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RESEARCH ARTICLE

NON ISOTHERMAL DECOMPOSITION KINETICS OF UREA

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ABSTRACT

A study was done of the thermal decomposition of urea at different heating rate by thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA). In this study the activation energy for the thermal decomposition of urea was measured using the Kissinger and Friedmann methods. The two methods produced consistent results revealing the complex decomposition process of urea.

INTRODUCTION

Kinetic analysis of thermal decomposition processes has been the subject interest for many investigators. Kinetics is related with the decomposition mechanisms (Vyazovkin, 2000). Although Kinetic studies can be performed in different devices, but thermogravimetry is the mostly used technique. In a TG experiment, modern equipment typically registers thousands of experimental points that can be used for kinetic analysis of the decomposition. Shortly after reporting how urea decomposes in an open reaction vessel (Schaber *et al*., 2004), researchers have examined the thermal decomposition kinetics of urea. It is apparent from the previous studies that the urea pyrolysis reaction is a very complex and diverse process (Schaber *et al*., 2004). At elevated temperatures, for instance, the primary reaction products are known to exhibit high reactivity and undergo a series of secondary reactions. Hence, this kinetics study is expected to improve our understanding of mechanism of pyrolysis of urea. A kinetic study based on the thermogravimetric analysis (TGA) and differential thermal analyzer (DTA) is known to be helpful in understanding the thermal decomposition of solid materials (Vyazovkin, 2000). These analyses can be done under variable experimental conditions. Traditionally, the reaction model has been chosen from a list of well known reaction models by fitting the experimental data with aid of statistical analyses (Vyazovkin, 2011). This model fitting method mostly uses single heating rates so that it produces a single set of kinetic parameters i.e. activation energy for a whole process. Moreover, the model fitting method is not effective in producing consistent E_α values from non isothermal data. As an alternative approach, the model free method has been demonstrated to produce reliable and consistent kinetic information from both isothermal and non-isothermal processes. The non-isothermal experiment has the advantage of resolving the problem of the isothermal experiment possibly occur during the time needed to reach the set temperature. Unlike the model fitting method, the model free method, which is based on iso-conversional principle, can measure the E_α as a function of the degree of conversion. Thus iso-conversional model free methods adequately reveal the multi step process of materials without making any assumption about the reaction models and consequently help to understand the underlying kinetic schemes.

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MATERIALS AND METHODS

Commercial urea obtained from Fischer Scientific of analytical grade (95%). It was recrystallized from water. This was the highest grade purity available. Urea was stored in an airtight container protected from moisture. Thermo gravimetric analysis of urea and measurements of mass losses (and the first derivative) versus temperature (TGA and DTG), measurements of heat flow versus temperature (DSC), measurements of temperature difference versus temperature (DTA) were determined using a SDT Q600 thermo gravimetric analyzer under N_2(g) (purge) (Fig. 1 and 2).

