

Mestrado Integrado em Engenharia Química

**FLOW REACTOR EXPERIMENTS  
FOR UREA DECOMPOSITION**

Differential Scanning Calorimetry and Gas Phase Analysis

**Tese de Mestrado**

Desenvolvida no âmbito da disciplina de  
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## Abstract

The Selective Catalytic Reduction system for bringing down NO<sub>x</sub> emissions from diesel engines is today considered a promising technology. In this system, ammonia is injected in the exhaust and reduces the NO<sub>x</sub> gases in a catalyst bed. But, due to practical reasons, a urea-water solution as a source of ammonia is used instead.

However, the thermal decomposition of urea is very complex and a reliable kinetic model is needed. As such, this work deals with the search of an experimental methodology using Differential Scanning Calorimetry and gas phase analysis to obtain reliable data from urea's decomposition; it also allows a deeper understanding on the decomposition of urea.

The effect of different heating rates, the influence of oxygen and NO for a urea solid sample, and the decomposition of a urea-water solution were studied.

Results verified that urea decomposes in two stages, starting right after its melting point (133 °C). It was also shown that heat and mass transfer limitations play an important role on product distribution and formation.

As for the oxygen experiments, no visible changes were noticeable, however, above 400 °C, NO was produced. This indicates that oxidation occurs but it is not certain which compound(s) is(are) being oxidized.

The NO experiments have also shown that above 400 °C, more nitric oxide is produced. At 900 ppm of NO there were no visible changes.

The urea-water solution decomposition experiment shows that, even though the relative production of ammonia is very high, the total recovery is less than for the solid samples. This leads to believe there is a shift in product distribution.

It is also proposed some future works and what could be improved to obtain better results.

## Resumo

O sistema de Redução Catalítica Selectiva para diminuir as emissões de NOx provenientes de motores diesel é hoje considerado uma tecnologia promissora. Neste sistema, é injectado amoníaco no escape e os NOx são reduzidos num leito catalítico. Mas, por razões práticas, é utilizado uma solução aquosa de ureia como fonte de amoníaco.

No entanto, a decomposição térmica da ureia é muito complexa e um modelo cinético fiável é necessário. Assim, com este trabalho pretende-se construir uma metodologia experimental usando Calorimetria Diferencial de Varrimento e análise de produtos na fase gasosa de modo a obter resultados fiáveis sobre a decomposição da ureia; permite também aprofundar os conhecimentos sobre esta mesma decomposição.

O efeito de diferentes programas de aquecimento, a influência de oxigénio e NO para amostras sólidas de ureia e a decomposição de uma solução aquosa de ureia foram as condições estudadas.

Os resultados mostram que a ureia decompõe-se em duas fases, iniciando-se a sua decomposição imediatamente após o seu ponto de fusão (133 °C). Mostrou-se também que limitações à transferência de massa e calor têm um papel importante na distribuição e formação dos produtos.

Quanto à influência do oxigénio, não são visíveis diferenças significativas, no entanto, acima de 400 °C, é produzido NO. Isto indica que ocorre oxidação, mas não é certo que compostos (ou composto) estão a ser oxidados.

A influência de NO mostra também que, acima dos 400 °C e a 450 ppm na alimentação, mais monóxido de azoto é produzido. A 900 ppm o mesmo já não acontece.

A decomposição da solução aquosa de ureia mostra que, apesar da produção relativa de amoníaco ser muita elevada, a recuperação total é menor comparativamente às amostras sólidas. Isto pode indicar que há uma mudança na distribuição dos produtos formados.

São também propostos alguns trabalhos futuros e o que pode ser melhorado para obter melhores resultados.



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## Table of Contents

Acknowledgements .....	iii
Abstract .....	iv
Resumo .....	v
Table of Contents .....	viii
List of Figures .....	x
List of Tables .....	xii
1. Introduction .....	1
1.1. Background .....	1
1.2. Problem description .....	4
1.3. Scope .....	4
2. Literature review .....	5
2.1. Decomposition products .....	5
2.2. Review of other experimental work .....	7
3. Material and methods .....	11
3.1. Experimental setup .....	11
3.1.1. DSC .....	12
3.1.2. FTIR .....	14
3.1.3. Mass flow controller .....	15
3.1.4. Gas tubes heating .....	16
3.1.5. Urea and gases used .....	17
3.2. Experimental procedure .....	17
3.2.1. Reproducibility of the calorimeter .....	18
3.2.2. Urea decomposition and gas phase analysis .....	19
4. Results and discussion .....	21
4.1. Reproducibility of the calorimeter .....	21

4.2. Effect of different heating rates (5, 10 and 30 K/min) .....	24
4.3. Influence of oxygen (7.5 and 15%) .....	30
4.4. Influence of NO (450 and 900 ppm) .....	32
4.5. Urea-water solution (32.5% by weight of urea) .....	34
5. Conclusions and future work .....	39
6. References .....	43

## Appendixes

## List of Figures

Figure		Page
1	Selective Catalytic Reduction (SCR) system .....	2
2	Thermogravimetric analysis of urea pyrolysis. Mass losses (-) and 1 <sup>st</sup> derivative (--) versus temperature were presented [15] .....	6
3	Urea powder decomposition experiment [10] .....	9
4	Urea solution decomposition experiment [10] .....	9
5	Experimental apparatus (red represents heated connections) .....	11
6	Differential Scanning Calorimeter .....	12
7	Furnace schematic; 1- Furnace, 2 – Reference, 3 – Sample .....	13
8	Fourier Transform Infrared Spectrometer .....	14
9	Dilution of the calorimeter exit gas .....	15
10	Mass Flow Controller .....	15
11	Pre-heating of the dilution gas .....	16
12	Reproducibility of the calorimeter; backgrounds .....	21
13	Reproducibility of the calorimeter; urea decomposition .....	22
14	Effect of different heating rates (5, 10 and 30 K/min); Calorimeter and gas phase analysis .....	25
15	Effect of different heating rates (5, 10 and 30 K/min); Distribution of ammonia and isocyanic acid .....	28
16	Effect of different heating rates (5, 10 and 30 K/min); Total recovery .....	29
17	Influence of oxygen (7.5 and 15 %); Calorimeter and gas phase analysis .	30
18	Influence of oxygen (7.5 and 15 %); NO production .....	31
19	Influence of NO (450 and 900 ppm); Calorimeter and gas phase analysis	32
20	Influence of NO (450 and 900 ppm); NO production .....	34
21	Urea-water solution (32.5 % by weight of urea); Calorimeter and gas phase analysis .....	35

22	Urea-water solution (32.5 % by weight of urea); Distribution of ammonia and isocyanic acid .....	36
23	Urea-water solution (32.5 % by weight of urea); Total recovery .....	37
24	New experimental setup .....	42

## List of Tables

Table		Page
1	Gas mixtures concentrations .....	17
2	Experiments program; reproducibility of the calorimeter .....	19
3	Test mass samples .....	19
4	Experiments program; urea decomposition .....	20
5	Urea melting enthalpy; literature values .....	23
6	Urea melting enthalpy; experimental results .....	23

## 1. Introduction

### 1.1. Background

Since the Industrial Revolution pollution has become a serious problem. Nowadays, knowing the damaging effects on the environment and on human health [1], efforts are being made to combat this problem.

One of the most debated subjects is air pollution [2]. Many compounds are released to the atmosphere every second and some are responsible for global warming [3] while others are known to cause diseases.

These compounds can include particulate matter, carbon dioxide or nitrogen oxides, which are emitted from different sources, where motor vehicles account for a big part.

Several legislations on air quality are already in place and more is yet to come. In Europe, the legislative package for light and heavy duty vehicles emissions, Euro 5 and 6 [5], is currently being prepared and aggressive cuts on emissions are expected. Therefore, there is a need for the interested parties (motor industry, research groups, etc) to work on feasible solutions that match the legislation requirements.

With air quality degrading in the last decades, new technologies and several improvements has been made available to reduce air pollution. Regarding motor vehicle gas exhaust systems, most of the efforts are focused on reducing the emissions of the three main gas pollutants: hydrocarbons, carbon monoxide and nitrogen oxides.

Means to reduce pollution can include fuel additives, as oxygenated compounds [12], or engine modifications, either of which is not enough to bring emissions to acceptable levels.

Post-combustion technologies are also available, with the catalytic converter being introduced in the 1970's. Over the years this technology evolved into the three-way catalysts, allowing reduction of all the three main pollutants at the same time [6].

With the increase of diesel powered vehicles, particulate matter (PM) also continues to pose a serious threat to human health [7]. But PM control technologies, such as diesel particulate filters, are being introduced on a larger scale.

However, according to EPA [4], nitrogen oxides, commonly referred to as NO<sub>x</sub>, are the only of the principal air pollutants to have increased its emissions over the last 30 years. Because of its reactivity, it contributes to the formation of ground-level ozone, acid rain, global warming and all the inherent dangers to these problems. This means that more efforts must be made to decrease NO<sub>x</sub> emissions.

Currently, diesel engines pose a serious challenge for NO<sub>x</sub> emissions due to their lean working conditions which makes controlling of these emissions difficult as the conversion from NO<sub>x</sub> to N<sub>2</sub> needs a reductant [6].

This way, one of the most promising technologies to achieve a reduction of NO<sub>x</sub> in diesel engines is the Selective Catalytic Reduction (SCR) [8]. The idea behind this concept is to inject ammonia into the exhaust system and NO<sub>x</sub> will be reduced on a catalyst bed; the process is usually called DeNO<sub>x</sub>.

But, due to the difficulty of ammonia storage in vehicles, the use of a urea-water solution as an ammonia source is becoming a more viable method (Figure 1).



Figure 1 – Selective Catalytic Reduction (SCR) system.

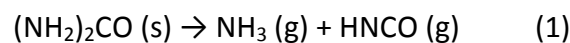
In practise a registered trademark, AdBlue, is used as a urea-water solution. It contains 32.5% by weight of urea and a freezing point of -11 °C (freezing-point depression). Even though it is safe to handle it still poses some challenges as the high freezing point could

be a problem for cold winters. This has led to the proposal of using solid urea instead of a water solution; but the implementation of this solution is quite challenging [8].

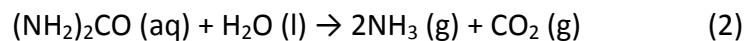
Independently of the form of urea used, its decomposition should be ideally complete before reaching the catalyst bed. However a mixture of urea together with decomposition products, such as ammonia and isocyanic acid, will hit the SCR catalyst. This has to do with different rates for the reactions involved and short residence times for the exhaust system. Corrosion problems caused by urea and its by-products are also important [8].

But, depending on how urea ((NH<sub>2</sub>)<sub>2</sub>CO) is delivered to the exhaust gas system [9], its main decomposition products are ammonia (NH<sub>3</sub>), isocyanic acid (HNCO) and carbon dioxide (CO<sub>2</sub>):

For dry solid urea,

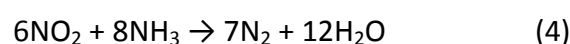
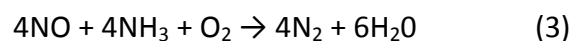


And for urea-water solutions,



For this last reaction, it is considered that HNCO is hydrolyzed into ammonia; some more details are given in the next chapter.

Ammonia would then be used as a reducing agent for NO<sub>x</sub> according to the following reaction schemes [10]:



This set of reactions would occur in a temperature range compatible with the exhaust system; this means, in a range of 250 – 450 °C [8].

