

Analytical Investigation of Urea Deposits in SCR System

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ABSTRACT

An aqueous urea solution is used as the source of ammonia for selective catalytic reduction (SCR) of NO_x to reduce the emissions of NO_x in the exhaust of diesel vehicles. However, the decomposition of urea into ammonia is not always complete, resulting in solid urea deposit formation in the decomposition tube or on the SCR catalyst. These solid deposits can impede the flow of the exhaust gases (and uniformity of NH_3 supply) and reduce SCR catalyst performance over time. To minimize the formation of urea deposit and to meet EPA NO_x emission regulations, it is important to understand the chemistry of formation or removal of the deposit in the decomposition tube and SCR catalyst. In this report, IR spectroscopy, UV-visible spectroscopy, thermogravimetric analysis and elemental analysis have been used to determine the chemical composition of the solid urea deposits formed by the thermal decomposition of urea. Small and bulk urea deposit samples that formed during engine dyno tests with exhaust temperatures between 200 and 425 °C were analyzed. The results showed that exhaust temperatures of 200-250 °C inside the decomposition tube yielded unreacted urea, biuret and cyanuric acid. However their proportions varied appreciably from test to test. At exhaust temperatures of 335-425 °C, the deposits consist of mostly cyanuric acid. Small scale tests results revealed that urea, biuret and cyanuric acid in the solid urea deposits were not completely removed even though the exhaust temperature exceeded the temperatures at which these compounds thermally decompose.

CITATION: Weeks, C., Ibeling, D., Han, S., Ludwig, L. et al., "Analytical Investigation of Urea Deposits in SCR System," *SAE Int. J. Engines* 8(3):2015, doi:10.4271/2015-01-1037.

INTRODUCTION

NO_x , a major air pollutant, contributes to smog, which causes asthma, respiratory and heart diseases. It is a high temperature by-product that forms in the diesel engine combustion chamber, where high temperatures created by compression in the cylinders ignites the diesel fuel. The US Environmental Protection Agency (EPA) has put in place stringent final tier 4 emission regulations on tail pipe NO_x levels (0.4 g/kWhr) for the year 2014 [1]. Although lower combustion temperature is one of the key ways to reduce the amount of NO_x formed it cannot be lowered while maintaining engine performance. Instead NO_x emission reductions are achieved by treating the exhaust stream from diesel engines.

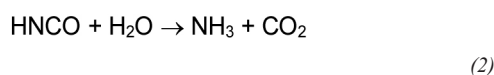
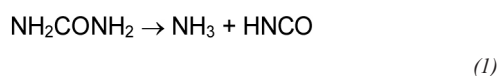
The diesel exhaust fluid-selective catalytic reduction (DEF-SCR) system is the leading and widely utilized technology to reduce NO_x emission from diesel engines (Figure 1). In this method, DEF (an aqueous 32.5wt% urea solution) is injected upstream of the SCR catalyst system to achieve EPA's target level of over 90% NO_x conversion. When the DEF is injected into the hot exhaust gas, urea dissociates into NH_3 , which is used to convert NO_x into N_2 . Although achieving over 90% NO_x conversion is a critical task to meet EPA regulations for Original Engine Manufacturers (OEMs), OEMs face challenges such as solid urea deposit formation that occurs at low temperatures in the DEF-SCR system [2], especially in severe cold

weather. Urea deposit formation is not only a concern in the operation of hardware components such as the DEF injector and mixer, but can also create backpressure problems, reducing engine performance or deposit build up on the SCR catalyst can lower NO_x conversion before the targeted service interval. In order to achieve over 90% NO_x conversion it is important to avoid urea deposit formation. While these solid deposits form from the injected urea DEF solution, they may contain urea decomposition products as well as urea [2,3,4]. Many factors including injector design and mounting geometry [3,4,5], mixer design [4, 5] and system temperature [3, 4] affect the extent of urea deposit formation. Bench tests of a DEF-SCR system indicated that the chemical composition of the solid deposit was temperature dependent [4] and a study on the thermal decomposition of urea in an open vessel showed that a variety of solid decomposition products can form at different decomposition temperatures [6].



Figure 1. Schematic diagram of DEF-SCR aftertreatment system. DOC- diesel oxidation catalyst, DPF- diesel particulate filter, SCR-selective catalytic reduction

The chemical complexity of the deposits that form in the DEF-SCR system is due to the side reactions that can occur during the thermal decomposition of urea to NH_3 . The thermal decomposition of urea generates two molecules of NH_3 by the reactions (1) and (2) [2, 3, 7].



The first step in the decomposition produces ammonia and isocyanic acid, and the latter subsequently reacts with water (facilitated by a metal oxide catalyst [2, 7]) to produce a second molecule of ammonia and carbon dioxide. The isocyanic acid produced in the first step of the urea decomposition can react with unreacted urea to form biuret and triuret and can also form heterocyclic compounds such as cyanuric acid, ammelide, ammeline and melamine (Figure 2) which are likely to contribute to deposit formation [2, 6, 8]. The further reaction of melamine to form oligomeric species (Figure 3) is also possible [9, 10].

