

DRY TOILET 2015
5th International Dry Toilet Conference



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W. John Steve KABORE is a researcher in environmental engineering and a PhD candidate at Hokkaido University, Japan. His research topic is related to Resource Oriented Sanitation (ROSan) aiming to reclaim nutrients from human excreta and reuse them in diverse fields such as agriculture. He focuses on the production of nitrogen slow released fertilizer from human urine. As a national from developing countries, he aims to provide solution to rural farming in those areas. Commercially available fertilizers are not affordable for farmers and the reuse of excreta is an alternative. He is now trying to conclude the main part of his research by studying the process (chemical kinetics) for an industrial scale production.

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Effect of Formaldehyde/Urea ratio on thermal properties of methylene urea from human urine
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Abstract

The effect of the Formaldehyde to Urea (F/U) ratio on methylene urea from human urine was evaluated. Elemental analysis, thermal analysis, SEM and XRD were performed on the samples. As results, F/U had no impact on the chain length of the polymers that precipitated. The temperature required to degrade the polymers was decreasing as F/U was increasing. For higher F/U ratio, the degradation rate was decreasing. The required enthalpy for the degradation was higher for low F/U. The particles were more crystalline and well consolidated as F/U was smaller.

Key words: TGA-DTA; DSC; methylene-Urea

Introduction

The world consumption of nitrogen fertilizer is gradually increasing and the total demand will be about 116 million tons in 2016 (FAO, 2012). Some of the human wastes contain important amount of nitrogen that is released in the environment. Recovering this nitrogen might be a solution to mitigate the world demand of nitrogen fertilizer. Considering that, Ito (2013) proposed the recovery of nitrogen from Human urine. Formaldehyde reacts with urea in urine and precipitates as solid polymers particles of methylene urea. From visual observation it was noticed that when the formaldehyde to urea ratio (F/U) was increased the precipitates respectively changed from consolidated blocs of particles to fine powder.

As methylene urea is a slow released fertilizer, it has a ability to be degraded in the soil system and slowly release the nutrient necessary for the growth of crops. The degradation follows four steps: (1) deterioration of the surface, (2) fragmentation into low molecular weight, (3) assimilation by microorganisms, (4) mineralization to produce the nutrients. However, abiotic parameters such as thermal properties have a strong influence and are able to condition such degradation process.

Therefore, the objective of this research was to study the effect of Formaldehyde/Urea (F/U) mixture ratio on the thermal properties of the polymers.

Material and Methods

Synthetic urine solution simulating real urine was used in the experiments. Its composition is summarized in Table 1 (Wilsenach et al., 2007). Two hundred millilitres of the synthetic urine was taken in a beaker, then its pH was adjusted at 2 with 1 mol/L hydrochloric acid solution (JIS special grade, Wako Pure Chemical Industries). The reaction temperature was kept at 25 °C in a water bath. Thirty six percent formaldehyde solution (JIS special grade, Wako Pure Chemical Industries) was added to the solution to start the reaction with mixing by a magnetic stirrer. The ratio of added amount of formaldehyde to the urea (F/U) in synthetic urine is collected in Table2. Samples were taken after 24 hours of reaction and filtrated with glass fiber filters (Advantec GB-140). Solid recoveries from filtrations were dried for another 24 hours at 105°C. All samples were then subject to Elemental analysis a using CN coder (Sumigraph NC-220F). Then, ThermoGravimetric - Differential Thermal Analysis (TG-DTA) to measure weight loss, temperature changes and degradation rate by Differential Thermo Gravimetry method (DTG) were perfomed. SII Exstar 6200 device was used for a

simultaneous TG-DTA and DTG with flowing purge gas technique with nitrogen for furnace atmosphere control at 100ml/min. 45 μ L alumina open crucible pan was used as reference and as sample container. Samples weight was about 10mg and experiments were replicated 3 times. Temperature regime applied to the samples was from room temperature up to 800°C at 10°C/min. However, for better peaks resolution, heating rate was reduced to 1°C/min within the range of 150-400°C (Figure 1) . For the measurement of specific heat of the samples, a means of Differential Scanning Calorimetry (DSC) was performed later under the same conditions of gas and temperature, using opened aluminium crucibles as reference and as sample holder. Granular shape of the precipitates was investigated using a scanning electron microscope (SEM).

