



## Effect of different heating rate on the thermal decomposition of urea in an open reaction vessel

Fouzia Rafat

Department of Chemistry (Research & P. G. Section), Vinoba Bhave University, Hazaribagh, Jharkhand, India

### ABSTRACT

A study was done of the thermal decomposition of urea at different heating rate by thermogravimetric analyzer (TGA). The temperature and enthalpy of fusion of urea were calculated based on TG experiments carried out using different heating rates varying from 5 to 15<sup>0</sup>C/min. Thus it was made possible to compare the contributions to the total thermal effect of urea fusion and thermal decomposition process.

**Keywords:** Thermogravimetric analysis (TGA), heating rate, differential thermal analysis (DTA), DSC, DTG

### INTRODUCTION

The first experiments on urea thermal decomposition were reported by F. Wohler[1] in 1829. Details of the reaction mechanism have been studied for many years and recently a temperature dependent reaction scheme based primarily on product distribution has been proposed.[2] Schaber et al found that this reaction proceeds by a very complex and diverse pathway. It has been known that the primary decomposition products exhibit high reactivity and undergo a series of secondary reactions.

The pyrolysis of urea is relevant to a variety of academic and industrial disciplines. Urea is a high demand fertilizer. It is now widely used in a great variety of applications. It is attractive because of its abundance in nature, its stability at room temperature, its ease of storage and its low toxicity in comparison with alternative substances.[3]

One of the most promising technologies to achieve a reduction of NO<sub>x</sub> in diesel engine is SCR[4] (Selective Catalytic Reduction). The idea behind the concept is to inject ammonia into the exhaust system and NO<sub>x</sub> will be reduced to N<sub>2</sub>. But, due to the difficulty of ammonia storage in vehicles, the use of urea as an ammonia source is becoming a more viable method.

The search for reliable information is mostly due to the fact that the decomposition reactions for urea are complex and depend on several conditions, either temperature, heating rate, pressure, open or closed vessel. And the influence of each parameter is not yet fully understood.

The focus of the current work is to present the comparable study of decomposition of urea at different heating rate, namely from 5 to 15<sup>0</sup>C/min.

### 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.

Thermogravimetric 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 thermogravimetric analyzer. Nitrogen was used as a purge gas with a flow rate of 100 ml/min. The experiments were performed in 25-380°C temperature range, heating rates varying from 5 to 15°C/min. About 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

Results show that depending on the heating rate, different behaviours in the thermograms are observed. This is due to the different reactions taking place in the vessel induced by the different conditions under which the pyrolysis of urea is performed.

The TG experiments proved that urea decomposes slightly before melting. (Fig.1) Chen and Isa[5] have also observed only a small mass change prior to urea's melting point which is consistent with our data. We analyzed the heating rate influence on the melting point and mass loss before melting point. It has been found that at a faster rate, melting point was higher while the mass loss was smaller. (Table) The melting point variation can be explained by cryoscopic effect. The resultant product of the decomposition acts as an impurity and decreases the melting temperature. Hence greater the mass loss, smaller be the melting point.