But despite being a very promising technology, urea-SCR still faces some problems; some include the volume of the catalyst, the ammonia slip [16], and a deeper understanding on how urea decomposes as the reaction paths shown above are known to be accompanied by other complex parallel reactions.

## **1.2. Problem Description**

Due to the complexity of urea's thermal decomposition, reliable data is needed for modelling purposes. Therefore, this study deals with the search of an experimental methodology using Differential Scanning Calorimetry and Gas Phase analysis to obtain reliable data from the decomposition of urea. Also, the analysis of the obtained results provides a further understanding on urea's decomposition.

## **1.3. Scope**

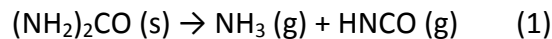
This work is divided in four parts. A first small literature review where the main products from urea's decomposition are presented and other works related to different experimental set ups. A second part where the equipment used is described as well the proposed experimental procedure. The third part consists of presenting the results together with its discussion. Finally, the conclusions are presented and recommendations for future work are explained.

## 2. Literature Review

### 2.1. Decomposition products

Ever since the decomposition of urea was first presented [13], the understanding of its products, by-products and reaction pathways have been the subject of several studies.

Knowing which products, to which extension or when are they formed is of obviously practical interest when modelling the SCR system. Nowadays the use of Computational Fluid Dynamics code to model this type of system is very common [19] and the construction of a reliable kinetic model is very important. One example of such model is when urea-water solution is sprayed into the exhaust system, causing the water to evaporate and a particle of solid urea results [8]. This would lead to the ideal path for the thermal decomposition of the urea solid particle:



(Basic chemical and physical properties of these three compounds can be found in Appendix A.)

Such example serves the purpose to show the possibilities of models that are possible to build, which, in turn, reinforces the need for reliable data for urea's decomposition.

The search for reliable information is mostly due to the fact that the decomposition reactions for urea are complex and depend on several conditions, either temperature, heating rate, pressure, open or closed vessel and mass and heat transfer limitations are also thought to be important [15]. And the influence of each parameter is not yet fully understood.

One study that is worth giving attention, given it is one of the most comprehensive of the subject at hand, was done by Schaber *et al* [15],

This study on the thermolysis of solid urea considers two main decomposition regions and involved thermogravimetric analysis of urea decomposition under nitrogen purge on an open platinum pan (Figure 2).

In a first region, above its melting point of 133 °C and up to 250 °C, urea starts to slowly vaporize and then begins to decompose according to reaction scheme (1). But other complications arise with increasing temperature as the production of biuret from urea and isocyanic acid or the formation of cyanuric acid, ammelide, ammeline or melamine. In this same region the decomposition of biuret back into HNCO is also said to occur.

After 250 °C, the *High-performance liquid chromatography* analysis (see Appendix B) showed there is no appreciable amount of urea, just some by-products that start to decompose into HNCO in this second region; above 350 °C and up to 500 °C, a mass loss of about 5 % leads to practically no residues left.

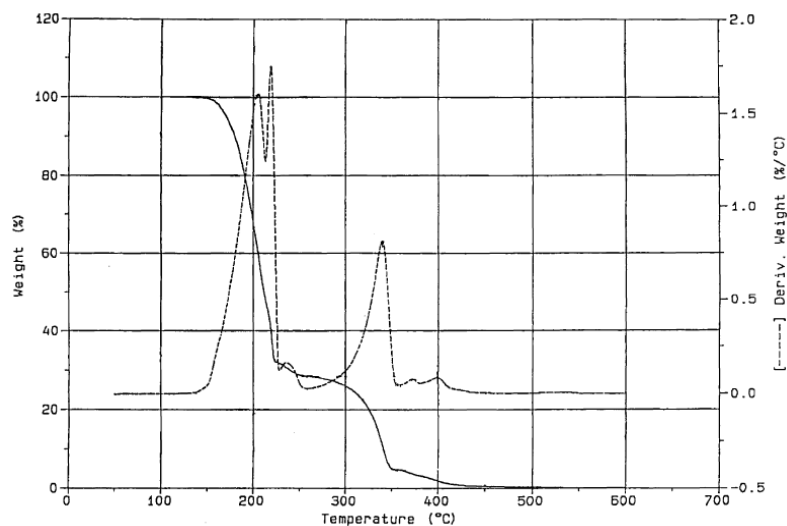


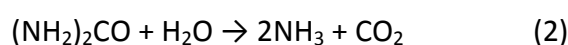
Figure 2 – Thermogravimetric analysis of urea pyrolysis. Mass losses (–) and 1<sup>st</sup> derivative (–) versus temperature [15].

The complexity of the reactions involved can be better understood with a reaction scheme proposed by Schaber *et al* [15] in Appendix C.

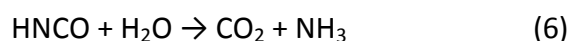
This means that the product distribution is temperature dependent and considering the operating temperature of the SCR system, it is obvious that the gas exhaust temperature will influence the production of ammonia.

In other words, to maximize the conversion of urea into ammonia, the temperature should be as low as possible [14], otherwise the formation of other products could become a problem.

Regarding the urea-water solution, there is not enough detailed information on possible by-products or pathways. However, it is known that, besides the main reaction (2), the by-products mentioned above for solid urea are also expected to be produced [10].



As previously mentioned, it should be noted that reaction (2) results from the merging of two other reactions; a first one where urea decomposes into ammonia and isocyanic acid (5) and a second one where HNCO is hydrolyzed into carbon dioxide and ammonia (6). The hydrolysis of isocyanic acid usually takes place at the SCR catalyst or at metal surface to some extent.



This brief description shows the amount of compounds that are at stake here.

## 2.2. Review of other experimental work

The use of flow reactors to study urea's decomposition has been done by other authors but with different conditions.

Gentemann and Caton [9] have studied the decomposition of a urea-water solution using a laminar flow reactor for the Selective Non-Catalytic Removal (SCNR) process. As the name for this system implies, it does not use any catalyst to reduce the NO<sub>x</sub> gases,

instead, urea or ammonia will act directly as the reducing agent. The working temperature for this system is higher than for the SCR system, in the range of 500 – 1000 °C. The presence of oxygen was also studied.

The experimental set up consisted of two mass flow controllers, one for nitrogen gas (inert conditions) and other for oxygen. Then, the urea-water solution would be injected into the gas stream by the means of a syringe. The decomposition would take place in a furnace, where a steel pipe lined with quartz tube works as the flow reactor. The quartz tube helps to prevent reactions that could occur on the metallic surface. At the end of the reactor, the stream is diluted with nitrogen to prevent further decomposition and to bring the mixture to the appropriate temperature for the FTIR gas cell that detects the decomposition products. The tubes before the reactor are heated to guarantee a pre-heating of the flow above the boiling point of water.

The results show that oxygen influences the decomposition for temperatures above 720 °C and that below this temperature thermal decomposition is the main reaction mechanism. Solidified urea was also found in the reactor, which is thought to have contributed to the unsteady behaviour of the experiment.

Another work, this time by Caton and Park [10], also studies the decomposition of a urea-water solution in a laminar flow reactor but in a temperature range of 220 – 520 °C.

The experimental setup is very similar to the previous work. One difference is how the urea-water solution is injected; a pressurized flask with the solution is enough to spray it at the entrance of the reactor. In the same way as the previous work, HNCO could not be calibrated due to its unstable nature.

The first experiment consisted of using powder urea at the reactor entrance and analyse its decomposition products (Figure 3).

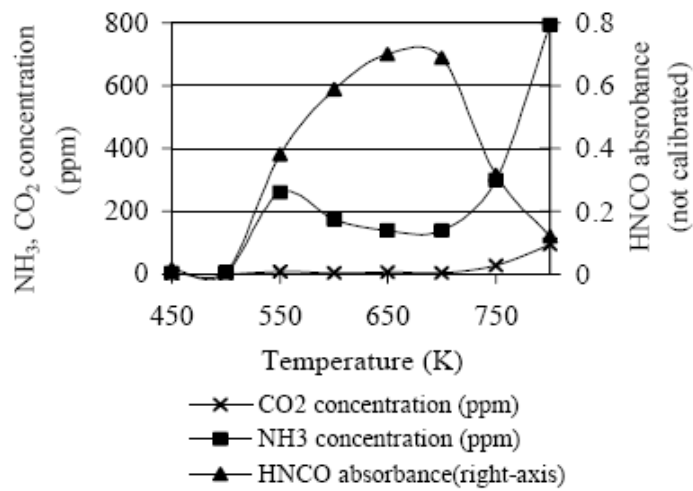


Figure 3 – Urea powder decomposition experiment [10].

The production of ammonia and isocyanic acid occurs at the same time, but when HNCO starts diminishing, the production of ammonia goes up. The presence of carbon dioxide is only seen at the end.

The urea-water solution decomposition produced the following results (Figure 4).

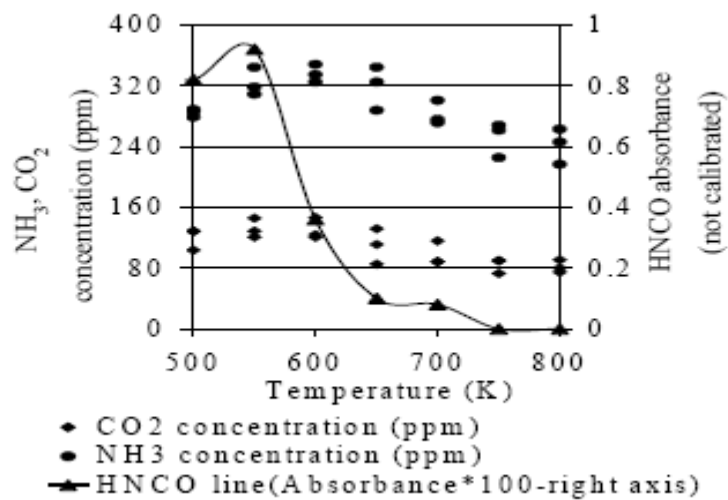


Figure 4 – Urea solution decomposition experiment [10].

The solution contained 1.27 % (by mass) of urea, which is much lower than the AdBlue solution for SCR systems. However, the production of ammonia and carbon dioxide reach a peak around the same temperature (300 °C); after this point both start decreasing. The authors consider that the production of these compounds does not satisfy reaction (2), which is justified by the production of biuret, cyanamide, ammelide or ammeline.

These experimental set up are important guidelines for this work. The obtained results are also worth comparing.

Even though the kinetic modelling of urea decomposition is not an objective in this work, other authors focus on this, and it is important to keep such results in mind for future works.

Oh *et al* [18] work derives a rate law for the decomposition of a urea-water solution spray to use in a SCR system for a marine diesel engine [18]. A two-step model is considered: in a first step, the urea-water droplets are vaporized and only then the decomposition starts.

In respect to the particle mass, a first-order rate law was presented, for a temperature range of 300-400 °C.

A similar work by Birkhold *et al* [19], with urea-water spraying and subsequent vaporization of water and decomposition of urea particles, considers an extended Arrhenius rate law where the decomposition temperature for this model is around 330 °C and constant.

### 3. Material and Methods

In this Chapter the proposed methodology for the study of urea decomposition is presented. It is based not only on other studies available from the literature but also on the conditions detailed below. It is meant for providing a further insight onto the complex decomposition of urea and, with equal importance, achieving a coherent experimental approach for future works.

As such, the apparatus should be able to cover a range of experimental conditions, including the operating temperatures of the SCR system and the temperature range for urea's decomposition, the possibility for different gas mixtures and different sample forms (solid or urea-water solution). To ensure inert conditions, argon and nitrogen were used.