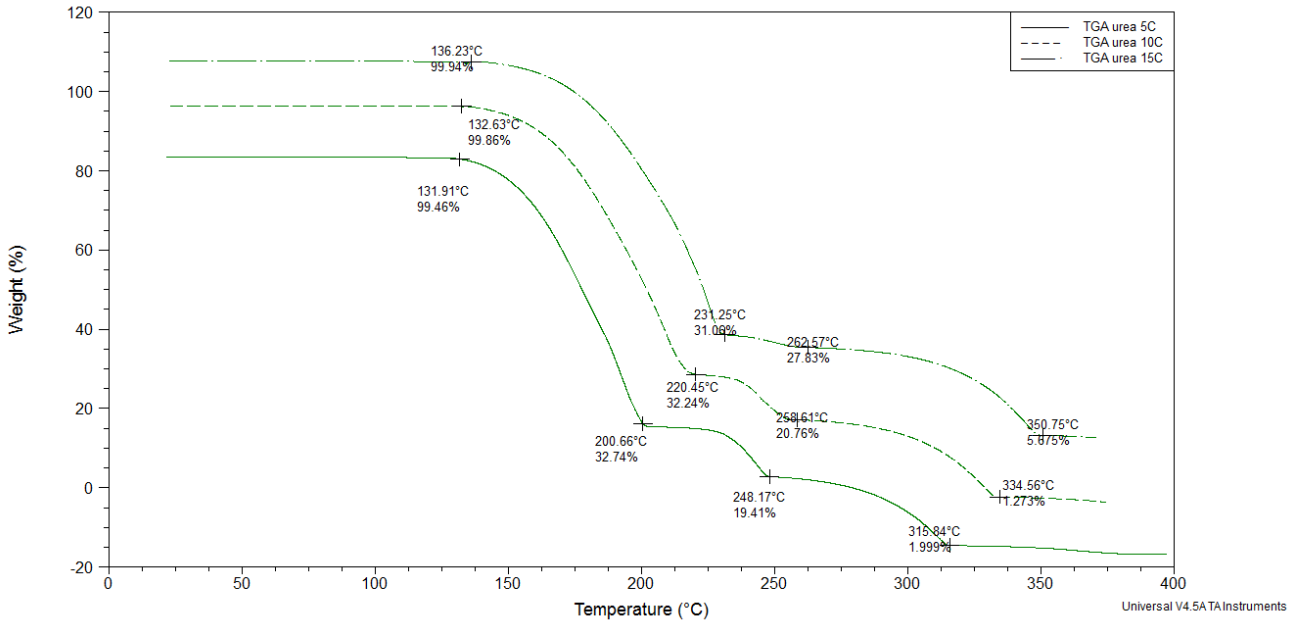


Fig. 1. The results of TGA study of urea thermolysis using different scanning rates

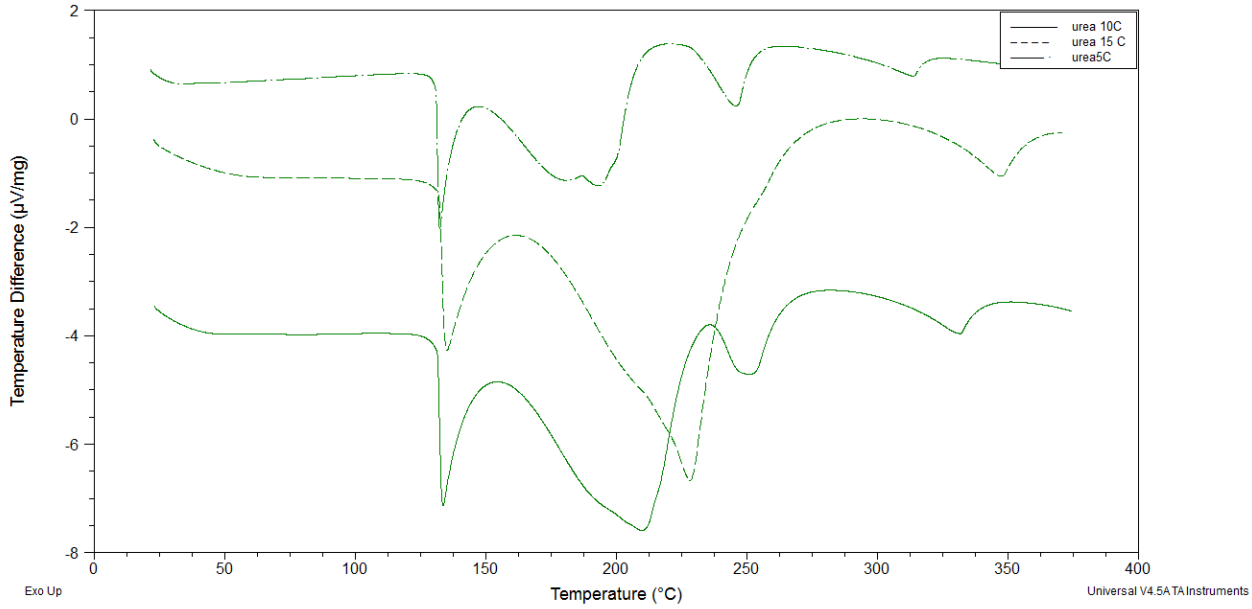


Fig. 2. The results of DTA study of urea thermolysis using different scanning rates

The experiments were performed in 25-380^{0}C temperature range, heating rates varying from 5 to 15^{0}C/min, typically 4-6 mg of sample was placed on a silica pan. Points of rapidly changing mass, slowly changing mass or where phase changes are known to occur (melting points etc.) were identified from the TGA, DTA, DSC and DTG plots.

