corrected from stage 1 by the following equations:

$$\frac{1}{T_{r0}} = \frac{1}{T_{r1}} = \frac{1}{T_0} + \frac{R}{E_1} ln\emptyset \tag{23}$$

$$\emptyset = 1 + \frac{m_b c_{p,b}}{m_s c_p} \tag{24}$$

Where, m_s is the mass of sample, c_p is the average specific heat capacity of sample, m_b is the test cell mass, and $c_{p,b}$ is the average specific heat capacity of test cell.

Step 3 is temperature Correction of each reaction stage:

$$T_{r1-cor} = T_{r0} + \emptyset(T_{r1} - T_0) \tag{25}$$

6

$$T_{r-cor} = T_{r1-cor} + T_{r2-cor} + T_{r3-cor} - 2T_{r0} \qquad (26)$$

Step 4 is temperature rate correction of each stage. The total rate is the sum of the temperature rate for all three stages in equation 27. The reaction time is able to be corrected according to the Enhanced Fisher method using equation 28:

$$\frac{dT}{dt}_{r-cor(\emptyset=1)} = \frac{dT}{dt}_{r1-cor(\emptyset=1)} + \frac{dT}{dt}_{r2-cor(\emptyset=1)} + \frac{dT}{dt}_{r3-cor(\emptyset=1)} \qquad (27)$$

$$t = \int_{T_{r0}}^{T_{r-cor}} \frac{dT}{\frac{dT}{dt}_{r-cor(\emptyset=1)}} \qquad (28)$$

Where subscript r refers to the entire reaction, 0 points to the initial value, $1, 2, 3$ refer to stage $1, 2, 3$ respectively.

These four steps comprise the new method we proposed, which provides more reasonable and accurate correction for complex reactions.

For application new method in adiabatic correction, the procedure includes five parts as follows:

Firstly, temperature determination of each stage (assume X as the number of stages):

$$Q_r = \sum_{i=1}^{X} Q_{ri} \qquad (29)$$

$$T_{ri} = Q_{ri}/mC_p + T_0 \qquad (30)$$

$$\emptyset = 1 + \frac{m_b c_{p,b}}{m_s c_p} \qquad (31)$$

Then, onset temperature correction of each stage:

$$\frac{1}{T_{r0}} = \frac{1}{T_{ri}} = \frac{1}{T_0} + \frac{R}{E_1} ln\emptyset \qquad (32)$$

Next is temperature correction of each stage and entire reaction:

$$T_{ri-cor} = T_{r0} + \emptyset(T_{ri} - T_0) \qquad (33)$$

$$T_{r-cor} = (\sum_{i=1}^{X} T_{r1-cor}) - (X-1)T_{r0} \qquad (34)$$

Followed is temperature rate correction of each stage and entire reaction:

$$\frac{dT}{dt}_{ri-cor(\emptyset=1)} = \emptyset exp\left[\frac{E_i}{R}(\frac{1}{T_{ri}} - \frac{1}{T_{ri-cor}})\right] \frac{dT}{dt}_{ri(\emptyset>1)} \qquad (35)$$

$$\frac{dT}{dt}_{r-cor(\emptyset=1)} = \sum_{i=1}^{X} \frac{dT}{dt}_{ri-cor(\emptyset=1)} \qquad (36)$$

Finally, time correction of entire reaction:

$$t = \int_{T_{r0}}^{T_{r-cor}} \frac{dT}{\frac{dT}{dt}_{r-cor(\emptyset=1)}} \qquad (37)$$

4.2 Correction results and analysis

To compare the differences between two adiabatic correction methods, the corrected results studied by the Enhanced Fisher method and our new method are shown in Figures 5 and 6. The circular points were corrected by the Enhanced Fisher method, in which the model parameters used in the correction were from the literature (Duh, et al., 1996). The rectangular points were corrected by the new method presented in section 4.1. In figure

7 and 8, temperature curves under VSP2 experimental conditions were simulated by accurate kinetics. The results showed that simulation curves matched the correction curves well by proposed method.

From the comparison of two corrected curves, the onset temperature and end temperature were almost the same. However, with constant temperature, the heat release rate corrected by the new method was larger than that corrected by the Enhanced Fisher method. In other words, the time of temperature rising in new method was shorter than that in Enhanced Fisher method. The main reason for this scenario was kinetics, which was non-catalytic kinetics in Enhanced Fisher method, but three stages autocatalytic kinetics in new method. The three-stage kinetics was close to the real kinetics of this esterification due to the well-fitting results of RC1 experiments. Accordingly, this accurate kinetics was used in correction and leaded to the more reasonable results. Furthermore, the shorter time resulted in the higher temperature rate, which illustrated that the risk may be ignored or be assessed too conservative after inaccurate adiabatic correction.

