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Author(s)	Kabore, John Steve Wendkouni
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Design of the process for the production of nitrogen slow release fertilizer from human urine

by

Wendkouni John Steve KABORE

A thesis submitted in partial fulfillment of the requirement for the degree of
Doctor of Philosophy in Engineering

Examination committee: Prof. Naoyuki Funamizu
Prof. Masahiro Takahashi
Prof. Takao Masuda

Laboratory on Engineering for Sustainable Sanitation, Division of Environmental
Engineering, Graduate School of Engineering, Hokkaido University, JAPAN

RESUME

Nationality: Burkina Faso
Current address: Kita 19, Jo Nishi 5, Kita-ku 2-33, Sapporo-shi, 203 Shine Biru Goushitsu

Name: John Steve Wendkouni Kabore
Date of birth: 22/09/1987

Educational background

03/09/2006	College Notre Dame d'Afrique, College Degree graduated
15/09/2007	Bachelor program, International Institute for Water and Environmental Engineering(2iE), Ouagadougou, Burkina Faso, enrolled
23/07/2010	Bachelor program, International Institute for Water and Environmental Engineering(2iE), Ouagadougou, Burkina Faso, graduated
25/09/2010	Master's program, International Institute for Water and Environmental Engineering(2iE), Ouagadougou, Burkina Faso, enrolled
24/07/2012	Master's program, International Institute for Water and Environmental Engineering(2iE), Ouagadougou, Burkina Faso, graduated
01/10/2013	Doctoral Program, Division of Environmental Engineering, Graduate School of Engineering, Hokkaido University, enrolled.
26/09/2016	Doctoral program, Division of Environmental Engineering, Graduate School of Engineering, Hokkaido University, expected to complete.

Professional background

None

Research background

09/2010-07/2012	International Institute for Water and Environmental Engineering (2iE), "Physical and chemical assessment of compost using shea husks as composting matrix", involved in during the period of Master program.
04/2013-09/2013	Division of Environmental Engineering, Faculty of Engineering, Hokkaido University, "Production of nitrogen slow release fertiliser from human urine" involved in during the period of research student.
10/2013-Present	Division of Environmental Engineering, Graduate School of Engineering, Hokkaido University, "Design of the process for the production of nitrogen slow release fertiliser from human urine" involved in during doctoral program.

Prize

None

I certify that the above are true records.
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(John Steve Wendkouni Kabore)

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3. S. Kabore, R. Ito, N. Funamizu, *Effect of the Formaldehyde to Urea Ratio on physicochemical Properties of Methylene Urea from Human Urine*. Chemical Engineering Journal. (Submitted)

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The Global Dry Toilet Conference, Tampere, Finland, 2015. **Title of presentation:** Effect of Formaldehyde/Urea ratio on thermal properties of methylene urea from human urine (S. Kabore, R. Ito, N. Funamizu)

The 13th IWA leading Edge Conference on Water and Wastewater Technologies, Jerez de la Frontera, Spain, 2016. **Title of presentation (poster):** Kinetics process for the production of nitrogen slow released fertilizer from human urine (S. Kabore, R. Ito, N. Funamizu).

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ABSTRACT

Title of dissertation submitted for the degree

Design of the process for the production of nitrogen slow release fertilizer from human urine.

人尿からの緩効性窒素肥料製造プロセスの開発

The present study was carried out to design the production of nitrogen slow release fertilizer from human urine. The world demand of nitrogen fertilizers keeps growing and most of them are made of fossil fuel which is limited resource. Common nitrogen fertilizers that are easily soluble in water like ammonia and urea may be subject to low utilization efficiency of nutrients by plants, evaporation, washing out by streaming, eutrophication of surface water by transportation and bad odor emission. Slow release fertilizers can solve these problems by increasing the efficiency to reduce the demand. On the other hand, human urine which supplies more than 90% of the total nitrogen in domestic wastewater appeared to have an important potential for the nitrogen fertilizer. Indeed, the potential amount of nitrogen which is yearly produced from the 7 billion people counts for more than 25% of the world demand of the nitrogen fertilizers. However, the direct application of urine in agriculture has same problems as common fertilizers because the main nitrogen component is urea which will biological hydrolyzed to ammonia. Our previous study showed a possibility to produce a slow release fertilizer of methylene urea from human urine, although the design of the process has not been taken into account. Therefore, comprehensive knowledge of the reaction process with the characteristics of the product and the reaction conditions was required to design the production.

In this thesis, the primary part of the study focused on the chemical reaction based on the reported evidence of by-products formation that reduces the nitrogen recovery, while the second part was the evaluation of the final product. Finally, the reactor design was discussed by developing a mathematical model for the production process through the explanation of the reaction mechanism.

In Chapter 1, the literature review on slow release fertilizers, the utilization of urine as fertilizer and the issues to be addressed is performed. This chapter summarizes the objectives of the thesis.

In Chapter 2, based on the observation that the formaldehyde to urea ratio (F/U) has an impact on the recovery percentage of nitrogen due to sub-reactions, the inventory of the involved chemical species was performed and a reaction model was proposed. It was found that the recovery was low for F/U lower than 1 because the formaldehyde was totally consumed while the urea was remaining in the liquid phase. For higher F/U, all urea reacted but the sub-reactions drove to by-products of low molecular weight that could not precipitate therefore reducing the recovery.

In Chapter 3, a simplified reaction model based on the findings of the previous chapter was proposed. The original mathematical model of the reaction in chapter 1 considered intermediate polymers (monomer and dimer), solid product (trimer) and intermediate by-products. The simplified reaction model was adopted because the concentration of the intermediate polymers and by-products could not be accurately measured. Therefore, only the initial reactants (urea and formaldehyde), the monomer, the trimer and some representative by-products were used. The model was divided in 3 parts that are the addition reaction, the polymerization and the sub-reactions. The related equations of the kinetics rate laws for each part were then written and solved. From a computer simulation, the reaction constants that fitted the experimental data were determined. The formation mechanism of the by-products and the relationship of the nitrogen recovery to the F/U ratio were explained. The optimum F/U ratio for the highest recovery was found from the simulation.

In Chapter 4, physicochemical properties of the fertilizer were evaluated. The controllability of those properties was possible through the formaldehyde dosage. The lower F/U ratios produced fertilizer of (1) higher crystallinity with (2) higher requirement of enthalpy for the degradation, (3) easy release of nitrogen in acidic solution.

In Chapter 5, the possibility to reduce the by-products and increase the recovery at high F/U was evaluated. The simulation of (1) the semi-batch and (2) batch reactors showed that (1) the increase of the number of injections of formaldehyde could reduce the formation dominant by-products and increase the recovery. (2) The use of concentrated urine positively impacts the polymerization reaction rate to increase the recovery.

In Chapter 6, a summary of the findings from the study is presented with recommendations.

The reaction model was developed and the mechanism explained.

The kinetics constants were determined and the optimum F/U for the highest recovery was found.

The controllability of the physicochemical properties of the fertilizer was possible through the dosage of formaldehyde. Lower F/U produces more crystalline particles with higher requirement of degradation parameters.

The batch reaction with concentrated urine can increase the recovery even at higher F/U ratio.

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Chapter 1
GENERALITIES

1.1- INTRODUCTION

The world population grew up from 1 billion to more than seven billion within the last two centuries (UNFPA, 2015). Feeding that population with such a dramatic growth is a nowadays concern. The agricultural sector which is the main provider of nourishment faces some challenges such as the inputs. For instance, the world demand of fertilizer keeps on increasing with the growth of the population. In 2020, the estimated demand will be about 116 million tons (FAO, 2016). However, the production of fertilizers appears to be expensive, particularly for nitrogenous ones as they are very dependent on natural gas, require high energy consumption and high fuel costs (Gellings and Parmenter, 2004). Indeed, in the world about 70.000 kilojoules are required to produce one pound of nitrogen fertilizer which is 4.5 times higher than that of phosphate and 5.7 times than potash (Gellings and Parmenter, 2004). The expensive costs for the production of fertilizers have an impact on the food price. From 2001 to 2014, the annual food price index increased from 94.6 up to 203.3 which is a significant jump of about 53% (FAO, 2015). The produced fertilizers are provided in solid (straight and slow release fertilizers), liquid and gaseous form (Agriculture extension service, 1999). Solid fertilizers are the most important group among them (Scherer, 2007).

Regarding water soluble or straight fertilizers, such as ammonium sulfate, urea, and the like, they are easily dissolved in water. The inadequate usage of the soluble nitrogen fertilizers may cause low utilization efficiency of nutrients by plants resulting to an increase in their amount for application, an increase of the labor cost for this application, and the eutrophication of surface and ground water.

Contrarily, slow release fertilizers that are made from slowly degradable material (Trenkel, 2010) can control the release rate of the nutrients by their own biodegradation rate and therefore reduce nutrients losses (Trenkel, 2010). A most complete definition is given by Trenkel (2010) who defines the slow release fertilizer as a fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference ‘rapidly available nutrient fertilizer’ such as ammonium nitrate or urea, ammonium phosphate or potassium chloride. Such delay of initial availability or extended time of continued availability may occur by a variety of mechanisms. These include controlled water solubility of the material by semi-permeable coatings, occlusion, protein materials, or other chemical forms, by slow hydrolysis of water-soluble low molecular weight compounds, or by other unknown means.

1.1.1- Human urine and the production of nitrogen slow release fertilizer

Human urine is an important source of nitrogen that can be recovered as a slow release fertilizer. Indeed, people daily discharge 12.5g of nitrogen with 90% of that amount coming from urine (Del Porto, 1999). The potential contribution of the 7 billion people in the world represents 30million of tons which is about 25% of the total demand. Besides, that source of nitrogen is free and equally distributed in the world. However, the excessive urine application inhibits plant growth due to the increase of the soil electrical conductivity (EC) (Mnkeni etal., 2008). The urine contains 0.5 wt. % of sodium chloride which could accumulate in the soil system. Ammonia evaporation may release bad odor for the people near the field and washout by rainwater may also occur (Galloway and Cowling, 2002). There is also the concern of crops contamination by pathogens contained in the urine bringing the long storage requirement period; At least 6 months at more than 20^{0}C (Höglund et al., 2002).
Ito *et al.* (2013) proposed the production of methylene urea — a nitrogen slow release fertilizer — from human urine. The urea contained in the urine reacts with formaldehyde under acidic condition to give a solid precipitate. However, the urea which is the main supplier of nitrogen may hydrolyze with a transformation into volatile ammonia NH_3 due to microbial contamination and then increase the pH of urine. Therefore, the handling of urine from collection to the production of slow release fertilizer is proposed with a regard to urea conservation (figure 1).

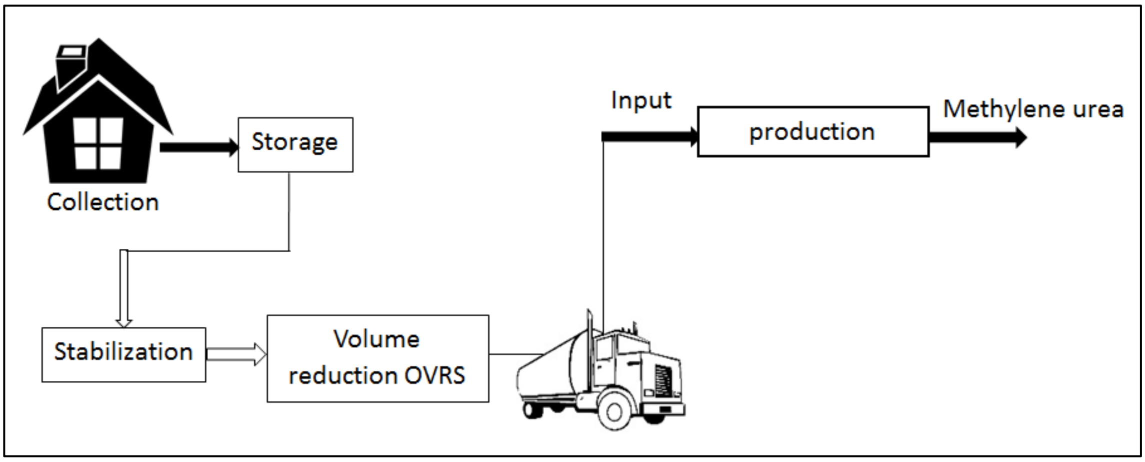

Figure 2 System for the production of methylene urea from human urine

The steps of the system are important, each one having its own consideration as discussed below:

- The collection

The use of urine dry diverting toilets avoids the direct contact of urine with feces and therefore the source contamination. Indeed, Hotta and Funamizu (2008) showed that the ammonification which is the change of urea into ammonia might be accelerated with the fecal contamination. From the separation, the urine can be safely collected with better fractions of nutrients to be recovered. The urine can be collected in ordinary jerricans or, if this is more suitable, in large tanks (Höglund, 2002).

- The storage and the stabilization

Generally it is recommended to store the urine at 20ºC for at least 6 months to inactivate pathogens such as rotavirus, campylobacter jejuni and cryptosporidium parvum (Höglund *et al*, 2002). This procedure generally referred as hygienisation is not suitable for the purpose of producing nitrogen slow release fertilizer. Indeed, the pH of fresh urine is normally between 4.8 and 7.5 but after collection it is around 9.0. When urine is excreted, the major fraction of the nitrogen is present as urea […] and converted to ammonium (Höglund). This form of nitrogen cannot react with the formaldehyde to be recovered. With no pre-treatment, about 10 days are sufficient to hydrolyze the urea (Takahashi, 2012).
In our case, there is the tremendous importance to prevent hydrolysis and ammonification by stabilizing the urine. Takashi *et al* (2012) proved that the urine can be kept for more than 2 months with no hydrolysis when the initial pH is decreased at 2 using acid. Hellström (1999) succeeded to keep the urine for more than 250 days with a pH below 4. However, the handling of acid might be dangerous sometimes, especially in household conditions. An alternative is the use of salt to inhibit ammonification. From Hotta and Funamizu (2008), it is known that about 150 g of NaCl addition per liter of stored urine can reduce the ammonification potential by 50% at room temperature.

- The volume reduction and the transportation

The volume reduction and the transportation are related in the sense that 80% of the urine is water. Reducing the volume of water may considerably reduce the costs required for the transportation by truck. To do so, different processes exist such as the freeze thaw, the reverse osmosis, the vapor compression distillation, the thermoelectric integrated membrane, lyophilization. However, all those processes are difficult to be used in the households. Pahore *et al.*(2010-2011) proposed the Onsite Volume Reduction System (OVRS) which is a method to reduce the volume of human urine at household level for small communities. The system is based on the natural atmospheric energy. It takes advantage of the wind flow to evaporate water from urine using a small size of gauze sheet. About 80% volume reduction can be achieved per day (Pahore, 2010-2011).

- The production

The production step here is mostly related to the high scale. This part requires the understanding of the reaction that occurs in the human urine and also the kinetics study so that the reaction rates can be computed to design the reactor. So far, little was known on this matter therefore bringing us to the research objectives of this thesis.

1.2- RESEARCH OBJECTIVES

The possibility to produce the methylene urea from human urine was proposed by Ito *et al.* From their results, when the formaldehyde is in excess, soluble nitrogen compounds still remain in the liquid phase and therefore decrease the recovery rate. This fact suggests the existence of additional pathways during the reaction. The objectives of this research were:

- To understand the phenomenon occurring in the human urine and propose the reaction model. To achieve this objective, different F/U ratios (low and high) were evaluated and the inventory of the chemical species was listed to propose an appropriate model of the reaction.

- To evaluate the proposed reaction model and the condition for better recovery percentage. The kinetics were studied to observe whether or not the proposed reaction model could accurately describe the experimental data. The optimum F/U ratio for the highest recovery was determined using a simulation of the model.

- To find the possibility to have a controllability on the nutrient release rate of the final product. Different F/U ratios were evaluated with physicochemical assessment of the fertilizer.

- To determine the appropriate chemical process regarding the reactor among the batch, semi-batch and continuous operations.

1.3- CONCLUSION

The use of human urine to produce the nitrogen slow release fertilizer is an important contribution to mitigate the world demand of nitrogen fertilizer. However, phenomena such as the decrease of recovery rate due to high and/or low F/U ratios are not explained. The reaction model is unknown and the final product itself is not yet discussed. We are bringing accurate answers in the upcoming parts of this thesis.

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Chapter 2

EFFECT OF THE FORMALDEHYDE TO UREA RATIO ON THE PRODUCTION RATE

2.1- INTRODUCTION

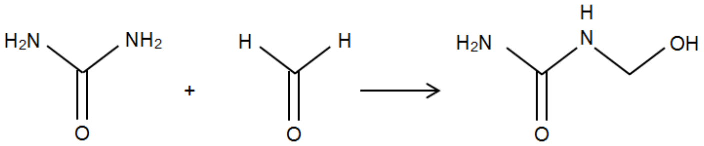
In the world, 100 Mtons of nitrogen fertilizer are annually produced and consumed [1] while the market is still growing. Most of them are produced from ammonia manufacturing industries. Inadequate usage of the soluble nitrogen fertilizers, such as ammonium sulfate, urea, and the like, may cause low utilization efficiency of nutrients by plants resulting to an increase in their amount for application, an increase of the labor cost for this application, and eutrophication of surface and ground water. This is because they are easily dissolved and can be washed out by streaming.

To overcome these problems, slow-release fertilizers are applied as a solution. Some of the slow-release fertilizers are made from slowly degradable materials [2]. They can control the release rate of the nutrient by their own biochemical degradation rate. Utilization of slow-release fertilizers can increase the efficiency of nitrogen fertilizer from 25 to 66% for tomato and from 22 to 79% for rice [3]. Using formaldehyde and human urine, Ito *et al.* (2013) [4] produced solid particles of methylene urea as a slow-release fertilizer, and the particles were the same as the commercially available one.

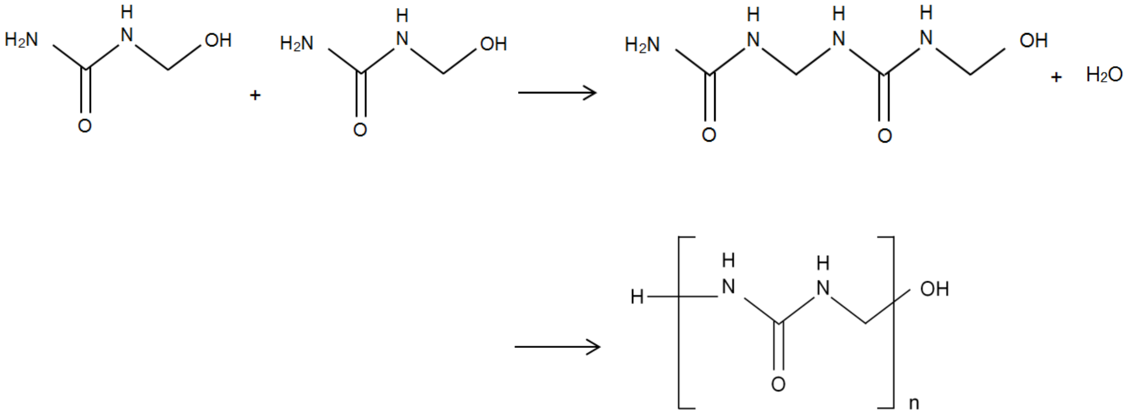
In the world, about 6 Mtons of excreta are disposed from human, and most of them are urine. So, recovery of nitrogen from urine also has the potential to reduce the nitrogen load into the environment.