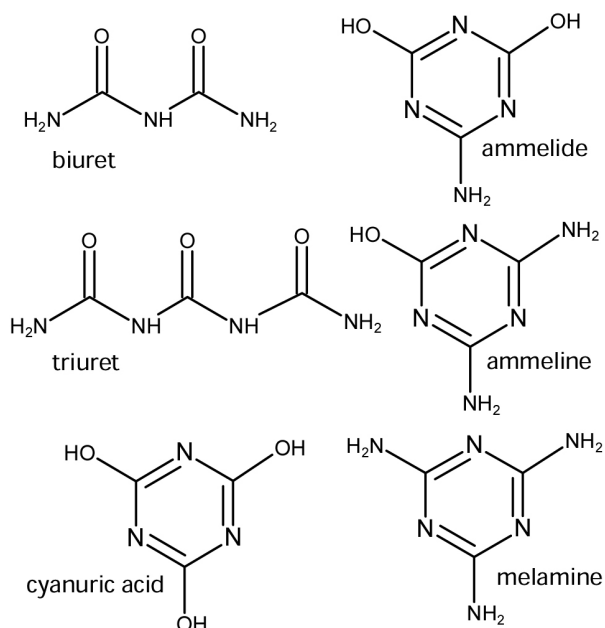


Figure 2. Possible urea decomposition products that could be part of the solid deposits in the exhaust treatment system.

In order to prevent the formation of solid deposits in the DEF-SCR system, or to efficiently remove deposits that form, it is important to know what the chemical composition of the deposit is. Zheng *et al.* [4] considered the effect of temperature on deposit formation in a study of a DEF-SCR system for diesel truck engines and reported the solubility of the deposits, their visual appearance and hardness, but did not explicitly determine the chemical composition. Dong and coworkers used thermogravimetric analysis and IR spectroscopy to characterize the chemical composition of the gaseous products of urea and urea deposit thermolysis as a function of temperature [3], but did not determine how temperature affected the chemical composition of the urea deposit itself. In this study we used thermogravimetric analysis (TGA), infrared (IR) spectroscopy, UV-visible spectroscopy, elemental analysis (for CHNOS) and solubility tests to study how temperature affected the chemical

composition of the solid residue produced in urea thermolysis and to characterize the chemical composition of urea deposits formed in DEF-SCR system over a wide range of operating temperatures.

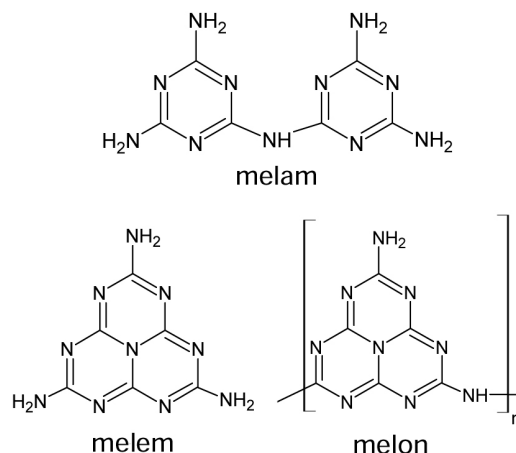


Figure 3. Oligomeric products that can form by the condensation of melamine.

EXPERIMENTAL METHODS

Reference Compounds

Urea (Baker, ACS grade), biuret (Fisher Scientific), cyanuric acid (Acros, 98%), ammeline (TCI America, 95%), and melamine (Alfa Aesar, 99%) were used as received and characterized by FTIR spectroscopy, UV-visible spectroscopy, TGA and elemental analysis to provide reference data for the characterization of the solid deposits collected from the DEF-SCR system.

Urea Thermal Decomposition Studies

Urea decomposition studies were carried out in the TGA (Mettler TGA/SDTA851[®] instrument) by heating a 20-30 mg sample of urea at 5 °C/min to 175 °C, 200 °C, 225 °C, 250 °C, 300 °C or 375 °C and maintaining the final temperature for 30 min to 2 h under a N_2 atmosphere. Samples run at lower temperatures were held at the target temperatures for longer periods of time to allow for the slower rate of decomposition at lower temperature. The residues left at the end of the TGA runs were characterized by IR spectroscopy.

Bulk (2-3 g) samples of urea were decomposed by heating in a silicone oil bath under a gentle stream of nitrogen. The oil bath temperature was maintained at 200 °C or 220 °C during the decomposition testing. Two different heating rates were used for the 200 °C decomposition: in one experiment the urea sample was placed in the oil bath while it was heated over the course of two hours to 200 °C, then maintained in the bath for three hours; this is referred to as the 200 °C slow heating experiment. In the second experiment the urea sample was placed in the oil bath once the temperature had reached 200 °C and maintained there for three hours; this is referred to as the 200 °C fast heating experiment. In the 220 °C experiment the urea sample was placed in the oil bath once the temperature reached 220 °C and maintained there for three hours. It was observed that some white solid condensed on the cooler portions of the apparatus during the heating period and IR spectroscopy showed that this was unreacted urea (data not shown). The solid decomposition residues collected from the heated part of the apparatus were characterized by IR and UV-visible spectroscopy.

Table 1. Summary of engine conditions under which urea deposit formed and the location where urea deposit was collected.