#### 3.1. Experimental Setup

The equipment used is represented in Figure 5. It consists of a Differential Scanning Calorimeter (DSC), a Fourier Transform Infrared Spectrometer (FTIR), a Mass Flow Controller (MFC), gas tube connections and heating and the correspondent equipment software.

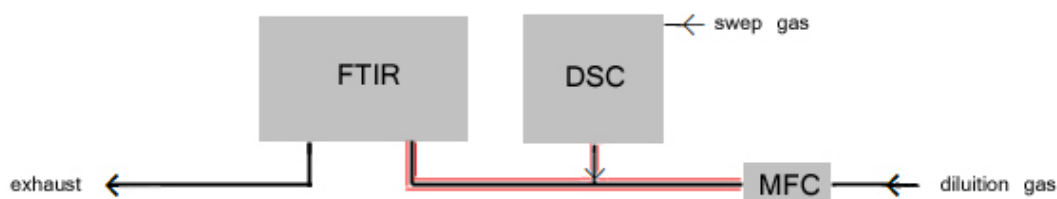


Figure 5 – Experimental apparatus (red represents heated connections).

The sample is placed in the DSC, which works as a flow reactor and, according to a pre-determined heating rate (K/min), the sample is heated until it reaches a desired temperature; the gas phase products are then analysed in the FTIR.

Considering the gas flow rate entering the calorimeter (10-30 cm<sup>3</sup>/min), the volume of the FTIR cell (aprox. 250 cm<sup>3</sup>) and how fast the phenomena occurring while heating urea happens, the calorimeter off-gas is diluted with nitrogen to an approximate

flow rate of 300 cm<sup>3</sup>/min, allowing shorter residence times in the FTIR cell. This also helps to bring the temperature in accordance with the FTIR pre-requisites. The gas tubing connecting the different equipments is also insulated and heated to assure a more constant gas temperature for analyses and to prevent urea and its by-products sticking to the pipe interior walls.

There was no need for exact flow rate measurements at this stage as a more qualitative perspective was the purpose of the current study.

### 3.1.1. Differential scanning calorimeter

The DSC used is shown in Figure 6. The calorimeter is a SENSYS TGA and DSC made by SETARAM; the temperature range is between -120 and +830 °C.



Figure 6 – Differential Scanning Calorimeter.

Its main components are a furnace, a central unit where the gas feed, the electrical power and the pressure are measured and controlled and software that controls all the DSC.

In the furnace there is one reference holder (usually empty) and one sample holder (Figure 7); each has a heater and a temperature sensor.

The urea to be analysed is placed in a silica cup, which is secured by a platinum/silica crucible, hanging approximately in the middle of the furnace, where the measuring sensors are placed.

In order to prevent unwanted reactions and provide a better cleaning of the system, the reference and sample holder are lined with silica piping.

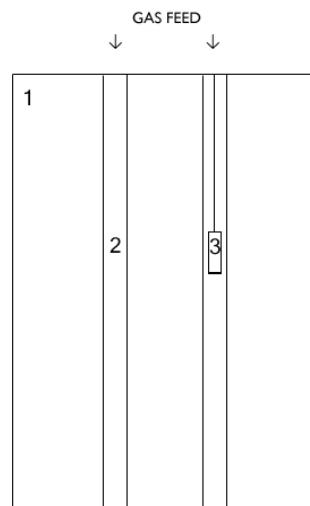


Figure 7 – Furnace schematic; 1- Furnace, 2 – Reference, 3 – Sample.

Both the reference and sample are heated according to the specified heating rate. Depending on the sample properties (heat capacity, melting enthalpy, endo or exothermal reactions...), to maintain the exact same heating rate for the reference and the sample, a different amount of heat must be provided. The difference in heat flux can be positive or negative and is represented as a peak in a heat flow vs. temperature (or time) plot. The area of each peak gives the enthalpy change for the occurring process.

The software provided by the DSC manufacturing company is SETSOFT, which allows the data acquisition and control of the DSC as well the background subtraction.

### 3.1.2. FTIR

The FTIR used is shown in Figure 8. It is a MKS MultiGas 2030-HS. The software is based on Labview.



Figure 8 - Fourier Transform Infrared Spectrometer.

The working principle of this equipment is the use of infrared radiation that is responsible for a certain response from different compounds. This way, it is possible to correctly identify the components going through the cell.

This equipment is calibrated for nitrogen as an inert gas. Even though the studied gas mixtures are prepared with argon, the dilution with nitrogen is considered to prevent any influences it could occur while measuring.

The use of this particular equipment has the main advantage of already being calibrated for the important gases to be measured. Such information becomes more important when HNCO is very difficult to calibrate (as seen in Chapter 2) [10].

The chosen measured gases were ammonia, isocyanic acid and nitric oxide as the most important for this work.

### 3.1.3. Mass flow controller

As previously mentioned, the carrier gas and urea's decomposition gas products exiting the calorimeter are diluted before reaching the FTIR (Figure 9).

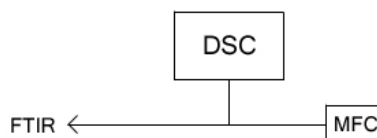


Figure 9 – Dilution of the calorimeter exit gas.

To achieve this, a Mass Flow Controller (MFC) is used. In order to obtain a flow rate around  $300 \text{ cm}^3/\text{min}$  before entering the FTIR, the MFC is capable of handling a maximum flow rate of  $3000 \text{ cm}^3/\text{min}$ .

The manufacturer is Bronkhorst and the MFC used is “EL-FLOW” (Figure 10).

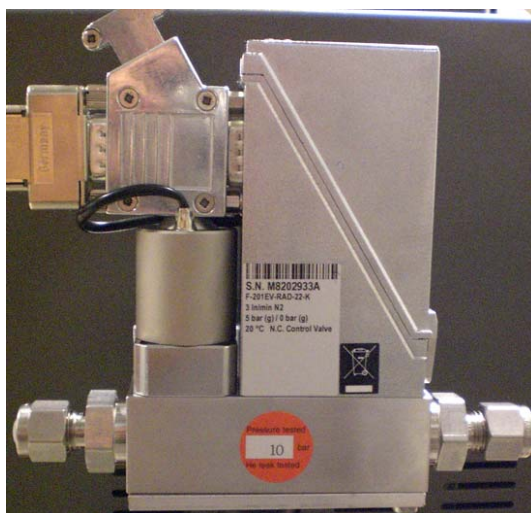


Figure 10 – Mass Flow Controller.

The MFC is already calibrated for nitrogen gas. However, to use different gases or gas mixtures, a conversion factor must be used, which is specific for each gas (Appendix D).

The MFC is controlled by a computer, and is connected to it by a RS232 port.

### 3.1.4. Gas tubes heating

The pre-heating of the gas starts right after the nitrogen flows through the MFC. It consists of a tube circuit heated and insulated (Figure 11). The temperature is set to 140 °C with a Labview in-house programmed software through means of a in-house made circuit box.

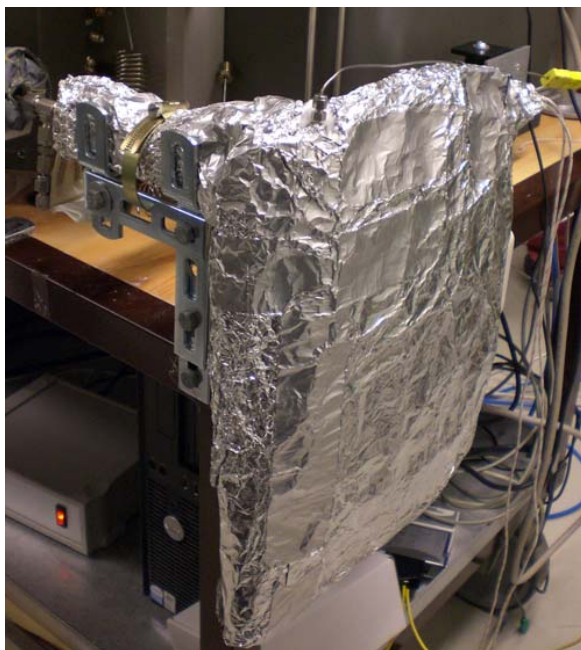


Figure 11 – Pre-heating of the dilution gas.

After the dilution, the nitrogen and the DSC off-gas are delivered to the FTIR through an insulated and heated tube. The temperature is set at 190 °C to satisfy the FTIR correct measurements conditions.

This pre-heating is useful to prevent condensation after dilution.

### 3.1.5. Urea and gases used

The urea (CAS 57-13-6) used is from Sigma-Aldrich. The product name is U1250, ReagentPlus™, purity over 99.5 % and granular form.

As for the gases used, their concentrations are presented in Table 1.

Table 1 – Gas mixtures concentrations.

Gases	Concentrations (molar fraction)
N <sub>2</sub>	99.9 % N <sub>2</sub>
O <sub>2</sub> /Ar	15 % O <sub>2</sub>
NO/Ar	900 ppm NO
Ar	99.9 % Ar

### 3.2. Experimental Procedure

A first approach consisted of several calorimeter runs, not only to test its reproducibility but also to analyse and compare different data. Thus, several experiments were carried out with some variables (gas flow and heating rate) similar to the literature [1].

These test experiments were followed by another group of experiments where urea's decomposition was studied, starting with the influence of different heating rates on the calorimeter, the presence of oxygen and NO and a urea-water solution, all coupled with gas phase analysis.

For each experiment a common procedure was established. For the calorimeter is as follows:

1. Turning on the calorimeter cooling water and the gas feed;
2. Programming the conditions to be studied;
3. Performing a background with an empty sample holder;

4. Repeating of the same conditions, this time with a urea sample;
5. Cleaning of the sample holder with warm water, ultra pure water and let it dry.

The background was then subtracted to the results for each sample.

When gas phase analysis was used, a common procedure was also necessary:

1. Cooling the FTIR with liquid nitrogen;
2. Starting the nitrogen gas flow through the MFC at the desired rate;
3. Heating the gas pipes to the desired temperature;
4. Taking the FTIR background right before starting the calorimeter program.

The gas flow rate going through the MFC was pre-set in order to prevent some oscillation in the DSC results as some preliminary experiments showed. This was most probably due to a backflow going into the calorimeter furnace; with a lower MFC flow rate, the oscillating behaviour was lowered.

### **3.2.1. Reproducibility of the calorimeter**

For each run, the calorimeter program (Table 2) was chosen in order to take urea's decomposition to completion (around 450 °C [15]), therefore, a temperature range between 20 and 500 °C was defined.

Table 2 – Experiments program; reproducibility of the calorimeter.

Temperature range (°C)	Heating rate (°C/min)	Time (min)
20 (Isotherm)	-	1
20-500 (Temperature ramp)	10	-
500 (Isotherm)	-	5
500-20 (Temperature ramp)	20	-

These experiments consisted of testing different sample masses. Considering the sample holder maximum capacity (aprox. 30 mg), two test masses were chosen accordingly (Table 3).

Table 3 – Test mass samples.

#	Mass sample (mg)
1	10
2	30

For each test mass two experiments were done with the corresponding background.

In order to ensure an inert environment, argon was used as the carrier gas.

### 3.2.2. Urea decomposition and gas phase analysis

The first variable to be tested was different heating rates for the calorimeter. The chosen speeds were of 5, 10 and 30 °C/min as shown in Table 4.

Table 4 – Experiments program; urea decomposition.

