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Pyrolysis kinetic analysis of sequential extract residues from Hefeng subbituminous coal based on Coats-Redfern method

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Abstract: Sequential extract residues (R_i, i=1, 2, 3, 4, 5) were obtained from Hefeng acid-washing coal (HF_{AC}) by petroleum ether, carbon disulfide, methanol, acetone and isometric carbon disulfide/acetone mixture, sequentially. Pyrolysis behavior of the samples was carried out using thermogravimetry analysis. Coats-Redfern method with different reaction order was used to analyze the pyrolysis kinetic of each sample, and the kinetic parameters, including correlation coefficient (R^2), activation energy (E), pre-exponential factor (A), were calculated. Results showed that the weight loss of extract residues was higher than HF_{AC}, and pyrolysis behavior varies greatly for residues, which may be due to unstable structure after extraction. From conversion-temperature (α-T) curves, pyrolysis process was divided into three stages: low-temperature stage (150-350 ºC), medium temperature stage (350-550 ºC) and high temperature stage (550-950 ºC). And the medium temperature stage made great

contribution to the process of pyrolysis, which was dominated by depolymerization and decomposition reaction, and the effect of kinetic fitting to this stage is better, with R^2 higher than 0.95. Relationship between kinetic parameters and reaction order showed that swelling effect might be an important reason for the discrepancy of E for each sample in the process of pyrolysis. And Ln(A)-E relationship has a great significance to predict E and the A under higher reaction order.

Key words: Extract residues; Pyrolysis; Coats-Redfern method; Kinetic analysis

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1. Introduction

In recent years, increasing consumption of coal, the main energy source in China, has caused serious environmental pollution problems. However, coal still play a leading role in Chinese primary energy consumption for a long time in the future. Therefore, clean and efficient utilization of coal has become the top priority [1-4]. Solvent extraction under mild conditions can separate organic matter from coal by the principle of similar phase dissolution, without damaging the environment, and the structure and composition characteristics of coal can be reflected by analyzing the molecular structure characteristics of the soluble molecules [5-6]. There are five kinds of intermolecular forces in coal, including entanglement interaction between alkyl and alkyl groups, π-π interaction between aromatic rings, weak hydrogen bond, strong hydrogen bond and hydrogen bond/π-π complex interaction. Different solvent can selectively destroy the intermolecular interaction in low-rank coal [7-9]. Therefore, sequential extraction with different solvent can effectively improve the extraction efficiency of organic matter in coal.

Macro-kinetics is widely used in study of coal pyrolysis characteristics and reaction

mechanism, which shows high theoretical and practical significance for improving clean and efficient utilization of coal [10-11]. Thermogravimetric analysis (TGA) is a kind of thermal analysis technology, which measures the change of material quality with temperature and time in a controlled environment. This method has a lot of advantages, such as simple pretreatment, no reagent and application [12-13]. By the establishment of kinetic model, pyrolysis process of coal can be quantitatively analyzed, which is convenient to understand the pyrolysis characteristics and mechanism of coal. Many theoretical models, including zero-order empirical model, single reaction model, multi-stage reaction model and distributed activation energy model (DAEM), have been put forward by researchers. In addition, many methods for calculating kinetic parameters are proposed according to the above model, including Coats-Redfern method, Kissinger method, Dzawa method and Doyle method. However, a universal model and method has not been developed due to the complexity and difference of coal structure. Among them, single reaction model, which considered the process of coal pyrolysis as an approximately first-order or n-order reaction and can well predict the kinetic parameters, has been widely concerned [14].

Liu et al. [15] investigated the effect of coal particle size on pyrolysis performance by Coats-Redfern method. It was found that the smaller the coal particle size is, the faster the surface heating rate, resulting in higher heat flux and lower activation energy. In addition, with the decrease of particle size, the specific surface area increased significantly, and the active sites increased, which could promote the release of primary pyrolysis products. According to TGA, Geng et al. [16] discussed the behavior of kinetics using Shenmu bituminous coal and its pyrolysis products. It was found that pyrolysis process involved many types of covalent and other chemical

bonds, resulting that cleavage of each bond need different activation energies. Du et al. [17] reported the pyrolysis kinetics of Shenfu coal, and divided the pyrolysis process into three stages. Low temperature stage was contributed by small molecules of gas and water. In the middle temperature region, a large amount of gas and tar vapors were evaporated, with semi-coke and coke formed in the process. And volume shrinkage could be observed in the high temperature range. Wu et al. [18] used *n*-level single reaction model to analyze the pyrolysis characteristics of Xinjiang bituminous coal. It was found that wonderful effect can be obtained in the violent pyrolysis stage when the reaction order n=2, and the reaction order n=1 is suitable for the polycondensation and secondary cracking stage.