Sample	Time duration (min)	Exhaust flow rate (kg/h)	DEF flow rate (g/s)	NO SCR in (ppm)	Location deposit collected	DPF out temperature (°C)	SCR in Temperature (°C)
A	280	486	0.2	255	Bottom of decomposition tube	226	212
B	190	207	0.228	298	Before mixer	251	206
C	195	217	0.228	338	Before mixer	249	204
D	190	220	0.23	382	Before mixer	247	202
E	190	217	0.23	387	Before mixer	249	205
F	190	220	0.23	383	Before mixer	251	201
G	366	1277	0.6	186	At dosing module	425	418
H	160	725	0.27	95	At mixer	340	335

Urea Deposit Samples

Urea deposits were collected from the exhaust system of a DEF-SCR used in bench tests. Most of the urea deposits were collected in the decomposition tube upstream of the urea mixer and [Table 1](#) summarizes the engine conditions under which each deposit formed.

Analytical Measurements

Thermogravimetric Analysis

TGA experiments were carried out on reference compounds and the urea deposit samples on a Mettler TGA/SDTA851^e instrument. The samples, typically 20-30 mg, were placed in alumina crucibles in the TGA furnace and heated under a gentle stream (60-70 mL/min) of nitrogen or air. The air supply used was breathing air grade and contained up to 1000 ppm of carbon dioxide and up to 10,700 ppm of water vapor. Urea decomposition studies were carried out in the TGA as described above. Decomposition studies of the reference compounds, cyanuric acid and melamine were carried out by heating samples to 450 °C at a rate of 10 °C/min under a nitrogen atmosphere. Five urea deposit samples were decomposed by heating to 200 °C and to 600 °C under both air and nitrogen atmospheres; fresh samples were used for each temperature. The samples were heated at a rate of 10 °C/min to the target temperature and then held at 200 °C for 60 minutes or held at 600 °C for 15 minutes.

Solubility Testing

The solubility of the residue collected from the bulk urea decomposition experiments and the urea deposit samples was determined in water, 95% alcohol (85.4-86.0% ethanol, 4.2-5.0% methanol, 4.5-5.5% isopropanol and 3.5-5.9% water), and cyclohexane by placing 20-25 mg of the sample in 20 mL of the solvent and allowing it to equilibrate at room temperature for one week. The rate of dissolution of selected urea deposit samples that were mostly soluble was determined by timing the dissolution of a 20 mg sample in 10 mL of the solvent with gentle shaking.

Infrared Spectroscopy

Finely ground samples of the reference compounds, the residues from the TGA urea decomposition studies and the urea deposit samples were used to record the IR spectra by the total attenuated reflectance method on a Nicolet IR2000 spectrometer.

UV-Visible Spectroscopy

UV-visible spectra from 190-800 nm were recorded on a Thermo Scientific Evolution 300 spectrometer. The solutions from the solubility testing were used to record the UV-visible spectra. The solutions were placed in a 1.00 cm path length quartz cell, and diluted with the pure solvent, if necessary, so that the maximum absorbance did not exceed 3. Concentrations that gave high maximum absorbances were used for some samples so that a weak shoulder on the intense short wavelength peak could be clearly identified.

Elemental Analysis

Carbon, hydrogen, nitrogen, sulfur (CHNS) and oxygen (O) composition were determined on a ThermoFinnigan Flash 2000 elemental analyzer. CHNS measurements were carried out on all urea deposit samples and O measurements were carried out on urea deposit samples C, G, and H. CHNS measurements used two cyanuric acid samples and two 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT) samples as the calibration standards. The K-factor calibration method was used for CHS determination and the quadratic calibration method was used for N determination. Oxygen measurements used two acetanilide samples and two benzoic acid samples as the calibration standards and the K-factor calibration method was used. Duplicates of the urea deposit samples were measured for both CHNS and O determinations, and the reference compounds urea, biuret, cyanuric acid and melamine were run as controls in every sequence of samples to check the accuracy of the calibration.

RESULTS AND DISCUSSION

Reference Compounds

The IR spectra of urea, biuret, cyanuric acid, ammeline, and melamine (Figure 4) were used as a comparison for the identification of the species present in the urea decomposition products and urea deposit samples. The assignments of selected bands are reported in the appendix (Table A1). The UV-visible spectra of urea, biuret, cyanuric acid, ammeline, and melamine (Appendix, Figure A1) mostly showed a single strong peak in the UV region at very low wavelength, cyanuric acid and ammeline also showed a weaker peak at longer wavelength. The maximum in the urea absorbance was below the 190 nm lower wavelength limit of the instrument, and the 192 nm maximum of biuret was very close to the limit, which makes it difficult to determine whether features in this region are due to urea, biuret or a combination of both.