Temperature range (°C)	Heating rate (°C/min)	Time (min)
20 (Isotherm)	-	1
20-500 (Temperature ramp)	5, 10 or 30	-
500 (Isotherm)	-	5
500-20 (Temperature ramp)	20	-

For the same reason stated above, the calorimeter program (Table 4) was chosen in order to take urea's decomposition to completion

Regarding the influence of other gases, the concentrations were chosen accordingly to an actual exhaust car system. This way,

- NO was studied using a 450 and 900 ppm mixture with Argon. The heating rate was of 10 °C/min.
- Oxygen was studied using a 7.5 and 15 % mixture with Argon. The heating rate was of 10 °C/min.

A urea-water solution of 32.5 % by weight was also studied under inert conditions (Argon). The heating rate was of 10 °C/min.

For the oxygen, NO and urea-water solution experiments, the temperature program is the one in Table 4, except for the heating rate that is 10 °C/min as stated.

For the solid samples experiments a mass around 14 mg was used. Urea pellets were used as preliminary experiments showed no differences between powder and pellets.

## 4. Results and discussion

### 4.1. Reproducibility of the calorimeter

These experiments are intended to test the reproducibility of the DSC. The first results are of the four backgrounds taken (Figure 12).

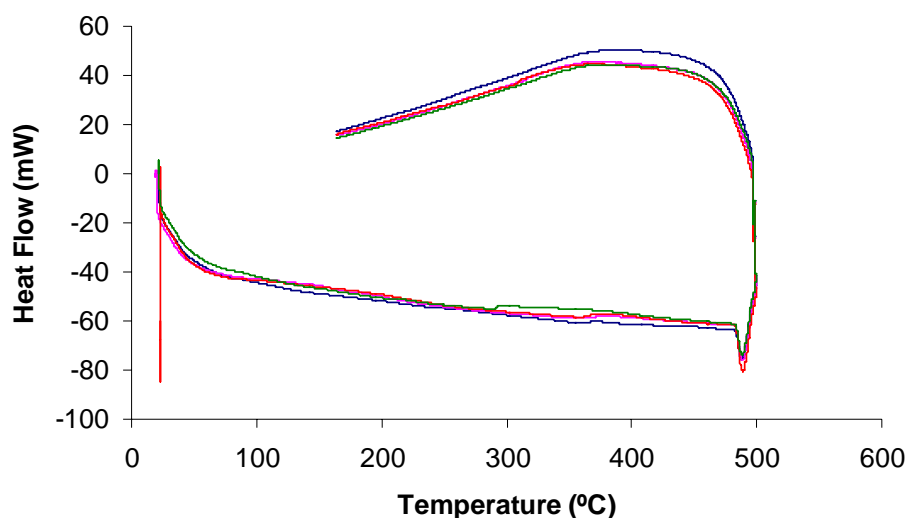


Figure 12 – Reproducibility of the calorimeter; backgrounds.

Starting at 20 °C, the sample holder and the reference were heated until both reached 500 °C, characterized by a negative heat flow. At maximum temperature a peak is always noticeable; this represents the beginning of the 500 °C isothermal followed by the cooling process, characterized by a positive heat flow.

For one of the backgrounds, a starting sharp endothermic peak, reaching a heat flow value around -80 mW is visible. This could be caused by some electrical disturbance, which is typical for DSC measurements. However, considering these events happens at a low temperature, it will not influence the results.

These results show that the backgrounds are consistently reproducible; this is a first step for obtaining coherent results. Also, the presence of oxygen or NO in the concentrations studied does not influence the background.

The importance of a background for each experiment has to do with subtracting the effects of the silica sample holder and the carrier gas flowing through the chamber.

Four other experiments were also done. This time, two of them with a 10 mg sample and other two with a 30 mg sample (Figure 13).

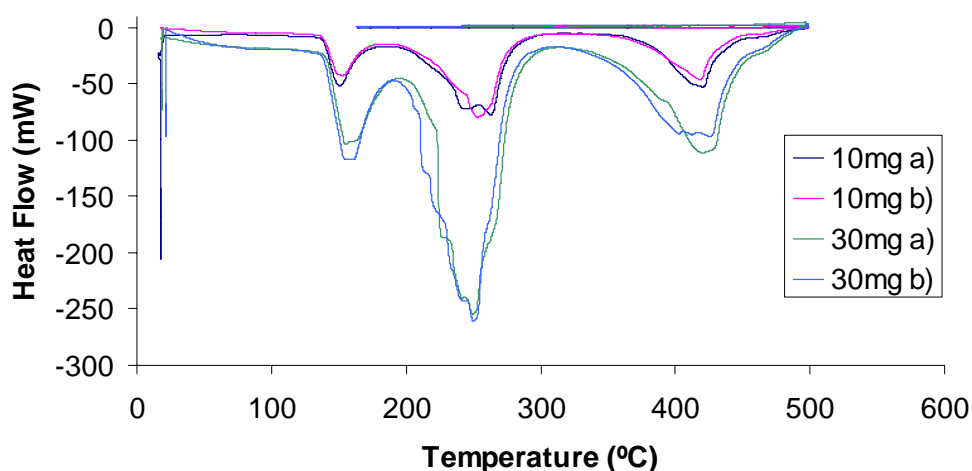


Figure 13 – Reproducibility of the calorimeter; urea decomposition.

Three peaks are clearly visible. The same trend is observed for each experiment. Starting from the left, the first peak is associated with the melting process; the other two represent two stages in urea decomposition.

As previously mentioned, there is some oscillation in the decomposition peaks and this is due to some backflow that occurred during dilution. Such problem was surpassed for the other experiments by lowering the dilution rate.

It should also be stated that from direct observation residues were found in the silica cup with a yellow/brown colour. And also, at the bottom of the DSC furnace, what it seems to be white crystals, appeared at the end of each experiment, and this is could be

urea, CYA, biuret, HNCO or some other compound that vaporized and re-solidified in this zone.

To obtain a quantitative measure of the reproducibility results, the melting enthalpy obtained from these experiments can be compared to the values found in the literature (Table 5).

Table 5 – Urea melting enthalpy; literature values.

<b>Melting enthalpy (kJ/mol urea)</b>	<b>Source</b>
13.5	Zordan et al [21]
14.1	Stradella and Argentero [22]
13.6	Ullmann's Encyclopaedia [20]
14.5	Koebel and Strutz [11]

Thus, the average melting enthalpy of urea found in the literature is  $13.9 \pm 0.2$  kJ/mol urea.

The melting enthalpies obtained for this work (Table 6) were done by calculating the area of the melting peaks and dividing it with by the number of moles of urea presented in the sample. Some guidelines [23] were followed to define the integration peak area.

Table 6 – Urea melting enthalpy; experimental results.

<b>Sample (mg)</b>	<b>Melting Enthalpy (kJ/mol urea)</b>
10 a)	13.4
10 b)	13.0
30 a)	13.7
30 a)	13.3

This meaning that, on average, the melting enthalpy for urea is  $13.4 \pm 0.3$  kJ/mol urea. Even though it is a bit below from the literature values, it is still consistent and another proof of the reproducibility of the calorimeter.

Of course there is always some error while calculating the melting enthalpy; first, choosing the exact area for integration can be difficult and, second, on this particular case, the melting is quickly followed by the first stage of decomposition, which makes it difficult to have a clear ending for the melting peak.

The on set temperature is around 133 °C, corresponding to urea's melting point.

On a brief statement about the decompositions stages, both have an overall endothermic effect and it seems that this decomposition happens at a higher temperature than what was seen from the Schaber *et al* [15] study. Possible explanations for this are presented for the next set of experiments.

#### **4.2. Effect of different heating rates (5, 10 and 30 K/min)**

These experiments compared the results for different heating rates (Figure 14).

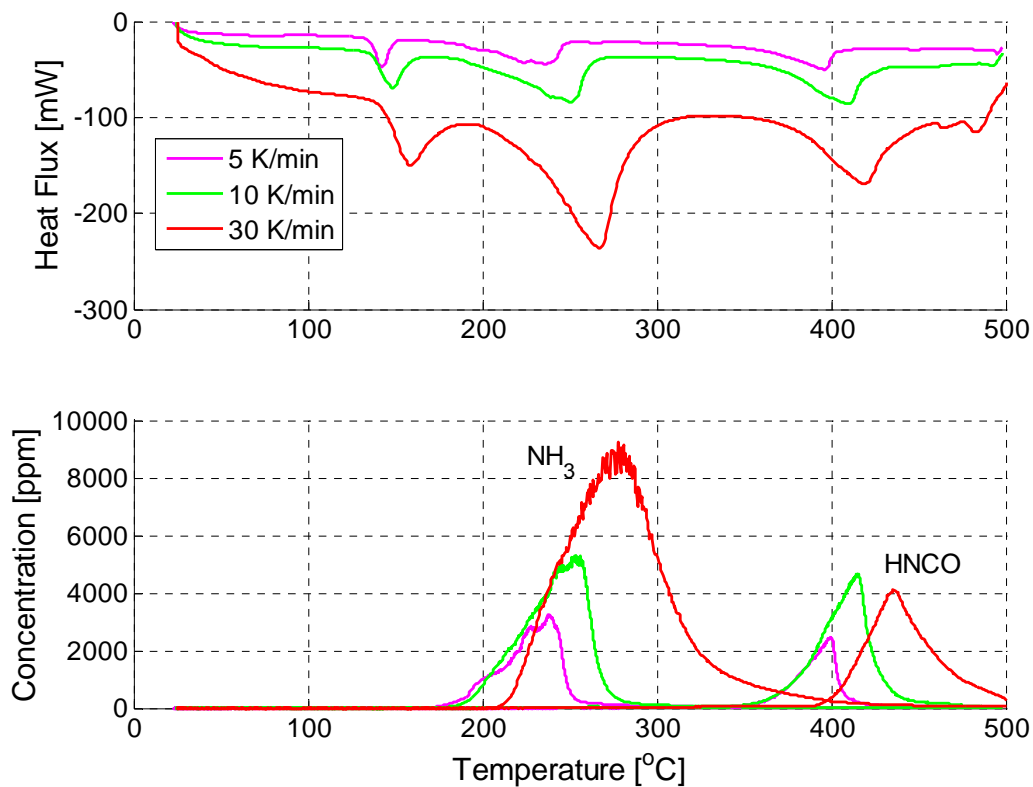
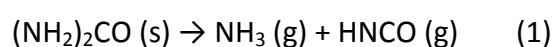


Figure 14 – Effect of different heating rates (5, 10 and 30 K/min); Calorimeter and gas phase analysis.

Starting with the calorimeter results, the same observed trend from the reproducibility of the DSC is also visible here. And taking a look at the results that these experiments were meant for (the effect of different heating rates), it seems that higher heating rates cause more spreading on the peaks. This corresponds to the existence of heat transfer limitations (urea melt and silica cup).

As for the gas phase analysis, the production of ammonia and isocyanic acid are presented. The ammonia release happens during the first stage of decomposition visible on the DSC results; the isocyanic acid release occurs during the second stage.

Remembering Chapter 2, specially reaction (1),



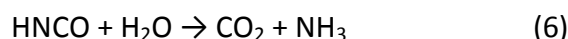
It seems that the production of ammonia and HNCO should occur at the same time, while in fact, there is practically no overlapping between the gas phase analysis peaks. But why is this happening?

It is known that HNCO plays an important role on the formation of by-products such as biuret, triazines or cyanuric acid and that these decompose back into isocyanic acid. So, it seems plausible to assume that these by-products are being formed in a first stage and then decompose again back into HNCO. But what could be triggering the formation of such by-products? If we consider that the urea sample is inside a silica cup, which itself does not let the carrier gas go all the way through the sample holder and the presence of urea melt, leads to believe that mass transfer limitations play a role.