Results and discussions

Elemental analysis

The molecular structure of the polymer $[UF]_n$ is presented on Figure 2. The weight percentage of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) were determined in the precipitates as shown in Table 3. The data of weight percentage were converted to moles ratio then, using the molecular structure of the polymer it was possible to approximate the degree of polymerization n from theoretical calculations. From this elemental analysis, we observed that all the polymers had the same chain length regardless the ratio with a degree of polymerization n equal approximately equal to 3. This mean the F/U ratio had no effect on the chain of the precipitated polymers.

TG-DTA

Figures 3-5 show respectively the results for F/U =0.5, F/U =1 and F/U =5. Analyses have been done by focusing on target temperatures: T_b , the beginning of degradation is the temperature corresponding to the first change of slope on TG curve. T_p , is the peak temperature of degradation represented by an endothermic peak on DTA and associated with maximum weight loss in the polymer. T_e is the temperature at the end of degradation and is associated to second change of slope on TG. The data on these temperatures are summarized in table 4. Comparative analysis of T_p from showed a decrease of the temperature required to degrade the polymers as F/U was increasing.

The TG curves showed that 10% weight loss occurred in all samples in the region of 25°C to 200°C just before the degradation. Visual observation of the polymers within this region didn't show any significant change on their physical integrity. Also, this weight loss was not associated to any discrete peak of DTA. Regarding these facts, the assumption made is that the weight loss was due to the presence of easy volatile particles in the polymers who disappeared by sublimation.

About 80% of the total weight was lost in the region of 200°C to 270°C by endothermic reaction as shown by DTA peaks orientation (under the baseline). The polymers absorbed heat during the degradation then remained as ash when T_e was reached. In the region of 400°C, the DTA showed a release of energy which is due to the transformation of the polymer into ash.

DTG

Figure 6 shows the degradation rates when the peak temperature for degradation in the polymers T_p , is reached. Polymers with high T_p requirements were also associated to high degradation rates (Table 5). As we already know from elemental analysis that the polymers have the same chain length, the difference observed on the degradation rate might be due to a difference in their crystallinity.

DSC

During their degradation the polymers absorbed power that can be converted to the enthalpy of degradation. The areas under the peaks of DSC represent this enthalpy of degradation (Figure 7) and Table 6 summarizes the data. Enthalpy requirement was increasing as F/U was decreasing. In this case also, we assumed that the F/U ratio affect the crystallinity of the polymer. Lower F/U produced harder crystal that required more enthalpy to be degraded.

SEM

After drying the precipitates, it was possible to observe that from low F/U ratios to higher ones, the precipitates respectively changed from consolidated blocs of particles to fine powder. Figure 8 shows that the precipitate from F/U=0.5 are mainly sharp crystals. In the contrary, Figure 9 and Figure 10 shows that the particles were becoming finer and tending to aggregate themselves as F/U was increased.

XRD

The results in Figures 11-13 show that the 5 peaks main have the same pattern and are located in same position of 2θ angle. This means the molecular structure is the same, even when F/U is changed. It is also a confirmation of elemental analysis results. However the peaks intensities were decreasing when F/U was increasing. Figure 14 shows the decrease of intensity of P1 and P2. These peaks were selected because they were present in both urea and formaldehyde XRD spectrums. The slopes of decrease followed by those peaks describe the diminution of crystallinity as F/U is increased. In this particular case, two parameters can affect the peak intensities: the atomic number of the atoms or the orientation of the particles. The latter appear to be the most expected. For well consolidated crystal, the particles are oriented on the same direction and the peaks intensities are high. This is why the peaks intensities for F/U = 0.5 were higher and the results of SEM showed some crystalline particles. At the opposite, crystals with random particles orientation have shorter peak intensities. The peaks intensities for F/U = 1 and 5 were getting smaller and SEM also showed that the particles were smaller and tending to be amorphous.

CONCLUSION

The results of this research allowed to know the effect of F/U ratio on the physical properties of methylene urea from human urine:

- The chain length or the degree of polymerization of the polymers was constant and not affected by F/U ratio.
- The temperature required to degrade the polymers was decreasing as F/U was increasing.
- For higher F/U ratio, the degradation rate was decreasing.
- The required enthalpy for the degradation was higher for low F/U
- The particles were getting smaller as F/U was increased.
- The crystallinity of the precipitate was affected by F/U.

