Mathematical model of biomass fast pyrolysis in fluidized bed

Maurizio Troiano¹*, Roberto Solimene², Piero Salatino¹

1 Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Napoli, Italy; 2 Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibile (STEMS), Consiglio Nazionale delle Ricerche, Napoli, Italy

*Corresponding author: maurizio.troiano@unina.it

Highlights

- An accurate description of chemical and physical phenomena is necessary for biomass pyrolysis.
- Multistep kinetic model allows to predict oil yield and composition.
- Solids holdup control needs to be considered for steady operation of fluidized bed.

1. Introduction

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 and it has the potential of converting all carbon in the feedstock. During fast pyrolysis, biomass decomposes very quickly to generate solid (biochar), liquid (bio-oil), and gases through a complex chemical network of seriesparallel thermally activated reactions starting with depolymerization of lignocellulosic biopolymers, fragmentation, rearrangement/isomerization, repolymerization, followed bv aromatization. volatilization, and condensation reactions [1]. 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. 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. 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.

In the present study, an assessment of fluidized bed fast pyrolysis of lignocellulosic 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. A 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 solids loading in the bed, namely, entrainment, elutriation, attrition, and bed drain/regeneration. The Ranzi et al. kinetic model (CRECK) is used to describe the pyrolytic decomposition of biomass [2]. An additional reaction considering the secondary heterogeneous reaction between oil and char is taken into account. Model results are helpful to assess 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.

2. Methods

The pyrolytic converter is modelled by means of a 1-D compartmental model, based on a simplified formulation of material balances on components involved in the pyrolytic process of lignocellulosic

biomass. The multistep reaction scheme, similar to the CRECK model [2] is used, considering serialparallel reactions of biomass main compounds. For instance, for the cellulose two degradation routes are proposed: towards the formation of char and water and towards the formation of active cellulose, which produces levoglucosan, other volatile species and char according to two parallel reactions. Furthermore, another reaction is considered in this work which represents in a lumped form the bundle of secondary heterogeneous reactions between vapours and char [3]. The reactor operates under steadystate conditions at ambient pressure. The temperature is uniform in the reactor (500 °C), and thermal equilibrium among phases holds. Cellulose particle size of 0.5 mm is considered. The pyrolytic converter is modeled according to a 1D distributed parameter model. The gas flow pattern is modeled according to the axial dispersion model with variable mixture density and velocity. Constitutive equations for entrainment, elutriation, attrition and drainage are considered.

3. Results and discussion

Oil and gas yields for cellulose pyrolysis are reported in Figure 1 (left) as a function of the residence time of the biomass in the reactor (drainage time τ_D). Oil yield first increases to reach a nearly constant value and then decreases for high values of τ_D . These trends can be explained considering that at low values of τ_D raw biomass is drained without being fully converted; therefore, low oil yields are obtained. For large drainage space times, instead, char accumulates in the bed and the extent of secondary reactions results in lower oil yields. Mass fraction of selected species of oil are reported in Figure 1 (right). Mass fractions values are in agreement with literature and their profile highlight the possibility to maximize the mass fraction of desired compounds by optimizing the drainage time and minimizing secondary reactions.



Figure 1. Oil and gas yields (left); mass fraction of selected species (right) as a function of the drainage time τ_D .

4. Conclusions

Fast pyrolysis of biomass has been investigated in a fluidized bed reactor by mathematical modelling. A compartmental one-dimensional model of the pyrolytic converter has been presented which includes a multistep reaction network to describe primary and secondary homogeneous reactions complemented by a heterogeneous volatile-char reaction step. The model also includes elutriation and attrition phenomena of biomass and char particles as well as bed drainage. Results allow to predict oil yields and composition in terms of selected species and to discriminate among different operating conditions to optimize the pyrolysis process.

References

- [1] A. Anca-Couce, Prog. Energy Combust. Sci. 53 (2016) 41-79
- [2] P. Debiagi, G. Gentile, A. Cuoci, A. Frassoldati, E. Ranzi, T. Faravelli, J. Anal. Appl. Pyrol 134 (2018) 326–335
- [3] M. Troiano, V. Ianzito, R. Solimene, E.T. Ganda, P. Salatino, Energ. Fuel 36 (2022) 9660–9671

Keywords

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