



Full Length Article

Modeling pyrolysis-induced microstructural changes in biomass: A cellular automata approach



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ABSTRACT

Lignocellulosic biomass is a chemically and morphologically heterogeneous material. This heterogeneity is in part responsible for the vast number of thermal decomposition products seen in pyrolysis events. While modeling of biomass pyrolysis has been a subject of much research in past years at length-scales ranging from macro to molecular, the majority of these works have focused on a range of continuum-based approaches. Though effective at capturing global outcomes, these approaches are less tractable as frameworks for capturing microstructural effects and upscaling molecular information. This work demonstrates the use of kinetic-cellular automata (k-CA) as an alternative platform for the modeling and simulation of biomass pyrolysis. Asides from being effective at capturing transport and chemical processes in highly heterogeneous system, k-CA is capable of modeling microstructural changes that occur as a result of chemical and physical transformations. A number of benchmark trials demonstrated the convergence of the k-CA to global continuum outcomes. Application of the k-CA to actual two-dimensional (2-D) biomass microstructures show promise for this platform as an intermediate length-scale tool capable of predicting char morphologies that mimic experimental outcomes at length-scales between those of atomistic events and those governed by macroscopically averaged approaches.

1. Introduction

Biomass pyrolysis is the thermal degradation of a lignocellulosic feedstock in the absence of oxygen to produce renewable fuel and chemical resources. These resources include a mixture of organic oxygenates (bio-oil) which are liquid at room temperature, permanent gases including H_2 , CO , CO_2 , and CH_4 and a solid carbonaceous phase referred to as char.

Along with the increasing population of the world, there is a commensurate increase in the demand for energy, for both domestic and industrial usage. This need, combined with the inevitable decline in the main energy source [1,2] – fossil fuel – demands that alternate sources of energy be developed. In addition to energy availability, the energy will eventually need to be renewable and sustainable (economically viable, environmentally acceptable, and socially equitable) [3]. Such has led to the investigation of various renewable technologies for the production of energy, fuels, and chemicals, biomass pyrolysis being among many alternatives. Because purposefully grown biomass feedstock would also support agricultural economies, there has been particular interest in such conversion technologies by government agencies. The “Billion-Ton Study” (BTS) sponsored by the US Department of Energy (DOE), states that more than a billion tons of biomass could be

available for biofuel production annually. The main benefit of converting solid biomass to liquid fuels is that transportable liquid fuel (bio-oil) has a higher energy density than the less portable solid feedstock [4]. Some of the ways of utilizing biomass pyrolysis products include: (1) condensation of the pyrolysis vapors to form bio-oil, (2) direct use of pyrolysis vapors to generate energy, (3) treatment of pyrolysis vapors to produce synthetic gas (syngas), (4) treatment of pyrolysis syngas to generate synthetic liquid fuels, (5) upgrading of pyrolysis vapors to produce non-energy products, (6) use of pyrolysis char as a valuable soil amendment, and (7) sequestration of atmospheric carbon dioxide [5].

Despite the promises of biomass pyrolysis, there are yet many challenges to overcome before this technology becomes commercially competitive [6], some of these include: poor fuel characteristics and chemical instability of direct pyrolysis derived liquids due to high oxygen content, and chemical complexity [7]. As a result, the commercialization and competitiveness of this technology with respect to other renewable alternatives depends on improving the quality and stability of the crude bio-oil. According to Mettler et al., one of the keys to unlocking the potential of biomass pyrolysis lies in fundamental models that are capable of describing the transport and reaction phenomena, and which can also capture the multiphase and multi-scale

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Nomenclature		t	time (s)
A	pre-exponential factor (s^{-1})	T_t	temperature (K)
E_a	activation energy (kJ/mol)	x	position or lattice site position
I	intensity	<i>Greek symbols</i>	
K	kinetic rate constant (s^{-1})	α	specie index
n	reaction order	β	heating rate ($^{\circ}C/min$)
N	occupation number	τ	step time
p	probability	ξ	mapping parameter
P	pressure (Pa)	η	reactivity term
R	universal gas constant (kJ/mol-K)	λ	lattice site spacing
SI	saturation index		

complexities of the system [6].

