Fast pyrolysis of lignin, macroalgae and sewage sludge

In the last twenty years, the fast pyrolysis process has been explored to produce bio-oil from biomass. Fast pyrolysis is a thermal conversion technology that is performed at temperatures 450 - 600 °C, high biomass heating rates (100 - 2000 K/s), a short gas residence time (less than 2 s) with no presence of oxygen. Fast pyrolysis can convert a large fraction of the biomass to bio-oil, and smaller fractions of char and gas. The pyrolysis centrifuge reactor (PCR) has been developed at the CHEC center at DTU Department of Chemical Engineering. The reactor is a compact design that uses a low flow rate of carrier gas, pyrolyse biomass without a heat carrier and obtain a biomass particle heating rate of 1000 - 1500 K/s by a high centrifugal force. The reactor can be constructed at a size that could be applicable locally at waste water treatment plants or pulp and paper plants, bio-ethanol plants or can constructed as a mobile unit of a tractor-propelled vehicle that is used on straw fields. A lot of work on PCR straw and wood pyrolysis with respect to pyrolysis conditions, moisture feedstock content, bio-oil properties, and PCR modelling is done before this PhD project. The bio-oil yields of approximately 68 and 60 wt%daf are obtained for wood and straw PCR pyrolysis, respectively and the bio-oils properties are similar to those of wood and straw pyrolysis from fluidized-bed reactors. Wood and straw, conventional biomasses, are extensively investigated and knowledge of wood and straw fast pyrolysis is available in the literature. Nonconventional biomass feedstock may also be applicable for fast pyrolysis processes. Among the forms of nonconventional biomasses: macroalgae, lignin (industrial residue) and sewage sludge may be attractive materials due to their low price, non-competitiveness with food crops and the possible utilization of solid wastes. Besides, a fast pyrolysis process can be used as a process to densify the biomass and produce bioslurry, a mixture of bio-oil and pyrolytic char. The bioslurry is found to be a possible feedstock for pressurized gasification plants. Thus, the aims of this project are to investigate fast pyrolysis properties of lignin, sewage sludge and macroalgae on a lab scale PCR and characterize their bio-oil properties. Bioslurry properties with respect to use as a feedstock for pressurized gasification is also investigated. Lignin and sewage sludge PCR pyrolysis provided bio-oil yields of 47 and 54 wt%daf, and oil energy recovery of 45 and 50 %, respectively. While the macroalgae PCR pyrolysis showed promising results with an organic oil yield of 65 wt%daf and an oil energy recovery of 76 %. The lignin, macroalgae and sewage sludge bio-oil properties were relatively different to those of the straw or wood bio-oils with respect to oxygen content, viscosity, HHV and mean molecular mass. The HHV of the lignin, sewage sludge and macroalgae oils were 29.7, 25.7 and 25.5 MJ/kg db respectively, and that are higher than that of typical biooil from conventional biomasses (23-24 MJ/kg db). Almost all metals feedstock contents were contained in the chars at temperatures of 550 - 575 °C for lignin, sewage sludge and macroalgae PCR pyrolysis. Therefore the bio-oils obtained low metal concentrations (especially alkali contents less than 0.09 wt%). Due to high feedstock nitrogen and sulfur contents, also a high level of nitrogen and sulfur of macroalgae and sewage sludge oils were observed compared to conventional bio-oil and this may limit their further industrial applications. The lignin char had a high proportion of small size particles, a HHV of 21 MJ/kg db and were almost free of chloride and sulfur, thus it is considered as a promising fuel for gasification or combustion; whereas macroalgae and sewage sludge chars containing high amounts of macronutrients as N, P, K, S, Mg and Ca and this could make the chars most valuable as raw materials for fertilizer production. The sewage sludge waste bulk volume (the char compared to the sludge) was reduced with 52 % by pyrolysis at 575 °C. It is seen that the fast pyrolysis process provides a promising method to reduce cost for landfilling and produce a bio-oil that can be used as a fuel. The pyrolysis temperature has a considerable effect on the product distributions of the lignin and sewage sludge PCR pyrolysis, as well as their bio-oil properties with respect to molecular mass distribution, identified GC-MS component compositions, water-insoluble fraction, viscosity, and HHV. A maximum of organic oil yields of lignin and sewage sludge PCR pyrolysis were obtained at optimal temperatures of 550 – 575 °C. The optimal oil properties with respect to industrial applications seem to observe at the optimal temperatures for obtaining a maximum oil yield. The Broido-Shafizadeh scheme1 and kinetic parameters of lignin and cellulose1 are applied in the PCR model developed by Neils Bech2 to model lignin pyrolysis. An acceptable fit between simulated and experimental data was obtained with only a modification of a ratio of gas to char selectivity (g of 0.45) of the char and gas formation reaction. The needed modification of g value is probably caused by presence of alkali and the lignin from a bioethanol plant. A fast pyrolysis can be used as a process to densify biomass. A bio-oil is mixed with char or wood to produce a bioslurry that is used as feedstock for a pressurized gasification process. In this work, the behaviors of slurry samples of wood, char and grinded char with respect to phase transitions, rheological properties, elemental composition, and energy density were investigated. Also pumping properties were investigated at temperatures 25, 40 and 60 °C and the solids loading of 0 - 20 wt%. The bioslurries obtained a volume energy density of 21– 23 GJ/m3 and an energy densification factor of 4.5 – 5 (when compared to beech wood). Their apparent viscosities were significantly influenced by the solid loading levels (0 – 20 wt %) and temperatures (25 – 60 °C). The slurry samples with 10 wt% char (having d80 of 276 μm) and 20 wt% grinded char (having d80 of 118 μm) were successfully pumped into a pressurized chamber (0 - 6 bar). v Extensive investigations were carried out with PCR experiments and PCR modeling. The PCR set-up has some limitations such as insufficient condenser cooling surface area, a small diameter of the condenser nozzle and high rotor speed for obtaining high bio-oil. The recognized limitations lead to that the old PCR set-up cannot be safely scaled up and perform well in a continuous mode. Thus a new set-up with significant modifications of reactor and bio-condenser has been manufactured to overcome these limitations. The new set up is possible to operate with hydrogen injection and catalyst fast pyrolysis modes.

**General information**
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