

MODELLING FAST PYROLYSIS IN A FLUIDIZED BED REACTOR: THE ROLE OF HETEROGENEOUS SECONDARY REACTIONS AND CHAR LOADING

Maurizio Troiano, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125, Napoli, Italy
maurizio.troiano@unina.it

Roberto Solimene, Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS), Consiglio Nazionale delle Ricerche, Piazzale V. Tecchio 80, 80125, Napoli, Italy

Piero Salatino, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale V. Tecchio 80, 80125, Napoli, Italy

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Biomass is one of the most promising renewable sources for the substitution of fossil feedstocks in the production of fuels and platform chemicals. Fast pyrolysis offers a direct route to produce liquid fuels and chemicals, with high feedstock flexibility and energy input efficiencies compared to alternative thermochemical pathways. Unlike biological processes, which can only valorize the non-recalcitrant fraction of biomass, fast pyrolysis has the potential of converting all carbon in the feedstock. Furthermore, fast pyrolysis fits well into extended-supply chain biomass valorization schemes, based on decentralized processing of raw feedstock and generation of biogenic intermediates (biofeedstocks) at satellite biomass harvesting/collection sites, which then feed into larger centralized processing or upgrading biorefineries.

During fast pyrolysis, biomass decomposes very quickly to generate solid (biochar), liquid (bio-oil), and gases through a complex chemical network of series-parallel thermally activated reactions starting with depolymerization of lignocellulosic biopolymers (cellulose, hemicellulose, and lignin), followed by fragmentation, rearrangement/isomerization, repolymerization, aromatization, volatilization, and condensation reactions. As a result, crude bio-oil is characterized by a heating value about half that of conventional fuel oil and by high viscosity, acidic pH and limited stability, which obligates bio-oil to be upgraded before further use. These potential drawbacks are driving research toward the improved design of pyrolytic converters and choice of process conditions that may maximize yield and selectivity toward valuable compounds. Clever chemical reaction engineering of the pyrolytic conversion represents a pivotal tool, with the aim of ensuring optimal chemical pathways for biomass conversion.

The present study is focused on fluidized bed fast pyrolysis, selected due to its versatility, robustness, and superior thermal performance over competing technologies especially for application to small-to-medium-scale decentralized plants for densification of raw biomass. Despite the inherent positive features of fluidized bed converters, particle heating and time-temperature history, biomass and volatile/gas residence times, gas and solid phase contacting, mixing, and flow pattern need to be carefully controlled to drive conversion along the prescribed chemical pathway. A specific concern regards the course of secondary reactions between depolymerization products and char, whose progress, possibly enhanced by prolonged residence times and uncontrolled backmixing, may alter the quantity/quality of the produced bio-oil. In fact, especially at low temperatures, contact with char may overtake vapor residence time as the determinant for secondary cracking reactions of vapors generated by biomass decomposition. Thus, char holdup in the pyrolyzer as well as the presence of entrained char in the hot parts of the reactor and the exhaust should be considered in reactor modeling and design. The recognition of the relevance of the heterogeneous vapor-char interaction to bio-oil production emphasizes the importance of proper control of char loading, establishing at steady state during operation of a fluidized bed biomass pyrolytic converter.

In the present study, a careful assessment of fluidized bed fast pyrolysis of biomass is undertaken. A one-dimensional (1D) model based on a simplified, although comprehensive, representation of the key features of the fluidized bed pyrolytic converter is developed. The reactor design and operating conditions are selected to minimize the expected secondary interaction between primary products of biomass pyrolysis and the biochar. Accordingly, a shallow fluidized bed with overbed feeding of relatively fine biomass particles is considered. The remarkable feature of the model is careful consideration of processes that control the establishment of a steady char loading in the bed, namely, entrainment, elutriation, attrition, and bed drain/regeneration. Primary pyrolytic decomposition of biomass and secondary reactions have been modeled using a semi-detailed reaction scheme. Model results are helpful to assess the role of heterogeneous secondary reactions and the proper management of char loading during fluidized bed fast pyrolysis, providing criteria and guidelines for optimal design and operation of a fluidized bed pyrolytic converter.