So, it is likely that the acid gas has trouble escaping the melt and the silica cup, thus leading to the production of such by-products which would then decompose into isocyanic acid.

This idea seems even more likely when comparing these results with the ones from the Park and Caton [10] experiment, already discussed in Section 2.2. In this study, a sample of dry urea was placed at the entrance of a flow reactor where the gas goes right through the sample, therefore, not confined to a closed space. And, as seen, the production of ammonia and HNCO happens at the same time.

Also, the ammonia production peak in the Park and Caton work occurs around 470 °C, for which the authors explain such finding being consistent with reaction (6),



(The water available for such reaction is supposed to have its origins when triazines and cyanamide are formed [15].)

In this study, the bulk of ammonia released happens before HNCO production is noticeable. It is not clear if this reaction could have occurred with some importance in this study, as the carbon dioxide production was not measured.

Nevertheless, what can be proposed to justify this difference is that with mass transfer limitations that do not seem to play a big importance in the Park and Caton study,

not only the production of by-products was less important, but also the HNCO production is not favorable at higher temperatures, at least for the conditions studied.

Regarding the shifting of the decomposition stages to higher temperatures, when compared to the Schaber *et al* study [15], can also be explained by the importance of heat and mass transfer limitations as the referred study was carried out in an open platinum pan.

However, what is not possible to infer from these results, is exactly which by-products are producing the HNCO that is visible in the gas phase analysis. Not only because the residues products were not analysed in this study but also because the Schaber *et al* experiment [15] shows that, in their first region (room temperature – 250 °C), biuret is produced and decomposes back into HNCO; only in the second region the decomposition of the other by-products, such as cyanuric acid, leads to the production of more HNCO.

In other words, it is not possible to know the exact importance that mass and heat transfer limitations have on product distribution and production.

What cannot also be ruled out for any isocyanic acid being visible in the first stage is the possible HNCO condensation (this compound has a condensation temperature of 23.5 °C at standard conditions [24]) due to problems with the cooling of the furnace.

This study can be taken a step further when normalizing the gas phase analysis results. Therefore, the production of ammonia and isocyanic acid is normalized in regards to the area of both peaks and the relative production for each compound is obtained (Figure 15).

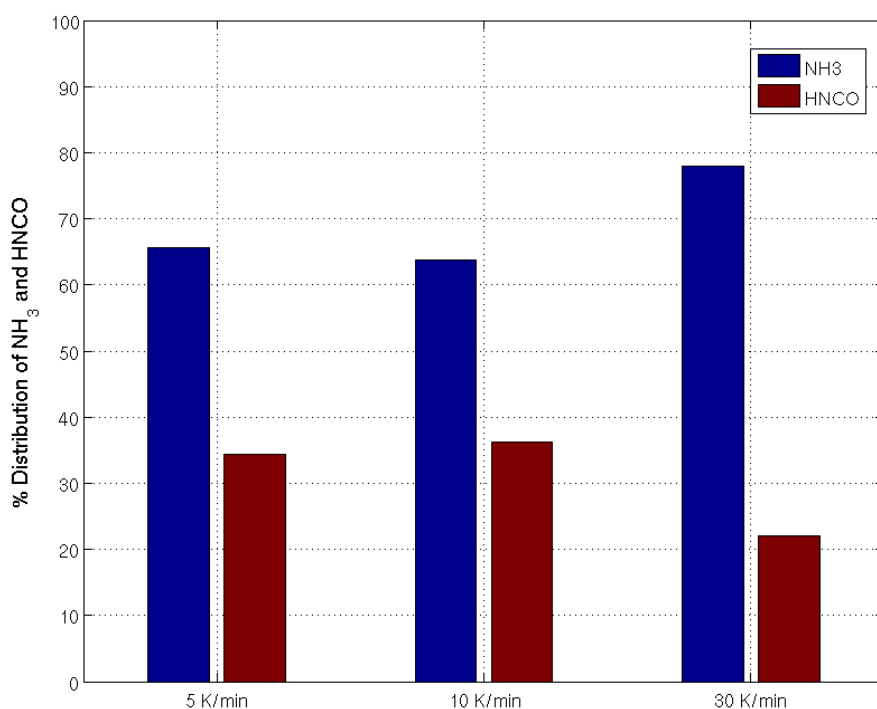


Figure 15 – Effect of different heating rates (5, 10 and 30 K/min); Distribution of ammonia and isocyanic acid.

This plot shows that the highest heating rate favours the production of ammonia. For the 10 K/min heating rate, there is a decrease in the ammonia production and increase in the HNCO production; this could be due to some reaction rate limiting step in conjunction to heat and mass transfer limitations.

But back to the 30 K/min experiment, where there is a big difference between the relative production of each compound. It seems there is a contradiction in these results. On one hand, there is more ammonia being produced and still practically no HNCO being produced at the same time. Should not this mean there are more by-products being produced? And that they would decompose back into HNCO and, therefore, result in a similar gas product distribution as with other heating rates? Looking back to the first results plot (gas phase analysis), there is a very small overlap between the ammonia and isocyanic production. Can this indicate a decrease in the importance of mass transfer limitations or, even perhaps, a shift in product distribution?

The totally recovered plot (Figure 16), which is a different kind of normalization where the ammonia and isocyanic production are compared to the initial quantity of urea, seems to provide a further insight on the occurring events.

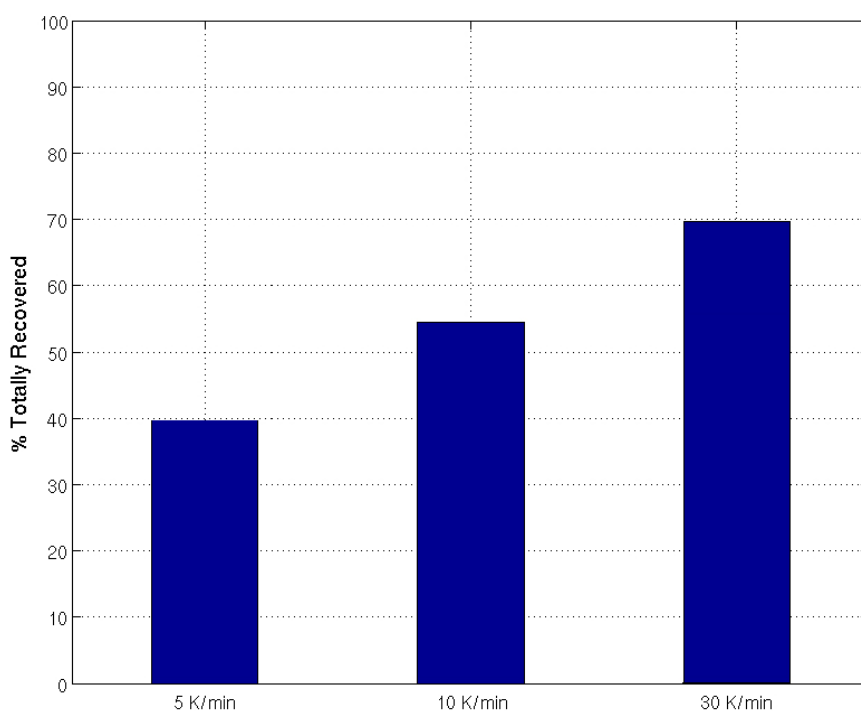


Figure 16 - Effect of different heating rates (5, 10 and 30 K/min); Total recovery.

This plot shows that with increasing heating rate there is higher recovery of ammonia and isocyanic acid. So, all this information seems to indicate that not only heat and mass transfer limitations play an important role on urea decomposition, but there is also a true increase in ammonia production (as both the relative production and total recovery increase) and, therefore, a shift on product distribution for higher heating rates.

### 4.3. Influence of oxygen (7.5 and 15 %)

The second set of experiments consisted of studying the influence of oxygen. Two different concentrations were chosen, 7.5 and 15% in an Argon mixture. The results are compared with the same temperature program but under inert conditions (Figure 17).

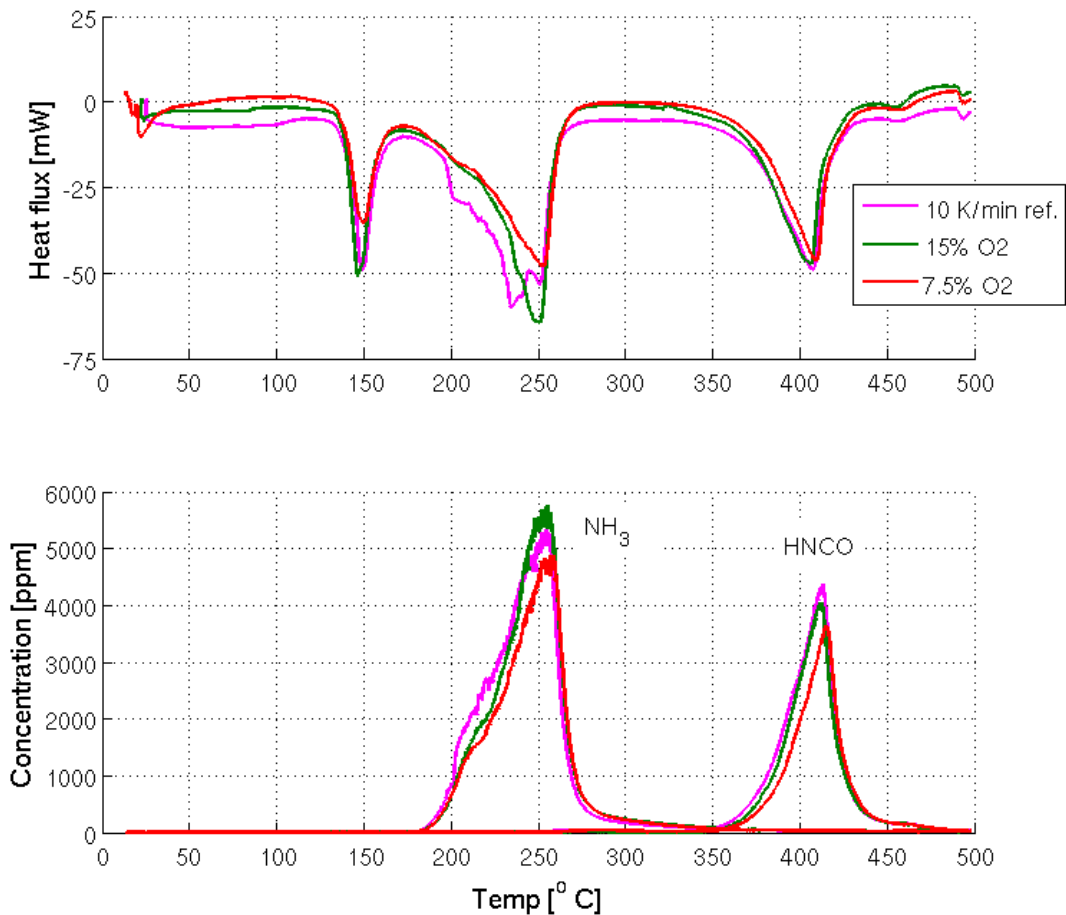


Figure 17 – Influence of oxygen (7.5 and 15 %); Calorimeter and gas phase analysis.

There are no appreciable differences between the results with oxygen presence and inert conditions. It is, however, worth discussion the production of NO at approximately 500 °C (Figure 18).