In this paper, pyrolysis kinetics of Xinjiang Hefeng acid-washing coal (HF_{AC}) and its sequential extract residues from petroleum ether (PE), carbon disulfide (CDS), methanol (*M*), acetone and isometric acetone/carbon disulfide (IMCDSAM) was discussed under the reaction order of n=1-5 with single reaction model by Coats-Redfern method. And the structure and pyrolysis characteristics of the samples were also investigated according to the kinetics parameters.

2. Experimental

2.1. Coal sample

The used subbituminous coal sample was selected from Hefeng, Xinjiang, China. **Table 1** shows the proximate and ultimate analyses of Hefeng coal (HF) and its acid-washing sample by hydrochloric acid and hydrofluoric acid.

It can be seen from **Table 1**, that HF shows the characteristics of high ash, high volatile matter, high ratio of hydrogen carbon and low sulfur. After acid-washing treatment, the ash content in HF_{AC} is greatly reduced, from 21.18% to 1.84%, with the removal rate high of 91.31%, indicating that acid-washing can effectively remove ash

in coal, thus we can study the pyrolysis characteristics of organic matter in coal, and the effect of ash can be ignored.

2.2. Sequential extraction process

The detailed process of aid-washing can be known from our group previous references [19,20]. HF_{AC} was successively extracted with petroleum ether (PE), carbon disulfide (CDS), methanol (*M*), acetone and isometric acetone/carbon disulfide (IMCDSAM) by ultrasonic assisted five-stage extraction. Residues obtained from each stage were recorded as R_i (i=1, 2, 3, 4, 5), and sequential extraction process is shown in **Fig. 1**. The yield, structural characteristics and composition distribution of the extract have been described in the literature [21].

2.3. Thermogravimetric analysis (TGA)

With N_2 as carrier gas, the pyrolysis behavior of HF_{AC} and R_i (i=1, 2, 3, 4, 5) was carried out on a thermogravimetric analyzer SDT-Q600 from TA company. The temperature is raised from ambient to 1000 ºC, with heating rate of 10 ºC/min.

2.4. Pyrolysis kinetics analysis

The pyrolysis kinetics of each sample was studied by conversion and other parameters. In this experiment, Coats-Redfern method was used to calculate the kinetics parameters for the process of pyrolysis with a single heating rate.

According to Coats-Redfern method, it generally has the following expression:

when n=1:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \qquad (1)$$

when $n\neq1$:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \qquad (2)$$

where α is the conversion; n is the reaction order; E is the activation energy, kJ/mol; T

is the kelvin temperature, K; φ is the heating rate, K/min; R is the constant, 8.314 J/(mol·K); *A* is the pre-exponential factor, min^{-1}.

According to the thermogravimetric analysis, the conversion is expressed as follows:

$$\alpha = \frac{m_0 - m_g}{m_0 - m_f}$$

where m_g is the mass of sample at a certain time (or temperature), mg; m_0 is the initial mass of sample, mg; m_f is the ending mass of sample reaction, mg.

The equations (1) and (2) are analyzed. Generally, for most reaction temperature regions and most *E*, the term of $E/RT \geq 1$, $2RT/E \rightarrow 0$. Hence, $(1-2RT/E) \approx 1$, then equations (1) and (2) can be simplified as follows:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\varphi E}\right) - \frac{E}{RT} \qquad (3)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\varphi E}\right) - \frac{E}{RT} \qquad (4)$$

When $n = 1$, let $y = \ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$; when $n \neq 1$, let $y = \ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$; let $x = \frac{1}{T}$.

When *n* takes different reaction orders and plot *y* against *x*, and the regression equation is carried out, with the slope of $-E/R$ and the intercept of $\mathrm{Ln}(AR/\varphi E)$. Activation energy and pre-exponential factor of the reaction can be calculated according to the regression equation.