RESULTS AND DISCUSSION

The energy of activation for the thermal decomposition was determined by the Kissinger (1957) and Friedman methods (1964) from non isothermal experiments. These methods are based on the following fundamental kinetic equations combined with the Arrhenius expression of the temperature dependent rate constant

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \quad (1)$$

Where (conversion)$\alpha = \left(\frac{m_0 - m_t}{m_0 - m_f}\right)$, m_0, m_t and m_f are the initial, time t and final mass of the solid respectively. T is the absolute temperature, A is the preexponential factor, E_α is the activation energy, R is the gas constant and f(α) is the reaction model. In a non-isothermal experiment introducing the heating rate $\beta = \frac{dT}{dt}$ into equation (1) gives

$$\frac{d\alpha}{dT} = \frac{A}{\beta}exp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \quad (2)$$

Integration of both sides of equation (2) gives

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} exp\left(\frac{-E_\alpha}{RT}\right) dT \quad (3)$$

The Kissinger method is based on the fact that the derivative of equation (1) is equal to zero at the maximum reaction rate. After differentiating, taking its logarithm form gives

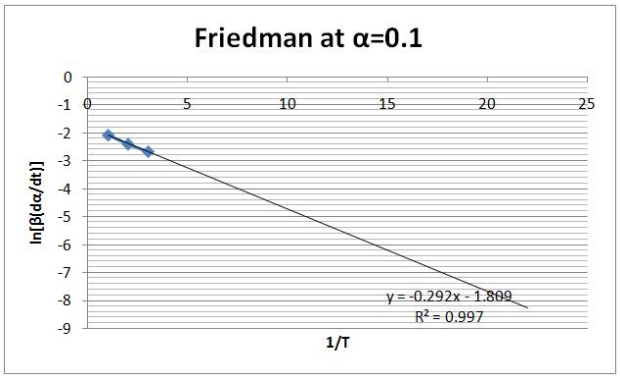
$$ln\left(\frac{\beta}{T_m^2}\right) = ln\left(\frac{-AR}{E_\alpha} f'(\alpha_m)\right) - \left(\frac{E_\alpha}{RT_m}\right) \quad (4)$$

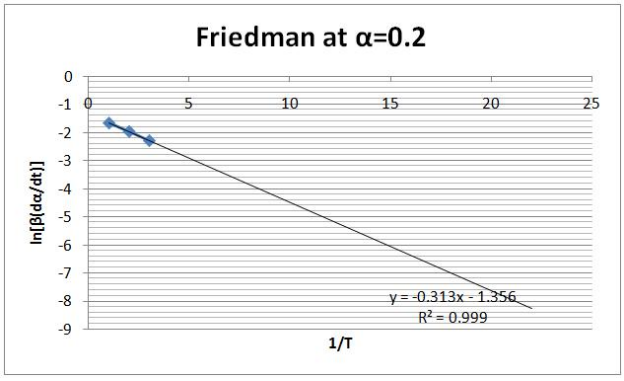
Where T_m is the temperature at the maximum mass loss rate and α_m is the conversion at that point. Since $f'(\alpha_\beta)$ is approximated to be a constant, the E_α can be obtained from the slope of the plot $\ln\left(\frac{\beta}{T_m^2}\right)$ against $\frac{1}{T_m}$ for a series of experiments at different βs. The Friedman method is an iso-conversion method consisting of taking the log of the equation (2)

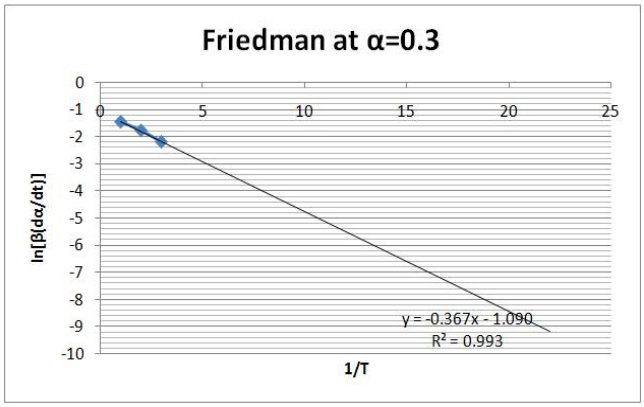
$$\ln\beta\left(\frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E_\alpha}{RT} \quad (5)$$