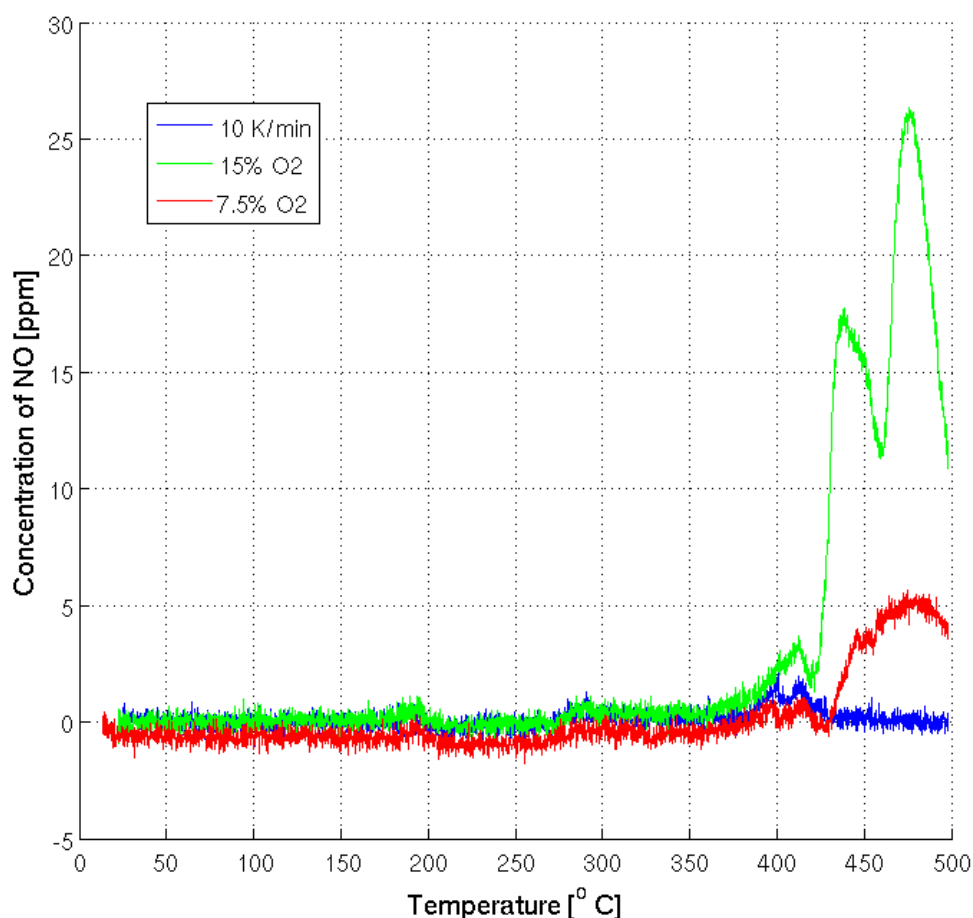


Figure 18 - Influence of oxygen (7.5 and 15 %); NO production.

The pattern is reproducible and happens right at the end of HNCO production (above 400 °C). It is worth noting that for this temperature there are no visible changes both in the calorimeter and gas phase analysis, as already mentioned.

It seems that oxidation is occurring. The key question is which compounds are being oxidized?

Glarborg *et al* [25] studied the oxidation chemistry of HNCO in a flow reactor. The operating temperatures were in the range of 750 – 1150 °C. These are well above the temperature at which this production of NO occurs, but it shows that isocyanic acid can oxidize into NO.

But what about the oxidation of the residues left in the silica cup? It is not known a possible oxidation of the urea decomposition by-products (such as triazines or

cyanuric acid) that gives off nitric oxide. And the residues that appeared at the bottom of the DSC furnace can also not be ruled out as a reactant in this oxidation, and this could also explain why there were no changes in the calorimeter results, as the sensors are placed in the middle of the furnace, where the silica cup is placed, and not in the bottom where this residues were.

#### 4.4. Influence of NO (450 and 900 ppm)

A third set of experiments consisted of studying the influence of NO. Two different concentrations were chosen, 450 and 900 ppm in an Argon mixture. The results are compared with the same temperature program but under inert conditions (Figure 19).

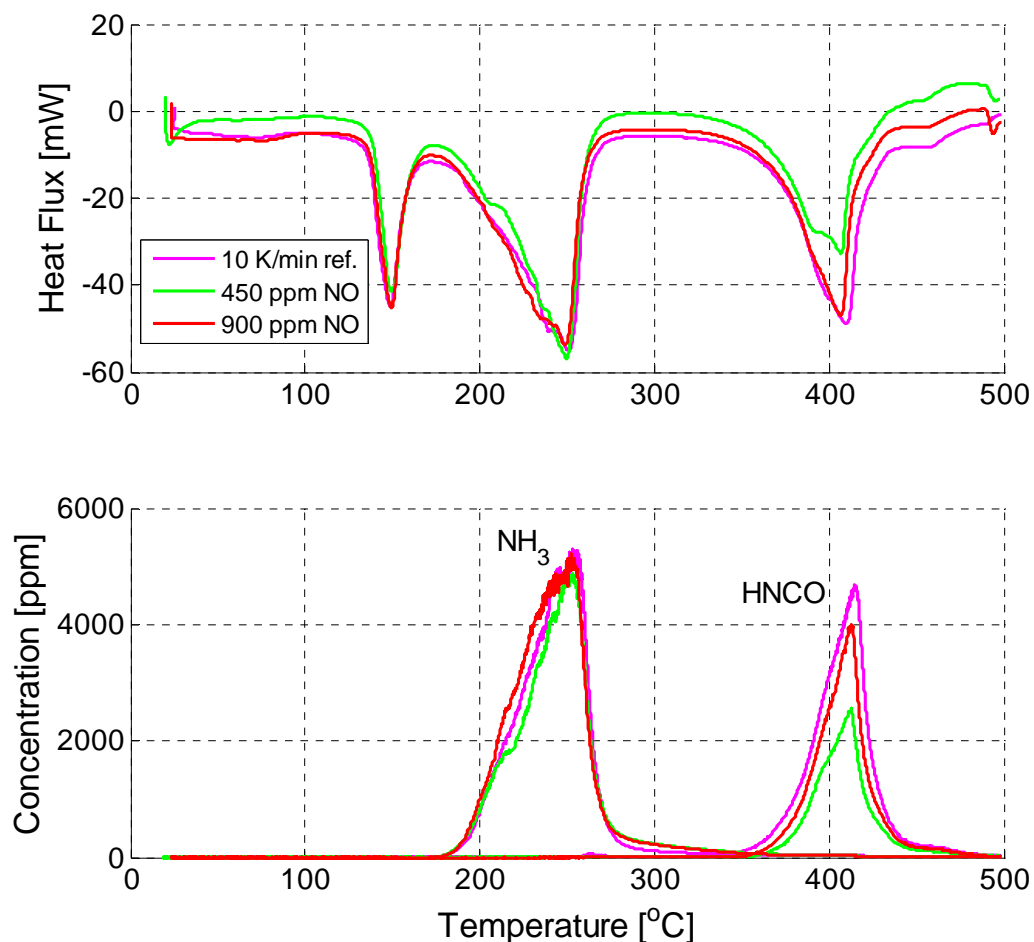


Figure 19 - Influence of NO (450 and 900 ppm); Calorimeter and gas phase analysis.

It seems that only the 450 ppm experiment presented visible changes, at least in the second stage of decomposition.

What could be happening is not the sort of answer that can be given by these results.

However, the NO concentration plots present some very interesting results (Figure 20). Above 400 °C there is an increase in NO for the 450 ppm experiment. Could this be related with the decrease in production of HNCO? Was a new compound formed during this second stage of decomposition that decomposed again into NO?

Either way, it seems that NO is causing, in some unknown way, the production of more NO and, at maximum release, producing approximately the same quantity that was introduced (it goes from aprox. 45 ppm to 80 ppm). It could be due to some oxidation but it should also be remembered that HNCO could condense at the exit of the furnace.

But to make the results even more interesting, the 900 ppm experiment showed no sign of NO production, indicating, therefore, that NO could now be acting as an inhibitor. It should not be ruled out the influence of mass and/or heat transfer limitations for this event or some fluctuations in the mass flow controllers.

Nevertheless, which mechanisms could be in place right now are not sure, only a further and more detailed study could shed some light.

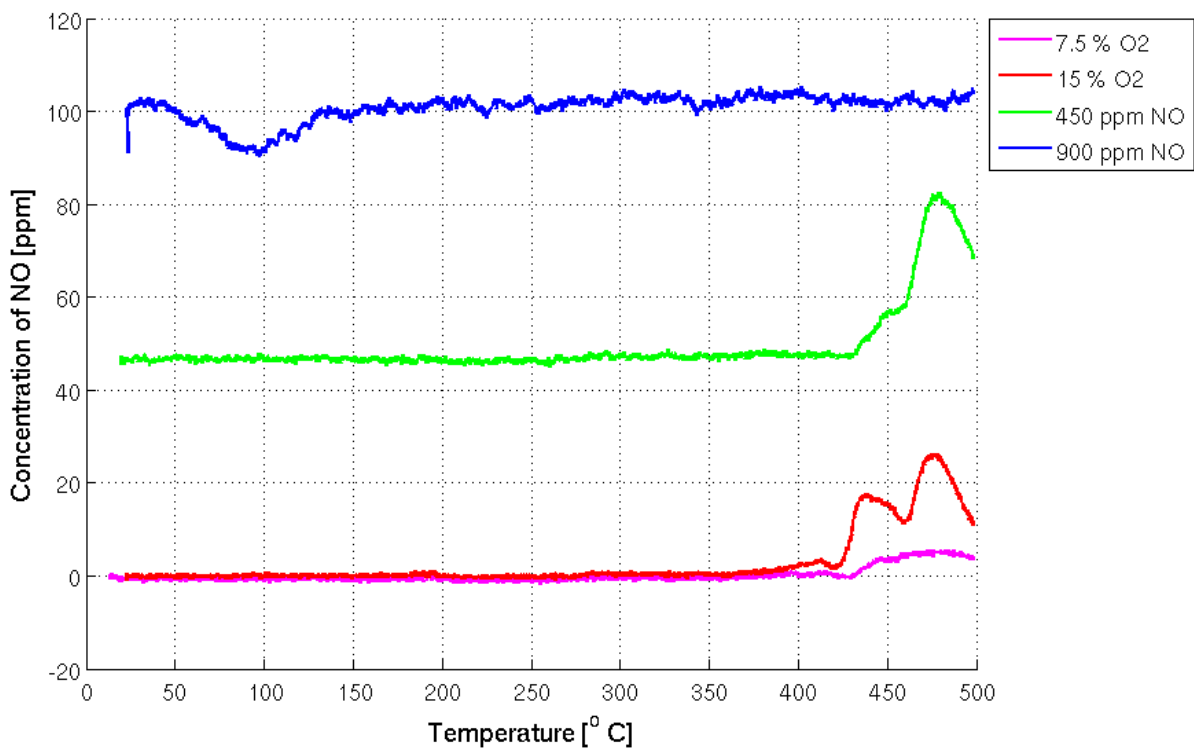


Figure 20 – Influence of NO (450 and 900 ppm); NO production.

The production of NO from the oxygen experiments was also placed in the same plot as both happen around the same temperature range.

A question is pertinent: what is the similarity, in terms of reaction mechanism and product distribution, between the four experiments? But the answer cannot be accounted from these results only.

#### 4.5. Urea-water solution (32.5 % by weight of urea)

A urea-water solution (32.5 % by weight of urea) decomposition of was also studied (Figure 21).