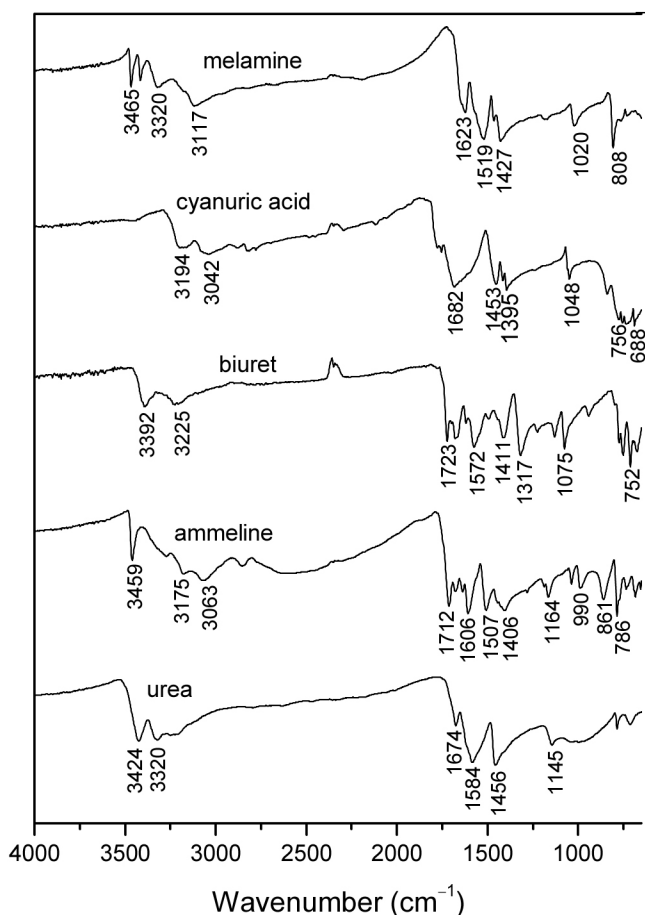


Figure 4. IR spectra of reference compounds

The TGA measurements show that urea decomposed in two steps (Figure 5). There was an initial mass loss of ~60% from 150-240 °C, with most of the remaining mass lost in a second decomposition step that occurred from 300-375 °C. Cyanuric acid (Figure 6) showed a small 2.7% mass loss at ~225 °C (this might be due to the presence of triuret as an impurity, since this is close to its 233 °C decomposition temperature[11]), but mostly decomposed in one step between 330-400 °C. Melamine (Appendix, Figure A2) showed a single decomposition step, losing 95% of its mass between 280-

390 °C. TGA measurements cannot distinguish between cyanuric acid and melamine as components of urea deposits because of the large overlap of the temperature ranges over which they decompose.

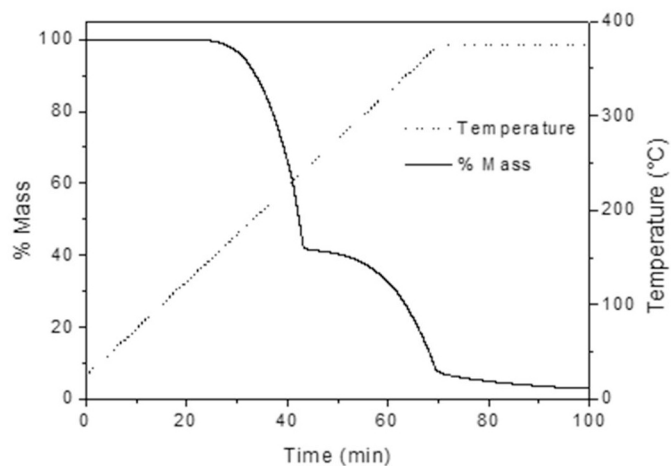


Figure 5. TGA trace for the decomposition of urea when heated at 5 °C/min to 375 °C and then held at 375 °C for 30 minutes under N₂ atmosphere.

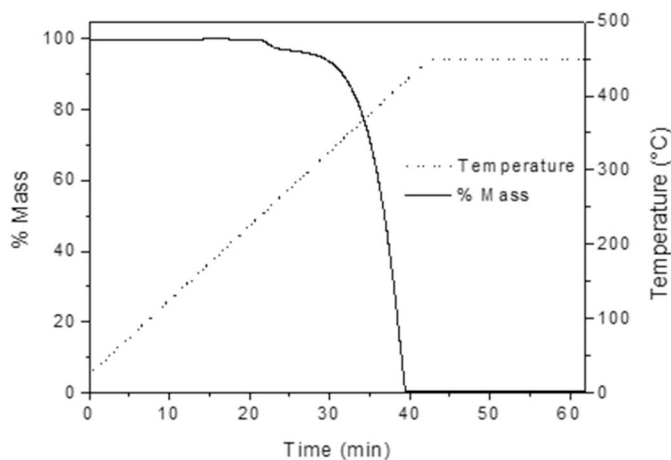


Figure 6. TGA trace for the decomposition of cyanuric acid when heated at 10 °C/min to 450 °C and then held at 450 °C for 20 minutes under N₂ atmosphere.

Urea Decomposition Studies

The IR spectra of the residues obtained after the thermal decomposition of urea at various temperatures in the TGA (Figures 7 and 8) were used to identify the major species present. After decomposition at 175 °C the bands at 3316 cm⁻¹ and 1452 cm⁻¹ showed that there was still unreacted urea present, even though the sample temperature was maintained at 175 °C for two hours. The other major product detected in the FTIR spectra of the 175 °C residue was biuret, with bands at 1080 cm⁻¹ and 1406 cm⁻¹ attributable to it. There may also have been some cyanuric acid present, as there was a band at 1048 cm⁻¹ and the 1452 cm⁻¹ band could also be due to cyanuric acid. The IR spectrum of the residue of the urea decomposition at 200 °C contained bands at 1564 cm⁻¹, 1409 cm⁻¹ and 1080 cm⁻¹ from biuret and bands at 1452 cm⁻¹ and 1056 cm⁻¹ from cyanuric acid. The IR spectra of the products of the decomposition of urea at 225 °C, 250 °C and 300 °C (Figure 8) were essentially identical and were very similar to the spectrum of cyanuric acid (Figure 4), indicating that it was the major

decomposition product at these temperatures and there was no evidence of unreacted urea in the IR spectra. The IR spectrum of the 375 °C urea decomposition product had the 1045 cm^{-1} band which indicated that there may have been some cyanuric acid present. However, the broad mass of highly overlapped peaks from 1100-1800 cm^{-1} makes it difficult to identify any other species conclusively and shows that the residue was a mixture of multiple products.

