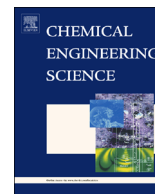




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Multiscale molecular modeling can be an effective tool to aid the development of biomass conversion technology: A perspective

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HIGHLIGHTS

- Challenges in developing biomass conversion technology are briefed.
- The role of molecular modeling in addressing specific issues is elaborated.
- The significance of condensed phase multiscale molecular simulations is reasoned.
- *State of the art* condensed phase molecular simulation tools are discussed.
- Molecular modeling literature in biomass is reviewed and a perspective is given.

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ABSTRACT

Lignocellulosic biomass is an alternate and renewable source of carbon. However, due to high oxygen content and diverse functionality, its conversion to fuels and chemicals is technologically challenging. Since physico-chemical characteristics of biomass and its derived components are very different from petroleum, fundamental understanding of their interactions with catalysts and solvents and of their behavior during thermochemical processing needs to be developed. In the present paper, we provide a perspective on how multiscale molecular modeling can assist in developing the science of biomass processing. The scope of this paper is limited to liquid phase catalytic and pyrolytic conversion of biomass. Car–Parrinello molecular dynamics (CPMD), a multiscale method that combines quantum mechanics and classical molecular dynamics and is an excellent choice to simulate biomass interactions in the condensed phase, is discussed. An overview of metadynamics, a method to accelerate CPMD dynamics, is also given. Revealing the chemistry of biomass pyrolysis, identifying liquid phase catalytic reaction mechanisms and developing a fundamental understanding of the role of solvents in biomass processing are the three main areas highlighted in this paper. Molecular modeling based investigations in these areas are reviewed and key findings are summarized. Limitations of the current approaches are discussed and the relevance of multiscale methods like CPMD and metadynamics is discussed. Potential studies that could implement multiscale molecular modeling methods to solve some of the challenging problems in developing biomass conversion technology are elaborated and an outlook is provided.

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1. Introduction

1.1. Lignocellulosic biomass: An alternate and renewable source of carbon

Second generation lignocellulosic biomass, consisting of lignin, cellulose and hemicellulose, is the biggest renewable source of carbon. It can be used to produce chemicals and fuels, without putting any stress on the nutritional needs of world population.

It also has the potential to reduce greenhouse gases, since the CO₂ released can be consumed in a relatively shorter time for growing the biomass (Chheda et al., 2007). One of the logistic constraints associated with the conversion of lignocellulosic biomass to biofuel is the transportation of biomass (Caputo et al., 2005; Chiamonti et al., 2007; Lange and Solutions, 2007). Hence, it is critical (to be able to commercialize the biomass to fuels and chemicals technology) to combine the handling and transportation of biomass and its processing, unlike petroleum fuels, where the crude is transported from multiple distant locations to a central processing facility. Setting up a “Bio-refinery” is also technologically challenging, since, unlike petroleum, biomass contains significant

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amounts of oxygen and is a solid material. To convert biomass to fuels and chemicals, C–O bonds need to be selectively cleaved, without breaking C–C bonds. Thus, utilizing the processing knowledgebase of petroleum may not be possible and novel catalysts, solvents and processes need to be developed.

The three possible pathways to process biomass are:

- (i) *Biochemical pathway*: Biochemical pathway involves the decomposition of biomass using microorganisms or enzymes into simple acids and sugars which can then be further converted into molecules which are suitable for use as fuels or as building block chemicals (BioEnergyTechnologyOffice, 2013). Though biochemical methods provide high selectivity and specificity, the resistant nature and broad variety of biomass feedstock, high cost and non-regenerative nature of enzymes, requirement of a very high purity of feed, narrow range of operating conditions, and the need to genetically engineer microorganisms for individual components separately pose some limitations (Balat, 2011).
- (ii) *Liquid phase catalytic processes*: Liquid phase processing of biomass, using inorganic homogeneous and heterogeneous catalysts, converts solid biomass into smaller molecules containing less oxygen. However, limitations associated with these methods are the necessity to pretreat the feedstock before its processing, the stability of catalysts, and the formation of unwanted by-products, to name a few (Lin and Huber, 2009).
- (iii) *Thermochemical methods*: Pyrolytic breakdown of biomass into bio-oil and char and further upgradation of bio-oil to bio-fuel is another possible pathway (Mettler et al., 2012a). Pyrolysis is gaining more popularity than gasification and combustion since it gives a liquid (bio-oil) product, which upon stabilization, can be stored and transported. Additionally, an economical comparison of a variety of biomass conversion platforms like pyrolysis, gasification and biochemical conversion, based on a 2000 t/day of biomass processing plant, has shown that pyrolysis has the lowest operating and capital cost (Anex et al., 2010). Pyrolysis is also thought of as a more friendly technology for decentralized biomass processing; however, it may not be possible to produce specific bulk chemicals using this method.