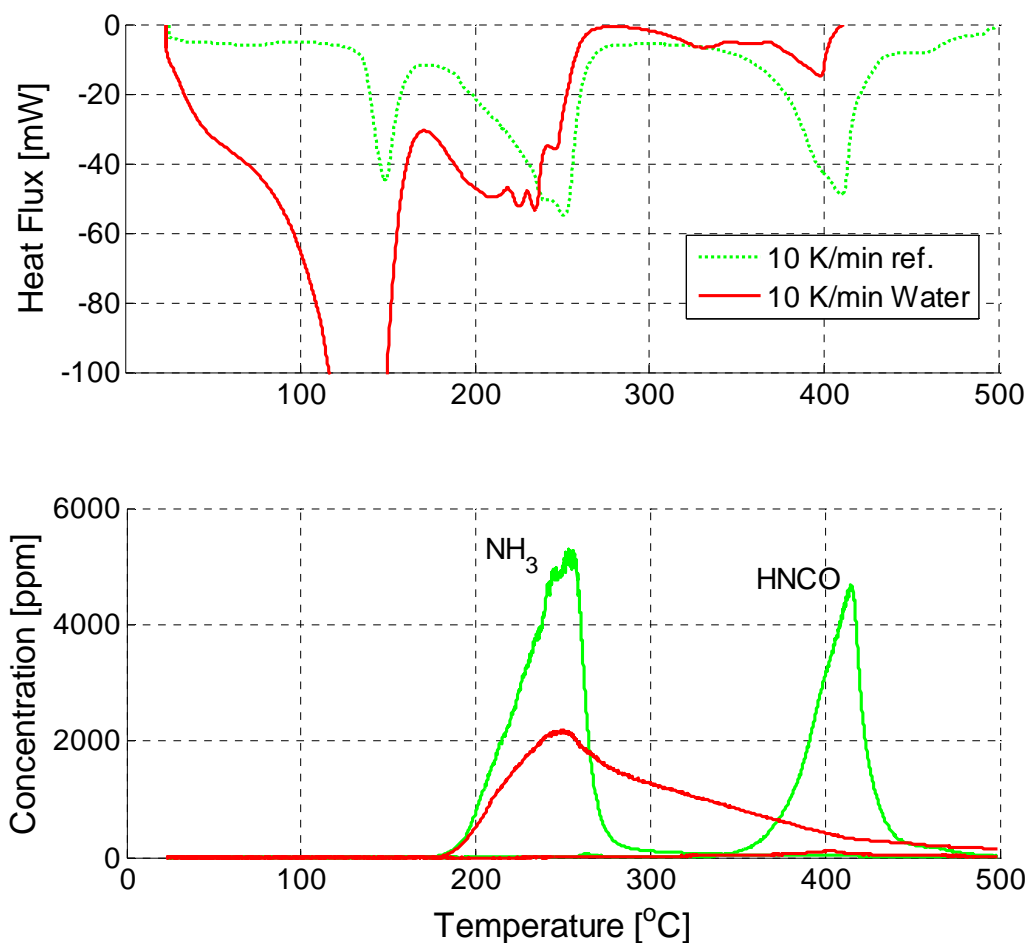


Figure 21 - Urea-water solution (32.5 % by weight of urea); Calorimeter and gas phase analysis.

Regarding the calorimeter results, they show a first very big peak, which is due to water vaporization, followed by the decomposition of urea.

The DSC results were zoomed in to get a better understanding of the occurring phenomena. The normal zoom version can be found in Appendix E, where water evaporation is responsible for the biggest peak.

The decomposition stages present a visible difference when compared to the solid sample and indicating that there are different reaction mechanisms in place.

The gas phase analysis shows a very interesting result. Of the measured gases, there is only production of ammonia, and this seems to extend throughout the two decomposition stages

So, why is there only production of ammonia and where did the isocyanic acid go?

The ammonia and HNCO distribution and recovery plots could perhaps give some more insight (Figure 22 and 23)

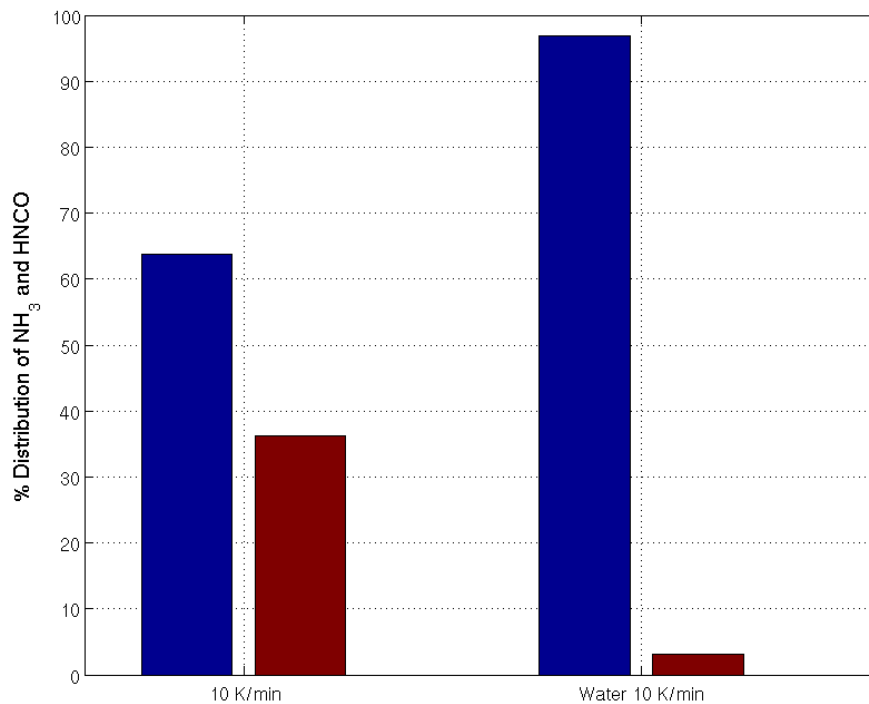


Figure 22 - Urea-water solution (32.5 % by weight of urea); Distribution of ammonia and isocyanic acid.

On this first plot, the big decrease in HNCO production is reinforced. Considering this extraordinary difference it does seem that different reaction mechanisms are in place.

It could be said that HNCO is being hydrolyzed into ammonia and carbon dioxide as the steel pipe would work as a catalyst. Taking a look at the second plot (Figure 23), a different explanation could be possible.

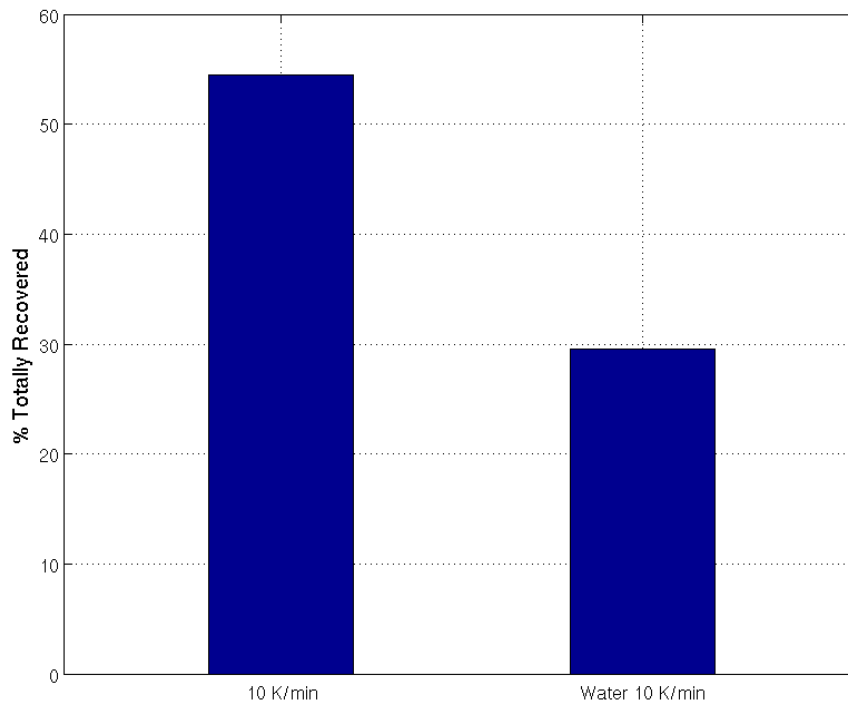
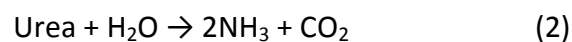


Figure 23 – Urea-water solution (32.5 % by weight of urea); Total recovery.

This plot shows a staggering difference between the recovery for the current experiment and the solid urea sample. The total recovery is now around 30% which, when compared to the 55% recovery in the solid urea, is definitely worth studying in more detail.

Going back to the hydrolysis hypothesis, for this to happen, the global reaction would be (2).



Which means, for every mole of urea decomposed, two moles of urea would be produced. Even though the carbon dioxide production was not measured, it does not seem plausible that HNCO is being hydrolysed given the big difference in the totally recovered plot.

So, it seems that the product distribution is now difference. How different, is not sure.

What is also worth mentioning are the heat transfer limitation that water can present. The first big peak in the DSC plot is a first sign that such phenomena could play an important role; not only water has an important heat capacity, but, most importantly, a big vaporization enthalpy.

And, if both decomposition stages are above water's normal boiling point, does this mean that the reaction between water and urea (and its by-products) happens in the gas phase? If so, should this be visible in the calorimeter results, or it happens through the entire pipe until reaching the FTIR? Or the decomposition stages visible in the DSC are mostly due to the residues and solidified urea in the cup?

All of this are important questions, but with the available information very difficult to answer.

## 5. Conclusions and future work

An experimental setup was put together using Differential Scanning Calorimetry and gas phase analysis, allowing an understanding on what sort of data can be obtained from the calorimeter and the FTIR and what problems can occur during the study of urea's thermal decomposition. This work also provided new and interesting results which are essential for a deeper understanding of urea's decomposition and for future experiments.

The calorimetric data has shown three distinct events; a first one corresponding to urea's melting and two more corresponding to the decomposition itself. Some problems occur, namely residues at the bottom of the DSC furnace or the backflow during dilution.

The gas phase analysis also showed the production of ammonia and isocyanic acid is compatible with each of the decomposition stage observed in the DSC. For the first region, ammonia is released; for the second region, HNCO is released.

But more than these observations, important conclusions were taken:

- heat and mass transfer limitations play an important role;

As it was shown, heat and mass transfer limitations shift the decomposition to higher temperatures and separates the production of ammonia and isocyanic acid into two distinct stages.

What is not known is how the competition between reaction rates and heat and mass transfer limitations works.

Of course there are also some uncertainties as the possible condensation of HNCO.

- oxidation increases the production of NO above 400 °C;

Even though this increase in NO production is visible, the reasons for this are not clear. It could be the oxidation of HNCO (which is known to oxidize into NO at higher temperatures), or the oxidation of the residues found.

- lower concentrations of NO leads to the production of more NO, while higher concentrations seems to inhibit;

These experiments have shown that at 450 ppm of NO, more nitric oxide is produced, while at 900 ppm there are no changes, at least visible changes in the DSC and gas phase analysis. This could also be due to some oxidation.

- ammonia production is expanded in a urea-water solution, but the total recovery is much lesser than for solid urea.

There was practically no production of isocyanic acid and nothing indicates that it was hydrolyzed. What can be said, however, is that there was a shift in product distribution.

Until now a qualitative view on the results was pursued. But it is also of great importance understanding how this methodology can be improved and what more can be studied in the future.