3. Results and discussion

3.1. TG analysis

Fig. 2 shows TG and DTG profiles of Hefeng acid-washing coal and its extract residues. It can be seen from **Fig. 2 (a)** that there are significant differences in TG profiles to the samples. The weight loss of HF_{AC} is smaller of 41.03%. TG profiles of

147 R_1 and R_2 are basically the same, with weight loss of 54.97% and 55.02%,
148 respectively. TG profiles of R_3, R_4 and R_5 are similar, with weight loss of 42.33%,
149 44.92% and 42.53%, respectively. When temperature is lower than 350 ºC, the weight
150 loss of each sample shows little difference, with the value about 10%. This stage is
151 mainly ascribed to the desorption and decarboxylation of adsorbed water and small
152 molecule gases, and the weight loss accounts for 18%-25% of the total pyrolysis
153 process. In addition, it is not difficult to see that the weight loss of the residues was
154 larger than that of HF_{AC}, which might be derived from that, after solvent extraction,
155 the molecular structure of coal is unstable and some solvents were remained in the
156 residues. Temperature from 350 ºC to 550 ºC is the main thermal decomposition stage,
157 which may be belonged to depolymerization and decomposition of larger molecular
158 structure in coal, accompanied by polycondensation reaction to generate some gases
159 (methane and its homologues, olefins, water, etc.).

160 It can be seen from DTG diagram in **Fig. 2 (b)** that the weight loss rate of R_1 and
161 R_2 is smaller than that of HF_{AC}. This may be due to the fact that volatile substances
162 are dissolved into the extractant after primary and secondary solvent extraction, which
163 might be leading to the molecular skeleton structure is more stable. Moreover, some
164 solvents may enter into the pores of coal molecular structure to form surface tension,
165 which makes pyrolysis process more difficult. While the weight loss rate of R_3, R_4
166 and R_5, from DTG profiles, is larger than that of HF_{AC}, which might be due to the
167 influence of swelling on the molecular structure of coal after many times solvent
168 extraction, and the volume expansion might be taken place to accelerate the process of
169 pyrolysis [22]. When temperature is higher than 550 ºC, aromatic substances
170 condense, and aromatic nuclei increase, and semi-coke forms coke rock. The weight
171 loss of R_1 and R_2 is the largest in this stage. This may be due to the polycondensation

reaction between residual solvents and substances in the residues, releasing a large amount of small molecular gases. The reason for the small weight loss of R_3, R_4 and R_5 might be concluded that the macromolecular channels formed by swelling under high temperature rapidly collapse and agglomerate to produce molecules.

It can also be seen from the DTG profiles that there are two weight loss rate peaks. The first weight loss rate peak appeared at about 100 ºC, corresponding to the evaporation of water and small molecular gases; the second weight loss rate peak is larger, appearing in the between of 400-500 ºC. This range is the main stage of the pyrolysis reaction, and more substances in the sample were depolymerized and small molecular gases were released. It can be seen that the peak value of weight loss rate of R_1 and R_2 is small of -0.14% $\cdot ^{o}C^{-1}$. The peak value of weight loss rate of R_3, R_4, R_5 and HF_{AC} are almost the same, and that of R_4 is larger of -0.22%$\cdot ^{o}C^{-1}$.

3.2. Conversion-temperature diagram

Fig. 3 (a) shows the relationship between pyrolysis conversion and temperature of Hefeng acid-washing coal and the corresponding extract residues. It can be seen that there is little difference for the conversion-temperature profiles of the acid-washing coal and its extract residues. Combined TG-DTG profiles with α-T diagram, pyrolysis process can be divided into three stages [23-25], as shown in **Fig. 3 (b)**. The samples contain a small amount of moisture, so the weight loss below 150 ºC is taken as the initial pyrolysis process. The intersection points A of tangent line of TG and DTG profile is taken as the dividing temperature point of the first stage (S1, 150-350 ºC) and B as the second stage (S2, 350-550 ºC), and the third stage (S3) is ranged from 550-950 ºC. It can be seen from **Fig. 3 (a)** that the change trend of conversion profiles is basically consistent in the stage of 150-350 ºC. And the conversions of extract residues are higher than that of acid-washing coal, which may be due to the

desorption of more small molecules in this stage (**Fig. 2 (a)**). In the stage of 350-550 °C, the conversions increase rapidly, which may be due to that this temperature region is the main stage of pyrolysis reaction, and a large number of substances are depolymerized and decomposed. Moreover, the conversion profiles are divergent in this temperature range, that is the increasing trend of the conversion of R_3, R_4, R_5 and HF_{AC} is more obvious. In the stage of 550-950 °C, the conversion of R_3, R_4, R_5 and HF_{AC} increases slowly, indicating that the pyrolysis process becomes gentle. The result may be caused from that the main reaction in this stage is polycondensation, which is difficult to take place.