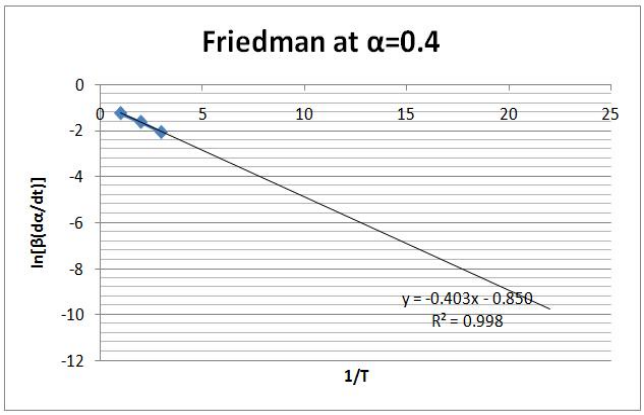
Dependence of E_α on conversion

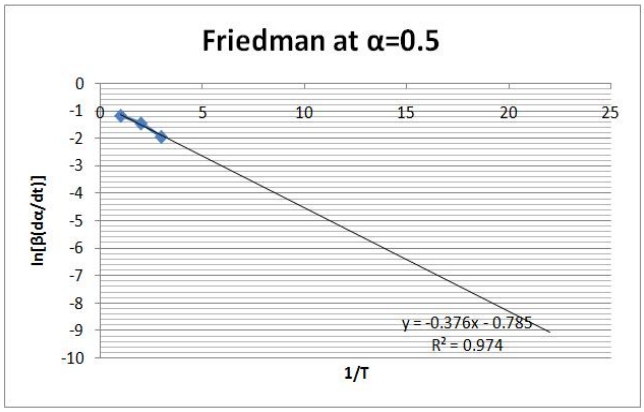
To understand how urea decomposes the dependence of E_α on conversion throughout the whole pyrolysis process was examined using isoconversional Friedman method. The Kissinger method generally produces E_α consistent with isothermal kinetic information. But since a single E_α is obtained based on the maximum decomposition rate temperature, this method has a weakness when it comes to identifying the kinetic scheme. On the other hand, the isoconversional method can measure the dependence of E_α on conversion in the whole process. In this study the E_α was measured in the coversion range of 0.05-0.95. According to Friedman equation the plot of $ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right]$ vs $\frac{1}{T}$ for the pyrolysis of urea is shown in Figures.