A previous experiment [5] found that the recovery of nitrogen as solid particles from urine gradually increased with the increase in formaldehyde dosage. The maximum was obtained at equimolar ratio of formaldehyde to urea (F/U) before decreasing at higher formaldehyde concentration. This indicates the existence of sub-reaction that does not give solid particles at high F/U ratio. Indeed, the reaction of urea and formaldehyde leads to different products like adhesive resins for plywood, slow-release fertilizer for agriculture among others. Focusing on the production of slow-release fertilizer, the general reaction to obtain the commercially available fertilizer is well known as follows [6]:

(1) Addition reaction under acidic condition



(2) Dehydration/condensation and polymerization



Nair and Francis (1982) reported the detailed reaction pathways of the production including by-products [7]. The reaction conditions of pH, temperature, and F/U ratio affect the series of reaction paths that lead to the final products [8–10]. For instance, Dunky (1997) [11] reported that the reaction to obtain adhesive resin starts under alkaline condition at F/U = 1.8 – 2.5 followed by condensation in acid medium with further addition of urea at different temperatures. He also reported that the low pH condition gives no branched polymer chain which is a more stable structure.

From the results of Ito (2013) *et al.* [4] and Takahashi (2012) [5], soluble nitrogen compounds still remain in the liquid phase and therefore decrease the recovery rate when-formaldehyde is in excess. This fact suggests the existence of additional pathways during the reaction. Indeed, Gürses *et al.* (2013) [12] reported the by-products of FUF and $FU(F)_2$ formed during the reaction of urea and formaldehyde at specific initial conditions, as shown in **Fig. 1**. The by-product $F_2U(F)_2$ is hypothetically possible but has not been observed experimentally [8].

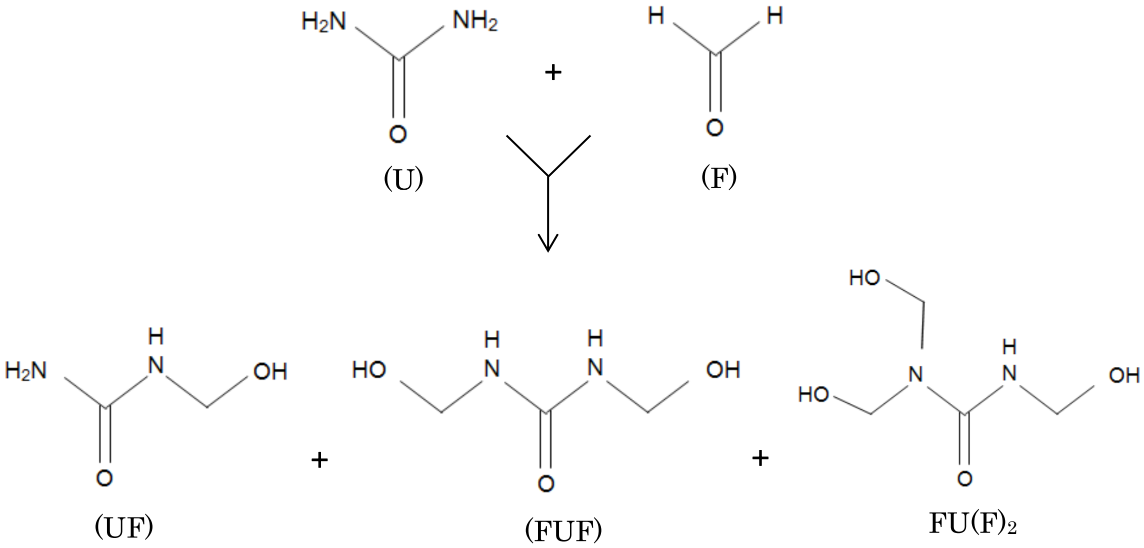


Fig. 1 Formation of monomethylol urea (UF), dimethylol urea (FUF) and trimethylol urea ($FU(F)_2$).

To design the reactor for the production of methylene urea from human urine, the reaction mechanism should be elucidated including soluble products of the intermediates. The objective of this research was to propose the model for the production of methylene urea by showing the presence of by-products, drawing the mass balance of nitrogen and carbon through the reaction, finding out the degree of polymerization and namely identifying those by-products in the liquid phase. That model is intended to be used in future studies to develop the kinetics of the reaction in human urine with a purpose of quantitatively describing the rates of formation and disappearance of the reactants.

2.2- MATERIALS AND METHODS

Synthetic urine solution was used to simulate real urine, whose composition is summarized in **Table 1** [13]. Two hundred milliliters of the synthetic urine was taken in a glass container which was tightly closed during the reaction to avoid escape of gas. The pH was adjusted at 2 with hydrochloric acid solution (JIS special grade, Wako Pure Chemical Industries, Japan). This specific value of pH was used based on the effect on the reaction rate described by Ito (2013) [4]. It was also based on the large capacity of acidic condition to avoid urea hydrolysis in the urine during storage and experiments [14,15]. The reaction temperature was kept at 25°C in a water bath. A specific volume of 36% 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 molar ratio of the added amount of formaldehyde to urea (F/U) in the solution for each experiment is summarized in **Table 2**. The conditions of F/U = 1 and 5 were to show the effect of F/U on nitrogen recovery and also the formation of by-products. The ratio F/U = 20 was selected to ensure the reaction without any production of solid particles of polymers and to maximize the formation of by-products. The solution was periodically taken and filtrated with glass fiber filter (GB 140, Advantec, Japan). The pH of the filtrate was adjusted to 7 with 1 mol/L sodium hydroxide (JIS special grade, Wako Pure Chemical Industries) to stop the reaction. The urea concentration, total nitrogen (TN) and formaldehyde concentration were respectively measured with an LC-MS (LC system 626, Waters, USA), a TN meter (TOC-VCSH, Shimadzu, Japan) and formaldehyde measurement agents (MBTH method 8110, Hach, USA) with a spectrophotometer (DR-2800, Hach). A liquid chromatography with organic carbon detection (LC-OCD, chromatograph for organics in water, model 8, DOC-LABOR DR. HUBER, Germany) was used to analyze the molecular distribution of polymers that remained in the liquid phase. The analyzer has an organic carbon detector (OCD), and an organic nitrogen detector (OND). The column used for the chromatographic analysis (Toyopearl HW-50s, Tosoh Bioscience, Japan) was a mode of gel filtration to classify the molecular weight of the samples. Molecular weights of dissolved species in F/U = 20 were measured by a mass spectrometer (JMS-T100LP, JEOL, Japan) with electrospray ionization mode (ESI) and methanol as solvent. The sample was previously concentrated with a low pressure evaporator at 35°C. Solid residue on the filter was weighed with an electric balance. The concentration of nitrogen in the solid phase was measured with a CN coder (Sumigraph NC-220F, Sumika Chemical Analysis Service, Japan). The detailed composition of the solid was measured by Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University, Japan.

The molecular weights and structures of all possible species from the reaction of urea and formaldehyde were computed and drawn using advanced chemistry software (Chemsketch®, ACD labs, Canada). The results of mass spectrometry (MS) were also evaluated using the same software to confirm the molecular weights of species in which fragmentation was possible to occur.

Table 1 Composition of synthetic urine.

	Concentrations	
Components	g/L	mmol/L
$MgCl_2 \cdot 6H_2O$	0.65	3.2
$NaCl$	4.60	78.7
Na_2SO_4	2.30	16.2
$Na_3(C_6H_5O_7) \cdot 2H_2O$	0.76	2.6
KCl	1.60	21.5
$C_4H_7N_3O$	1.10	9.7
$CaCl_2 \cdot 2H_2O$	0.65	4.4
KH_2PO_4	4.20	30.9
NH_4Cl	1.00	18.7
$(NH_2)_2CO$	25.0	416
$Na_2(COO)_2$	0.02	0.15
$C_6H_8O_6$	0.10	0.57

Table 2 Amount of formaldehyde and corresponding ratio to urea.

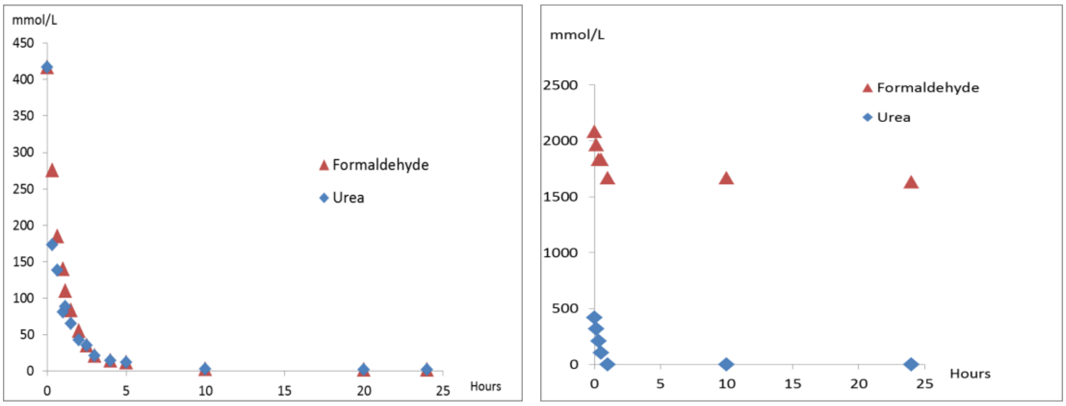
Volume of urine (mL)	F/U ratio	Volume of formaldehyde (mL)
200	1	6.95
	5	34.8
	20	139

2.3- RESULTS AND DISCUSSION

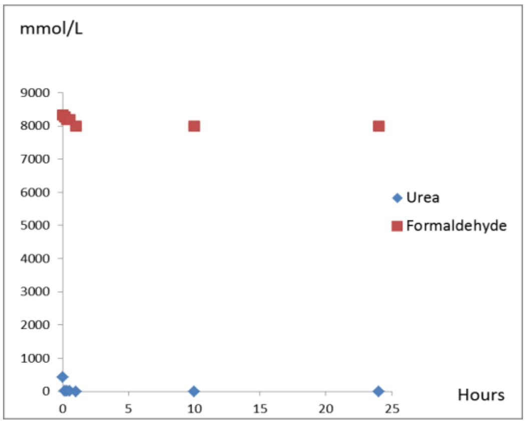
2.3.1- Mass balance of nitrogen and carbon

Figures 2 show the time course of concentrations of urea and formaldehyde during the reaction. In the case of F/U = 1 (**Fig. 2(a)**), the concentrations of urea and formaldehyde decreased with time synchronously. From 0 to 10 hours, the concentrations of urea and formaldehyde respectively decreased from 416 mmol/L to 2 mmol/L and from 416 mmol/L to 2 mmol/L. The total corresponding consumption for each urea and formaldehyde was 414 mmol/L, so, the stoichiometric reaction of urea and formaldehyde has occurred in F/U = 1 case.

Regarding F/U = 5 and F/U = 20 (**Fig. 2(b)** and **2(c)**), the initial concentration of urea, 416 mmol/L, respectively decreased to 12 mmol/L and 1 mmol/L in 30 minutes. Initial concentrations of formaldehyde respectively decreased from 2,080 mmol/L to 1,630 mmol/L and from 8,330 mmol/L to 8,000 mmol/L. The decreases of urea and formaldehyde concentrations were respectively 404 mmol/L and 452 mmol/L for F/U = 5, and 415 mmol/L and 334 mmol/L for F/U = 20. These differences on the consumption of urea and formaldehyde suggest that other reactions different from the main reaction to produce methylene urea has occurred.



(a) F/U = 1. **(b)** F/U = 5.



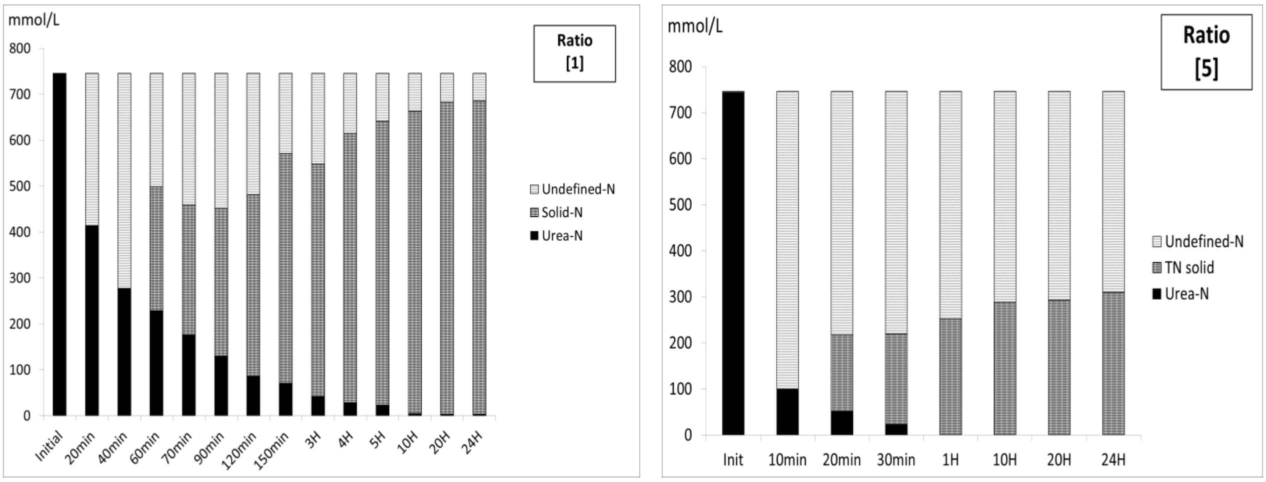
(c) F/U = 20.

Fig. 2 Time courses of urea and formaldehyde consumption at different F/U ratios.

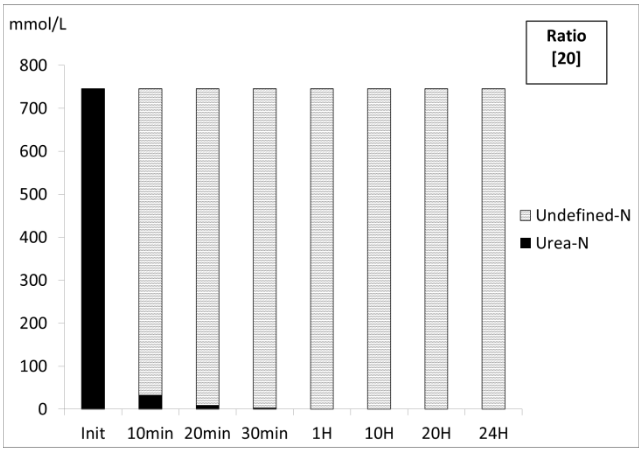
To analyze the fate of the total nitrogen from supplied urea, the mass balances for F/U = 1, 5 and 20 are respectively illustrated in **Fig. 3**. At the beginning of the reaction, the urea-nitrogen (Urea-N) decreased, while undefined nitrogen (Undefined-N) appeared in the liquid phase. Then some of the Undefined-N turned into precipitation (Solid-N) in the case of F/U = 1 and 5. The amount of soluble product considered as undefined-N was calculated by subtracting from the total nitrogen, the amount as Urea-N and that as Solid-N. For all F/U ratios, the initial concentration of Urea-N decreased to 0 mmol/L during the 24 hours of reaction. These phenomena showed that the reaction of urea and formaldehyde occurred first to form soluble components. Then the precipitate appeared following the polymerization reaction described by equations (1) and (2). The solid precipitate developed from the products of the reaction of urea and formaldehyde through the Undefined-N.

After 24 hours, Solid-N and Undefined-N were about 680 mmol/L and 60 mmol/L, respectively, for F/U = 1, 310 mmol/L and 435 mmol/L, respectively, for F/U = 5, and 0 mmol/L and 745 mmol/L, respectively, for F/U = 20.

Increase of F/U ratio also increased the concentration of Undefined-N to which the concentration after 24 hours was about 60, 435 and 745 mmol/L for F/U = 1, 5 and 20. Therefore, high F/U seems to lead to the formation of soluble polymers and by-products.



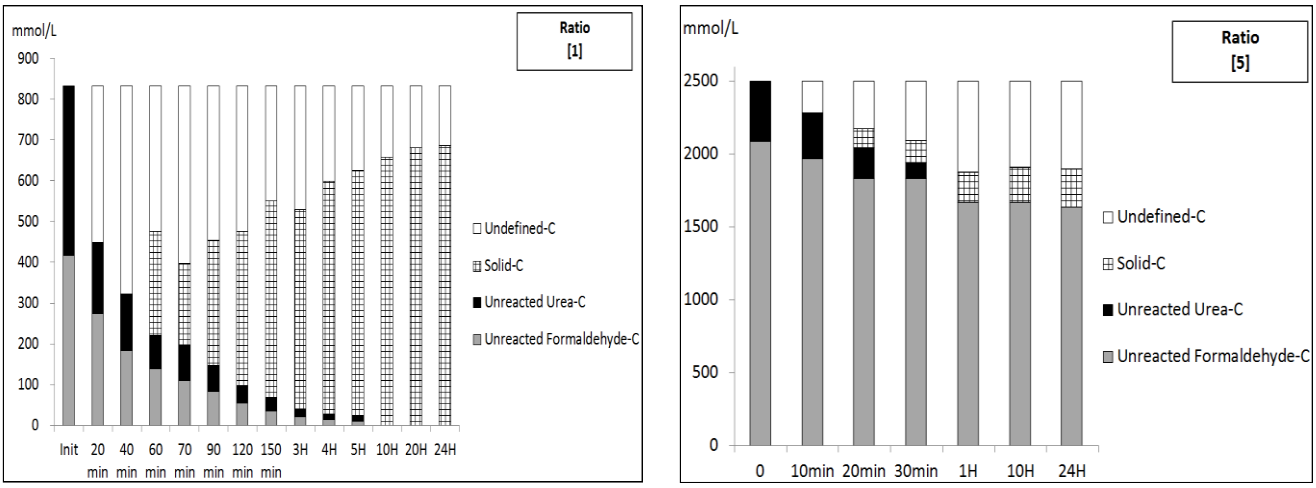
(a) F/U = 1 **(b)** F/U = 5



(c) F/U = 20

Fig. 3 Nitrogen balances at different F/U ratios.

Figure 4 shows the mass balance of carbon of the reaction for F/U = 1 and 5. In the case of F/U = 1, the urea carbon (Urea-C) reacted with the same molar amount of formaldehyde carbon (Formaldehyde-C) which was 414 mmol/L. Concentration of unreacted Formaldehyde-C was still high in the liquid after 24 hours for F/U = 5, however, all Urea-C was consumed. Indeed, at the end, about 416 mmol/L Urea-C reacted with 751 mmol/L of Formaldehyde-C. This situation showed that excess formaldehyde reacted with urea comparing to the case of equimolar mixture (F/U = 1) and could explain what happens when too much formaldehyde is used to produce methylene-urea. A mole of urea might react with more than one mole of formaldehyde. For F/U = 20, the standard deviation was about 8% and for huge initial concentration of formaldehyde (8,330 mmol/L) the accuracy was not enough to calculate the amount of consumption by reaction.