3.3. Coats-Redfern kinetic analysis

In order to discuss the pyrolysis kinetic characteristics of the samples, kinetic fitting of each sample in the temperature range of 350-550 °C was carried out by Coats-Redfern method, and the fitting diagram of reaction order n=0.5-5 was obtained, as shown in **Fig. 4**. It can be seen that each reaction order has little effect on R_1 and R_2, which may be due to the samples have a stable and similar main structure. And our previous work [19] showed that extraction process has an effective effect to organic matter, while does not change the main structure of coal. The fitting curves of R_3, R_4, R_5 and HF_{AC} have a large deviation when n=3, indicating that different reaction order can obviously affect the fitting effect. And this phenomenon needs to be further explored from the pyrolysis reaction mechanism.

3.4. Calculation of kinetic parameters

According to the fitting curves, the kinetic parameters, including regression equation (y), correlation coefficient (R^2), activation energy (E), pre-exponential factor (A), were calculated under different reaction orders by Coats-Redfern method. Results were shown in **Table 2**.

It can be seen that the values of R^2 are above 0.9500, indicating that the fitting correlation of each sample is better. Activation energy can reflect the difficulty of pyrolysis reaction. It is not difficult to see that the variation for activation energy is very large after extraction. Residues had lower activation energy than HF_{AC}, indicating that coal after extraction more conducive to pyrolysis. Pre-exponential factor is a constant determined by the nature of the reaction. The value of a varies greatly in different reaction order. Many studies [25-27] have found that the pre-exponential factor has great difference under different reaction conditions. The value of A increases with the increase of heating rate and reaction order, and it is also found that there is a "compensation effect" between activation energy and pre-exponential factor. Coats-Redfern integral formula assumes that the term E/RT is far greater than 1, that is, $2RT/E \rightarrow 0$. Therefore, the smaller the $2RT/E$ value, the better the calculation results of kinetic parameters can meet the preconditions of the formula.

3.5. Relationship between kinetic parameters and reaction order

Pyrolysis is a macroscopic process, and kinetic parameters can reflect the comprehensive performance of pyrolysis process. The higher the reaction order, the more complex the pyrolysis process. The relationship between kinetic parameters and reaction order in the temperature range of 350-550 °C is shown in **Fig. 5**.

Fig. 5(a) shows the relationship between activation energy and reaction order. It can be seen from **Fig. 5(a)** that activation energy increases with the increases of reaction order for each sample, indicating that the higher the reaction order, the more complex the pyrolysis reaction might be. While activation energy presents significant difference for HF_{AC} and its residues, which could be related to the composition difference of each sample after sequential extraction. Ma et al. [28] found that coal sample showed swelling effect in solvent, which is a process of gradual expansion,

247 micro-explosion, pore collapse and formation of fragments, and swelling coefficient
248 with different solvent varies greatly. After the process of ultrasonic-assisted sequential
249 extraction, with pore structure of coal sample collapse, with weak bridge bond
250 destroyed and cross-linked network structure slacked, the extract residues could be
251 swelled under different solvents. Therefore, swelling effect might be an important
252 reason for the discrepancy of activation energy for each sample in the process of
253 pyrolysis.

254 **Fig. 5 (b)** shows the relationship between correlation coefficient R^2 and reaction
255 order. The values of R^2 were all above 0.95, indicating that the correlation effect was
256 acceptable. Correlation coefficient R^2 increases firstly and then decreases with the
257 reaction order, and the value of HF_{AC} reaches the maximum of 0.972 when the
258 reaction order n=2, while the values of all the residues reach the maximum when
259 reaction order n=1.5, indicating that kinetic parameters show more accuracy when
260 reaction order n=1.5-2.