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Figures and tables

Chemicals	Concentration (mmol/L)
MgCl ₂ ·6H ₂ O	3.2
NaCl	78.7
Na ₂ SO ₄	16.2
Na ₃ (C ₆ H ₅ O ₇)·2H ₂ O	2.6
KCl	21.5
C ₄ H ₇ N ₃ O	9.7
CaCl ₂ ·2H ₂ O	4.4
KH ₂ PO ₄	30.9
NH ₄ Cl	18.7
(NH ₂) ₂ CO	417
Na ₂ (COO) ₂	0.15
C ₆ H ₈ O ₆	0.57

Table 1: Components of synthetic urine

Volume of Urine (mL)	F/U ratio	Volume of Formaldehyde (mL)
200	0.5	2.48
	1	6.95
	5	34.75

Table 2 Amount of formaldehyde and corresponded ratio to urea.

F/U ratio	Element in weight %				Element in moles %				Corresponding chain length
	C	H	N	O	C	H	N	O	
0.5	0.304	0.055	0.379	0.262	1.545	3.383	1.654	1	3
1	0.316	0.056	0.364	0.265	1.591	3.386	1.571	1	3
5	0.323	0.056	0.346	0.275	1.564	3.270	1.439	1	3

Table 3: Conversion to determine the chain length of the precipitate

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Ratio	Temperature °C		
	T _b	T _p	T _e
0.5	208.12	264.24	283
1	197.11	253.18	274.03
5	196.31	237.97	266.42

Table 4: Temperatures related to change of state in the polymers

Ratio	T _p (°C)	DTG (µg/min)
0.5	264.24	254
1	253.18	219.25
5	237.97	186.72

Table 5: Degradation temperatures and degradation rates

Ratio	Power (µW)	Approximative enthalpy (kJ/g)
0.5	8198	1.383
1	5280	1.014
5	3973	0.653