To address this challenge, the authors propose to model biomass pyrolysis using a kinetic-cellular automata (k-CA) platform that captures at the mesoscale level, transport, kinetic, and microstructural events. The voluminous prior research done on the modeling of biomass pyrolysis has focused on the application of continuum-based macroscopic and microscopic balance equations, e.g. ordinary differential or partial differential formulations and molecular-scale modeling. Microstructural changes, as illustrated in real-time by Haas et al. [8] using light microscopy (LM), however, are not easily described by such continuum-based mathematical descriptions, hence the need for an alternative modeling approach. Biomass shrinkage has been observed and empirically quantified by many investigators: biomass obtained from wood has shown shrinkage of up to 70–80% for tulip poplar at 800 °C [9], 35% for *Eucalyptus delegatensis* at 420 °C [10] and 65% for birch at 700 °C [11]. It is expected that such physical changes in structure of the biomass/char during pyrolysis should have implications for predicting conversion and conversion rates since the characteristic length for both heat and mass transfer (of the biomass undergoing pyrolysis) vary with time, not to mention changes in the physical properties, e.g. thermal conductivity. This implies that shrinkage should be incorporated into particle-scale pyrolysis models since such physical change is liable to affect heat transfer and mass transport within the particle [12]. Despite the importance of shrinkage, it has understandably been disregarded in most pyrolysis models [13–15]. This may be due to the intractable nature of using nonlinear PDEs to model microstructural changes; the few examples that considered shrinkage are confined to using correlations of empirical volume-based shrinkage data [12,16].

A comprehensive literature review on modeling of lignocellulose pyrolysis finds a single citation that suggests the use of k-CA. The paper [17], while offering a comparison of a simple reaction schema solved both by using continuum mechanics and k-CA, does not provide details regarding specifics of the k-CA approach, neither did it model the structural changes during pyrolysis. In this work, a k-CA was used to simulate both chemical and microstructural (physical) changes that occur during biomass pyrolysis for the first time (to our knowledge). This feat demonstrates the capability of k-CA for solving complex multi-physical problems for highly heterogeneous systems.

2. Literature review

2.1. Modeling chemical changes

The development of mathematical models for pyrolysis can greatly assist the large-scale development and optimization of thermal biomass conversion processes [15]. This includes the prediction of reactor yields, the understanding of pollutant emissions, the examination of effective control strategies, and the development of energy integration schema. The modeling of biomass pyrolysis has been approached in a number of ways including formulations using Lagrangian [18] or Eulerian reference frames [19], bulk (macroscopic) or particulate

(microscopic) forms, and models that account for different biomass shapes, among others. In most cases, such models assume that biomass is homogeneous or has a homogenous matrix with porous inclusions. Particle-based modeling, however, has received much attention since pyrolytic behavior of a single particle is needed before extending to an ensemble of particles that reflect conditions within reactors [15,20]. Yet, other studies focused specifically on the modeling of multi-particle systems with the aim of optimizing the process conditions and reactor configuration [19].

Park et al. illustrated that the distribution of products (gas, char, and oil yield) depends on the heating condition; as such, many particle-based models consider heat transfer effects [21]. Williams and Besler observed that the effect of heating rate on product yield is relatively small but has more effect on the characteristics of the primary vapors and the surface area of the char [22]. The slight disparity in the reported impact of heating rate (and hence temperature changes) on products of pyrolysis may be attributed to the size of the particles which could make the effect of thermal and mass diffusion more pronounced. For kinetic studies, the size of the biomass sample used must be small so that chemical decomposition can be attributed only to the chemistry of the biomass, and not heat transfer or mass transport effects, therefore, modeling biomass pyrolysis of large dense particles requires the incorporation of transport factors.

In terms of modeling reaction kinetics, the majority of studies considered only mass loss changes that occur (generally based on thermogravimetric methods); such kinetics lump the volatile reaction products together making permanent gases and condensables indistinguishable, see [23–25] for example. Fewer works utilized distributed kinetics wherein individual product concentrations are tracked to one extent or another (generally based on using a thermogravimetric method coupled with mass spectrometry [26,27]).

2.2. Modeling physical changes – char genesis and characteristics

Microscopic images of biomass show the complex anisotropic and heterogeneous nature of the composite lignocellulosic matter. The heterogeneities are due to many factors including density variations, composition of matter, and grain inclination [6]; these factors likewise vary with the extent of biomass decomposition. Such present formidable challenges for traditional continuum-based models, hence the need for a tractable platform that can account for such heterogeneities as a function of decomposition extent.

This work introduces the use of kinetic-cellular automata (k-CA) to model biomass kinetics and concomitant microstructural changes. Byrne and Nagle showed the volume shrinkage upon pyrolysis for tulip poplar to be 75–80% [9]. Other works show varying amounts of shrinkage depending upon the biomass source; it was reported that shrinkage is related to both the reaction temperature and extent of conversion for cylindrical birch samples which showed different shrinkage along the longitudinal, tangential, and radial directions [12,28]. Likewise, Haas et al. reported that the porosity of the

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