4.3   Verification

The experiment simulated by TSS (thermal safety software) was also compared, in which a phi-factor $\emptyset$ equal to one was assumed, and the kinetic model used for simulation was obtained from RC1 test, i.e., the same as the new correction method.

From Figures 7 and 8, the correlation coefficients between simulation curves and corrected curves were 0.976 and 0.968, respectively, which validated the appropriateness of proposed new method as well as the accuracy of the reaction kinetics.

5   Conclusion

(1) A three-stage reaction kinetics for the esterification of acetic anhydride by methanol is successfully modeled. The specific parameters in this model are estimated, which are close to literatures' value.

(2) A new adiabatic correction method suitable for complex reactions is proposed. The procedure for application of this method is described in section 4.1. What is more, this method is applied successfully in esterification of acetic anhydride by methanol.

(3) Results in this study demonstrate that adiabatic correction would be more reliable and accurate when combining real reaction kinetics with experimental results. The adiabatic correction may not conservative enough by simplified one stage kinetics, which may lead to the risk level much lower than real one in safety assessment.

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Figures and tables

Table 1 Experimental Conditions for RC1

RC1	Mass of acetic Anhydride (g)	Mass of methanol (g)	Dosing rate (g/min)	Experimental temperature (°C)	Molar ratio
Test 1	432.6	135.7	2	50	1:1
Test 2	432.6	135.7	3	55	1:1
Test 3	432.6	135.7	2	60	1:1
Test 4	432.6	203.7	3	55	1:1.5

Table 2 Experimental Conditions for VSP2

VSP2	Mass of acetic Anhydride (g)	Mass of methanol (g)	Test mode	Phi value	Molar ratio
Test 5	31.1	9.5	HWS (3 k/20min)	1.254	1:1
Test 6	31.1	19	HWS (3k/20min)	1.211	1:2

Table 3 parameters measured from RC1

Test	C_{p1} (J·g^{-1}·K^{-1})	U_1 (W·m^{-2}·K^{-1})	C_{p2} (J·g^{-1}·K^{-1})	U_2 (W·m^{-2}·K^{-1})	$q_{r\,(max)}$ (W)	Q (kJ)
1	2.03	118.0	2.02	114.4	27.2	207.4
2	2.03	118.1	2.04	115.5	40.0	210.0
3	2.02	119.3	2.08	118.4	53.3	213.8
4	2.02	113.6	2.20	116.4	39.2	244.9

Table 4 kinetics calculation results for each step

Step	Parameter	value
$A + B \rightarrow C + D$	$\ln(A_1/s^{-1})$	16.05
	E_1(kJ/mol)	67.09
	n_1	0.46
	m_1	0.58
$B + D \rightarrow W + C$	$\ln(A_2/s^{-1})$	19.59
	E_2(kJ/mol)	81.02
	n_2	0.40
	m_2	0.70
$A + W \rightarrow 2D$	$\ln(A_3/s^{-1})$	15.72
	E_3(kJ/mol)	73.77
	n_3	2.90
	m_3	0.47