Table 6: Conversion of power absorption to enthalpy

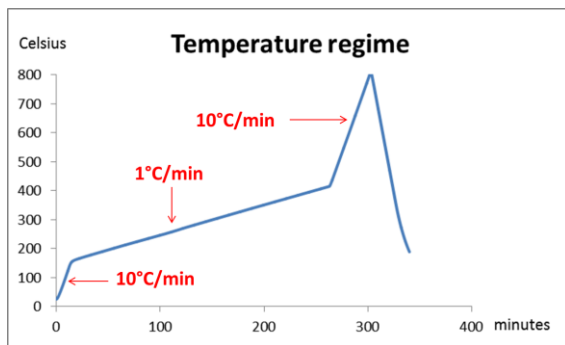


Figure 1: Temperature regime

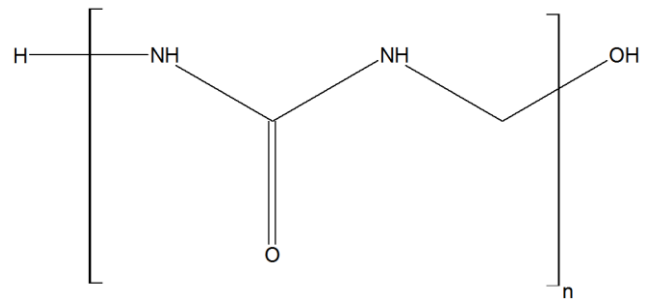


Figure 2: Molecular structure of the polymer [UF]_n

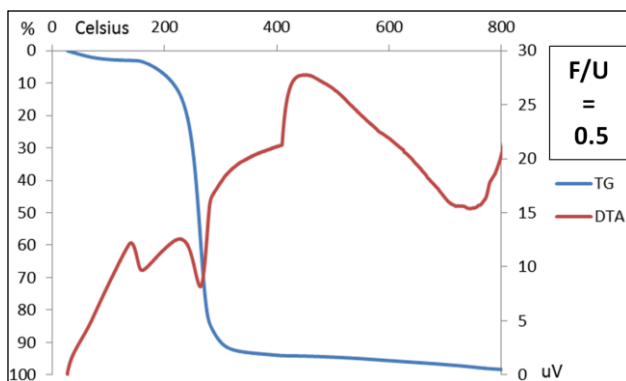


Figure 3: TG-DTA F/U = 0.5

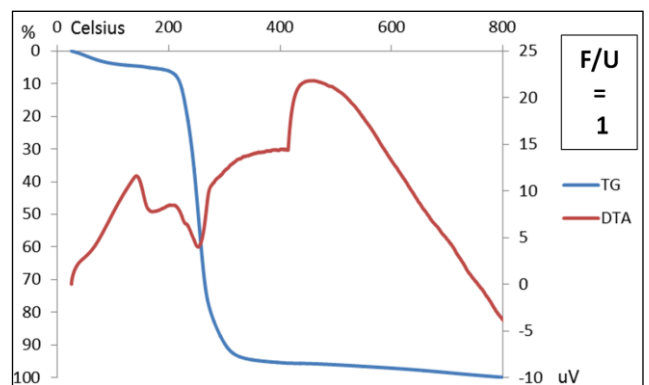


Figure 4: TG-DTA F/U = 1

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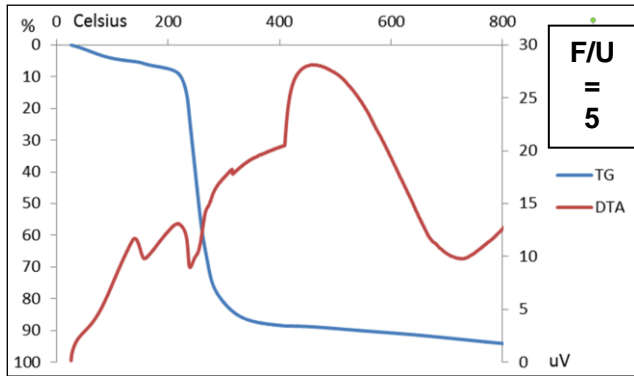