261 **Fig. 5 (c)** shows the relationship between $2RT/E$ and reaction order. $2RT/E \rightarrow 0$ is
262 the precondition for the calculation of kinetic parameters for Coats-Redfern method.
263 The lower the value, the higher the reliability of the model is. It can be seen that the
264 value of $2RT/E$ decreases with the increase of reaction order, indicating that high
265 reaction order can better meet the condition of Coats-Redfern method.

266 Literatures [29-31] found that pre-exponential factor increases when activation energy
267 increases, and the factor decreases when the activation energy decreases, which is
268 called “dynamic compensation effect”. Meng et al. [32] also discovered that there was
269 “dynamic compensation effect” between activation energy and pre-exponential factor
270 in the process of coal gasification, and the gas diffusion has a significant impact on
271 the compensation effect.

The "dynamic compensation effect" can be expressed by mathematical formula as follows:

$$\mathrm{Ln}(A) = qE + p \quad [33]$$

Where q and p are the compensation parameters.

In order to further explore the compensation effect of activation energy and pre-exponential factor, the diagram of Ln(A)-E is plotted, and the profiles are shown in **Fig. 5(d)**. It can be found that the relationship between activation energy and pre-exponential factor is almost a line. And there is a one-to-one correspondence between the activation energy and the reaction order, which could be used to predict the activation energy and the pre-exponential factor under higher reaction order.

4. Conclusions

In this paper, thermogravimetric analyses of acid-washing coal and its extract residues were carried out. Results showed that the weight losses of all stages for extract residues were higher than that of HF_{AC}. Coats-Redfern method was used to fit the pyrolysis kinetics under the reaction order of n=0.5-5 at different temperature stages, and the kinetic parameters were calculated according to the fitting curves. Results showed that, in the medium temperature range, the correlation coefficient R^2 is larger, and the fitting effect is better. Relationship between kinetic parameters and reaction order showed that swelling effect might be an important reason for the discrepancy of activation energy for each sample in the process of pyrolysis, and that high reaction order can better meet the condition of Coats-Redfern method. And Ln(A)-E relationship can be used to predict the activation energy and the pre-exponential factor under higher reaction order.

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Figures

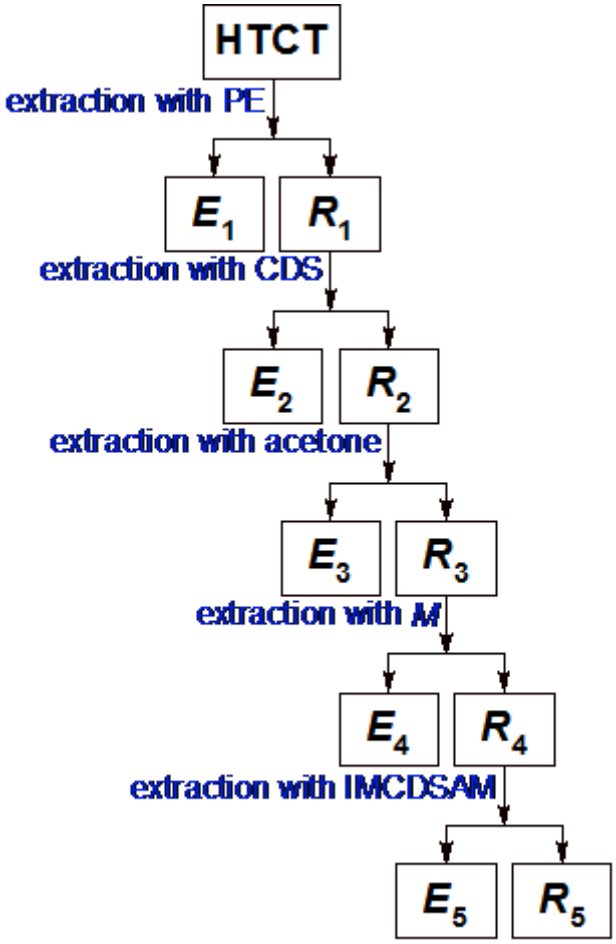

Figure 1

Sequential extraction process of HFAC.