Table 5 kinetics comparison

model	stages	E(kJ/mol)	$\ln(A/s^{-1})$
Autocatalytic kinetics	$A + B \rightarrow C + D$	67.09	16.05
	$B + D \rightarrow W + C$	81.02	19.59
	$A + W \rightarrow 2D$	73.77	15.72
non-catalytic kinetics (Widell, 2006)	$A + B \rightarrow C + D$	69.90	16.9
non-catalytic kinetics (Duh et al., 1996)	$A + B \rightarrow C + D$	72.6	17.40
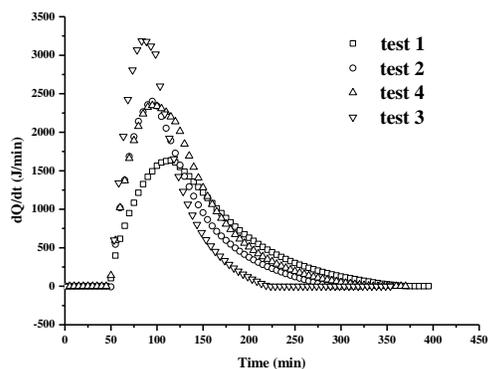
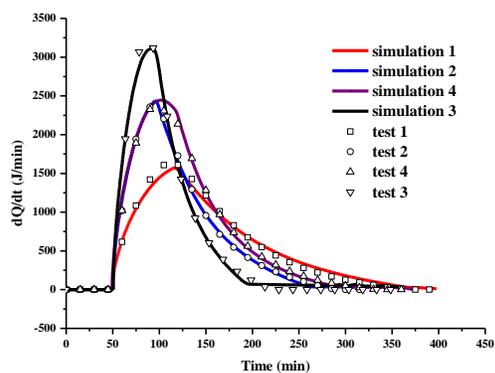Figure 1 RC1 experimental curves
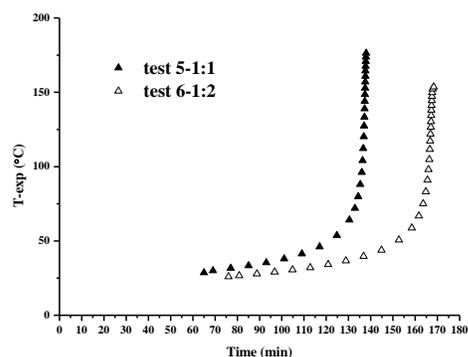
Figure 2 VSP2 experimental curves

Figure 3. dQ/dt simulation curves for RC1 experiments
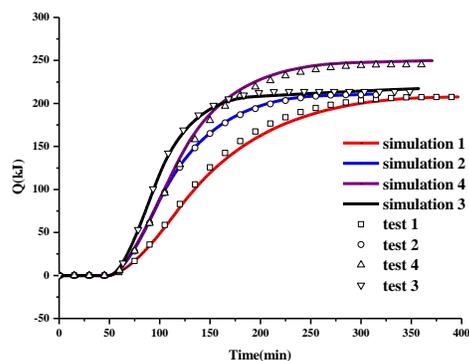
Figure 4. Q simulation curves for RC1 experiments
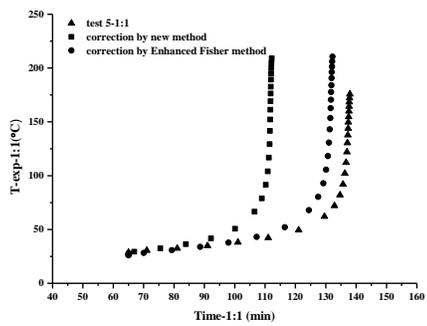
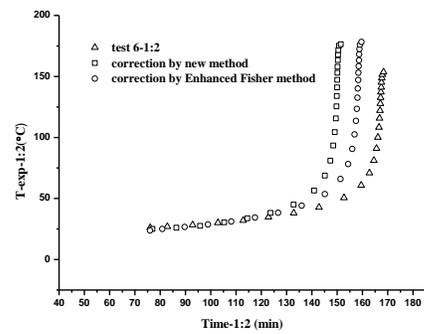Figure 5 two correction results for test 5-1:1

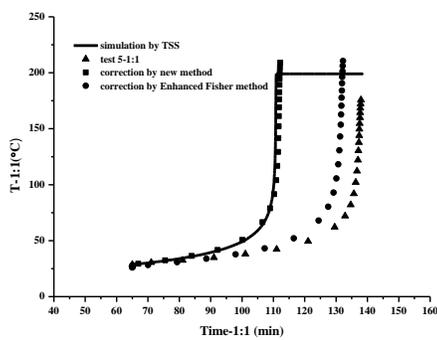Figure 6 two correction results for test 6-1:2

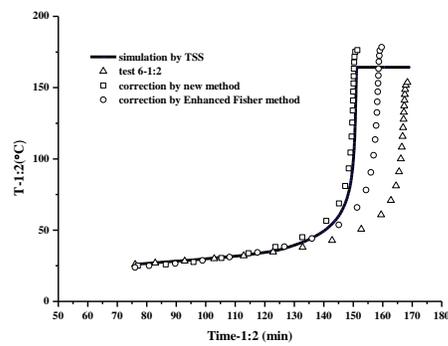Figure 7. Test 5-1:1 comparison results for corrected curves

Figure 8. Test 6-1:2 comparison results for corrected curves

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