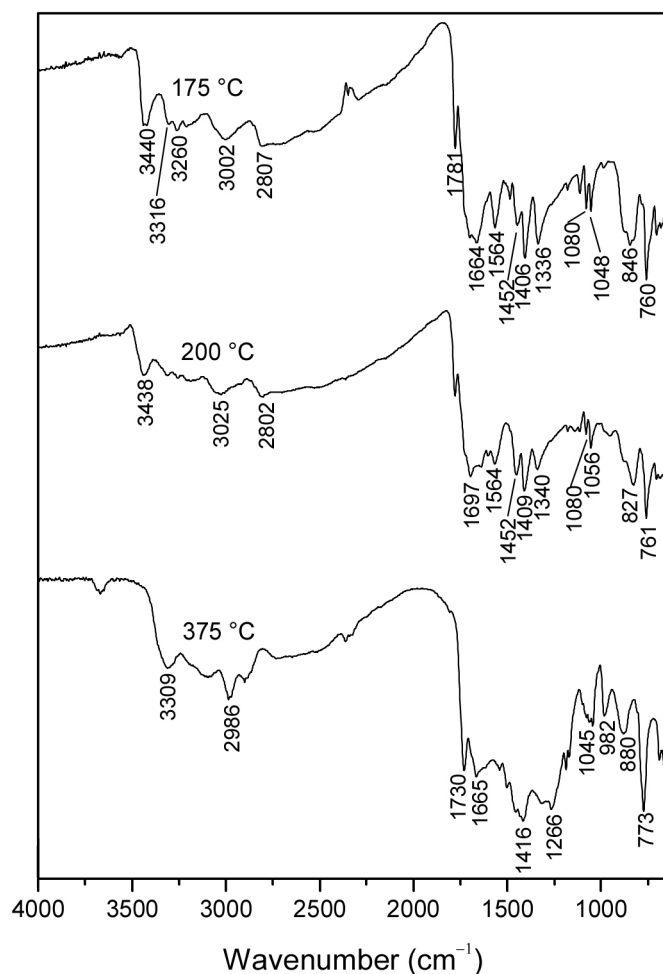


Figure 7. IR spectra of pure urea decomposition residues from samples heated in the TGA at 175 °C, 200 °C, and 375 °C and then held at that temperature for 30-120 minutes.

The products of the bulk decomposition experiments on urea were also examined to see whether the sample size or the heating rate affected the product distribution. The IR spectra (Figure 9) show that the spectrum of the 200 °C slow heating experiment was very similar to the spectrum of the 220 °C fast heating experiment. The residues of these two experiments were predominately a mixture of biuret (identified by the band at 1414 cm^{-1}) and cyanuric acid (identified by the bands at 1455 cm^{-1} , 1056 cm^{-1}). The spectrum of the residue of the 200 °C fast heating experiment was slightly different to that of the 200 °C slow heating experiment, and comparison to the reference samples indicated that it was a mixture of cyanuric acid (3196 cm^{-1} , and 1459 cm^{-1} bands) urea (3426 cm^{-1} , and 1141 cm^{-1} bands) and biuret (1414 cm^{-1} band). The differences in the spectrum of the 200 °C fast heating experiment were probably due to differences in the relative amounts of cyanuric acid and biuret and the possible

presence of urea. The formation of the same products with different heating rates at 200 °C indicates that changing the heating rate does not substantially alter the chemical species that form during urea decomposition, but it can affect the relative amounts of the different species formed. The IR spectra of the residues from the bulk urea decomposition at 200 °C with slow heating was very similar to the residue from the sample heated in the TGA at 200 °C (Appendix, Figure A3). This is not surprising, as the sample in the TGA was heated gradually (5 °C/min) to 200 °C. The main significance of this result is that it shows that the urea decomposition products obtained by decomposing small samples in the TGA are similar to the decomposition products of larger urea samples heated to the same temperature at similar rates. This means it is reasonable to assume that the results of TGA urea decomposition studies will accurately represent the urea decomposition products formed at that temperature in other systems. This is important because the TGA instrument is the preferred apparatus for studying the temperature dependence of urea decomposition as it provides the most precise control of temperature and heating rate.

