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Satisfactory results from modelling of NOx formation in CFD during combustion of Municipal Solid Waste (MSW) in grate-fired waste-to-energy plants is highly depended on accurate descriptions of the temperature field in the free-board above the waste bed. Accurate modelling of the temperature field relies on an accurate determination of the boundary conditions; the species concentration, gas temperature and gas velocity from the waste bed into the computational domain. In this study the gas temperature and the gas concentration profiles of O2, H2O, CO, CO2, CH4, C2H2, C2H4, NH3 and HCN along the waste bed were measured. The measurements were performed on a 9 ton/h grate-fired waste-to-energy plant, Affald+ unit 4 in Denmark. The species concentration profiles were determined by gas extraction using a 6 m water cooled probe and FTIR spectroscopy, while the gas temperatures were determined by suction pyrometer. The major combustible gasses were determined to be CO, CH4 and C2H4, which are only found above the first half of the grate. Furthermore, it was determined that during grate-fired MSW combustion the majority of the NOx precursors are released as NH3; more than 80%. The influence of NOx precursor composition on the NOx formation was examined through CHEMKIN simulations. It was shown that for reliable modelling of the NO formation at high excess air ratios, λ > 1.1, it is important to determine the correct ratio between NH3 and HCN. The importance of an accurate precursor determination increases considerably with decreasing temperatures.