(a) F/U = 1

(b) F/U = 5

Fig. 4 Carbon balances at different F/U ratios.

2.3.2- Degree of polymerization of dissolved molecules

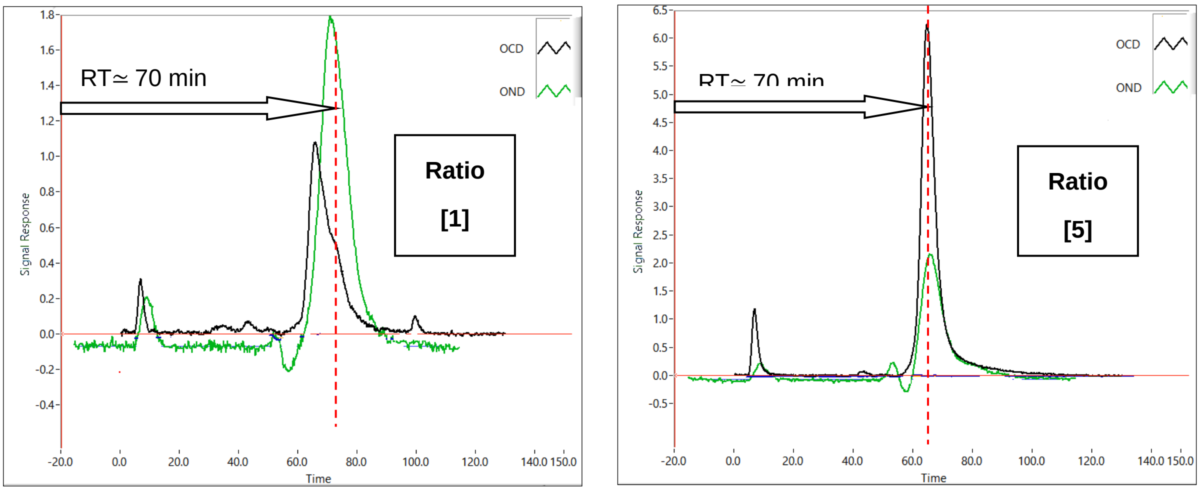
Table 3 summarizes the elemental composition of the recovered solid particles for F/U = 1 and 5 and **Table 4** summarizes the theoretical elemental composition related to the degree of polymerization. The displayed data in both tables is the ratio of the elements to the respective carbon content. By comparing theoretical oxygen ratio from **Table 4** and the experimental one in **Table 3**, *n* value of 3 or 4 were the corresponding degree of polymerization for the recovered solids. This showed that polymers with lower degree of polymerization than these values did not precipitate and therefore gave evidence of the absence of high molecular weight polymers in the liquid phase. **Figures 5** illustrates the results from LC analysis of the liquid samples at 24 hours. The elution peaks were detected at about 70 minutes for all F/U ratios, which corresponded to a molecular weight of less than 350 Da from the catalogue specification. Referring to the structural formula of the polymer which is H-[NH-CO-NH-CH_2]$_n$-OH, less than 350 Da corresponds to an average degree of polymerization *n* lower than 5, which supports the results of the elemental analysis.

Table 3 Ratio of the elemental composition of recovered solid.

F/U	H/C	N/C	O/C
1	2.13	0.99	0.63
5	2.10	0.92	0.64

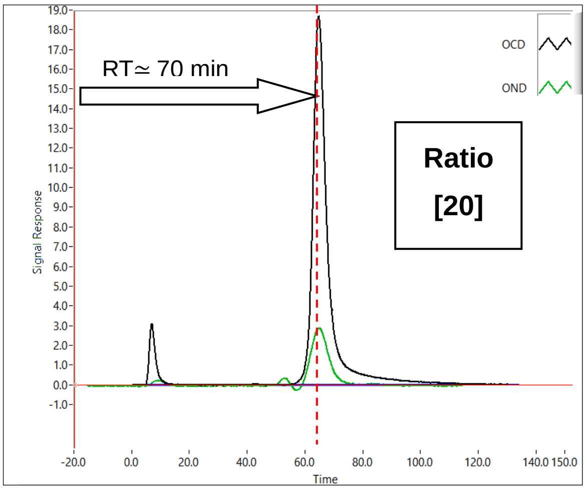
Table 4 Theoretical ratio of the elemental composition of solid polymer.

Polymerization degree, *n*	H/C	N/C	O/C
1	3.00	1.00	1.00
2	2.50	1.00	0.75
3	2.33	1.00	0.67
4	2.25	1.00	0.63
5	2.20	1.00	0.60
6	2.17	1.00	0.58



(a) F/U = 1

(b) F/U = 5



(c) F/U = 20

Fig. 5 Chromatograms of LC-OCD at different F/U ratios. RT: Retention Time, OCD: response of organic carbon detection, OND: response of organic nitrogen detection.

2.3.3- Detection of by-products

The general reaction for the production of commercially available methylene urea is described in equations (1) and (2). To analyze the mass spectrometry results, it was important to target the possible products that could be formed during the reaction process. **Table 5** is a summary of those species appearing between the equations.

Figures 6 shows the mass spectrometry profiles with the negative and positive electrospray ionization mode. The boxes inside are the zoom on their relative abundances and on their molecular weight to charge ratio, *m/z*. The circled peaks are the ones that matched the theoretical molecular weights of considerable components. Low molecular weight polymers were detected and also some by-products from side paths of the reaction. These by-products appeared to be polymers with incomplete sequences. The by-products $FU(F)_2$, $(F)_2U(F)_2$, $[UF]_5$, UFUFUFUFU and UFUFUFUFUFU were not detected. Indeed, $FU(F)_2$ is a product that appears in alkaline solution at temperature above 60°C [16]. Therefore formation of such specie was not possible from our reaction conditions. Regarding $(F)_2U(F)_2$, ithas never been observed experimentally at least in detectable quantity [8] and neither from our results. Species $[UF]_5$, UFUFUFUFU and UFUFUFUFUFU also were not considered because they have degrees of polymerization equal or higher than the precipitate which means they are supposed to be out of the liquid phase in case their production took place. For this reason, molecular weight from the MS result matching these products is not from the reaction course.

Data of detected molecular weights are summarized in **Table 6**, where U is urea, F is formaldehyde, $[UF]_n$ is polymer of methylene urea with the polymerization degree, *n*, while FUF, UFU, UFUFU, and UFUFUFU are by-products. Their available structures are shown in **Fig. 7**. Most compounds were found in positive mode and ion adduction condition was also determined.

During the mass spectrometry process, some species were detected in both positive and negative modes. Basically, in ESI, a proton is attached to the molecular ion in positive mode $[M]^+$ and detached from the molecular ion in negative mode $[M]^-$. However, fragmentation such as dehydration can be observed, when molecules contain alkyl carbon with a hydroxyl functional group. In such case, the molecular weights of the dehydrated species have 18 Da less than that of their original forms [17,18]. Here 18 Da is the molecular weight of water. These fragmentations were observed for all polymers and FUF. The fragmentations $[M\text{-}18]^+$ and $[M\text{-}18]^-$ are the ones of the dehydrated molecules respectively in positive and negative mode. The phenomenon for the rest of the by-products did not occur because their molecular structures are free from hydroxyl functional group attached to an alkyl carbon.

Another type of fragmentation is dehydrogenation which is the loss of H_2 [17–19]. $[M\text{-}H]^+$ is the detachment of H_2 plus attachment of proton [17]. This dehydrogenation was observed for $[UF]_2$, UFU and UFUFU. In the case of FUF, the dehydrogenation occurred with also the loss of water $[M\text{-}18\text{-}H]^+$.

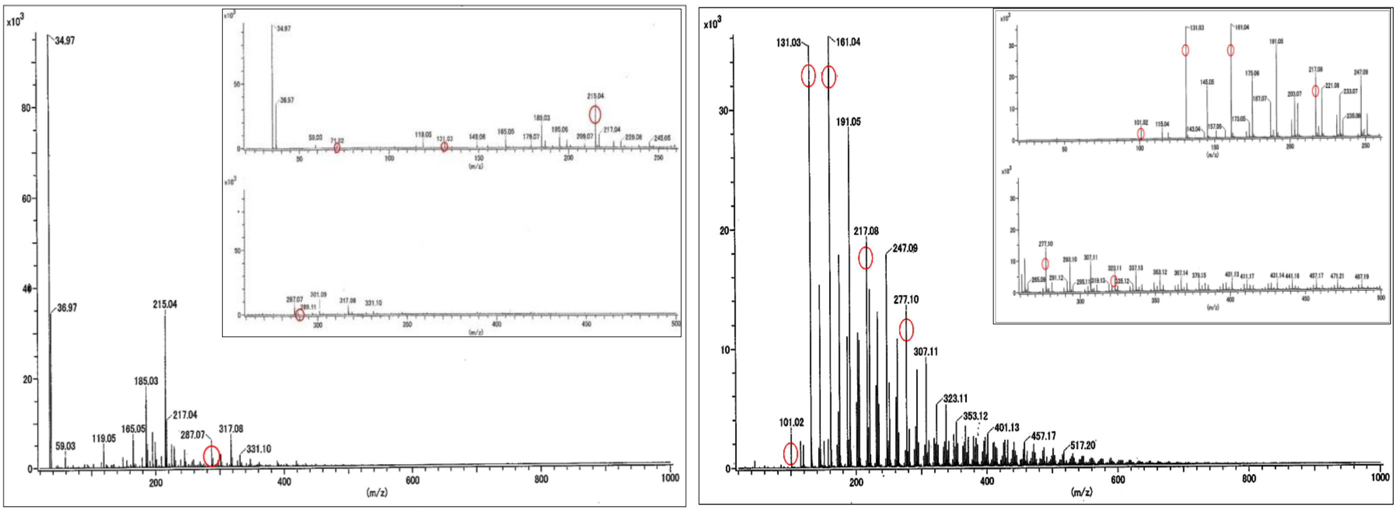
The fragmentations of the different molecules were carefully analyzed by comparing the experimental data of mass spectrometry with computer-generated results using their molecular structures.

Relative abundance was highest for the dimer, $[UF]_2$ and lowest for the monomer but it does not necessarily reflect the concentration of the concerned compounds.

Some peaks of mass spectrometry still have some high relative abundance but they did not match the theoretical calculation of MW.

Table 5 . Possible products from the reaction course. (Y/N = Yes/No)

	Possible products	Nominal molecular weight (Da)	Detection in MS
Main products	[UF]	90	Y
	$[UF]_2$	162	Y
	$[UF]_3$	234	Y
	$[UF]_4$	306	Y
	$[UF]_5$	378	N
Sub Products	FUF	120	Y
	UFU	132	Y
	$FU(F)_2$	150	N
	$(F)_2U(F)_2$	180	N
	UFUFU	204	Y
	UFUFUFU	276	Y
	UFUFUFUFU	348	N
	UFUFUFUFUFU	420	N



(a) Negative electrospray.

(b) Positive electrospray

Fig. 6 Mass spectrum at F/U = 20.

Table 6 . Summary of mass spectrometry data. (* = Dehydrated)

	Products	Theoritical MW	MS results	Ionization mode	Fragmentation
Polymers	$[UF]_1$ *	72	71.02	ES-	$[M-18]^-$
	$[UF]_2$	162	161.04	ES+	$[M-H]^+$
	$[UF]_2$ *	144	145.05	ES+	$[M-18]^+$
	$[UF]_3$	234	235.08	ES+	$[M]^+$
	$[UF]_3$ *	216	217.08/215.04	ES+/ES-	$[M-18]^+/[M-18]^-$
	$[UF]_4$	306	307.11	ES+	$[M]^+$
	$[UF]_4$ *	288	287.07/289.11	ES+/ES-	$[M-18]^+$ / $[M-18]^-$
By-Products	FUF *	102	101.02	ES+	$[M-18-H]^+$
	UFU	132	131.03/131.03	ES+/ES-	$[M-H]^+/[M]^-$
	UFUFU	204	203.07	ES+	$[M-H]^+$
	UFUFUFU	276	277.1	ES+	$[M]^+$

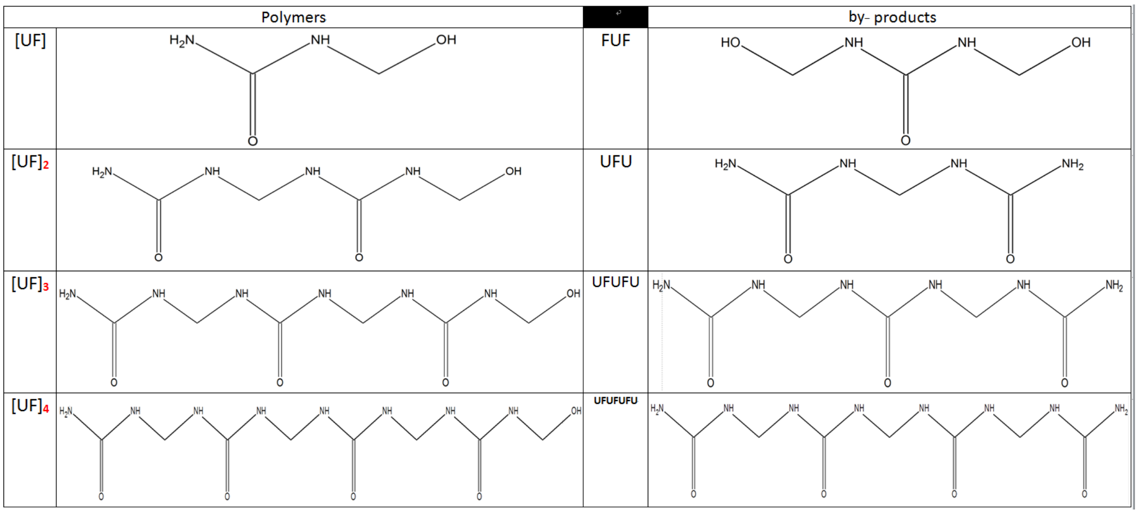


Fig. 7 Molecular structures of detected dissolved compounds.

2.3.4- The Reaction model

From the above results, a reaction model can be proposed as illustrated in **Fig. 8**. The main product is solid polymers of methylene urea, and the main path is the same reaction described in equations (1) and (2). It is comprised by an addition reaction between urea and formaldehyde to produce the monomer $[UF]_1$ which is then involved in a step-growth polymerization. The molecular weight increases until reaching the final degree of polymerization (*n*) for precipitation.

However, in the case of human urine, side reactions should be included to describe the formation of by-products which are FUF, UFU, UFUFU, and UFUFUFU. There are some pathways that can be considered. After the addition reaction, the monomer $[UF]_1$could either react with a molecule of formaldehyde or urea to respectively produce FUF and UFU. The latter might also get involved in a chain reaction with the monomer $[UF]_1$to produce UFUFU and UFUFUFU. These two by-products could also be respectively produced from the main path in case the dimer $[UF]_2$ and the trimer $[UF]_3$ respectively react with a molecule of urea.

It is important to mention that this reaction model is qualitative. The number of different species does not reflect their concentrations. Their participation in the reaction process should be discussed on a quantitative basis. For instance, in the case of high F/U ratio, the concentration of FUF will be higher compared to those of all other by-products. This discussion requires the kinetic studies based on this reaction model. As the mechanism is now determined, the kinetic model has to be developed in the future perspectives.

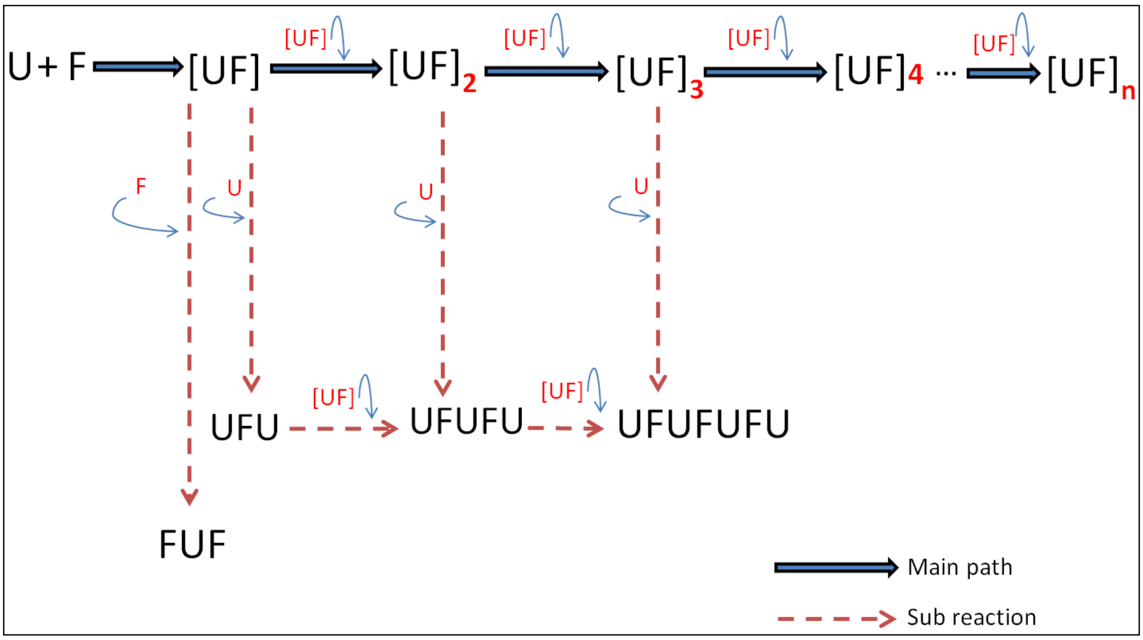


Fig. 8 Pathways of the reaction and product formation.

2.4- CONCLUSIONS

Chemical reactions to produce methylene urea polymers from urea and formaldehyde in synthetic urine have been investigated by drawing nitrogen and carbon balance through the reaction, molecular distribution analysis in the liquid phase, elemental analysis of precipitations and identifying possible molecules as intermediates for different F/U ratios. From the results, we obtained the conclusions below:

(a) The nitrogen balance showed the consumption reaction of Urea-N to produce soluble molecules considered as Undefined-N then followed by the precipitation reaction to produce Solid-N. Complete consumption of urea was observed in all F/U ratios. Higher F/U ratio gave a rapid consumption reaction, despite the low yield of Solid-N. The carbon balance also showed complete consumption of urea and increase of soluble molecule as Undefined-C, followed by the production of solid polymers as Solid-C. The comparison of consumed amount of urea and formaldehyde indicated an equimolar reaction at F/U = 1 and a non-equimolar reaction for higher F/U ratios.

(b) The liquid chromatography showed that unidentified nitrogen compounds had a nominal molecular weight less than 350 Da. Referring to the chemical formula of methylene urea, the degree of polymerization of the low molecular polymers was lower than 5. Elemental analysis also supported this fact by showing the composition of the elements to estimate the degree of polymerization as 3 or 4.

(c) Eleven molecules comprised by polymers and by-products were identified in the liquid phase by mass spectrometry and their possible structures were illustrated.

(d) The reaction model for the production of methylene urea from human urine was proposed.

