Fast pyrolysis of biomass at high temperatures

This Ph.D. thesis describes experimental and modeling investigations of fast high temperature pyrolysis of biomass. Suspension firing of biomass is widely used for power generation and has been considered as an important step in reduction of greenhouse gas emissions by using less fossil fuels. Fast pyrolysis at high temperatures plays a significant role in the overall combustion process since the biomass type, the reaction kinetics and heat transfer rates during pyrolysis influence the volatile gas release. The solid residue yield and its properties in suspension firing, including particle size and shape, composition, reactivity and burnout depend significantly on the operating conditions of the fast pyrolysis. Biomass fast pyrolysis experiments were performed in a laboratory-scale wire mesh reactor and bench scale atmospheric pressure drop tube / entrained flow reactors with the aim to investigate the effects of operating parameters and biomass types on yields of char and soot, their chemistry and morphology as well as their reactivity using thermogravimetric analysis. The experimental study was focused on the influence of a wide range of operating parameters including heat treatment temperature, heating rate, particle size, residence time, inorganic matter and major organic biomass compounds. Woody and herbaceous biomass were used as fuels. Char yields from the drop tube and entrained flow reactors were lower than those obtained in the wire mesh reactor, emphasizing the importance of heating rate on the product yields. The char yield decreased significantly between 10 and 600K s⁻¹, but continued to decrease with increasing heating rate, and was lowest for the drop tube / entrained flow reactors with estimated heating rate of > 10⁴ K s⁻¹. The heat treatment temperature and potassium content affected the char yield stronger than the heating rates and differences in the plant cell wall compounds between 800 and 3000K s⁻¹. The heat treatment temperature affected more the herbaceous biomass char yield compared with wood.

The differences in the char yield for particle size fractions in the range of 0.05mm were negligible, leading to the conclusion that the biomass particle can be assumed isothermal, when its size did not exceed 0.425 mm. Compared to smaller particles, the larger pinewood particles (dₜ > 0.85 mm) required more than 1 s holding time for the complete conversion at intermediate and fast heating rates. The influence of heating rate on the char yield was less pronounced for larger particles (from 0.85 to 4 mm) obtained at temperatures > 1250°C in the wire mesh reactor, single particle burner and drop tube reactor, due to the predominance of internal heat transfer control within the large particles.

Potassium compared to all other ash elements in the fuels had the highest influence on the char yield. The effect of potassium on the char yield was stronger at low and intermediate heating rates where potassium catalyzed the repolymerization and cross-linking reactions, leading to higher char yields. Silicon compounds abundant in herbaceous biomass had a negligible influence on the char yield and reactivity. However, a very high content of silicon oxides in biomass (> 50% of the overall biomass inorganic matter) significantly affected the char morphology, as observed for forrice husk. For this fuel, the high content of low-temperature melting amorphous silicon oxides led to the formation of a glassy shell on rice husk chars at 1000-1500°C. The ability of char to melt in fast pyrolysis followed the order pinewood > beechwood, straw > rice husk, and was related to the formation of metaplast. Different particle shapes of beechwood and leached wheat straw chars produced in the drop tube reactor which have similar potassium content suggested a stronger influence of the major biomass cell wall compounds (cellulose, hemicellulose, lignin and extractives) and siliconates on the char morphology than alkali metals. In this study, potassium lean pinewood (0.06 wt. %) produced the highest soot yield (9 and 7 wt. %) at 1250 and 1400°C, whereas leached wheat straw with the higher potassium content (0.3 wt. %) generated the lowest soot yield (2 and 1 wt. %). Soot yields of wheat and alfalfa straw at both temperatures were 5% points lower than wood soot yields and 3% points higher than leached wheatstraw soot yield, indicating that potassium plays a minor role on the soot formation. The leaching of alkali from wheat straw additionally resulted in a removal of lignin, leading to the decreased formation of polycyclic aromatic hydrocarbon precursors, and thereby to lower soot yields. Pinewood soot particles generated at 1250°C were significantly larger (77.7 nm) than soot particles produced in pinewood (47.8 nm) pyrolysis at 1400°C, beechwood (43 nm) and wheat straw (30.8 nm) devolatilization at both temperatures. The larger pinewood soot particles were related to the formation of tar balls known from smoldering combustion. The major difference in nanostructure of pinewood, beechwood and wheat straw soot was in the formation of multi and single core particles. Pinewood soot particles generated at 1250°C were mainly multi core structures compared to pinewood soot generated at 1400°C, combining both single and multi core particles. Beechwood and wheat straw soot samples had multi and single core particles at both temperatures. In thermogravimetric analysis, the maximal reaction rate of pinewood soot was shifted to temperatures about 100°C higher than for the other samples in both oxidation and CO₂ gasification, indicating a significantly lower reactivity. Soot samples produced at 1400°C were more reactive than soot generated at 1250°C. The beechwood and wheat straw soot samples were more graphitic than pinewood soot based on the electron energy loss spectroscopy (EELS) analysis. In contrast to expectations of graphic structures to react slower than amorphous samples, beechwood and wheat straw soot were 35 and 571 times more reactive than pinewood soot prepared at 1400°C. The presence of potassium in wheat straw soot mainly as water-soluble KCl, KOH, KHCO₃ and K₂CO₃ and to a minor extent bonded to the soot matrix in oxygen-containing surface groups (e.g.carboxyl, phenol/lático) or intercalated in soot graphene layers led to a higher reactivity in CO₂ gasification compared to low-alkali containing pinewood soot. The results showed that potassium has a dominating effect on the soot reactivity compared to nanostructure and particle size. A mathematical model of biomass fast pyrolysis was developed to predict the gas and char yield of wood and herbaceous biomass at heating rates > 600K s⁻¹. The model includes both kinetics and external and internal heat transfer assuming that mass transfer is fast. The model relies on the concept applied in fast pyrolysis of cellulose through the formation of an intermediate liquid (so-called metaplast) which reacts further to form char and gas. The kinetics of the fast pyrolysis was described through the Brodoo-Shafizadeh scheme for biomass. The catalytic effect of potassium which is a major ash element influencing the char yield was included in the model.

General information