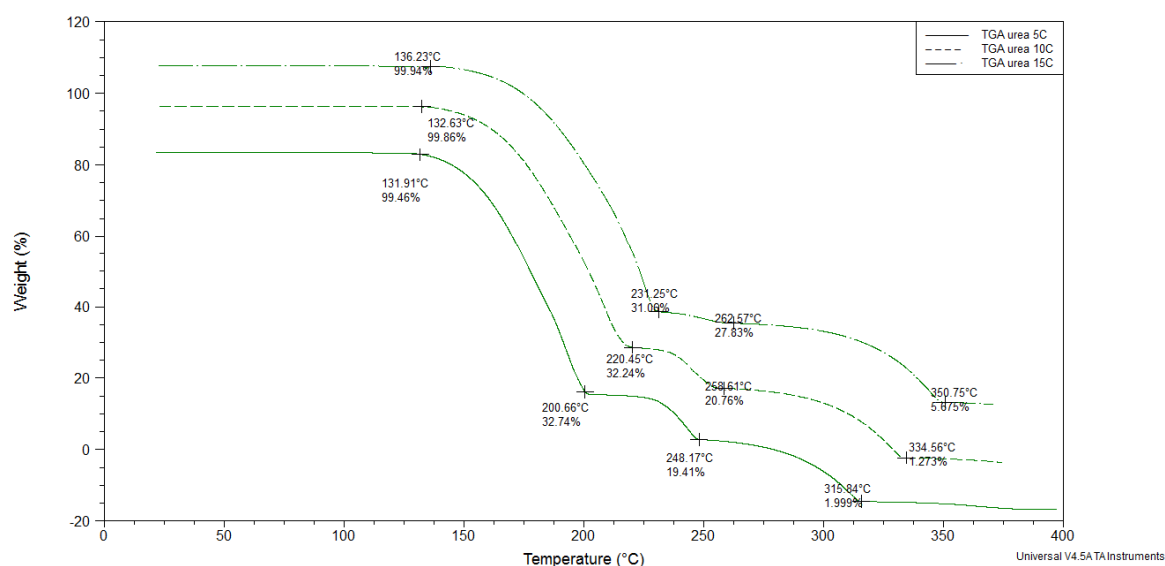
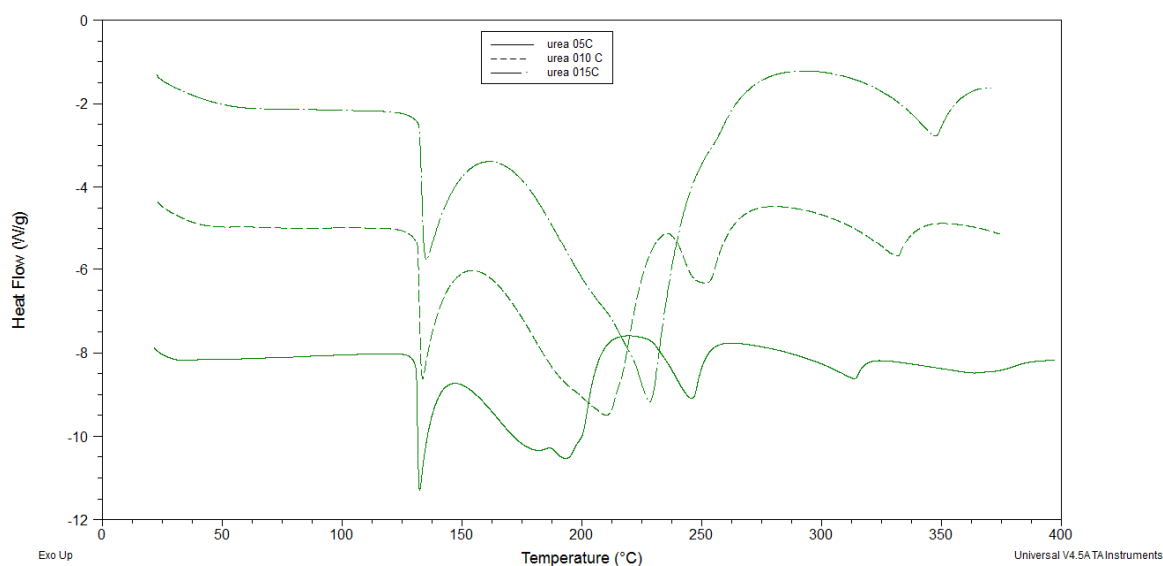


Fig.1 The results of TGA study of urea thermolysis using different scanning rates

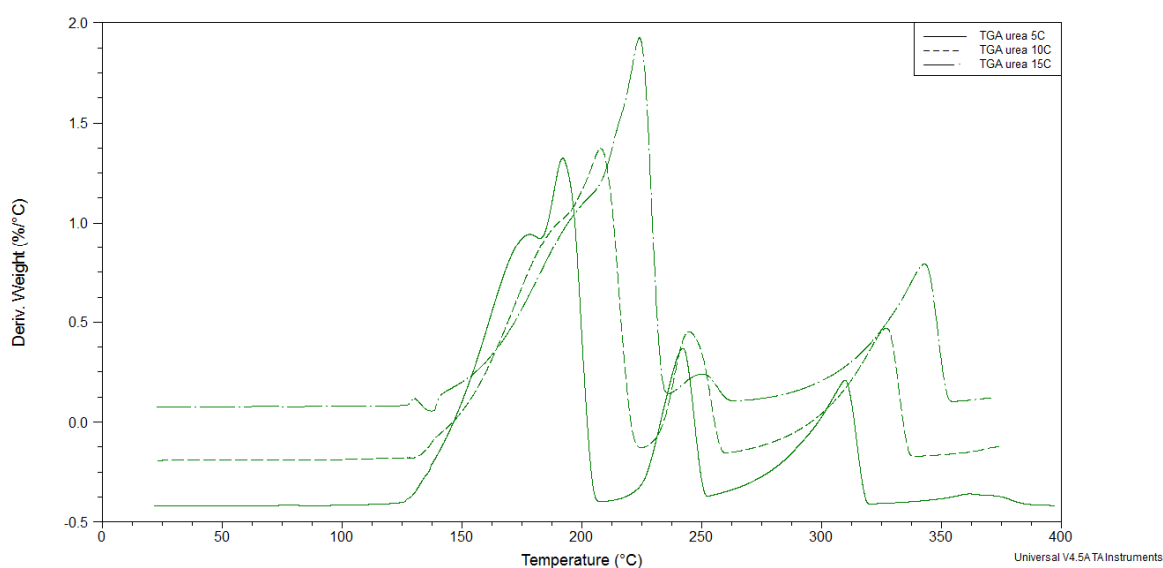
The results of DSC plot could be used directly to estimate heat of fusion. Increasing heating rate leads to an increase of heat of fusion. The values are given in Table. From the DSC plot it also appears that on increasing the heating rate, temperature range where liquid urea may exist also increases. It may be explained on the basis that at a high heating rate, heat is dissipated much more easily and hence decomposition starts at a comparatively higher temperature and also have high heat of fusion.