2.5- REFERENCES

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CHAPTER 3

EVALUATION OF THE REACTION MODEL: KINETICS

3.1- INTRODUCTION

The world demand of nitrogen fertilizer is gradually increasing and will be about 116 million tons in 2020 (FAO, 2012). People daily discharge 12.5 g of nitrogen with 90% of that amount coming from urine (Del Porto, 1999). The potential amount of nitrogen produced from the 7 billion people is about 30 million tons. This counts for 25% of the total demand in the world. Therefore, the reuse of urine could provide an alternative source of nitrogen fertilizer. The energy consumption necessary for producing conventional ammonia based fertilizers could also be reduced. However, the direct application of urine in agriculture faces problems that might be considered. Excessive urine application inhibits plant growth due to the increase of the soil electrical conductivity (EC) (Mnkeni etal., 2008). The urine contains 0.5 wt. % of sodium chloride which could accumulate in the soil system. Ammonia evaporation may release bad odor for the people near the field and washout by rainwater may also occur (Galloway and Cowling, 2002). There is also the concern of crops contamination by pathogens contained in the urine bringing the long storage requirement period; At least 6 months at more than 20^{0}C (Höglund et al., 2002).

On the other hand, slow release fertilizers made from slowly degradable materials can control the release rate of the nutrient by their own biochemical degradation rate therefore reducing nutrients losses (Trenkel, 2010). During the fabrication process, intermittent controlled pH condition and addition of urea is also done (M Dunki). Ito *et al* (2013) succeeded to produce solid particles of methylene urea from urine at room temperature (25_ C) at pH 1–5. Formaldehyde reacted with the urea to give precipitate. The concentration of urea decreased with elapse of time at all pH values while the rate was high at low ones. The experiments were performed using both synthetic and real human urine. The elemental analysis of the precipitates showed that they were identical to the commercial methylene urea. Kabore *et al* (2016) studied the recovery rate and they found that it was gradually increasing with the increase in the ratio of formaldehyde to urea (F/U). The maximum was obtained for the equimolar F/U, and then decreased at higher F/U. They also found that the reaction in human urine was different from the one used to produce the methylene urea available on the market. Indeed, in the case of human urine sub-reactions leading to by-products have to be considered. They therefore proposed a reaction model that considers the main reaction path producing methylene urea and also secondary paths leading to the related by-products.

To design a reactor to produce the slow released fertilizer from human urine, the kinetics constants of the reaction have to be determined. Basically, those constants are necessary to compute the reaction rates (r), the volume (V) and the residence time (t). In realistic situation, the design includes a series of reactors with recirculation of the species. In such cases, the kinetics parameters are necessary to also compute the periodical concentrations of the different species.

The objectives of this research paper were (1) to evaluate the kinetics parameters for the proposed mathematical model of the reaction, (2) to perform a simulation with the mathematical model for obtaining quantitative data and for designing the reactor and (3) to analyze the contribution of the soluble products on the recovery of nitrogen and therefore determining the optimum F/U ratio condition for the highest recovery of nitrogen.

3.2- MATERIALS AND METHODS

3.2.1- Preparation of samples

Synthetic urine solution whose composition is summarized in table 1 was used to simulate real urine (Wilsenach et al., 2007). Two hundred millilitres of the synthetic urine was taken in a tightly closed glass bottle during the reaction to avoid escape of gases. The pH was adjusted to 2 with concentrated hydrochloric acid solution (JIS special grade, Wako Pure Chemical Industries). This specific value of pH was used based on the effect on the reaction rate described by Ito (2013). It was also based on the large capacity of the acidic condition to avoid the hydrolysis of urea in the urine during storage and experiments (Hellstrom *et al.,* 1998; Hotta and Funamizu 2008). The reaction temperature was kept at 25 °C in a water bath. A specific volume of 36% 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 F/U in the solution for each experiment is summarized in table 2. The solution was periodically taken during 24 hours, and then filtrated with glass fibre filter (GB 140, Advantec). The pH of the filtrates was adjusted to 7 with 1 mol/L sodium hydroxide (JIS special grade, Wako Pure Chemical Industries) solution to slow the reaction.

Table 1 Composition of synthetic urine

	Concentrations	
Components	g/L	mmol/L
$MgCl_2 \cdot 6H_2O$	0.65	3.20
$NaCl$	4.60	78.70
Na_2SO_4	2.30	16.20
$Na_3(C_6H_5O_7) \cdot 2H_2O$	0.76	2.60
KCl	1.60	21.50
$C_4H_7N_3O$	1.10	9.70
$CaCl_2 \cdot 2H_2O$	0.65	4.40
KH_2PO_4	4.20	30.90
NH_4Cl	1.00	18.70
$(NH_2)_2CO$	25.03	416
$Na_2(COO)_2$	0.02	0.15
$C_6H_8O_6$	0.10	0.57

Table 2 Amount of formaldehyde and corresponding ratio to urea.

Volume of urine (mL)	F/U ratio	Volume of formaldehyde (mL)
200	0.5	6.95
	1	34.75
	2	139

3.2.2- Measurements in liquid phase

The urea concentration, the total nitrogen (TN) and the formaldehyde concentration were respectively measured with a LC-MS system (LC system 626 with Shodex RSpak DE-413 column, Waters), a TN meter (TOC-VCSH, Shimadzu, Kyoto Japan) and formaldehyde measurement agents (MBTH method 8110) with a spectrophotometer (DR-2800, Hach). The total organic carbon (TOC) was measured using a liquid chromatography with organic carbon detection (LC-OCD, chromatograph for organics in water, model 8, DOC-LABOR DR. HUBER).

3.2.3- Measurements in solid phase

Solid residues on the filters were dried at 105^{0}C for 24 hours and weighted with an electric balance. The concentration of nitrogen and carbon in the solid phase was measured with a CN coder (Sumigraph NC-220F, Sumika Chemical Analysis Service).

3.2.4- Simulation and computing

The original mathematical model of the reaction proposed by Kabore *et al.* (2015) considers the reactants of urea and formaldehyde (U and F), solid products of methylene-urea ($(UF)_3$), intermediate polymers (UF and $(UF)_2$), and by-products (FUF, UFU, UFUFU and UFUFUFU). However, the simplified model, as shown in Figure 1, was adopted because the concentration of the intermediates and by-products cannot be accurately measured. So, the reactants U and F, the solid products of $(UF)_3$, the intermediate UF, and the by-products of FUF and UFU are considered.

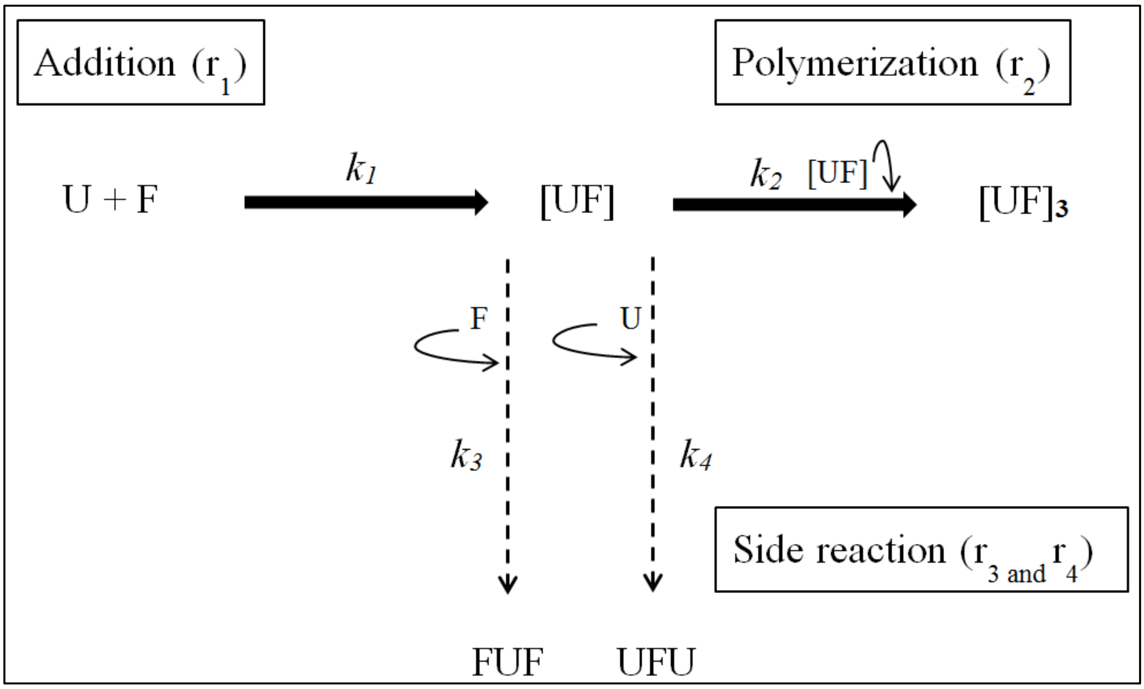


Figure 1 Simplified reaction model

The soluble products concentration which is the sum of intermediate and by-products in the experimental data can be estimated from the mass balances of carbon and nitrogen as respectively described in equations (1) and (2):

$$\text{Soluble products}_{\text{exp,C}} = \text{TOC} - [\text{U}]_{\text{C}} - [\text{F}]_{\text{C}} \tag{1}$$

$$\text{Soluble products}_{\text{exp,N}} = \text{TN} - [\text{U}]_{\text{N}} - [\text{F}]_{\text{N}} \tag{2}$$

where, $[\text{U}]_{\text{C}}$, $[\text{U}]_{\text{N}}$, $[\text{F}]_{\text{C}}$ and $[\text{F}]_{\text{N}}$ are respectively carbon and nitrogen concentrations of U and F. Regarding the simulated data, the soluble product concentration is defined as the sum of UF, FUF and UFU in equations (3) and (4) respectively for carbon and nitrogen content:

$$\text{Soluble products}_{\text{sim,C}} = [\text{UF}]_{\text{C}} + [\text{FUF}]_{\text{C}} + [\text{UFU}]_{\text{C}} \tag{3}$$

$$\text{Soluble products}_{\text{sim,N}} = [\text{UF}]_{\text{N}} + [\text{FUF}]_{\text{N}} + [\text{UFU}]_{\text{N}} \tag{4}$$

With, $[\text{UF}]_{\text{C}}$, $[\text{UF}]_{\text{N}}$, $[\text{FUF}]_{\text{C}}$, $[\text{FUF}]_{\text{N}}$, $[\text{UFU}]_{\text{C}}$ and $[\text{UFU}]_{\text{N}}$ are respectively the carbon and nitrogen concentrations of UF, FUF and UFU. The conversion factors were introduced to calculate the carbon and nitrogen content from molar concentrations of components based on their molecular structures as shown in table 3. The equations related to the elementary rate laws and the reaction rates are collected in table 4. These equations were computed with the Runge Kunta method. The least square method on the area difference between simulated and experimental data was applied for optimization of the reaction coefficients.

Table 3 Conversion factors to carbon and nitrogen content

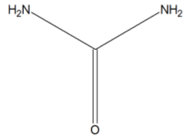
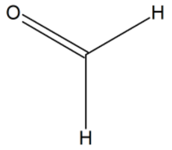
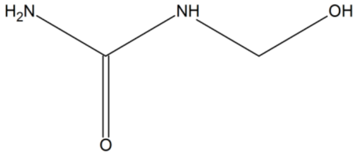
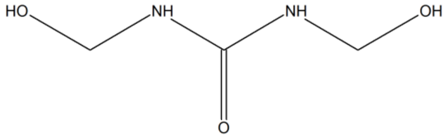
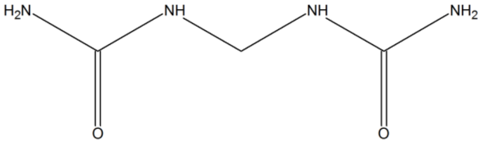
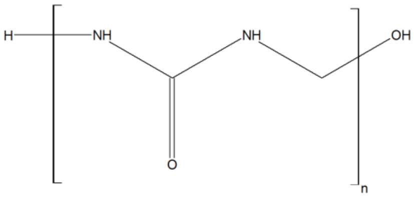
Species	Structures	mol-C/mol	mol-N/mol
U (urea)		**1**	**2**
F (formaldehyde)		**1**	**0**
UF (Intermediate)		**2**	**2**
FUF (side compound)		**3**	**2**
UFU (side compound)		**3**	**4**
$[UF]_3$ (solid)		**2**	**6**

Table 4 Simulated equations

Species	**Elementary rate laws**
U (urea)	$\frac{d[U]}{dt} = -k_1[U][F] - k_4[UF][U]$
F (formaldehyde)	$\frac{d[F]}{dt} = -k_1[U][F] - k_3[F][UF]$
UF (Intermediate)	$\frac{d[UF]}{dt} = -k_1[U][F] - 3k_2[UF]^3 - k_3[F][UF] - k_4[U][UF]$
$[UF]_3$ (solid)	$\frac{d[UF]_3}{dt} = k_2[UF]^3$
FUF (side compound)	$\frac{d[FUF]}{dt} = -k_3[F][UF]$
UFU (side compound)	$\frac{d[UFU]}{dt} = k_4[U][UF]$
Rate r_1	$r_1 = k_1[U][F]$
Rate r_2	$r_2 = k_2[UF]^3$
Rate r_3	$r_3 = k_3[F][UF]$
Rate r_4	$r_4 = k_4[U][UF]$

3.2.5- Experiment in real human urine

The data of the experiment performed by Ito et *al.* (2013) using real human urine have been collected to evaluate the precision of the model for real case. In that experiment, the F/U ratio was about 0.5 and the reaction time set to 24 h. The kinetics parameters of our model were then applied to those original data. The time course of urea concentration was observed.

3.3- RESULTS AND DISCUSSION

3.3.1- Experimental data

Figures 2(a) and (b) respectively illustrate the time courses of carbon and nitrogen concentrations of the species for F/U = 1. The dots represent the experimental data. The carbon and nitrogen concentration of U and carbon concentration of F decreased with time to indicate that they were just consumed to produce intermediates. The nitrogen concentration of F does not appear because formaldehyde structure is free from this element. The concentrations of soluble products increased then decreased, but they did not reach 0. This fact suggests a rapid production and consumption of the intermediate at first stage while the remaining soluble products may contain by-products which do not produce precipitates. The concentrations of solid products increased with time. The recovery rate of nitrogen as the solid products for F/U=1 was 85% after 24 hours.

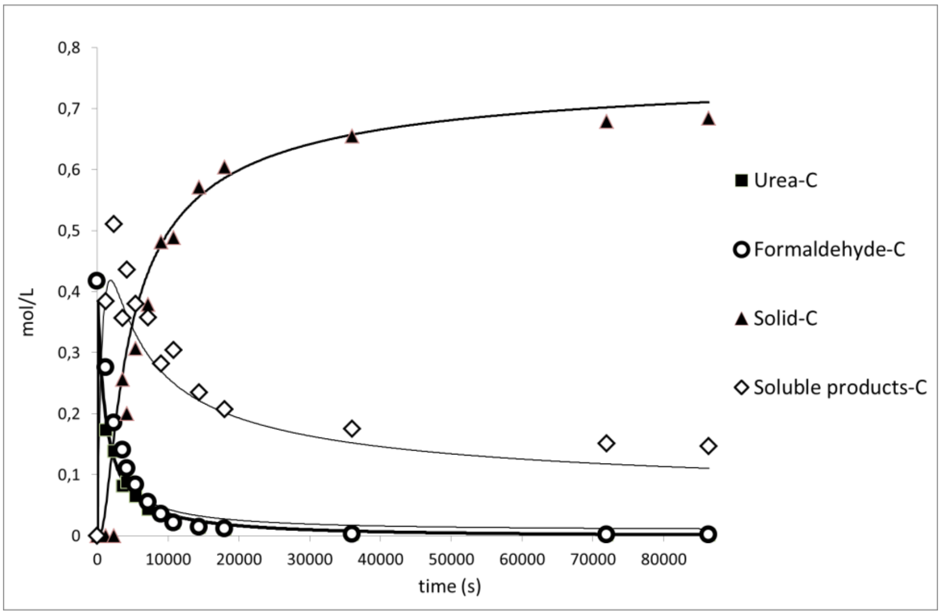


Figure 2(a) Time course of carbon of the different species for F/U = 1

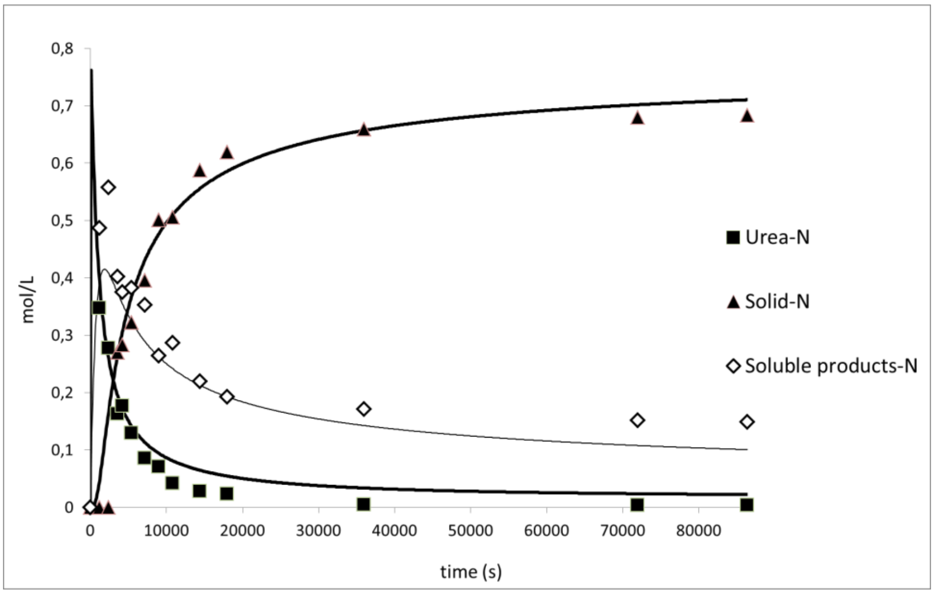


Figure 2(b) Time course of nitrogen of the different species for F/U = 1

Figures 3(a) and (b) respectively show the carbon and nitrogen concentrations for F/U=2. The concentrations gave same trends as F/U = 1, but the excess F was observed at final stage of the reaction. The recovery rate of nitrogen, 70%, was lower than F/U=1, although most of U was consumed in the reaction. This also indicates the existence of by-products. Figure 4(a) and (b) respectively show the carbon and nitrogen concentrations for F/U=0.5. These figures also give same trend on the concentrations. The U remains after 24 hours, although the F was almost consumed. The nitrogen recovery was 50%.