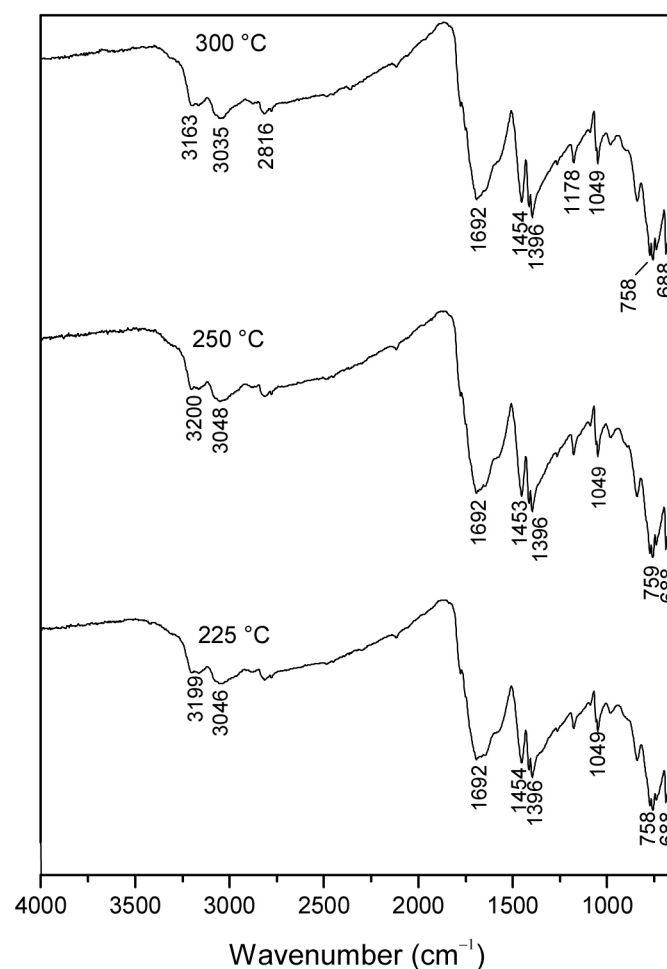


Figure 8. IR spectra of pure urea decomposition residues from samples heated in the TGA at 225 °C, 250 °C, or 300 °C, then held at that temperature for 30 min-2 hours.

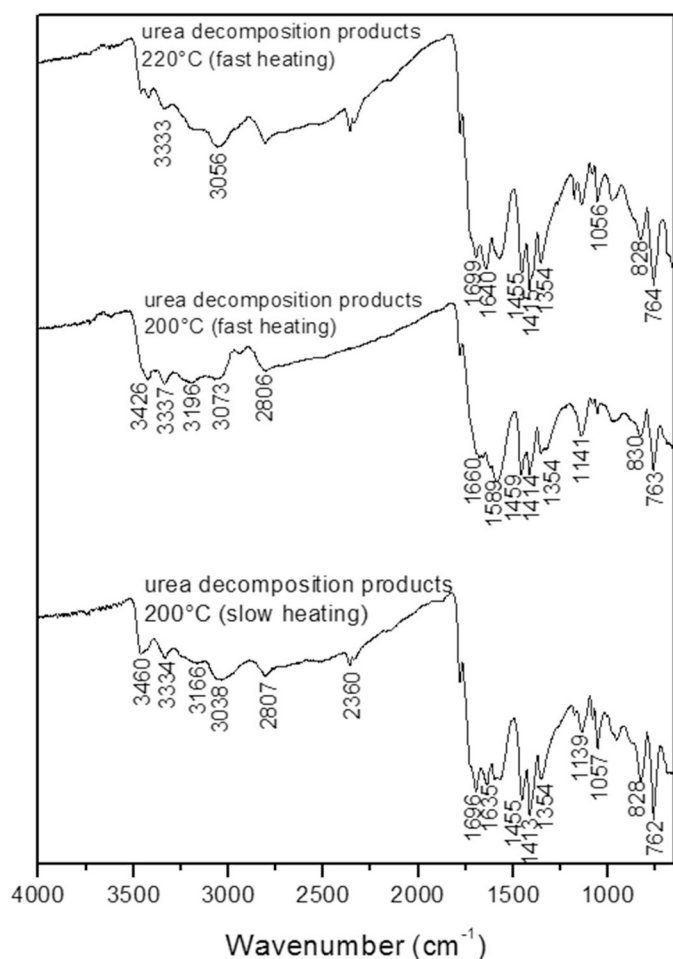


Figure 9. IR spectra of the residues from the decomposition of pure bulk urea samples at 200 °C or 220 °C.

The presence of both 192 nm (due to biuret) and 213 nm (due to cyanuric acid) bands in the UV-visible spectra of the residues from the decomposition of bulk urea at 200 °C and 220 °C (Appendix, Figure A4) showed that they contained both biuret and cyanuric acid, which is consistent with the results of the IR spectra. Any unreacted urea would absorb at similar wavelengths to the biuret, so the UV-visible data does not rule out its presence in small amounts. The larger relative intensity of the 213 nm peak in the spectrum of the 200 °C slow heating sample shows that it contained a larger proportion of cyanuric acid than the samples heated rapidly at 200 °C or 220 °C. This is consistent with the finding from the IR spectra that different heating rates can affect the relative amounts of the urea decomposition products.