In each case three major stages of mass loss are observed. (Fig.1) The pyrolysis reaction of urea in an open reaction vessel can be divided into three major reaction regions. These regions are dominated by different chemical processes associated with the mass loss stages observed in the TGA.

Schaber et al[6] reported that in the first decomposition region urea decomposes to biuret. We found that when it was heated at a faster rate, the temperature at the start of the first decomposition and the final temperature on completion of first decomposition were higher than that obtained at a slower rate of heating. Furthermore, the difference between these two temperatures was also higher for faster rate.



**Fig.II** The results of DSC study of urea thermolysis using different scanning rates



**Fig.III** The results of DTG study of urea thermolysis using different scanning rates

Changing heating rate leads to a simultaneous decrease of the effect temperature and an increase of the heat effect. If the heating rate increases, higher temperature is required to set off the decomposition process. At the same time, the amount of decomposition products decreases, which explains the difference between the effect temperature and heat effect. Fig. I-IV show that while heating rate steadily decreases with a reduction in effect temperature, the heat effect rises. We observed decreasing mass loss with increasing scanning rate.

The endothermic minima respond to the decomposition of urea into biuret, which in all three cases takes place at slight different temperature range but the reaction heats absorbed are closely similar to each other. The exothermic peaks are much more varied, at a temperature range of 250-300°C. They are undoubtedly related to the crystallisation process as could be proved by DSC plot. The area under exothermic peak should be proportional to the concentration of the crystalline polymer.

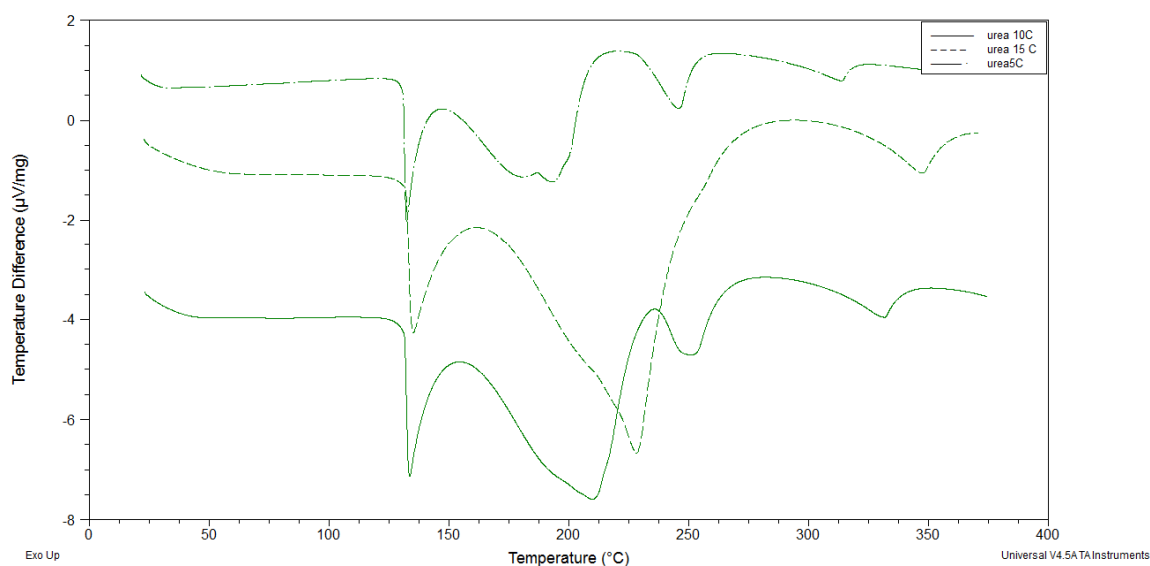


Fig.IV The results of DTA study of urea thermolysis using different scanning rates

Table 1

Heating Rate ( $\beta$ )	Temperature range where liquid urea exists ( $^{\circ}\text{C}$ )	Heat of fusion (kJ/mol)	Melting temperature ( $^{\circ}\text{C}$ )
5 $^{\circ}\text{C}/\text{min}$	4.46	12.4	132.48
10 $^{\circ}\text{C}/\text{min}$	7.0	13.1	133.71
15 $^{\circ}\text{C}/\text{min}$	9.91	13.5	135.21

## REFERENCES

- [1] Wohler F. *Ann.Phys.*,15 (**1829**) 619-630.
- [2] Schaber P.M., Colson J., Higgins S., Dietz E., Thielen D., Anspach B. & Brauer J. *Am.Lab.* 31 (**1999**) 13-21.
- [3] Rollinson A.N., Jones J.M., Dupont V. & Twigg M.V. *Energy Environ. Sci.*, 4 (**2011**) 1216-1244.
- [4] Salanta G.,Zheng G., Kotrba A. & Rampazzo R. *SAE Int. Tech. Paper* (**2010**) 01-1938.
- [5] Chen J.P. & Isa K. *J. Mass spectrum. Soc. Jpn.* 46 (**1998**) 299-303.
- [6] Schaber P.M., Colson J., Higgins S., Thielen D., Anspach B. & Brauer J. *Thermochimica Acta*, 424 (**2004**) 131-142.