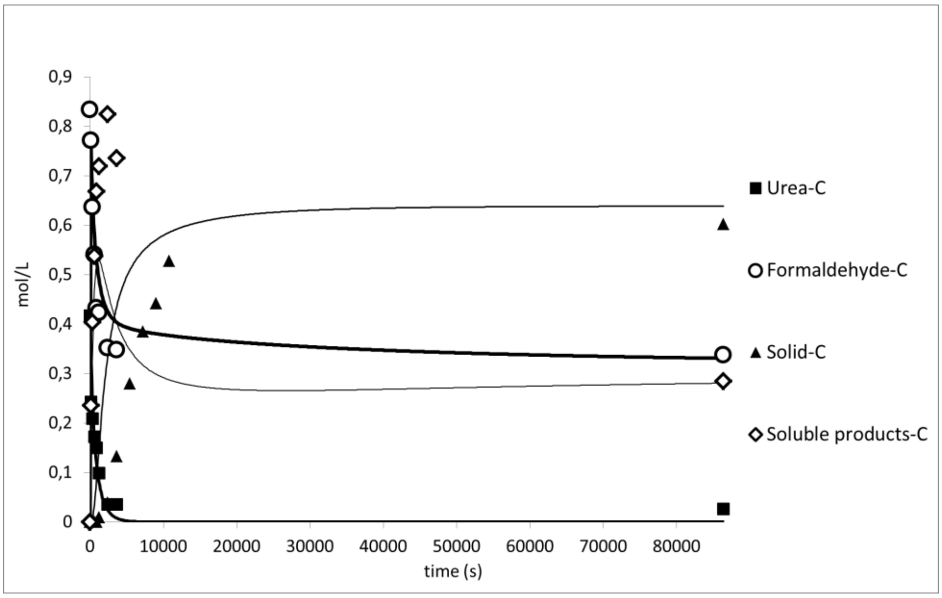


Figure 3(a) Time course of carbon of the different species for F/U = 2

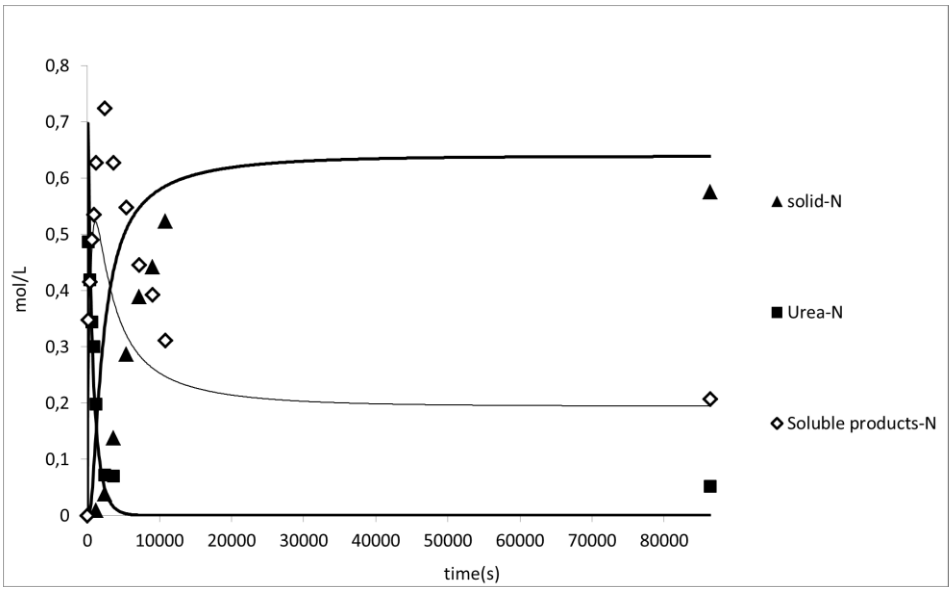


Figure 3(b) Time course of nitrogen of the different species for F/U = 2

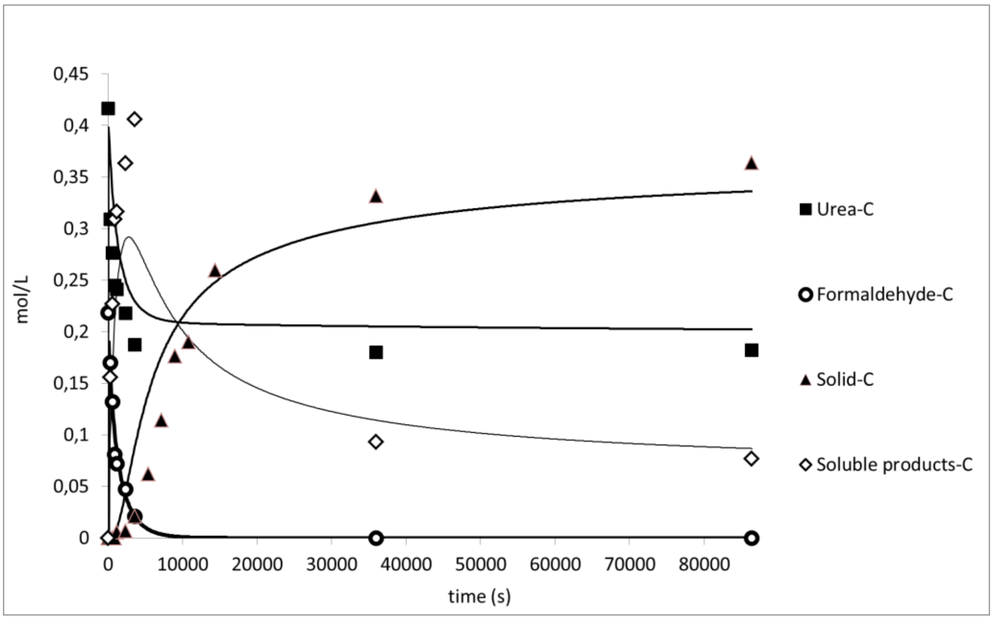


Figure 4(a) Time course of carbon of the different species for F/U = 0.5

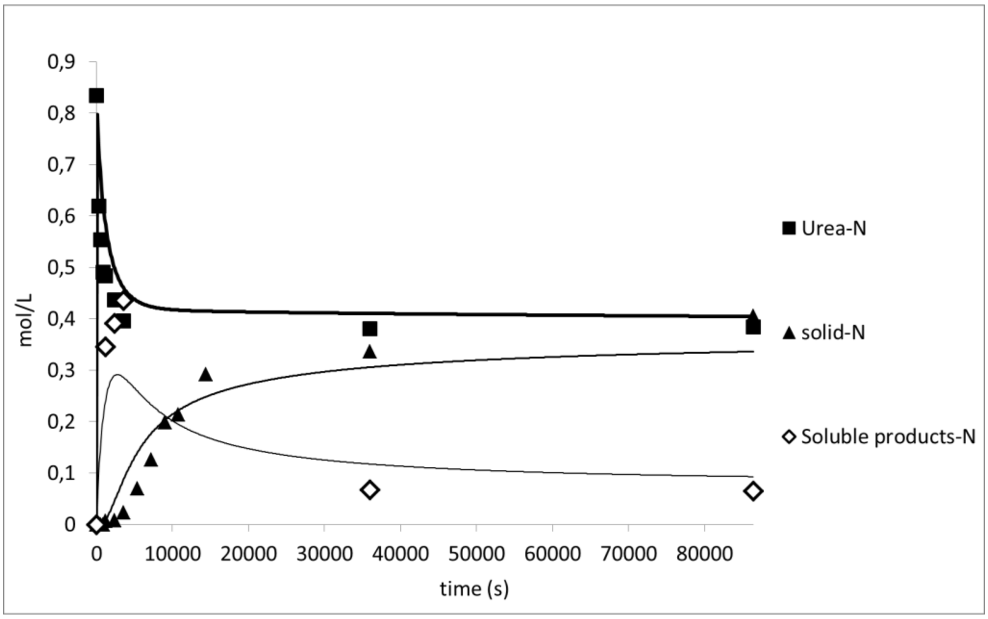


Figure 4(b) Time course of nitrogen of the different species for F/U = 0.5

3.3.2- Application of the mathematical model

The mathematical simulation with the simplified reaction model was performed to find the optimized reaction constants using the data of F/U=1. The solid lines in the figures 2-4 show the simulation results. The obtained reaction constants were $k_1 = 2.24 \times 10^{-3}$ ($L^{-1}.mol^{-1}.s^{-1}$), $k_2 = 2.05 \times 10^{-3}$ ($L^{-2}.mol^{-2}.s^{-1}$), $k_3 = 5.96 \times 10^{-5}$ ($L^{-1}.mol^{-1}.s^{-1}$) and $k_4 = 8.13 \times 10^{-6}$ ($L^{-1}.mol^{-1}.s^{-1}$). The simulation results also showed good fit for F/U=2 and 0.5. To maximize the recovery rate of nitrogen as solid particles, minimizing the concentration of soluble products is necessary. Figures 5(a)-(c) respectively illustrate composition of soluble products for F/U=1, 2 and 0.5. The reaction time was extended to 10 days to check whether the equilibrium of those soluble products was reached. At equimolar condition, a very rapid increase and decrease of intermediate UF was observed. Slight increase of the by-product UFU was found with higher concentration than FUF. This is due to the fact that the reaction rate coefficient to produce UFU is larger than that of FUF. When the F concentration was higher than U like F/U=2 condition, the rapid increase of UF followed by its complete consumption was similarly observed. But in contrast, the concentration of FUF was greater than UFU, because the high concentration of F gave higher production rate of FUF comparing to the one of UFU. At excessive U condition as F/U=0.5, the trends were similar to equimolar condition.

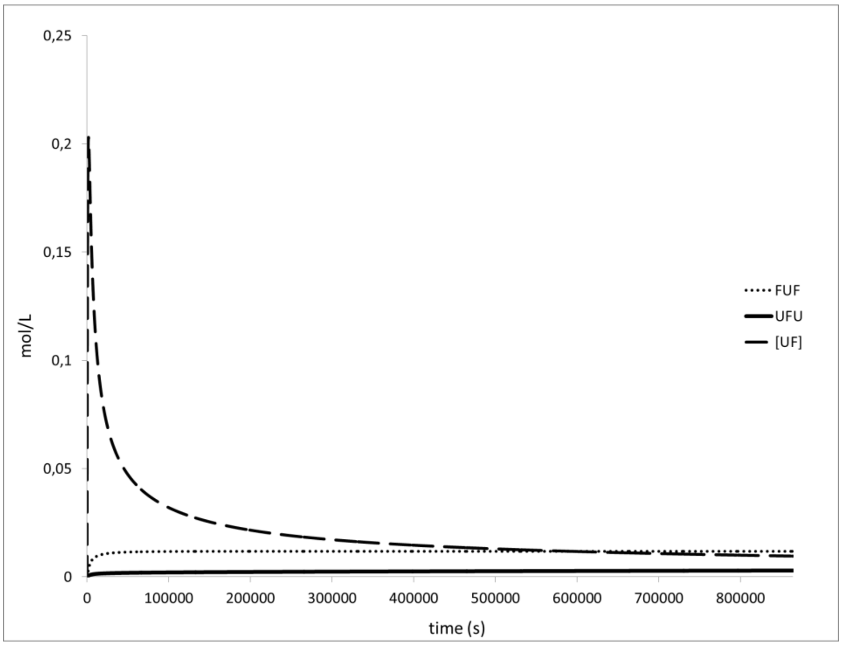


Figure 5(a) Contribution of FUF, UFU and [UF] for 10 days reaction time

F/U = 1

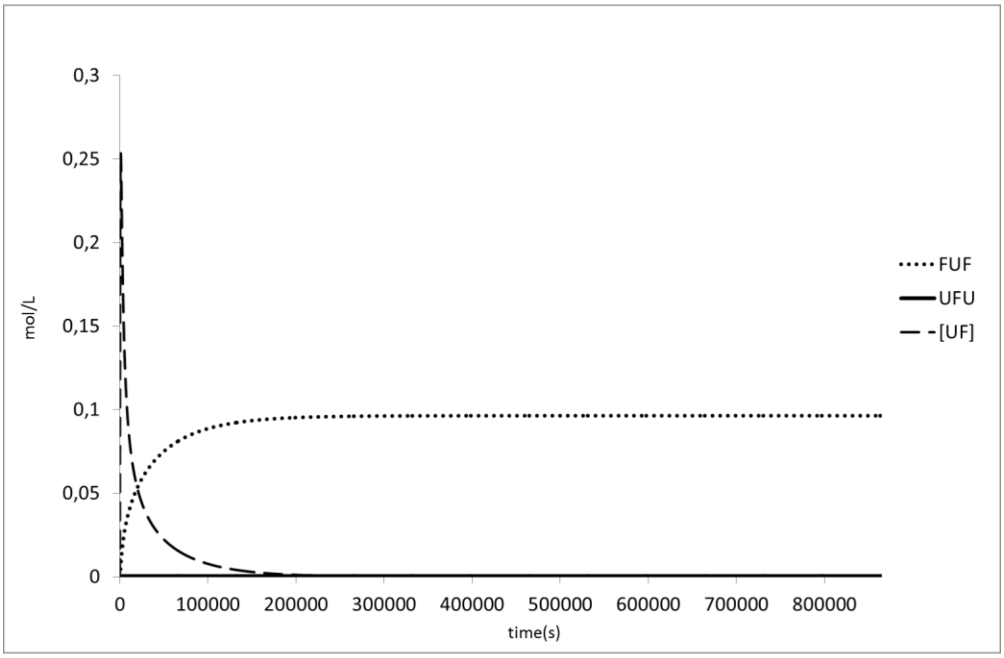


Figure 5(b) Contribution of FUF, UFU and [UF] for 10 days reaction time

F/U = 2

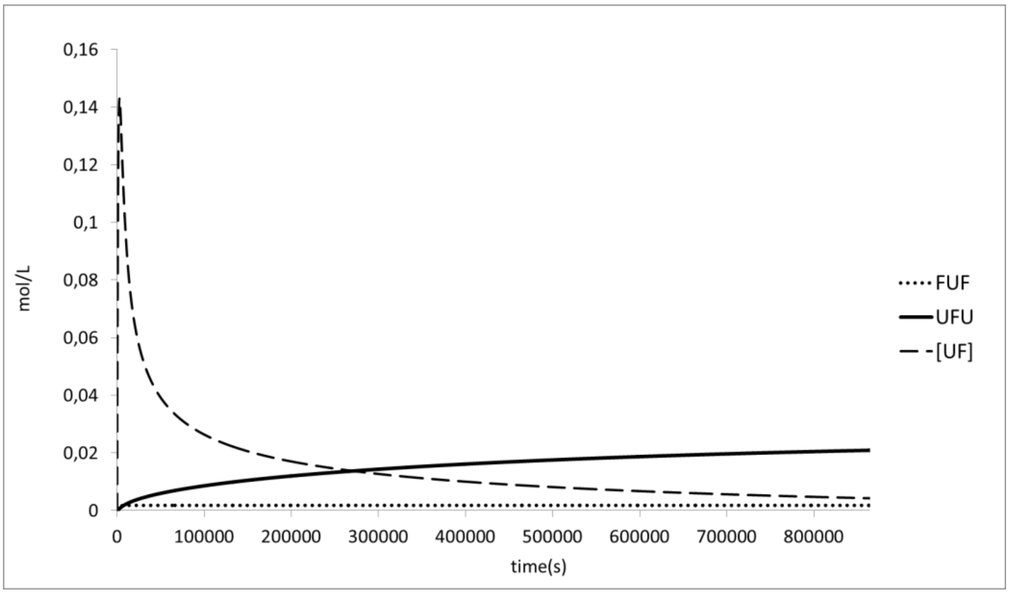


Figure 5(c) Contribution of FUF, UFU and [UF] for 10 days reaction time

F/U = 0.5

Figure 6 shows the relation of the F/U ratio to the recovery at 24 hours of reaction. The recovery pattern is based on the three experimental ratios (F/U = 1, 2 and 0.5) while the solid line is from simulated F/U ratios. Nitrogen recovery was gradually increasing with the addition of formaldehyde until the highest recovery at F/U = 1.2. When the F/U was higher than the peak, the recovery decreased with increase in F/U because of formation of FUF as discussed previously. So, the F/U should be controlled around 1 to maximize the nitrogen recovery.

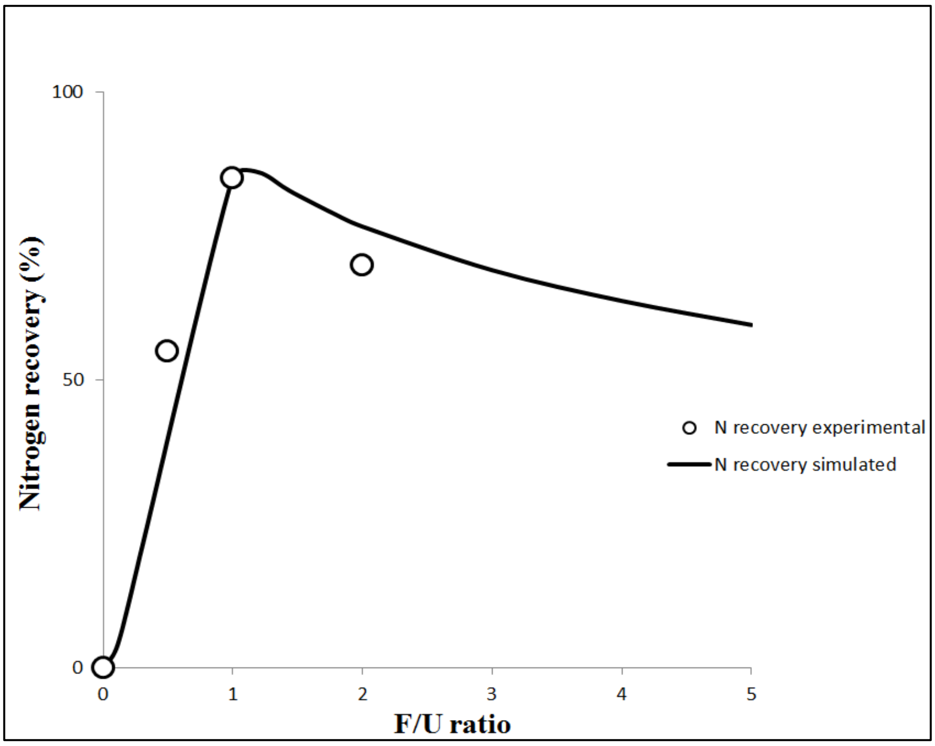


Figure 6 Recovery of nitrogen at equilibrium based on the F/U ratio

3.3.3- Experiment in real human urine

Figure 7 is the consumption of urea in real human urine. During the first stage which is the addition reaction with formaldehyde, the concentration of urea rapidly decreased and then reached the equilibrium. The behaviour of urea is essential as it is the one converted into slow release fertilizer throughout the reaction. The experimental and simulated data are shown for Urea-C and Urea-N respectively in Figures 7(a) and (b). As expected, the model was applicable with good fitting using the kinetics constants deter- mined in this study.

