Fuel 210 (2017) 625–638

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Comparison of multi-component kinetic relations on bubbling fluidized-bed woody biomass fast pyrolysis reactor model performance

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ARTICLE INFO

Keywords:
Biomass fast pyrolysis
Multi-component devolatilization mechanisms
Pyrolysis modelling

ABSTRACT

Modelling of the thermochemical conversion process of biomass has been widely studied in the past. However, only a handful of works have been devoted to modelling pyrolysis at the bubbling fluidized-bed reactor level. Often, the most significant shortfalls of these models lie within the implemented devolatilization schemes, especially when only simple single-component mechanisms without product specification are used. This work compares the performance of two multicomponent, multistep kinetic reaction schemes implemented into a fluidized-bed level reactor model of fast pyrolysis. The first kinetic scheme only provides information on the amount of char, bio-oil, and gas yields whereas the second model provides compositional specifications of the resulting bio-oil and gases. This article compares the totals yields of char, bio-oil and gas with experimental data from a 5 to 10 kg/h fluidized bed fast pyrolysis system using three distinct biomass feedstocks. The results show that the model without compositional specification gave better agreement with the specific experimental results compared, especially for the yield of gas and char. The model with compositional specification gave good predictions of some components in the bio-oil, such as water, but modifications were shown to improve model accuracy to better account for the competition between transglycosylation and fragmentation reactions of cellulose.

1. Introduction

Over the past century the majority of energy consumed has originated from fossil sources, primarily coal, oil, and natural gas. However, the importance of finding cleaner, renewable alternatives for energy production is significantly growing due to the negative environmental impact of fossil fuels. Among current developments in the field of renewable energy, the exploitation of biomass for the production of bioenergy and biofuels is a promising option to replace some fossil sources of energy. Biomass is a renewable energy resource derived from the carbonaceous waste of various human and natural activities [1]. It could be of various types including: forestry crops and residues (wood, bark), agriculture crops and residues (straw, stover) and parts of municipal solid wastes, to name a few. Bioenergy generated from biomass offers several advantages over energy produced from fossil sources. The principle advantage is that biomass represents a carbon neutral energy source when harvested in an appropriate and sustainable manner. This means that replacing fossil fuels in energy production with biomass could reduce net greenhouse gas emissions. Despite the potential environmental benefit, the increased use of biomass for energy faces several challenges in developed nations. These challenges include: the low energy density of biomass, the large variability in resources and supply, the cost of transport, storage, and handling systems, and the lack of commercial demonstration of conversion technologies due to costly initial investments [2].

One way to address some of the challenges with biomass for energy applications is to make use of thermochemical conversion technologies to convert raw biomass sources into a more convenient energy intermediates. Thermochemical conversion involves thermally deconstructing biomass and transforming the resulting intermediates into a range of fuels and other products. Research in fast thermochemical conversion processes commonly focuses on the production of either gaseous intermediates or liquid intermediates [3]. One such thermochemical conversion process, fast pyrolysis, involves the prompt heating of biomass to 450 °C–600 °C in the absence of oxygen to ultimately produce a liquid intermediate termed biomass fast pyrolysis oil or bio-oil [4]. Under these conditions, organic vapours are initially produced and rapidly quenched to yield the pyrolysis oil. Non-

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http://dx.doi.org/10.1016/j.fuel.2017.08.092
Received 25 June 2017; Received in revised form 17 August 2017; Accepted 25 August 2017

condensable gases (NCGs) and biochar are also by-products of the fast pyrolysis of biomass, which are yielded in smaller amounts than the bio-oil under typical conditions. The NCGs consists mainly of CO_2, CO, and CH_4, as well as traces of H_2 and C_2-C_3 compounds [5].

The bio-oil can be used, directly or with minimal treatment, for heat and electricity generation just as solid biomass fuels. Presently, bio-oil is being used in a handful of commercial installations to replace liquid fossil fuel oils in institutional heating systems which have been retrofitted to handle the different properties of the liquid [6–9]. Additionally, with more severe treatment, such as hydrodeoxygenation, separation and fractionation, the bio-oil may be upgraded into a finished fuel suitable for a wide variety of applications including biofuels, biomaterials and chemicals. Typically, 60–75% of the feedstock mass is converted to bio-oil [4] which can have a volumetric energetic density of up to 20 times higher than the original biomass [10]. Bio-oil produced from fast pyrolysis can be a uniform, single phase liquid or it can separate into multiple phases depending on various factors including feedstock moisture, feedstock extractives, production conditions and reactor design Often, when a non-uniform bio-oil is produced, it consists of a water-rich aqueous phase containing a variety of highly water soluble oxygenated organic compounds and an organic-rich phase which contains insoluble heavy organic species [11], each of which are suited for different applications. While the production of bio-oil can be attractive, the liquid has some distinct characteristics that traditional fossil fuels do not share which can present challenges. Importantly, bio-oil is thermally unstable whereby exposure to elevated temperatures may cause separation and solidification of the bio-oil or some fraction of it. The nature and reactivity of the polar oxygen-containing functional groups in the oxygenated components is reported to be the main cause for the unstable character of the bio-oil. Coking on burner nozzles for the combustion of the bio-oil or coking upon injection into hot catalysts beds for the upgrading of bio-oil are frequently observed problems [12]. In addition to the thermal instability exhibited at the temperatures of combustion equipment or catalyst beds, polymerization of certain components at room temperature causes an increase in fluid viscosity or causes phase separation over the course of months which is problematic for long-term bio-oil storage [13]. Finally, the bio-oil is acidic because the resulting components from the thermal decomposition conditions employed in the fast pyrolysis process include significant amounts of carboxylic acids. This renders the bio-oil corrosive towards some traditional materials of construction for fuel handling systems including low alloy steels and aluminum.