It was already mentioned that backflow can be a problem but this was solved just by lowering the dilution rate. What could not be solved were the residues in the bottom of the DSC furnace. Perhaps a better insulation and heating just at the exit of the furnace could improve the situation, but considering the residues were found inside the furnace in a place where the sample is not heated and is pretty much insulated from the exterior, is not certain how much this would decrease the amount of residues.

However, these residues at the bottom could also provide a further insight for the events that urea is going through. That is, an HPLC analysis could help knowing what exact compounds are present. The same analysis should be done to the residues in the silica cup.

But this would only allow knowing the product distribution at the end of each experiment. This could be overcome by carrying out several isothermal experiments at different temperatures and then analyse the obtained residues. This would give a more clear perspective of the solid product distribution and enhance the knowledge on mass and heat transfer limitations.

Also, the individual study of the decomposition of compounds such as biuret or cyanuric acid could also be done and this would give some more insight on possible oxidations for example.

Reliable data also means having correct measurements such as the flow rates of the carrier gas. As such, a set of Mass Flow Controllers for each different gas mixture should provide a more accurate measure for the set of conditions to be studied.

What can also be studied is the influence of mass and heat transfer limitations. One way to do this could be using a silica tube with a small porous bed in the middle (available in the laboratory from the calorimeter supplier) where the urea sample could be placed, allowing the carrier gas to go right through sample. This could, however, present some setbacks, as some decomposition products are sticky and could make the cleaning process very difficult.

As for the urea-water solution, a different and new way to obtain data could be the use of a cordierite monolith where the solution is impregnated in the material.

In fact, this last option is currently being implemented in the laboratory. This way, it is easier to account for mass and heat transfer limitations.

A picture of part of this experimental setup can be seen in Figure 24.

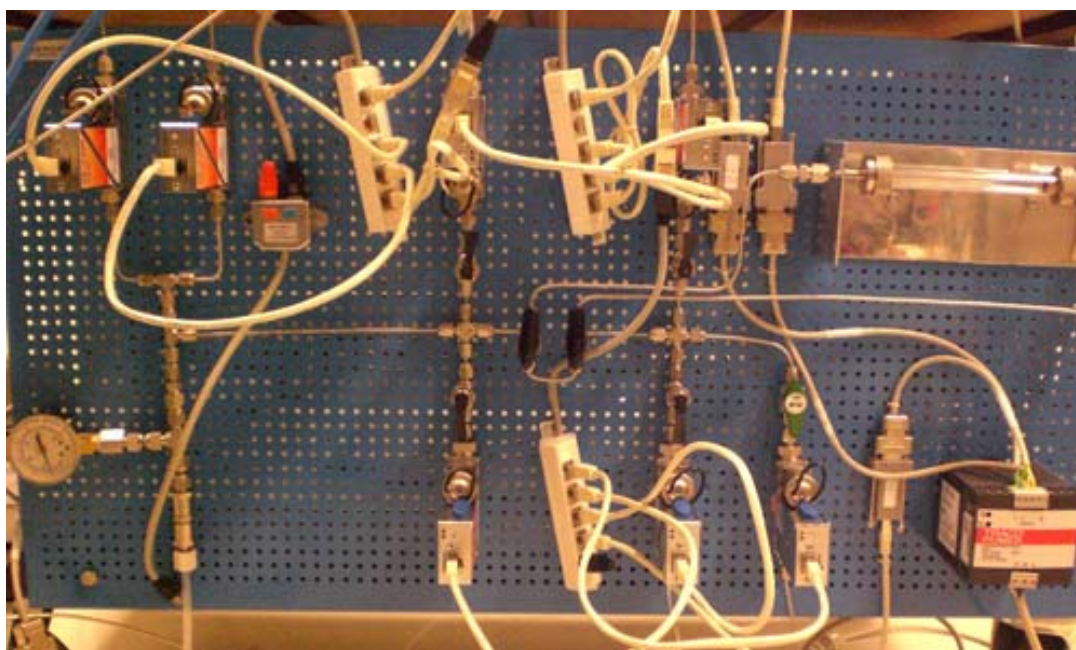


Figure 24 – New experimental setup.

This new experimental setup consists of a set of Mass Flow Controllers for the different conditions to be tested and a new feature, a catalyst to produce pure water in the gas phase (via hydrogen and oxygen). To prevent unwanted condensations at the bottom of the DSC furnace, a simple mechanism was also installed.

Preliminary results show only one decomposition peak (right after the melting). This is one more verification that heat and mass transfer limitations play a very important role as the urea-water solution is now impregnated in a monolith and not in a silica cup.

As final remarks, a few notes on kinetic modelling should be mentioned, even though such work is not the purpose of the current study.

Therefore, it is possible to obtain kinetic data from both the calorimeter and gas phase analysis, namely rate constants, reaction orders, activation energies and reaction enthalpies, in this last case, just from calorimetric data [26].

One of the advantages of using both a calorimeter and gas phase analysis is that a kinetic model is possible to derive independently of the data source (DSC or FTIR). As such, it allows comparing the obtained parameters or even constructing a more robust model using both data simultaneously [26].

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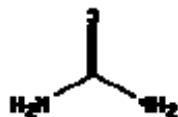
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## Appendixes

## Appendix A

Basic chemical and physical properties of some important compounds [24] (at standard conditions).

- urea

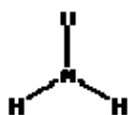


Molecular formula:  $(\text{NH}_2)_2\text{CO}$

Molar mass: 60.0553 g/mol

Melting point: 132.7 °C (decomposes)

- ammonia



Molecular formula:  $\text{H}_3\text{N}$

Molar mass: 17.03056 g/mol

Melting point: -77.73 °C

Boiling point: -33,34 °C

- isocyanic acid



Molecular formula:  $\text{CHNO}$

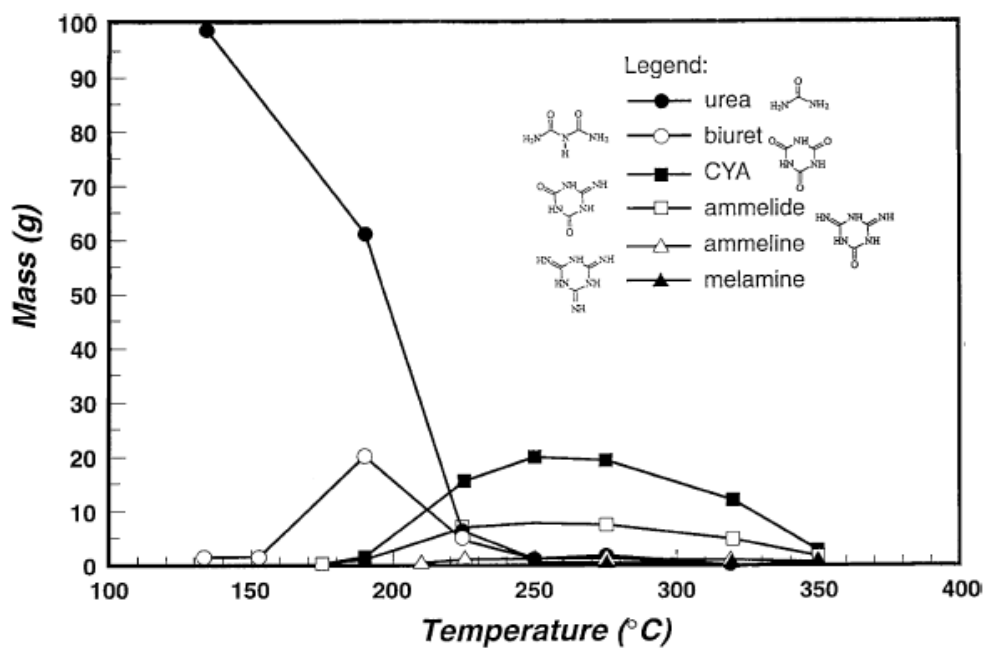
Molar mass: 43.0248 g/mol

Melting point: -81 °C

Boiling point: 23.5 °C

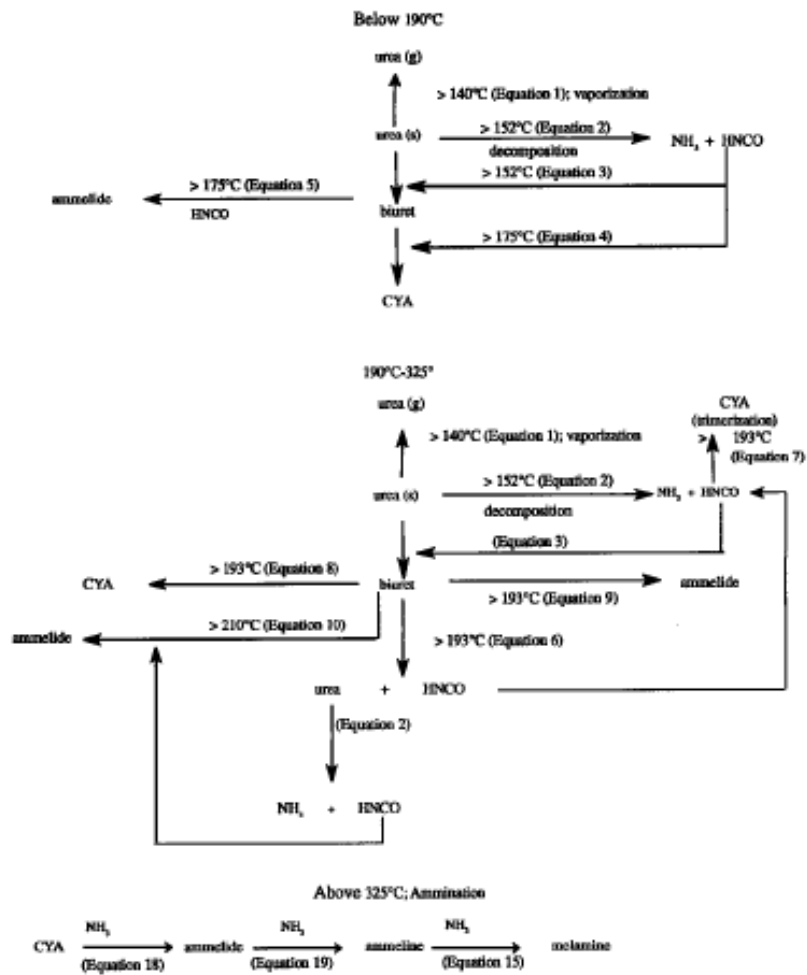
## Appendix B

Temperature-dependent plot of urea's decomposition products (open reaction vessel) – HPLC analysis [15].



## Appendix C

General temperature-dependent reaction scheme for urea's decomposition as proposed by Schaber *et al* [15].



## Appendix D

### Mass Flow Controller gas flow rate correction

The actual gas flow rate is obtained multiplying the displayed flow rate with the conversion factor for the gas used. When using a gas mixture, the conversion factor must be adjusted according to the following relation:

$$\frac{1}{C_{mix}} = \frac{V_1}{C_1} + \frac{V_2}{C_2} + \dots + \frac{V_n}{C_n} \quad (1)$$

Where  $C_{mix}$  is the conversion factor for the mixture,  $C_i$  the conversion factor for gas  $i$  and  $V_i$  is the volumetric fraction of gas  $i$  in the mixture.

The manufacturer provides a table with conversion factors relative to nitrogen (normal conditions).

## Appendix E

Urea-water solution (32.5 % by weight of urea); Calorimeter and gas phase analysis (Normal zoom version).