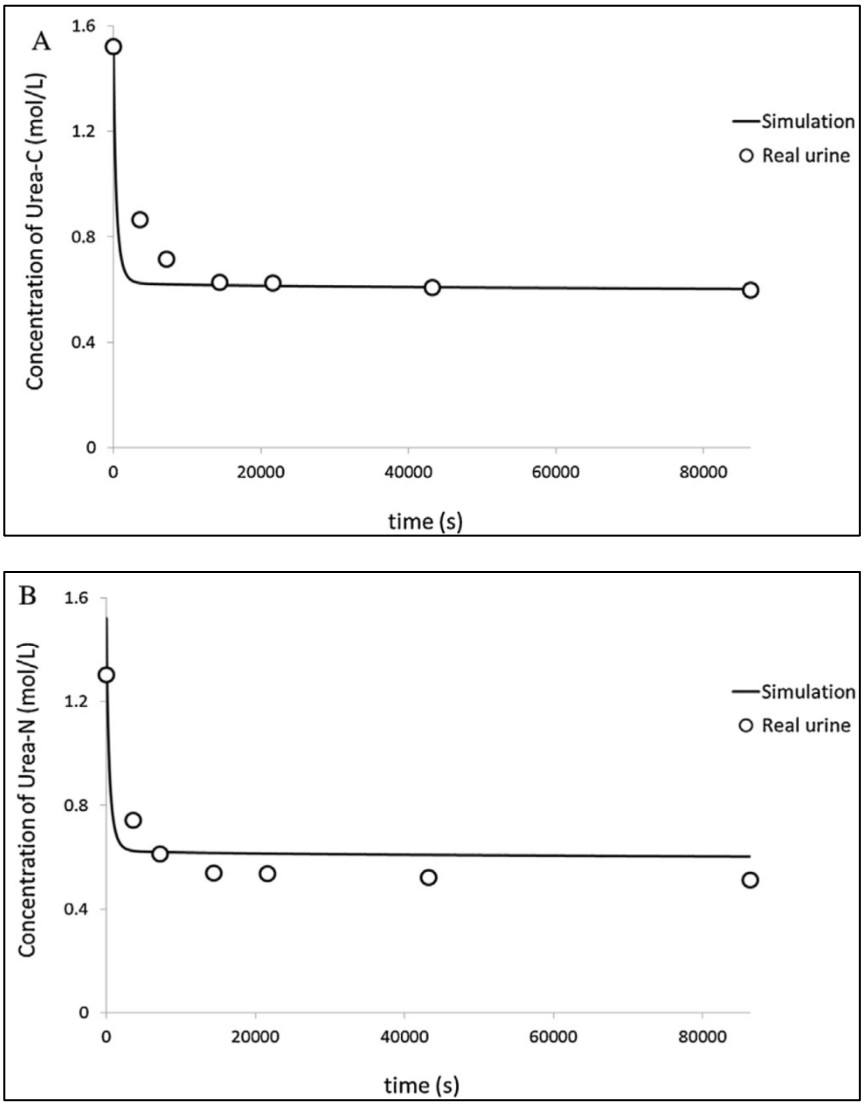


Figure 7 (a) Application of the model to real human urine (Urea-C).

(b) Application of the model to real human urine (Urea-N).

3.4- CONCLUSION

The kinetics for the production of methylene urea from human urine was investigated in this study. A simplified reaction model was proposed and the reaction constants at 25ºC were determined for each reaction. Constants k1 = 2.24 x 10^{-3} (L^{-2} mol^{-2} s^{-1}) for the addition reaction of urea and formaldehyde to produce the monomer [UF]; k2 = 2.05 x 10^{-3} (L^{-2} mol^{-2} s^{-1}), for the polymerization process leading to the precipitate; k3 = 5.96 x 10^{-5} (L^{-1} mol^{-1} s^{-1}) for the side reaction that forms the soluble product of FUF and k4 = 8.13 x 10^{-6} (L^{-1} mol^{-1} s^{-1}) for the side reaction that forms the soluble product of UFU. The model also fitted and described the cases of low and high F/U ratio. Side reaction leading to UFU was predominant for the first one while the other side reaction forming

FUF was predominant for the latter. The optimum F/U ratio condition for the highest recovery of nitrogen must be set up to 1.2 at pH 2 and at room temperature (≈25ºC). The current findings in the reaction kinetics allow the design of the reactor regarding the calculation of the volume, the reaction rates and the determination of the residence time. Future perspective may focus on further minimization of the by-products during the production through a system of reactors.

3.5- REFERENCES

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CHAPTER 4

PHYSICOCHEMICAL PROPERTIES OF THE FERTILIZER

4.1- INTRODUCTION

Domestic wastewater contains nutrients from human excreta. Nitrogen is the most abundant nutrient and approximately 80% of the fraction of the total nitrogen in grey water is from human urine (Höglund et al., 2002). Source separation of urine and its collection a potential to be reuse in agriculture. Indeed, the potential amount of nitrogen produced from the 7 billion people is about 30 million tons. This counts for 25% of the total demand in the world. Therefore, the reuse of urine could provide an alternative source of nitrogen fertilizer. However, the direct application of urine in agriculture faces problems that might be considered. Excessive urine application inhibits plant growth due to increasing soil electrical conductivity (EC) (Mnkeni et al., 2008). The urine contains 0.5 wt. % of sodium chloride which could accumulate in the soil system. Ammonia evaporation may release bad smell for the people near the field and washout by rainwater may also occur (Galloway and Cowling, 2002). There is also the concern of crops contamination by pathogens. Indeed, the urine has to be stored for at least 6 months at more than 20^0C (Höglund et al., 2002).

An alternative to those problems is the use of slow release fertilizers. The release of nutrient from these fertilizers is driven by their own biochemical degradation rate therefore reducing nutrients losses (Trenkel, 2010). Utilization of slow-release fertilizers can increase the efficiency of nitrogen fertilizer from 25 to 66% for tomato and from 22 to 79% for rice (Trenkel, 1997). Such improvements may vary from a slow release fertilizer to another depending on the synthesis process as they are polymers. Ito *et al.* (2013) produced solid particles of methylene urea, a slow-release fertilizer by a reaction of formaldehyde and urea in human urine under acidic condition. The particles were the same as the commercially available one. The recovery rate was gradually increasing with the increase in the ratio of formaldehyde to urea (F/U). The maximum was obtained for the equimolar F/U, and then decreased at higher F/U. The effect of F/U ratio on the reaction process and on the kinetics was previously discussed by Kabore *et* *al. (2016).* An assumption that the F/U could affect the degradation of the precipitated polymers has been made. Generally, degradation reflects changes in material properties such as mechanical, optical or electrical characteristics in crazing, cracking, erosion, discoloration and phase separation. Depending upon the nature of the causing agents, polymer degradations have been classified as photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation and biodegradation (Grassie and Scott, 1984).

This paper focuses on the precipitated polymers from different F/U ratios. The first objective was to determine the effect of F/U ratio on the properties of the polymers *i.e.* (1) Degree of polymerization (2) crystallinity (3) molecular structure and (4) thermal degradation. The second objective was to investigate the controllability of the nitrogen release.

4.2- MATERIALS AND METHODS

4.2.1- Preparation of samples

Synthetic urine solution whose composition is summarized in table 1 was used to simulate real urine (Wilsenach et al., 2007). The synthetic urine was used to avoid the fluctuation of chemicals that occurred in the real human urine. Two hundred millilitres were taken in a tightly closed glass bottle during the reaction to avoid escape of gases. The pH was adjusted to 2 with concentrated hydrochloric acid solution (JIS special grade, Wako Pure Chemical Industries). This specific value of pH was used based on the effect on the reaction rate described by Ito *et al* (2013). It was also based on the large capacity of the acidic condition to avoid the hydrolysis of urea in the urine during storage and experiments (Hellstrom *et al.,* 1998; Hotta and Funamizu 2008). The reaction temperature was kept at 25 °C in a water bath. A specific volume of 36% 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 amount of formaldehyde added to urea in the solution for each experiment is summarized in table 2. The solution was taken and filtrated after 24 hours with glass fibre filter (GB 140, Advantec), and then dried at 105˚C for another 24 hours.

Table 1 Components of synthetic urine

	Concentrations	
Components	g/L	mmol/L
$MgCl_2 \cdot 6H_2O$	0.65	3.20
$NaCl$	4.60	78.70
Na_2SO_4	2.30	16.20
$Na_3(C_6H_5O_7) \cdot 2H_2O$	0.76	2.60
KCl	1.60	21.50
$C_4H_7N_3O$	1.10	9.70
$CaCl_2 \cdot 2H_2O$	0.65	4.40
KH_2PO_4	4.20	30.90
NH_4Cl	1.00	18.70
$(NH_2)_2CO$	25.03	416
$Na_2(COO)_2$	0.02	0.15
$C_6H_8O_6$	0.10	0.57

Table 2 Amount of formaldehyde and corresponding ratio to urea

Volume of urine (mL)	F/U ratio	Volume of formaldehyde (mL)
200	0.5	3.48
	1	6.95
	5	13.9

4.2.2- Elemental Analysis

To determine the degree of polymerization of the polymers, the content of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) of the dried precipitates were analyzed by the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution (Hokkaido University, Japan).

4.2.2- Crystallinity and molecular structure

The crystal precipitates from the different F/U ratio were analysed by a powder X-ray diffraction (p-XRD) analyser (RINT-2000, RIGAKU). The particles shape was observed by a scanning electron microscope (SEM-EDS, SSX-550, Shimadzu corp.).

4.2.3- Thermal analysis

TG-DTA DTG and DSC

The weight loss, the temperature changes and the degradation rate were measure by simultaneous Thermogravimetric - Differential Thermal Analysis (TG-DTA) and Differential Thermogravimetry method (DTG). About 10mg of sample was inserted into 45µL alumina open crucible pan while another empty pan was used as reference. Flowing purge gas technique was used with nitrogen for furnace atmosphere control at 100mL/min (EXSTAR TG/DTA 6000, SII). 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). Specific heat of the samples was measured by a means of Differential Scanning Calorimetry (DSC) under the same conditions of gas and temperature, using 45µL opened aluminium crucibles pan as reference and as sample holder (EXSTAR 6000 W/DSC 6200).

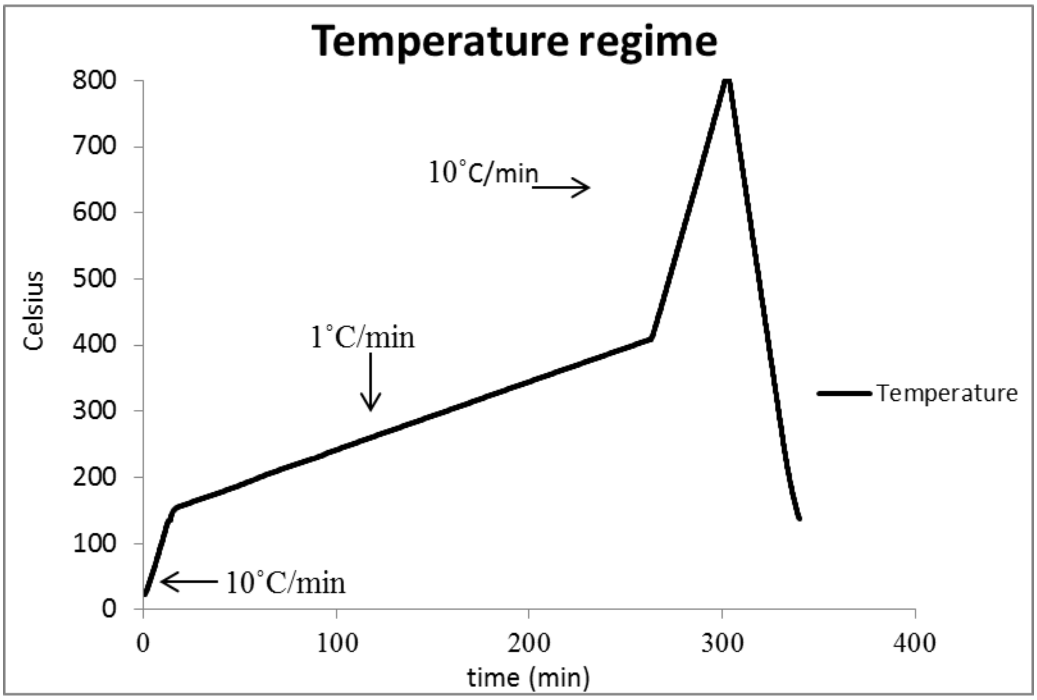


Figure 1. Temperature regime

4.2.4- Measurements in acidic solution

A concentration of 20g/L citric acid solution was used to degrade 1g of commercial ureaform and precipitate from F/U = 0.5; 1 and 5 in 1 litre. The method was based on the procedure of the Food and Agricultural Material Inspection Center (FAMIC). The total nitrogen contained in the precipitates as shown in Table 3 was measured with a CN coder (Sumigraph NC-220F, Sumika Chemical Analysis Service). Samples were periodically taken during 100 days to measure the concentration of the released urea. The urea concentration was determined with a Liquid Chromatography-Mass Spectrometry (LC-MS) (LC system 626, Waters, USA) and then converted to urea nitrogen (Urea-N) using the appropriate conversion factor.

Table 3. Nitrogen content in the solid samples

	TN (mg/g)
Ureaform	436
R05	415
R1	386
R5	364

4.3- RESULTS AND DISCUSSIONS

4.3.1- Elemental Analysis

The molecular formula of the polymer of methylene urea $[UF]_n$ 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 4. The data of weight percentage was 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, all the polymers had approximately the same chain length regardless the ratio with a degree of polymerization *n* about 3.

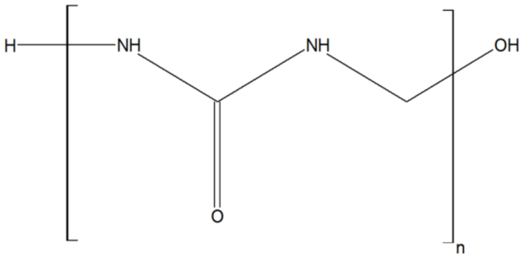


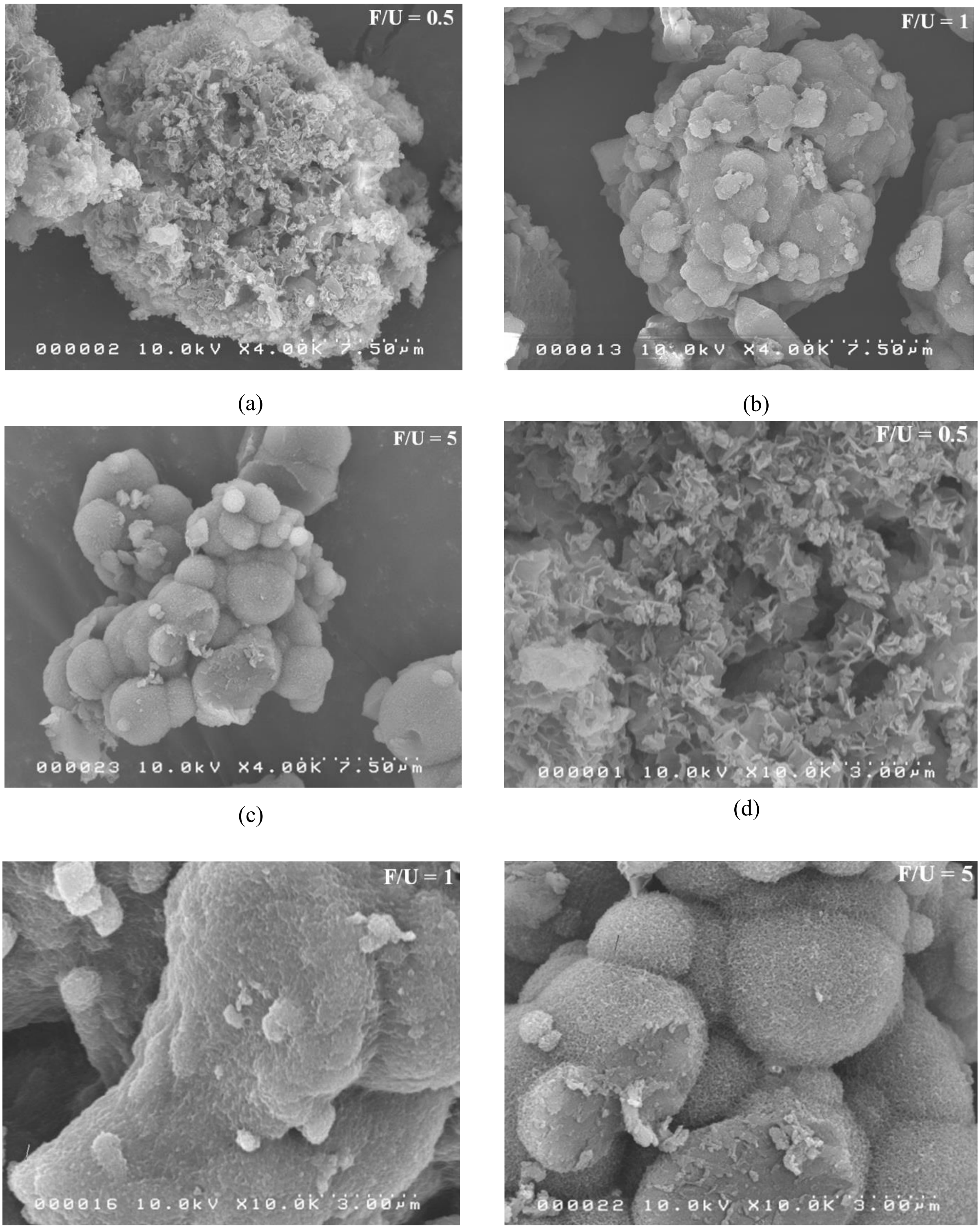
Figure 2. Polymer of methylene urea

Table 4. Weight percentage of elements and corresponding chain length

	Element in weight %				Element in moles %				Corresponding chain length *n*
F/U ratio	C	H	N	O	C	H	N	O	3
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

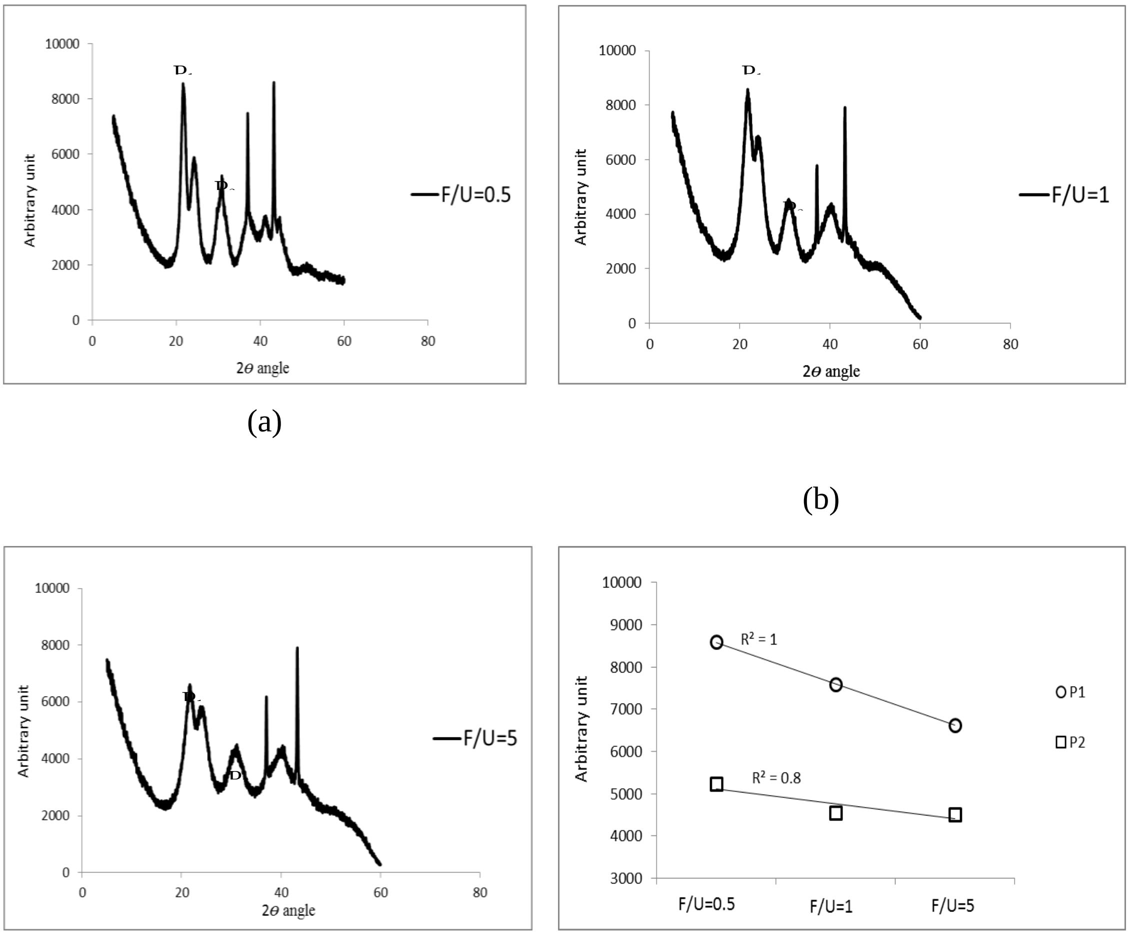
4.3.2- Crystallinity and molecular structure

Figure 2 shows the particle shape from the different samples. The particles appeared to change with the F/U ratio. They were rough and angular for F/U = 0.5 (figure 2(a)) and tend to turn spherical with the addition of formaldehyde (figure 2(b) and 2(c)). This result confirmed the visual observation of the solid state after drying. The surface of the particles in figure 3 were rough for F/U = 0.5 (figure 2(d)) and were getting relatively smoother with increasing F/U (figure 2(e) and 2(f)). However, the precipitates were structurally same as shown in the X-ray diffraction data (XRD) in figure 3 (a, b and c). Indeed the structure determines the diffraction pattern while the arrangement of the atoms within the unit cell determines the relative intensities (Cullity, 1956). Four major peaks were located at the same 2θ angle regardless the F/U ratio. However, the peaks' intensity was decreasing therefore reflecting a difference in the arrangement of the atoms which may result in a change of crystallinity. The marked peaks P_1 and P_2 can be found in XRD performed on standard samples of urea and formaldehyde respectively. Figure 3(d) shows the evolution of those two peaks for different F/U ratio. There clearly is a correlation between the F/U ratio and the crystallinity. The slope is a change from more to less crystalline as the F/U increased.