The residue from the bulk decomposition of urea at 200 °C with slow heating was found to be mostly soluble in water, and largely insoluble in 95% alcohol and cyclohexane. This is consistent with the identification of cyanuric acid and biuret as its major constituents, as biuret and cyanuric acid are slightly soluble in water and biuret is soluble in alcohols, while cyanuric acid is insoluble in alcohols.[11]

Overall, the bulk and TGA urea decomposition studies (Figure 10) showed that at lower temperatures, 175-200 °C, the major products formed from urea were biuret and cyanuric acid. At 225-250 °C the major product was cyanuric acid, and at the highest temperature tested,

375 °C, the a small amount of residue left contained some cyanuric acid and small amounts of other species with ammelide tentatively identified. These results are consistent with the results of the study by Schaber *et al.*[6] on the pyrolysis of urea in an open reaction vessel. They found that biuret was produced from 150-190 °C, cyanuric acid was the major decomposition product as the temperature increases beyond 190 °C and continues up to 250 °C. The urea decomposition in the 190-250 °C range also produces ammelide and ammeline, but in smaller amounts than cyanuric acid. There are some differences in temperature dependence of the product distribution, which may be due to Schaber and coworkers immediately cooling the samples once the target temperature was reached while we held the samples at the target temperature for up to three hours.

Urea Deposit Samples Collected from the Decomposition Tube of the DEF-SCR System

IR Spectroscopy

The IR spectra of the urea deposit samples are shown in Figures 11 and 12. The spectra of urea deposit samples B, C and D contained bands at 3423 cm⁻¹, 1583 cm⁻¹, 1455 cm⁻¹ and 1145 cm⁻¹ which showed that urea was a major component, while the spectrum of sample E contained features from both urea (3421 cm⁻¹, 1455 cm⁻¹ and 1145 cm⁻¹ bands) and biuret (1413 cm⁻¹ band), with a weak band at 3200 cm⁻¹ that was possibly due to cyanuric acid. In particular it should be noted that the IR spectrum of sample C (Figure 11) was essentially identical to the reference spectrum of urea (Figure 4). Samples B, C, D and E were all collected from the decomposition tube when the exhaust temperature was maintained at ~250 °C at the DPF outlet and ~200 °C at the SCR inlet. It should be noted that these exhaust temperatures at which substantial amounts of unreacted urea and biuret collected in the decomposition tube, were well above the 150 °C at which urea decomposition begins, and the 190 °C at which biuret decomposition starts. However, unreacted urea and biuret were not the only components of the deposits that formed in the 200-250 °C temperature range. Sample F formed under essentially identical exhaust conditions to samples B, C, D and E, yet the IR spectrum (Figure 12) indicated that its major components were biuret (1414 cm⁻¹ band) and cyanuric acid (3193 cm⁻¹, 1456 cm⁻¹ and 1051 cm⁻¹ bands). The IR spectrum indicated that the major components of sample A (Figure 11) were cyanuric acid (1396 cm⁻¹ and 1050 cm⁻¹ bands) and biuret (1572 cm⁻¹ band), and though the engine exhaust had a narrower range of temperatures, 212-226 °C when it formed, this was still within the range for other tests where urea and biuret were the main constituents of the deposits. One possible reason for the presence of appreciable amounts of cyanuric acid in sample A is that it was obtained from a test 90 minutes longer than the other tests conducted in the 200-250 °C temperature range, and it may be that conversion of the initial deposit of unreacted urea and biuret to cyanuric acid was slow in this temperature range. The presence of cyanuric acid and biuret as major products in samples A and F was consistent with the results of pure urea decomposition in TGA and bulk studies where all samples formed in the 200-250 °C range contained cyanuric acid. For the samples collected at the highest temperatures, G (418-425 °C) and H (335-340 °C), the bands at 3051 cm⁻¹, 1690 cm⁻¹, 1454 cm⁻¹ and 1397 cm⁻¹ showed that the major component was cyanuric acid (Figure 12).