It may not be possible to choose one of the aforementioned methods as an ideal choice for biomass conversion, and it is likely that an optimal combination of these would be the most efficient option. The scope of the present paper would be limited to non-biological pathways.

1.2. Technological challenges in developing biomass conversion technology

Some of the main technological challenges associated with developing liquid phase processing and high temperature pyrolysis technologies are listed in Table 1.

In pyrolysis, the quality and quantity of bio-oil is not only dependent on the type of the feedstock, but also varies significantly

with reactor design and operating conditions. The most common type of reactor implemented for pyrolysis is the fluidized bed reactor, which is also suitable for industrial scale pyrolysis (Bridgwater, 2012). Operating temperature, residence times, cooling rates and particle size greatly affect the product distribution (within bio-oil and the char to bio-oil ratio) (Ozbay et al., 2006; Uzun et al., 2006; Tsai et al., 2007; Garcia-Perez et al., 2008; Shen et al., 2009; Heo et al., 2010; Bridgwater, 2012) Since bio-oil is a direct product of the reactions that happen in the reactor, its quality and quantity are governed by those reactions. However, reaction chemistry, kinetics and transport effects are inter-related and they are significantly affected/alterd by operating conditions of the reactor and the reactor design. Despite of numerous studies in the field of pyrolysis, understanding of condensed phase pyrolysis reactions remains very poor (Mettler et al., 2012a, 2012b). Most of the research reports are either based on the reaction mechanism knowledge in the aqueous phase biomass processing technology (temperatures around 100 °C) or based on the experimentally observed effect of operating conditions on the macroscopic product distribution, without taking into account transport effects. Isolated experimental investigation into pyrolysis reactions and kinetics is extremely difficult due to several factors, such as, fast reactions, short residence times, high temperatures and transport limitations. Additionally, due to lack of knowledge of the reaction chemistry, studies investigating transport effects assumed few pseudo and lumped reactions (with fitted kinetic parameters) for pyrolysis (Blasi, 1996; Di Blasi, 1996; Hagge and Bryden, 2002; Babu and Chaurasia, 2004a, 2004b; Chaurasia and Kulkarni, 2007; Zabaniotou and Damartzis, 2007; Sadhukhan et al., 2008; Sreekanth and Leckner, 2008; Sadhukhan et al., 2009; Dufour et al., 2011; Haseli et al., 2011a, 2011b, 2012a, 2012b; Peters, 2011; Anca-Couce and Zobel, 2012; Blondeau and Jeanmart, 2012; Lin et al., 2012; Okekunle et al., 2012; Sharma et al., 2014). The prediction capability of such models remains very limited. Hence, a reaction-transport model, containing detailed information of reaction kinetics and heat and mass transfer under fluidized bed reactor conditions, which will allow chemical engineers to optimally design and operate pyrolysis reactors from first principles, instead of relying on the conventional trial and error approach, is not present in the literature.

In the case of liquid phase catalytic processing of biomass, the development of economically viable processes for biomass conversion also requires gleaning fundamental insights into the conversion technologies and reaction mechanisms associated with them. Since biomass processing involves a variety of reactions like hydrolysis, oxidation, hydrogenation, hydrogenolysis, isomerization, dehydration, to name a few (Chheda et al., 2007; Climent et al., 2011), it is desirable to have multifunctional catalysts in order to develop an economically viable process system. The search for novel catalysts also necessitates developing the fundamental understanding of the catalytic reaction mechanism and the associated kinetics.

Biomass conversion reactions are carried out in a solvent and the solvent is believed to participate in the reactions (Zope et al., 2010), instead of just being a benign solvation medium. Solvent dynamics is also believed to affect reaction kinetics; and preferential solvation of selected biomass species is believed to alter the conversion and selectivity in biomass reactions (Caratzoulas and

Table 1

List of some of the grand technological challenges associated with the development of biomass conversion technology.

High temperature pyrolysis	Liquid phase catalytic process
Convolved and unknown reaction chemistry	Role of solvent
Heat and mass transport	Novel catalysts for high selectivity
Controlling the product distribution	Catalytic reaction mechanisms and pathways
	Separation

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