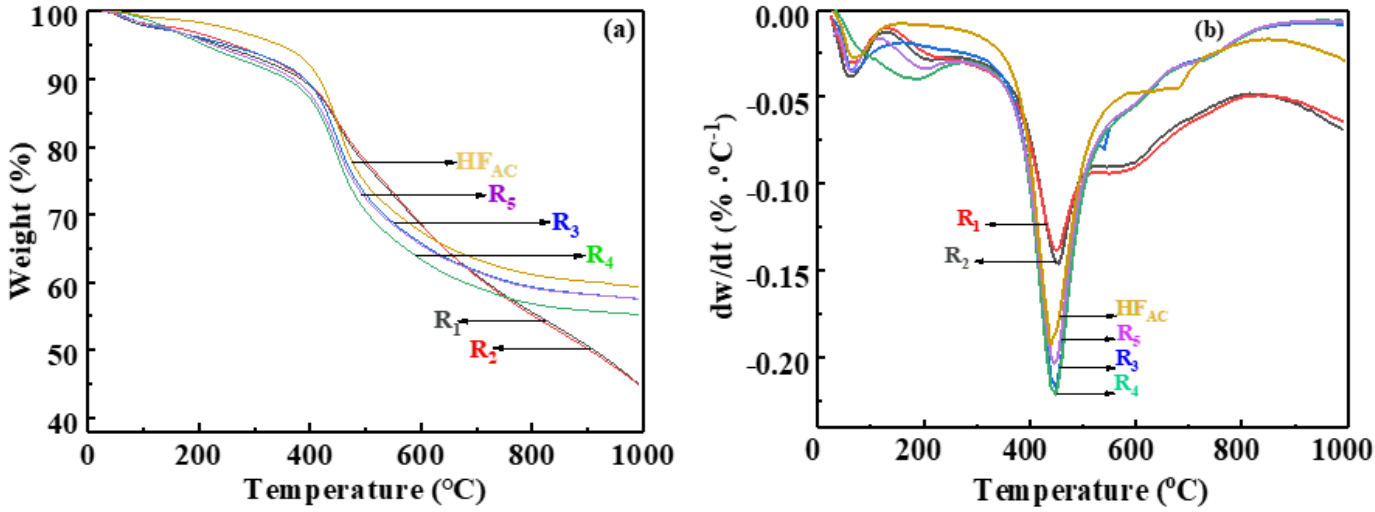

Figure 2

TG-DTG diagram of HFAC and its extract residues

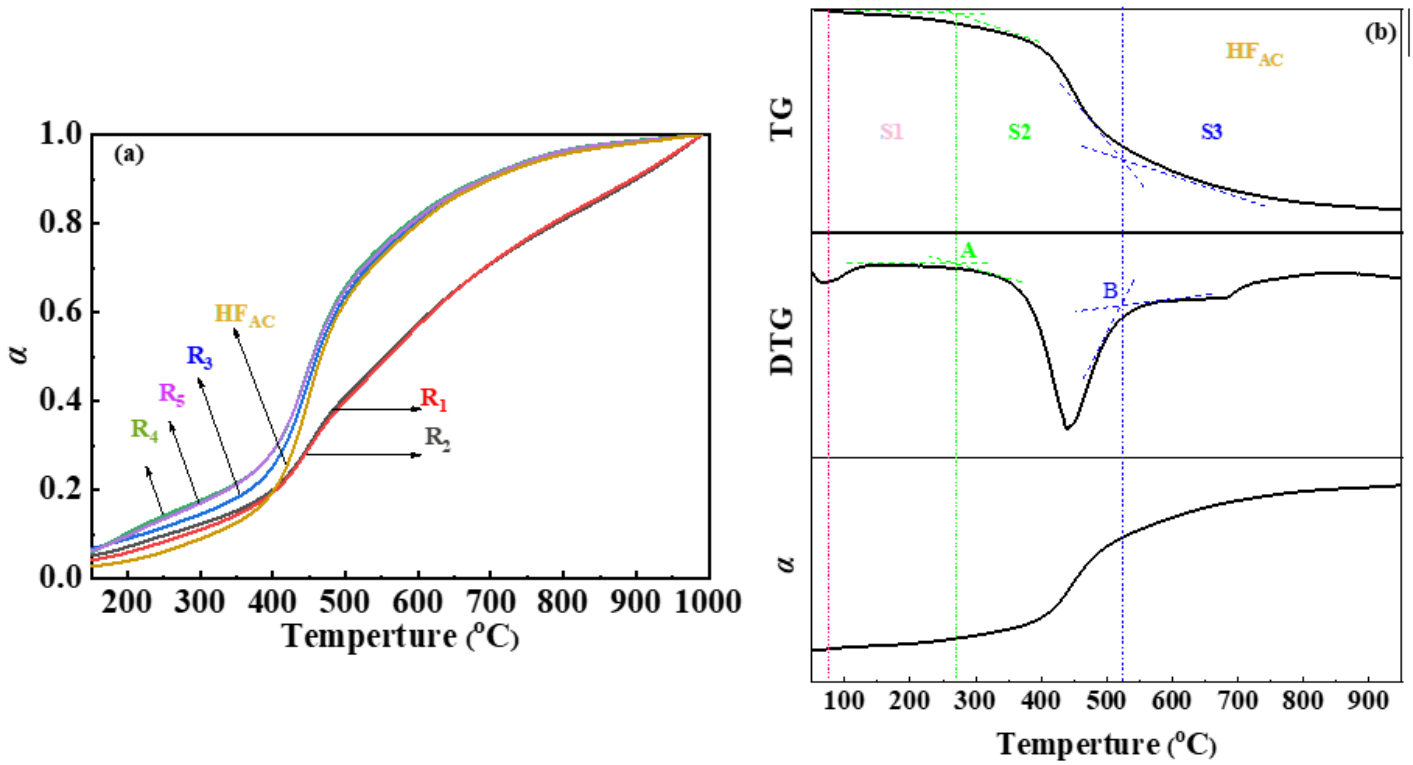