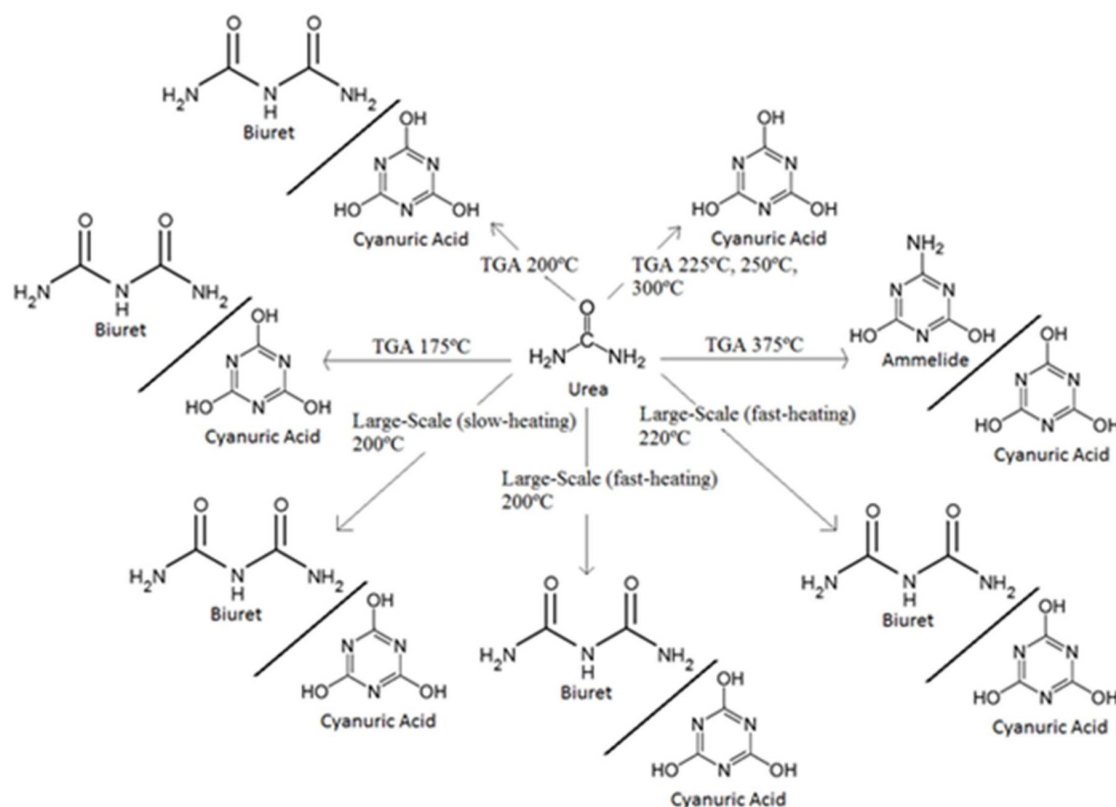


Figure 10. Temperature dependence of the major decomposition products of urea.

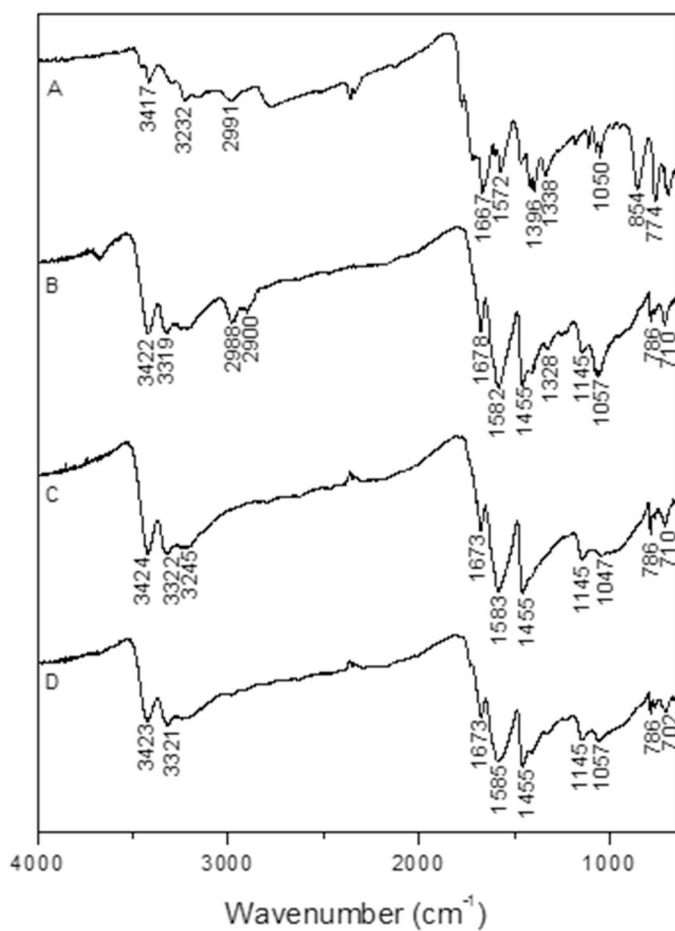


Figure 11. IR spectra of urea deposit samples A, B, C and D.

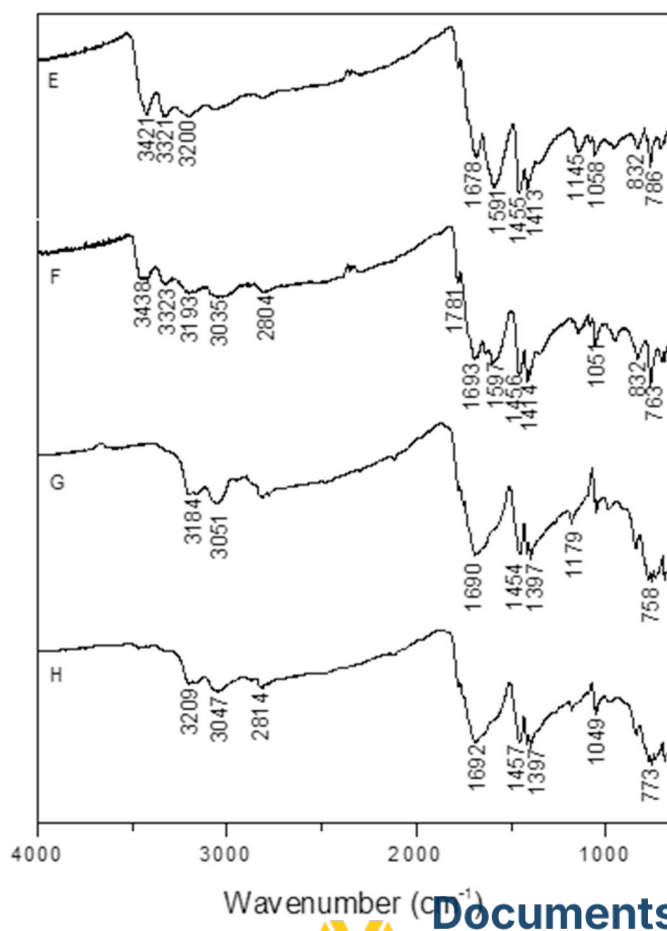


Figure 12. IR spectra of urea deposit samples E, F, G and H.