(a) (b) (c) (d) (e) (f)

Figure 3. SEM of samples from the different F/U ratio



(a)

(b)

(c)

(d)

Figure 4. XRD of samples from the different F/U ratio

4.3.3- Thermal analysis

TG-DTA

Figures 5-7 show respectively the results for F/U =0.5, F/U =1 and F/U =5. Analyses have been done 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 to the maximum weight loss of the polymer. T_e, is the temperature at the end of degradation and is associated to second change of slope on TG curve. The data on these temperatures are summarized in Table 5. Comparative analysis of T_P from the different ratios showed a decrease of the temperature required to degrade the polymers as F/U was increased.

A weight loss of 10% occurred in all samples in the region of 25°C to 200°C just before the degradation (Figure 5-7). 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. Considering that, the assumption made is that the weight loss was due to the presence of easy volatile particles in the polymers who disappeared by sublimation and also by dehydration.

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. 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.

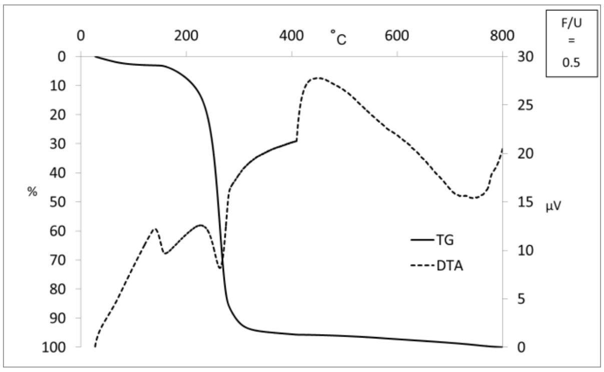


Figure 5. Thermal analys F/U = 0.5

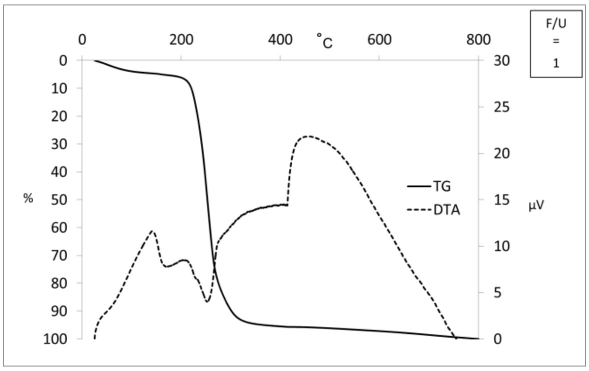


Figure 6. Thermal analys F/U = 1

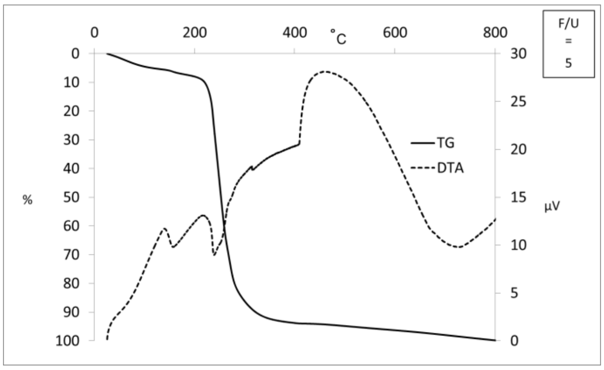


Figure 7. Thermal analys F/U = 5

Table 5. Temperatures related to the changes in the polymer

		Temperature ^{0}C	
Ratio	T_b	T_p	T_e
0.5	208.12	264.24	283.00
1	197.11	253.18	274.03
5	196.31	237.97	266.42

DTG

Figure 8 shows the degradation rates when the peak temperature T_p for degradation in the polymers, is reached. Polymers with high T_p requirement were also associated to higher degradation rates (Table 6). Elemental analysis showed that the polymers have the same chain length. Therefore the difference observed on the degradation rate was due to the difference of crystallinity. Indeed, as the F/U increased crystallinity decreased with less demand of degradation energy.

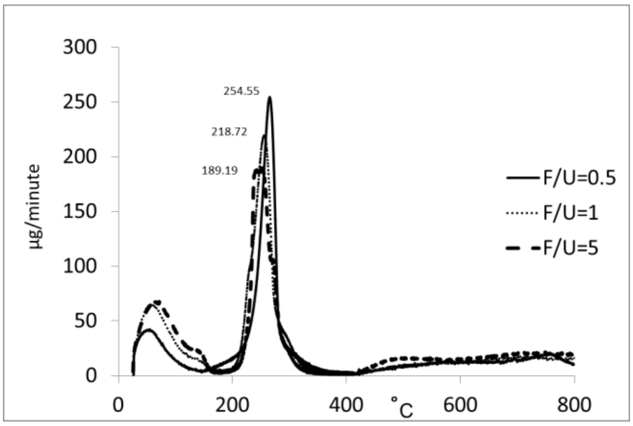


Figure 8. Degradation rate F/U = 0.5, 1, 5

Table 6. Degradation temperatures and associated degradation rates

F/U	T_p (°C)	DTG (μg/min)
0.5	264.24	254.55
1	253.18	218.72
5	237.97	189.19

DSC

The orientation of DSC peaks shows an endothermic reaction that occurs in the polymers (Figure 9). The peaks in the region before 0-20 minutes are due to the 10% weight loss observed previously with the TG-DTA. The ones in the region of 100-140 minutes are related to the degradation of the polymer. The power absorbed by the samples was increasing for low F/U ratio summarized in Table 7. The area under those peaks in this region represents the enthalpy of degradation and the demand was higher for smaller F/U ratio due to their crystallinity.

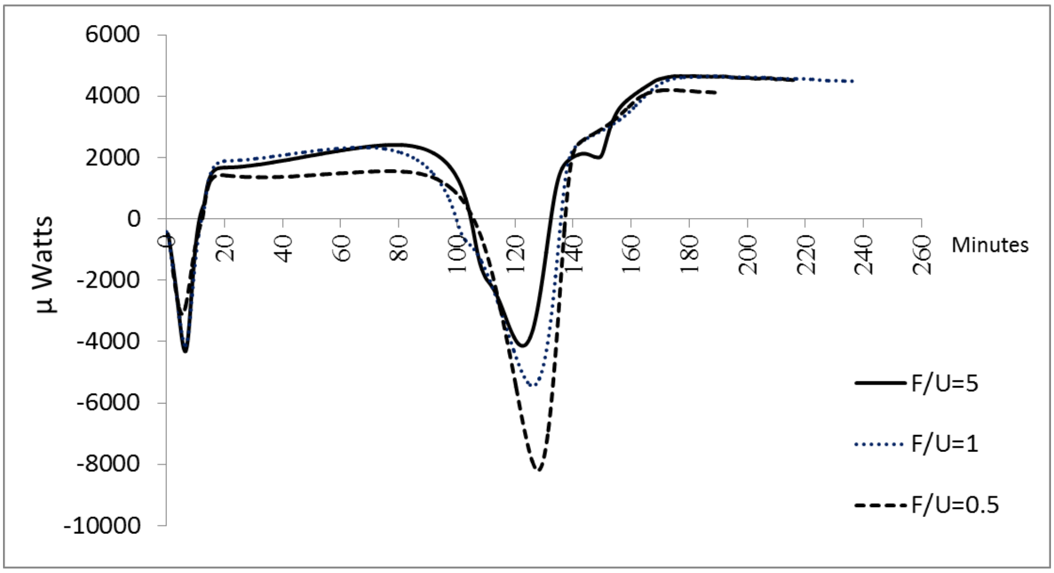


Figure 9 Differential Scanning Calorimetry of the samples

Table 7. Absorption of power and enthalpy of degradation

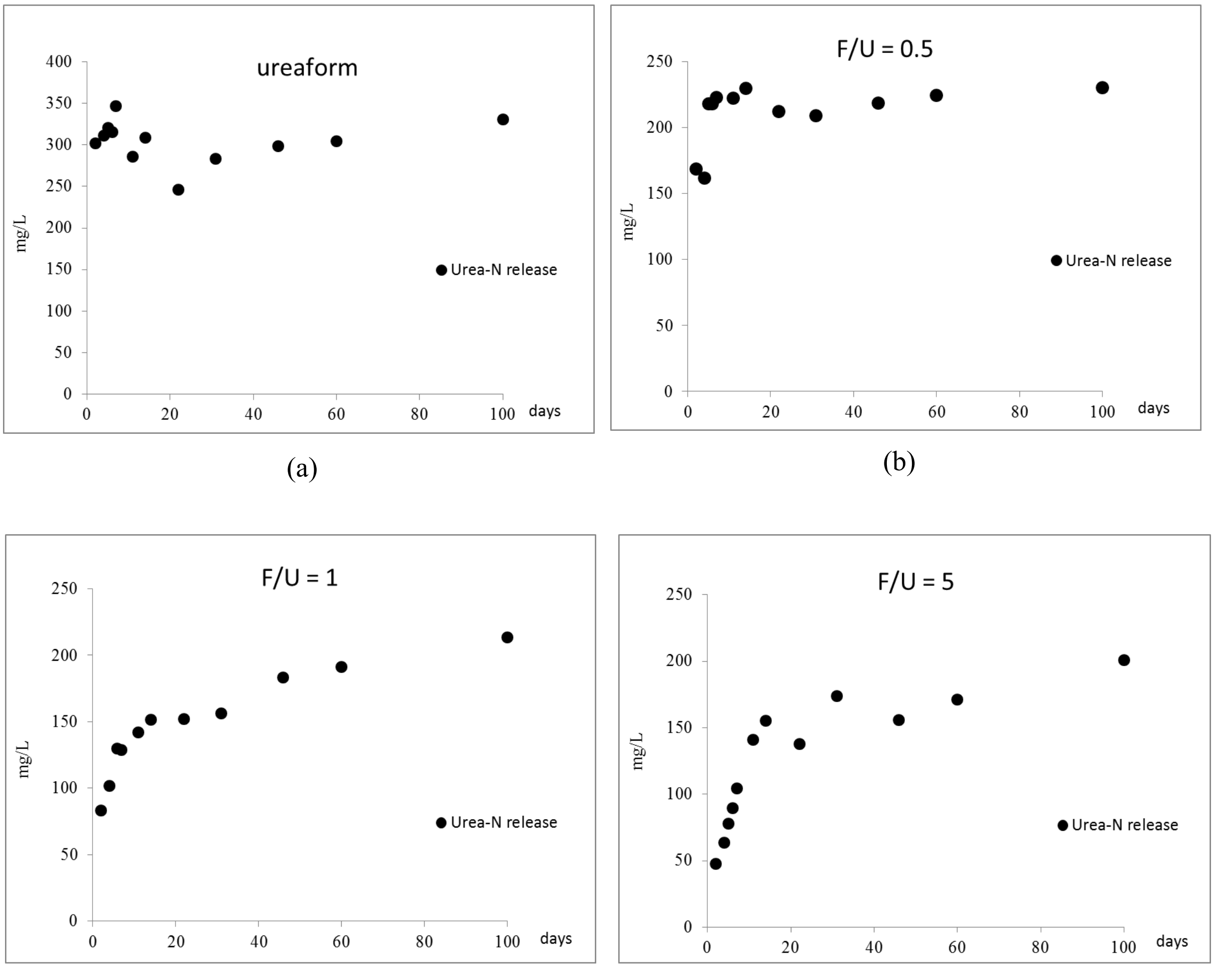
	Power absorption mW	Enthalpy ΔH kJ/g
F/U = 0.5	8.19	1.38
F/U = 1	5.27	1.01
F/U = 5	3.97	0.65

4.3.4- Measurements in acidic solution

The mineralization of ureaform in the soil has been described by a series of consecutive chemical processes (Alexander and Hans, 1990):

$$\textit{Ureaform} \rightarrow \textit{Urea} \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

Controlling the release rate of urea has therefore an impact on the availability of the different forms of nitrogen. Figure 10 ((a)-(d)) shows the release pattern of urea-nitrogen (urea-N) respectively from ureaform and samples from F/U = 0.5, 1 and 5 during 100 days. An immediate release of urea-N was observed for ureaform and F/U = 0.5 (figure 10(a) and 10(b)). This release was constant and respectively accounted for 80% and 50% of their initial total nitrogen. At the opposite, a gradual release of urea-N occurred for F/U =1 and 5(figure 10(c) and 10(d)). The released urea-N for these samples was about 50% of their total nitrogen content. The differences can be explained by the fact that nitrogen slow release fertilisers contain different fractions of nitrogen that are considered as water insoluble nitrogen (WIN) and hot water insoluble nitrogen (HWIN) (Clark *et al*, 1956). The slow release properties are generally conferred by the percentage of those fractions. This experiment shows that a controllability of the urea-N release is possible by changing the F/U ratio.



(a) (b)

(c) (d)

Figure 10 Release pattern of urea nitrogen

4.4- CONCLUSION

The effect of the formaldehyde to urea ratio (F/U) on some physic-chemical properties of methylene urea from human urine was evaluated in this study. The degree of polymerization ($n = 3$) of the precipitates was not affected by the F/U while the crystallinity was getting for lower ratio.

The crystallinity had in impact on all thermal properties. Indeed, the temperature of degradation (T_p), the degradation rate (DTG), the power absorption and the enthalpy (ΔH) were decreasing as the F/U ratio was increased.

The controllability of the urea-N release was possible by changing the F/U ratio. However, further research must be performed to determine the different fractions of nitrogen in the polymers and the effective nitrification scheme in the soil system.

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CHAPTER 5

SIMULATION OF THE REACTOR FEEDING PROCESS

5.1- INTRODUCTION

The chemical reaction to produce the commercial methylene urea is known as a two stages linear reaction of (1) an addition reaction of urea and formaldehyde followed by (2) a dehydrated condensed polymerization (Salthammer et al, 2010). The case of urine appeared to be different with an importance to the formaldehyde to urea ratio (F/U). In previous studies it was shown that the recovery percentage of nitrogen was increasing with the increase of the formaldehyde dosage (Kabore *et al,* 2015-a). The maximum was obtained at equimolar F/U before decreasing at higher concentration, due to the formation of by-products or rapid consumption of reactants depending on the different cases. The related mechanism was explained by Kabore *et al* (2016-a), who also proposed a reaction model and the kinetics studies (2016-b).

The dosage of F/U also has an impact on the physicochemical properties of the final product (Kabore *et al,* 2015-c). For instance, higher F/U conditions will lead to lesser recovery percentage with fertilizers having more and more rapid release rate of nitrogen. The agricultural application requires variants of the fertilizer based on crops requirements. There is the importance to minimize the by-products while maximizing the recovery percentage from various F/U ratios during the production. The experimental results obtained from previous studies were from the batch process. As lower recovery occurred at high F/U, the control of the feeding process of formaldehyde may influence the formation of by-products.

The main objective of this present chapter was to determine the appropriated process to increase the recovery of nitrogen and reduce the by-products at high F/U ratio while controlling the feeding of formaldehyde.

5.2- MATERIAL AND METHODS

5.2.1- Effect of intermittent injection of formaldehyde in the urine

The simplified reaction model proposed by Kabore *et al.*(2016-b) was used in this study. The equations of the kinetics rate laws and the kinetics constants k they proposed were used in a computer simulation. The feeding modes were changed to emulate the process of injections in the semi-batch reactor at F/U = 2. The table 1 summarizes the process based on the number of injections.

Table 1. Summary of the injections method

i	F_i	t_i
2	$\frac{F_0}{2}$	$\frac{t}{4}$
4	$\frac{F_0}{4}$	$\frac{t}{4}$
6	$\frac{F_0}{6}$	$\frac{t}{6}$

i = number of injections

F_0 = the total concentration of formaldehyde to put in 1 liter of urine to match F/U = 2.

F_0 = 0.832 mol/L

F_i = concentration of formaldehyde injected

t_i = time interval between consecutive injections

t = total reaction time = 24 hours

A comparison of the recovery of nitrogen and the formation of by products from this simulation process and the simulation from batch reactor was conducted.