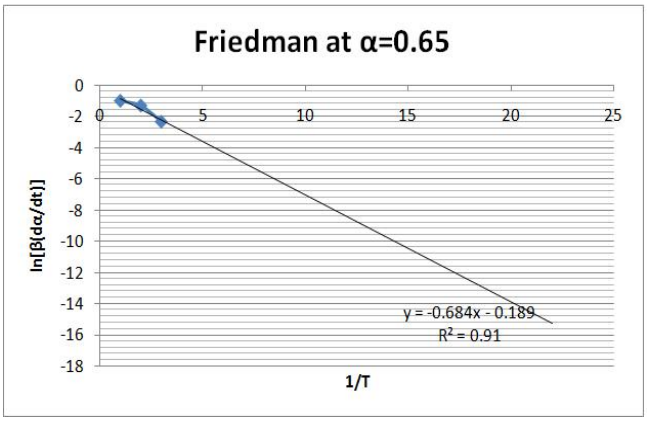


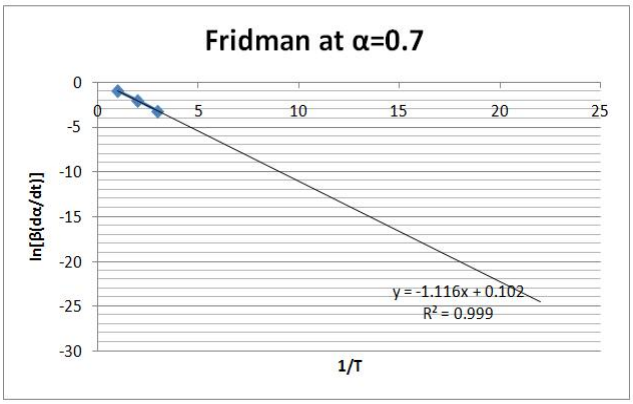


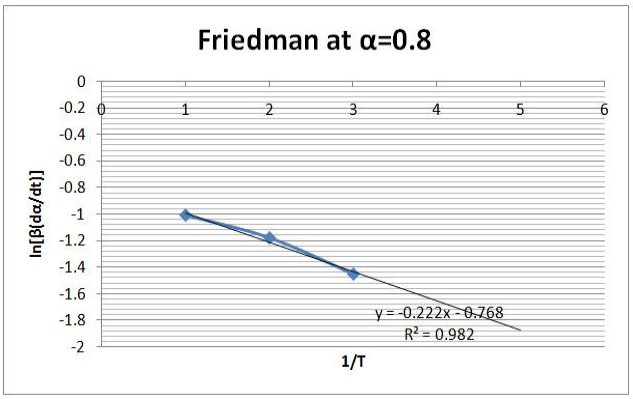


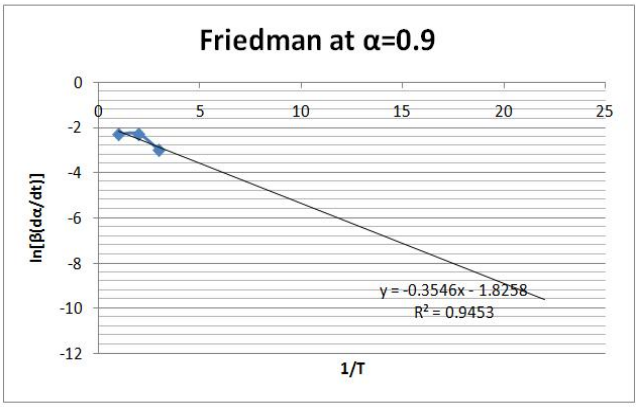


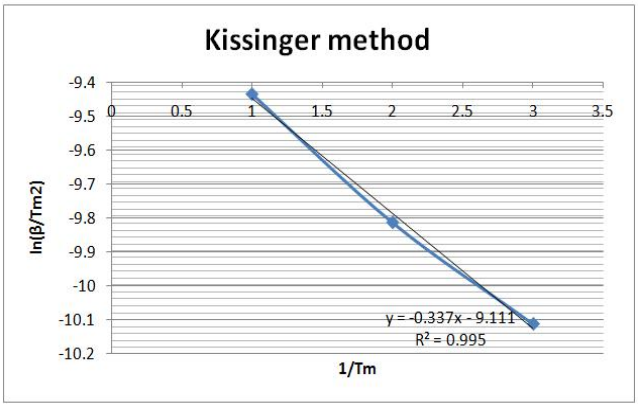




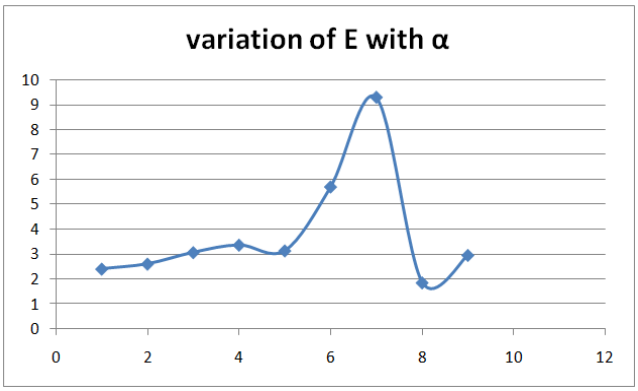








Decomposition of urea exhibited straight lines (r > 0.99) in the entire conversion range studied, signifying the feasibility of the method. The E_α values determined by the Friedman method are plotted against conversion. Recently Vyazovkin (2000) have studied the type of reaction steps (single or multiple) depending upon the variation of E_α with α. If E_α is roughly constant over the entire conversion range then the process is dominated by a single reaction step. On the other hand, if it has peaks then multiple step process dominates. In our case, multiple peaks are obtained confirming the multi step and complex decomposition of urea.



The average value of E_α (3.8J/g) obtained by Friedman method is a little higher than determined by the Kissinger method.

Conclusion

The kinetic study helped better understanding the decomposition steps of urea. Decomposition of urea exhibited straight lines (r > 0.9) in the entire conversion range studied, signifying the feasibility of the method. Peaks are obtained in the variation of E_α with α indicating the complex process.

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