Accurate reactor models for fast pyrolysis can provide several benefits due, in large part to the cost, effort and expertise required to run experiments at a sufficiently large scale to generate representative results. Given the variety of potential biomass sources, quantity of pretreatment options for the biomass, and the variety of reactor configurations, the number of possible permutations and combinations of factors that would need to be experimentally explored to complete a comprehensive optimization of the process are enormous. Reactors models which are responsive to changes in feedstock inputs such as particle size, moisture level, and feedstock composition while providing mass, energy and compositional data, can be very useful for implementation in process simulations in order to accurately forecast the impact of changing parameters on process economics and identifying optimum feedstock pre-treatment, reactor design and operating conditions. Additionally, improving the accuracy of fast pyrolysis models may allow for a better understanding of the fundamental influencing parameters such as product yield or composition.

To produce more accurate reactor models for biomass fast pyrolysis, the specific goal of this work is to compare two multi-component and multi-step devolatilization schemes with experimental results. One of the schemes only predicts the total yield of char, bio-oil and gas while the second scheme offers predictions about the chemical composition of the bio-oil in addition to the total yields.

2. Biomass fast pyrolysis devolatilization schemes

2.1. Challenges of biomass fast pyrolysis kinetic mechanism formulation

Modelling of the thermochemical conversion of biomass in practical systems requires a strong interaction between chemical and physical processes. Transport phenomena in various types of reactors are well documented but there is a need for an appropriate description of reaction kinetics in these systems. The variety and complexity of reaction schemes for biomass fast pyrolysis make kinetic modelling an interesting and challenging study. In fact, there exist certain difficulties in reaching a clear consensus for defining intrinsic kinetic pathways and equation constants [14]. Since the mid-late 20th century, several variations of the devolatilization mechanisms have been proposed [15–30]. Undoubtedly, one of the largest concerns in the analysis of kinetic data is the validity and reproducibility of the kinetic constants for general application. Modelling the kinetics of biomass fast pyrolysis is a challenge because of the variety in raw materials involved, the inconsistencies in experimental apparatuses and the wide range of operating conditions used [31]. In fact, several literature sources have consecutively used different apparatuses with variable heating procedures to study biomass component decomposition over narrow temperature ranges; most of which have reported problems from systematic errors in comparing the applied methods [28]. However, recent advancements in thermogravimetric technology have allowed for the analysis of sample devolatilization over larger (and higher) temperature ranges, refining kinetic data comparisons. Another major difficulty encountered in carrying out measurements of sample weight loss for kinetic equation fitting procedures is the exclusion of heat transfer limitations to obtain data under pure kinetic control. Particularly, experimental deviations in sample size and heating rates present non-negligible effects of particle internal and external heat-transfer resistances. Gronli et al. [29] attributed the discrepancies of different experimental results primarily to variations in the "thermal lag" of the instruments used; which is directly correlated to the different heating rates applied and sample sizes used. In addition, each type of biomass has a unique composition with specific physiochemical properties which will greatly alter kinetic behaviour [32] and present limitations in terms of formulating general pyrolysis mechanisms.

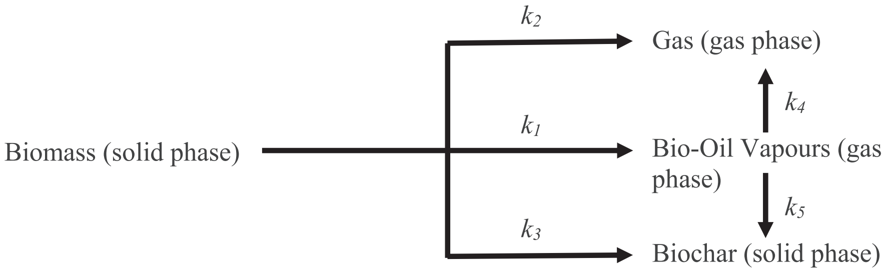

Fig. 1. Single-component mechanism of woody biomass pyrolysis [18].