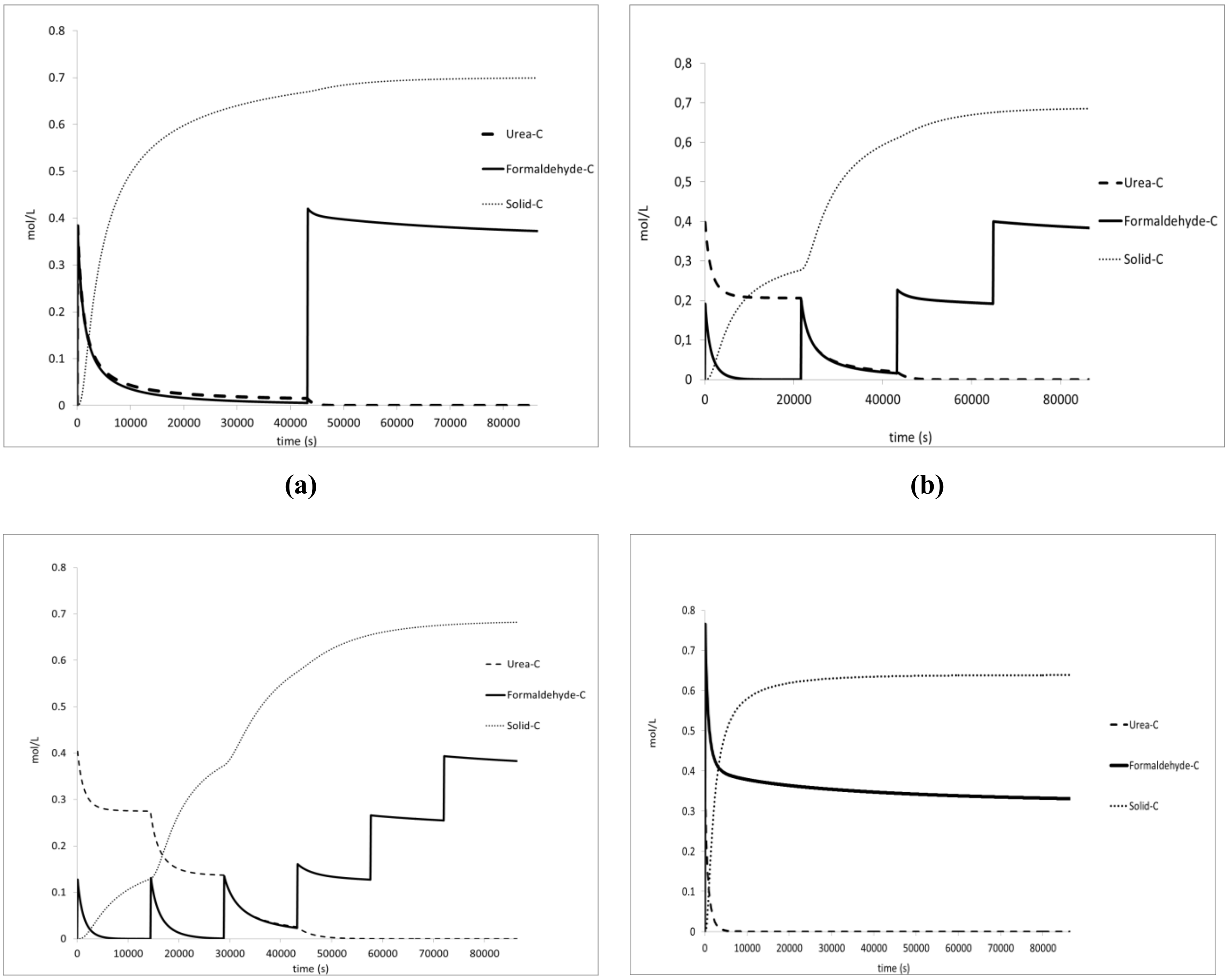
5.2.2- Effect of initial concentration of urea and formaldehyde

The reaction of the polymerization to produce the fertilizer is a third order one. Three molecules of the monomer [UF] are required to obtain a solid precipitate. This suggests that the more the monomer is produced, the more it can grow in the polymerization process. As the production of the monomer is from the addition reaction of urea and formaldehyde, the idea was to double their initial concentrations in the first simulation process and half their concentrations in a second simulation process to observe the sensitivity of the monomer. The initial concentrations of urea and formaldehyde to match F/U = 2 are respectively 0.416 and 0.832 moles per liter of urine.

5.3- RESULTS AND DISCUSSION

5.3.1- Effect of intermittent injections of formaldehyde in the urine

Figures 1 (a, b, c) are respectively the simulation results of injections number 2, 4 and 6. The results are showed in terms of carbon content, in order to consider the time course formaldehyde. The conversion process had been explained in the chapter 3. The recovery as the number of injections was increased was 79, 80 and 83%. The batch reactor in figure 1(d) had a recovery of nitrogen of 76%. This difference in the recovery is due to rate of formation of by-products when the formaldehyde supply is controlled. Indeed, as the addition reaction of urea and formaldehyde is fast, those reactants will produce the monomer UF in equimolar condition until urea disappears in the urine. The formation of by products may occur for late injections of excess formaldehyde that will react with the remained monomers and therefore slow down the polymerization process.

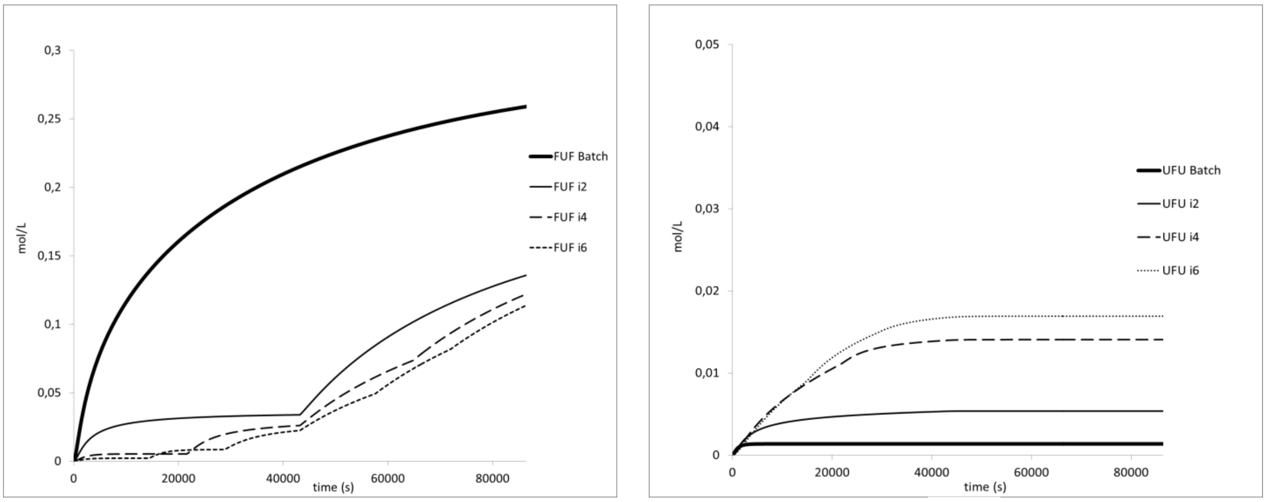


(a) (b)

(c) (d)

Figure 1. Simulation results – **(a)** 2 times injection of formaldehyde – **(b)** 4 times injection of formaldehyde – **(c)** 6 times injection of formaldehyde – **(d)** Batch reactor

The considered by-products are FUF and UFU. They are respectively produced when one mole of the monomer [UF] reacts with another mole of formaldehyde or urea. However, the production rate of UFU is ten times lower than that of urea. Figure 2 (a) and (b) shows that FUF is the dominant by-product due to its reaction rate and the excess formaldehyde. In figure, there is the observation that high number of injections reduces the formation of by-products. As a comparison, the concentration of FUF after 6 injections was 15 times lower than that from the batch reactor. The important presence of FUF in the batch reactor is related to the readily available excess formaldehyde at the beginning of the reaction. In such a case, the reaction rate of this by product is high; the monomer [UF] reacts quickly with the formaldehyde F to produce FUF. On figure 2(b) the equilibrium of UFU is reached for the batch reaction process and all the injections of the semi-batch because of the absence of urea. The relationship between the number of injections and the formation of UFU was opposite to that of FUF. An increase of the number of injections leads to the higher concentration of UFU because it is related to the consumption rate of urea. The situation that leads to some remaining urea in presence of the monomer [UF] will foster the formation of UFU. For this reason, the concentration of UFU in the batch reactor is minimal since the major part of urea reacted with the supplied formaldehyde at once. On the contrary, when the concentration of formaldehyde is divided to increase the number injections, small part of urea reacts with it to form the monomer [UF] that may react with the excess urea in waiting for the next injection of formaldehyde.

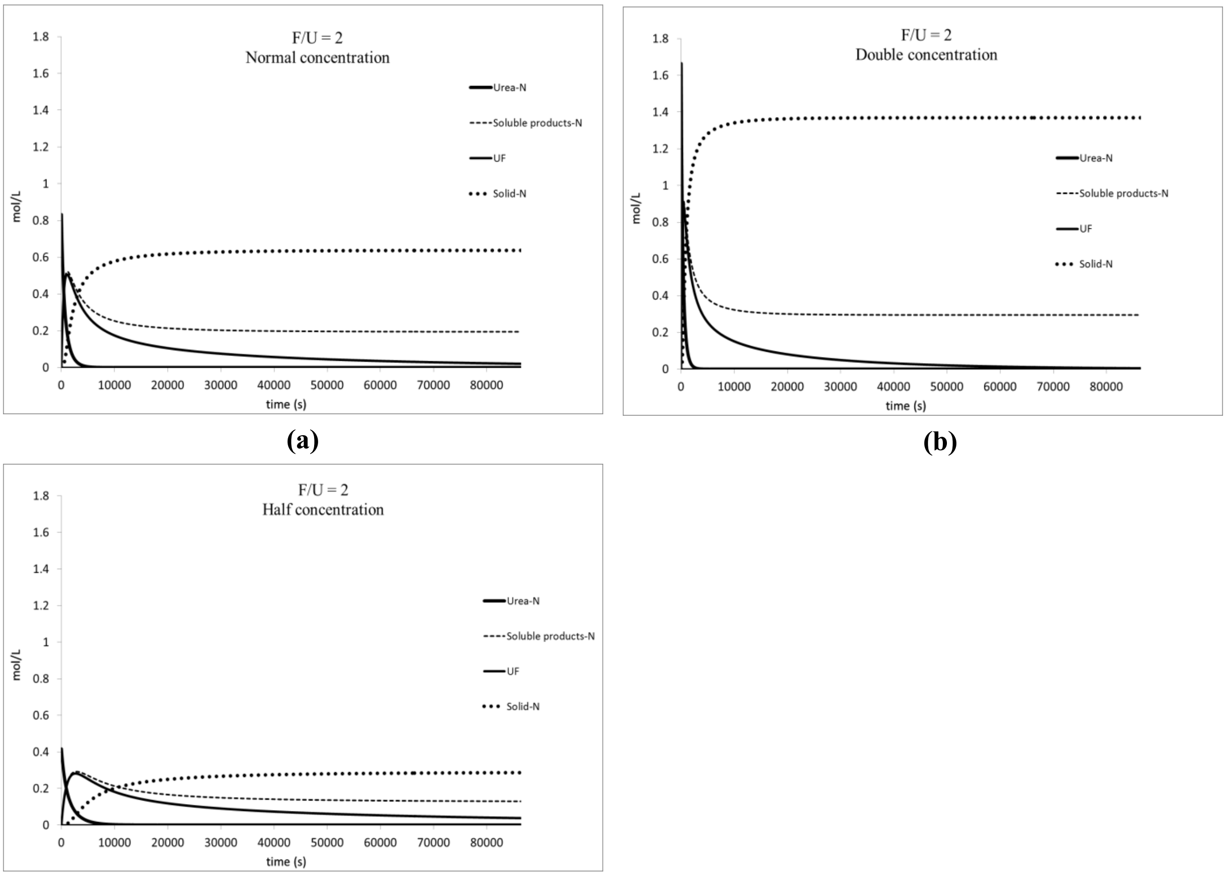


(a) **(b)**

Figure 2. Simulation results – **(a)** Evolution of FUF – **(b)** Evolution of UFU

5.3.2- Effect of initial concentration of urea and formaldehyde

Figure 3 (a, b and c) are respectively the results of 24 hours reaction for F/U = 2 when the initial concentrations of urea and formaldehyde are normal, double and half. The nitrogen content of the respective products is considered here. The recovery of nitrogen was 76%, 68% and 82 % respectively for the normal, half and double concentration. Such dependence of the recovery based on the initial concentrations was related to the rate of the monomer. Indeed, for double concentration of urea and formaldehyde, the production and consumption rate of the monomer was high. It means the polymerization could run faster and produce more precipitate. In about 15 hours, **[**UF**]** could polymerize and totally disappear from the liquid phase. In comparison, the monomer remained in the liquid phase after 24 hours. This suggests that the polymer is sensitive to the initial concentration of urea and formaldehyde. Practically, the use of concentrated urine can increase the recovery of nitrogen at higher F/U ratio.



(a)

(b)

(c)

Figure 3. Effect of initial concentration of urea and formaldehyde **(a)** Normal concentration **(b)** Double concentration – **(c)** Half concentration

5.4- CONCLUSION

In this study, possibility to reduce the by-products and to increase the recovery of nitrogen at high F/U ratio was evaluated. The semi-batch process for the production of methylene urea from human urine was simulated and compared to the simulated data from the batch reactor. Different injections numbers were performed for F/U = 2. In all processes, the recovery of nitrogen was higher than the recovery of the batch reactor. It also was observed that this difference of recovery was dependent on the number of injections that influenced the formation of by-products. FUF was the main by-product due to the excess formaldehyde. An increase of the number of injections decreased the concentration of FUF because of the controlled amount of supplied formaldehyde that completely reacts with the urea. At the opposite, the concentration of UFU was increasing with the number of injections but with slow reaction rate. Even with the possibility to reduce the formation of by-products and increase the recovery of nitrogen with the semi-batch reactor, it is important to mention the uncertainty on the product obtained by using the intermittent feed of formaldehyde. It might be different of the one from the batch reactor as the F/U ratio changes in the reactor at every injection.

The effect of initial concentration of urea and formaldehyde in the batch reactor showed that the recovery can also be increased when using more concentrated urine. In such case, the rate of the monomer is higher and the polymerization which is a third reaction order is facilitated.

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Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

The production of methylene urea from human urine has been assessed all along the chapters of this present research. The use of human urine is a contribution to nutrient reclamation and reuse while the extraction of nitrogen as a slow release fertilizer is a solution to the problems encountered while using soluble fertilizer or applying directly urine on crops. Indeed, in comparison, the nitrogen slow release fertilizer is not easily soluble in water, can increase its efficiency for better nutrient uptake by crops, cannot be easily washed out by streaming water and does not have bad odour emissions. The production of this fertilizer is a polymerization process of formaldehyde reacting with the urea contained in the urine.

The aim of this final chapter is to synoptically provide an overview of the findings related to the production process and further considerations to be taken account.

6.1- The reaction model and the F/U ratio

6.1.1- Findings

The reaction model in this study was proposed based on the evidences from mass spectrometry. We found that comparatively to the reaction used for the production of the commercial methylene urea, the case of human urine had additional paths that were considered as sub-reactions leading to by-products. Those by-products affected the nitrogen recovery percentage. The formaldehyde to urea ratio (F/U) has a very important role in the formation of those by-products. As the F/U was increasing, the recovery also gradually increased until the maximum of 90% was reached at F/U = 1 and then started to decrease for higher F/U. This was due to the fact that in the case of low F/U, the formaldehyde was quickly consumed while the urea was remained in the urine. The monomer produced after the addition reaction could react with the remaining urea to give the by-products UFU. For higher F/U, the urea was consumed but the recovery was low because the monomers could react with the remaining formaldehyde to give by-product FUF.

6.1.2- Recommendation

To avoid higher concentrations of by-products and for a maximum recovery of the nitrogen — about 90% — the process should be performed using F/U around 1. Simulation data showed that 90% recovery was possible at F/U = 1.2.

6.2- The reaction kinetics

6.2.1- Findings

The production of the commercial methylene urea is performed under stringent conditions of pH, temperature and concentrations of reactants. We succeeded to produce the same fertilizer using moderate conditions of pH and room temperature. Based on the reaction model we proposed the kinetics parameters that are the reaction constants k_1, k_2, k_3, k_4. The associated rate equations allow the design of a prospective reactor in the case high scale production is planned later on.

6.2.2- Recommendation

The reaction constants are temperature sensitive as described by the Arrhenius equation. Therefore any design based on our findings is for a production at room temperature (≈25ºC). The reaction constants are: $k_1 = 2.24 \times 10^{-3}$ ($L^{-1}.mol^{-1}.s^{-1}$), $k_2 = 2.05 \times 10^{-3}$ ($L^{-2}.mol^{-2}.s^{-1}$), $k_3 = 5.96 \times 10^{-5}$ ($L^{-1}.mol^{-1}.s^{-1}$) and $k_4 = 8.13 \times 10^{-6}$ ($L^{-1}.mol^{-1}.s^{-1}$).

6.3- Properties of the produced fertilizer

6.3.1- Findings

A slow release fertilizer as stated within the appellation is a fertilizer that can retard the release of the nutrients and therefore increase its efficiency. Depending on the crops requirements, variants of the slow release fertilizer based on the nutrients release rate might be used. We have found that the F/U ratio has an impact on the final product. Indeed, the physical state of the recovered fertilizer was transiting from rougher to smoother as the F/U was increased. We therefore assumed the possibility to get the controllability of the final product. The elemental analysis showed that the precipitate obtained from different F/U ratio were the same. The abiotic parameters such as the thermal properties and the crystallinity were assessed including the release pattern in acidic solution. The F/U = 0.5 gave very crystalline particles with higher energy requirements for the degradation (enthalpy and degradation temperature). About 50% of the nitrogen was immediately released at once (first day) in the dissolution test in acidic solution and the equilibrium was reached. In comparison, for higher ratio — F/U = 1 and F/U = 5 — the crystallinity and the energy requirement for the degradation were respectively decreasing. Considering the release rate, about 50% of their respective total nitrogen content was gradually released during the 100 days while the equilibrium was not yet reached.

6.3.2- Recommendation

We preconize the use of fertilizer from F/U = 0.5 for application on crops that requires an immediate availability of nitrogen. For application with slow release requirements, F/U = 1 and F/U = 5 are more suitable. For more general considerations, slow release properties were obtained for F/U ≥ 1.

6.4- The reactor feeding process

6.4.1- Findings

It was possible to reduce the by-products formation at higher F/U ratio with either the intermittent feed of formaldehyde or the increase of the initial concentrations of urea and formaldehyde for 24 hours of reaction.

For the semi-batch process, an increase of the number of the injections could decrease the concentration of predominant by-product which was FUF.

Regarding the batch reactor, concentrated urine (double concentration of urea) allowed the recovery of 82% of the nitrogen.

6.4.2- Recommendation

The controllability of the physicochemical parameters of the fertilizer was observed on precipitates from batch reactor. Even though it is possible to reduce the by-products and increase the recovery in the intermittent process, the effect on the final product is undetermined when using a semi-batch. Indeed, there is an uncertainty on the homogeneity of the product recover from the semi-batch reactor. In this reactor, the F/U ratio changes at every injection until the total amount of formaldehyde supplied at the end matches the desired F/U. Therefore, the batch reactor with concentrated urine appears to be suitable for the production.