Figure 3

Diagram of conversion to temperature. (a): α-T ; (b): TG/DTG/α-T

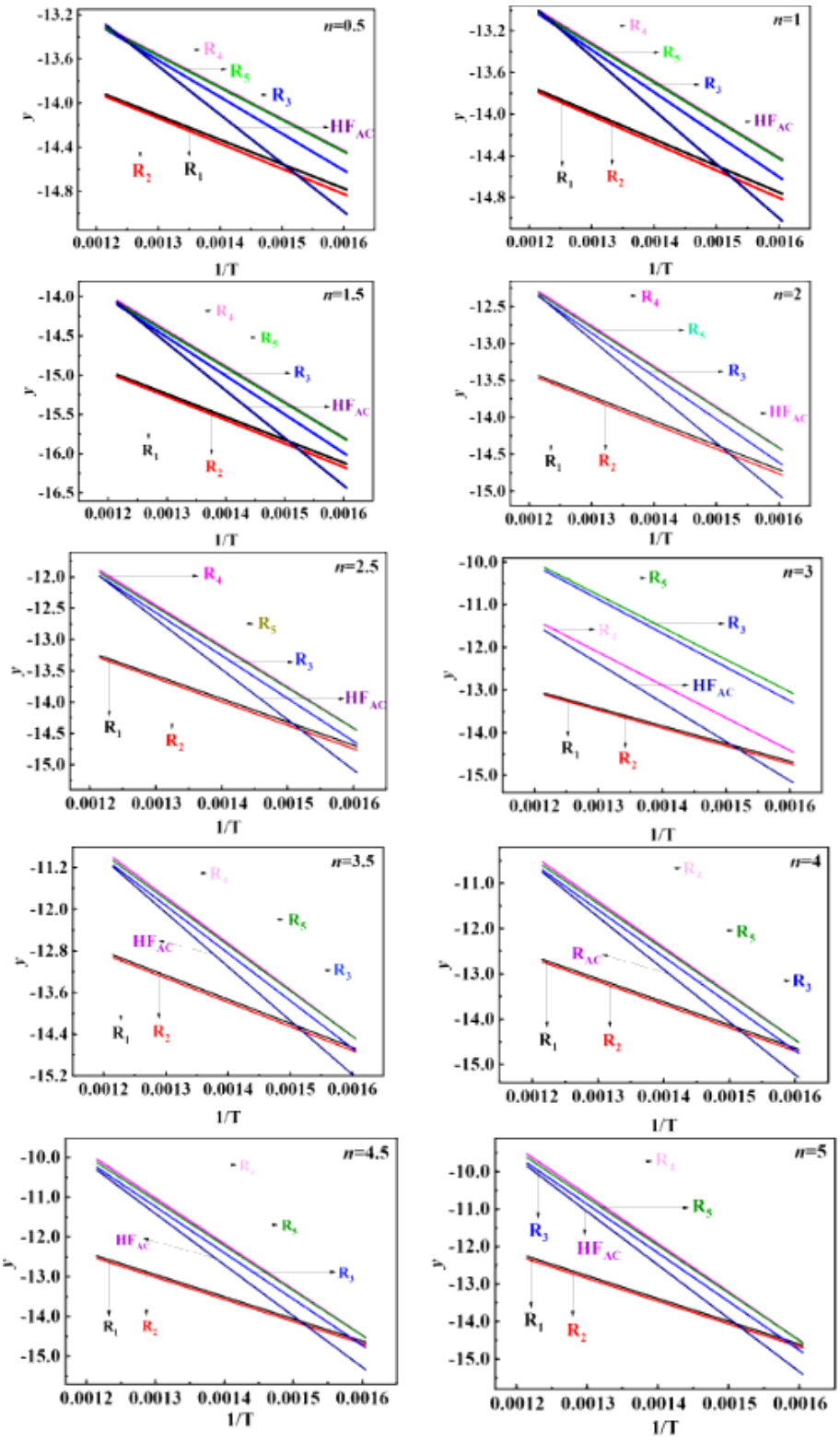

Figure 4

Fitting curves of each