Figure 5 TG-DTA F/U = 5

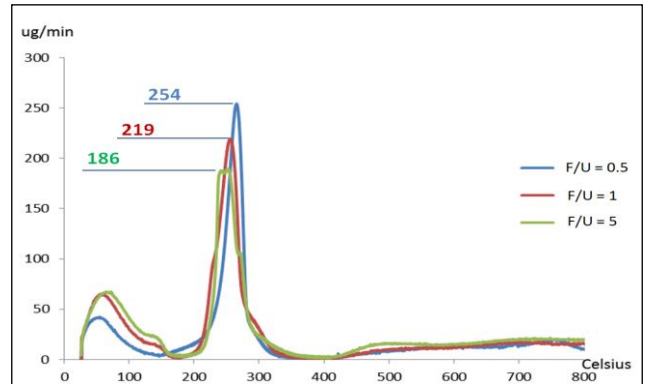


Figure 6: Degradation rate of precipitated samples
F/U = 0.5, 1, 5

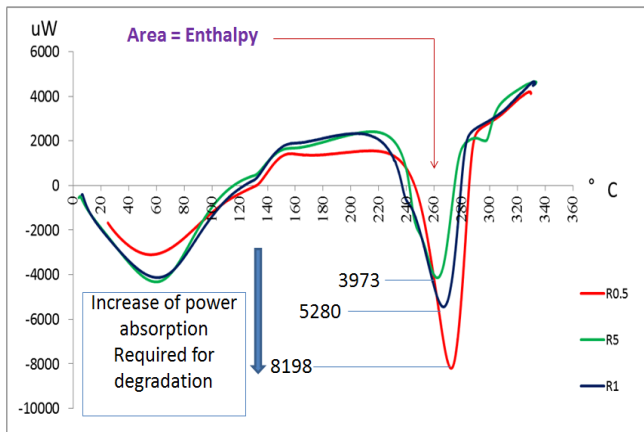


Figure 7 : DSC F/U = 0.5, 1, 5



Figure 8 : SEM F/U = 0.5

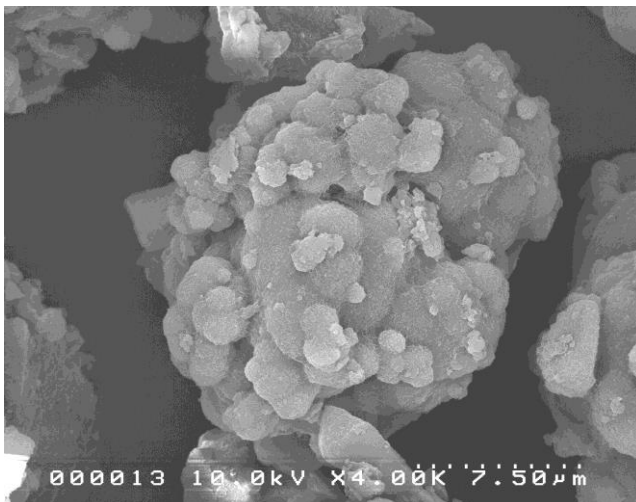


Figure 9 : SEM F/U = 1

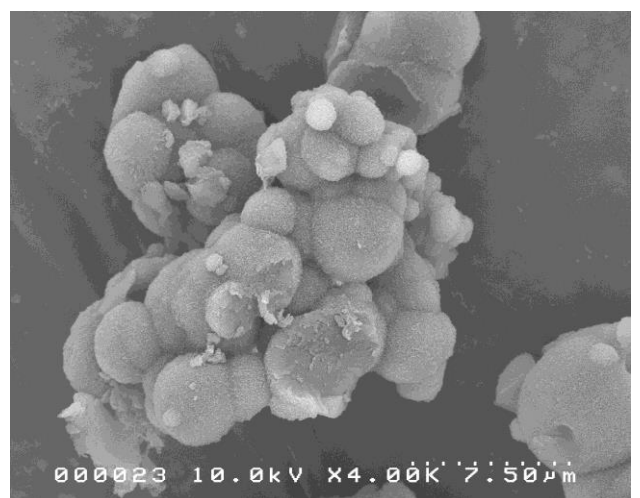


Figure 10 : SEM F/U = 5

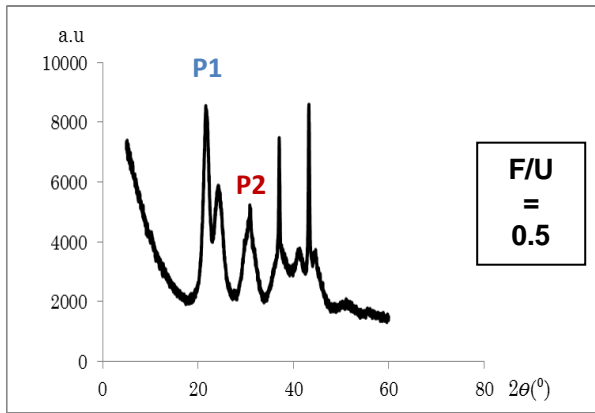


Figure 11 : XRD pattern F/U = 0.5

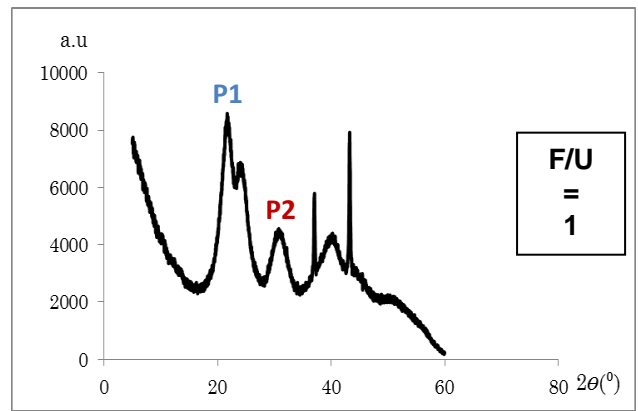


Figure 12 : XRD pattern F/U = 1

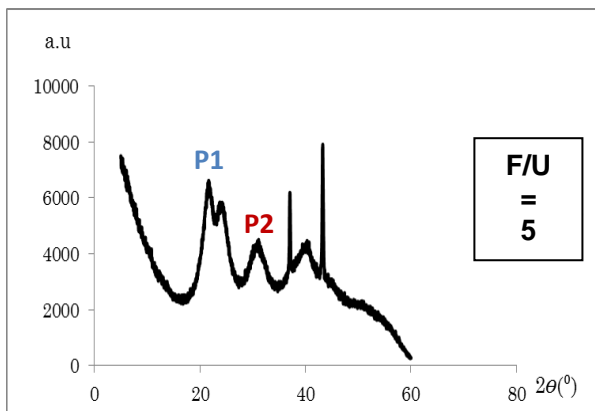


Figure 13 : XRD pattern F/U = 5

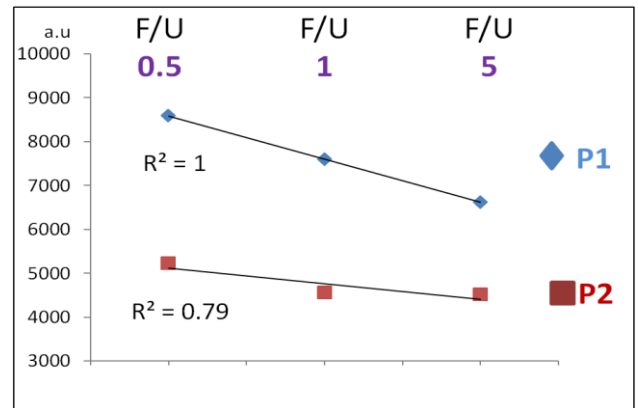


Figure 14 : Decrease of particles crystallinity