# Ammonia Formation Rates in Biomass Pyrolysis

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**Introduction** For the development and design of advanced biomass conversion equipment, accurate experimental data of fundamental processes are highly important. Therefore, this paper aims to contribute to a better description of the chemical and physical processes occurring in biomass pyrolysis. The results of biomass pyrolysis experiments from the experimental set-ups at Eindhoven University of Technology, in which biomass is heated very fast (up to 1000 K/s) on a metal grid, are highlighted. Specific focus is on the product evolution rate of ammonia (NH3), an important precursor for NOX formation. The gas phase concentration of ammonia is followed on-line using single-frequence IR light, and also determined off-line by FT-IR based on the gas spectrum in the mid-infrared region.

**Background** Whatever conversion takes places in biomass conversion equipment, it will always be preceded by, or at least influenced by biomass pyrolysis. Therefore, a lot of experimental effort and modelling has focused on this process. Many researchers have studied cellulose, which constitutes around 50% of woody biomass, as a model component. The well-known Broido-Shafizeh mechanism that describes the rate of weight loss of cellulose was developed in the 1970's [1,2]. Later work of Antal and Varheygi [3,4,5] must also be noted. Many other papers on the weight loss rate due to biomass decomposition have appeared, for various feedstock and temperature regimes. These existing models give some information on the product species formed, but only in terms of product classes: gas, tar and char. For a pyrolysis model to be implemented in modern CFD process simulations, its output should be on a molecular level, i.e. give information about individual components. The development of such a model is a very difficult task, for several reasons:

- The biomass sample must be heated very fast to minimize reactions already occurring in the warm-up phase. For TGA equipment with a low heating rate of 10-100 K/min, the error introduced by the weight loss during this phase is unacceptable.
- An analysis method is required to measure the product formation rates of individual components almost instantaneously.
- The amount of reactions occurring and reaction products formed is enormous.

To circumvent the first problem, a so-called heated grid reactor can be used, a unique facility to measure the rate of pyrolysis and/or gasification reactions of very fine biomass and coal particles [6,7]. It is described in more detail later. As an analysis method, rather than slow methods based on gas chromatography, and other methods where a gas sample must be taken and removed from the gas mixture, an in-situ spectroscopic technique is preferred. Therefore, we use a Tuneable Diode Laser (TDL) with fast frequency scanning properties to measure the temporal evolution of the Infra Red absorption at a specific frequency in the mid infrared region. By selecting the right frequency, the production rate of any component which absorbs infrared light can be determined, such as carbon monoxide [8] or in this case, ammonia. In conjunction to the TDL, we also use Fourier Transformed InfraRed (FT-IR) for two reasons. Firstly, due to the large number of products formed during the complex pyrolysis processes, care must be taken to avoid interference from other components. Secondly, while the TDL gives information about the relative rate of the concentrations of formed species, FT-IR can give more reliable information about the total amount formed.

**Experimental** The heated grid reactor consists of a metal wire mesh (stainless steel, platinum or other material) placed between two electrodes in a reactor chamber, see Fig.1. The maximum operating temperature is given by the melting point of the metal. The reactor can be operated in pressurized conditions, or under vacuum, depending on the application. Gases can enter and leave the chamber from different ports located below the grid. Sintered porous material in the ports reduces the gas speed, to prevent the sample being blown away. The grid temperature is measured with a thin thermocouple (0.1 mm junction) placed on the mesh close to the sample. Optical windows are placed on the top and at both sides of the reactor (CaF2), so that the pyrolysis process can be investigated with a CCD camera (or any other alternative optical equipment). The evolved gases can be analyzed with a FTIR (Fourier Transform InfraRed spectrometer), as in Fig.2, and single-frequency IR. This is done in the mid infrared region, specifically for ammonia in the spectral range of 900-1200 cm-1.

**Results** It was found that very little ammonia is produced from fresh wood, since wood typically contains < 1wt% of nitrogen. However for other fuels such as MDF it is substantial; apparently the glue in the MDF is a nitrogen source. N-rich model components have also been studied, notably urea and melamine. These components release nitrogen in the form of NH3, HCN and HNCO. The production rates of these components are expressed in the form of first order kinetics. These kinetic data are vital for an accurate description of NOx formation in biomass conversion equipment, and aim to contribute to the use of renewable fuels without creating harmful emissions to the environment.

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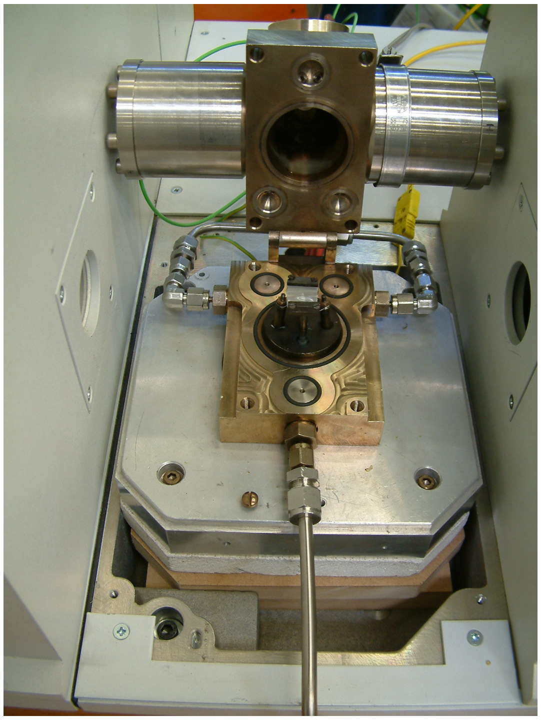

*Figure 1: Heated grid reactor (opened)*

*Figure 2: Heated grid reactor in FT-IR compartment*