sample with reaction order n=0.5-5.

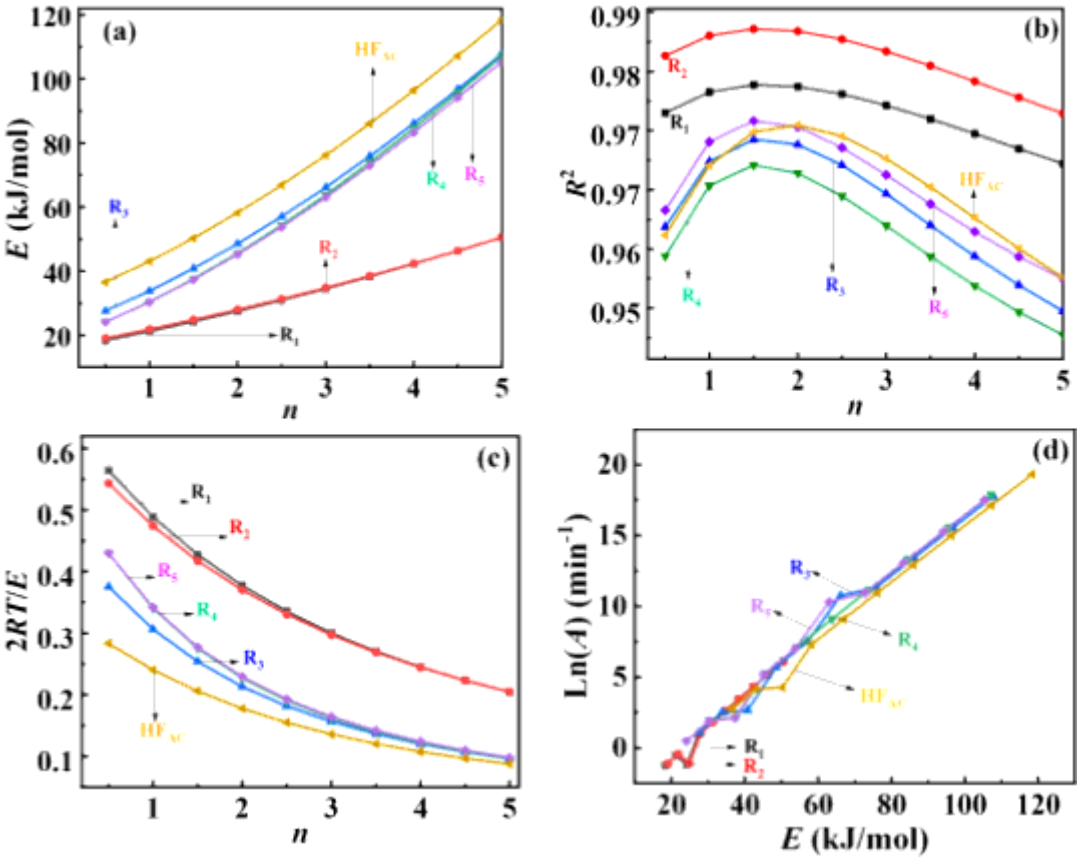

Figure 5

Relationship between kinetic parameters and reaction order.