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Product quality optimization in an integrated biorefinery: Conversion of pistachio nutshell biomass to biofuels and activated biochars via pyrolysis

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ABSTRACT

An economically viable transition to a renewable, sustainable energy future hinges on the ability to simultaneously produce multiple high value products from biomass precursors. Though there is considerable literature on the thermochemical conversion of biomass to biofuels and biochars, there are few holistic examinations that seek to understand trade-offs between biofuel quality and the associated pyrolysis conditions on activated carbons made from the resulting biochars. Using an Ordinary Least Squares regression analysis, this study probes the impact of pyrolysis and activation temperature on surface areas and pore volumes for 28 carbon dioxide-activated carbons. Activation temperature has the largest single impact of any other variable; increasing the temperature from 800 to 900 °C leads to an increase in surface area of more than 300 m^2/g. Contrary to some prior results, pyrolysis temperature has minimal effect on the resulting surface area and pore volume, suggesting that optimizing the temperature at which biofuels are extracted will have little impact on carbon dioxide-activated carbons. Increasing pyrolysis temperature increases methane formation but decreases gaseous hydrocarbons. Bio-oil obtained at lower pyrolysis temperatures shows fewer oxygenated compounds, indicating a greater stability, but higher pyrolysis temperatures maximize production of key biorefinery intermediaries such as furans. By analyzing data in such a holistic manner, it may be possible to optimize the production of biofuels and activated carbons from biomass by minimizing the amount of raw materials and energy necessary to maximize fuel quality, surface areas and pore volumes, thereby increasing the economic incentives for thermochemical conversion of biomass.

1. Introduction

There is a global reliance on fossil fuels for the majority of worldwide energy generation, resulting in uncertainty about future energy supplies due to economic, political, and environmental volatilities [1]. As the world shifts towards a renewable energy future, one of the most crucial areas to address is in energy for transportation. The United States Energy Independence and Security Act of 2007 Renewable Fuel Standard mandates that 16 billion gallons of cellulosic biofuel be blended into transportation fuels by 2022, a part of which must be biodiesel produced from biomass [2]. Moving beyond cellulosic ethanol, researchers are investigating various integrated pathways to produce renewable fuels, chemicals, and materials [3].

Thermal decomposition methods, including pyrolysis, are promising methods to deliver this biofuel from a variety of biomasses, including marine macroalgeto mitigate green tide issues [4].

Terrestrial sources such as olive pits have been shown to biofuels and activated carbons while mitigating land disposal of carbonaceous biomasses [5]. Unlike biological conversion processes,

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pyrolysis enables conversion of the entire plant material as a feedstock [6]. However, though pyrolysis is able to produce biofuels and biochars from a variety of biomasses, there is little research that tackles a holistic optimization of the pyrolysis process in terms of the *quality* of products produced. Rather, most studies on biomass pyrolysis optimization seek to maximize the *quantity* of each product produced, such as from laboratory-based studies on pertinent reaction conditions [7]. Other studies approach the integrated biorefinery from an economic cost-benefit analysis using "standardized" reaction conditions [8]. Some studies approach pyrolysis biorefinery optimization from the context of the supply chain [9]. Others probe the greenhouse gas emissions from various pyrolysis options to find an optimized pathway that reduces atmospheric impacts of fuel production [10]. Still others present new systems technologies that can embrace many of these latter aspects simultaneously [11]. While some studies go so far as to probe the optimal pyrolysis conditions for oil quality [12], none (that the authors could locate) probe the optimal conditions for all three pyrolysis products – bio-oil, pyrolysis gas, and biochar – which likely hampers work that seeks to understand how to maximize the pyrolysis process of an integrated biorefinery in terms of all three products. Society is at a critical juncture in the global quest for a renewable, sustainable future; with oil prices starting 2016 under $30 per barrel, the economics of pyrolysis as a platform to bio-oils – even if the production of bio-oil can be lowered to below $26 per barrel [13] – is a hard sell. Additional revenue streams, beyond biochars, must be created to make this environmentally attractive energy product more fiscally appealing. Improving techno-economic analyses for the design of efficient bio-refineries requires knowledge of the technical trade-offs between energy inputs, product yield, and product quality [14], the latter of which – after a comprehensive review of the literature – appears to be the most lacking.

Pyrolysis, or thermal decomposition in an oxygen-limited environment, yields three products in different ratios depending on the processing conditions: bio-oil, pyrolysis gas, and biochar [15]. Pyrolysis removes volatiles, many of which contain heteroatoms, from a raw solid sample, increasing the relative carbon content and creating voids, thereby developing the material's porosity, and simultaneously evolving condensable and non-condensable fuels. Starting material, particle size, heating rate, pyrolysis temperature, hold time, and activation method are all factors that influence the yields and properties of bio-oil, pyrolysis gas, and chars [16]. Different types of biomass contain different percentages of hemicellulose, cellulose, lignin, and ash. Since these components volatilize at different temperature ranges, the impact of increasing peak pyrolysis temperature varies among feedstocks and products [17]. In general, the maximum liquid product yield from pyrolysis occurs between 450 and 600 °C [18]. This depends on the specific process parameters employed, i.e. heating rate and energy input [19]. Liquid product compositions also depend on the biomass characteristics, i.e. particle size and biomass precursor [20]. Though there is a significant amount of work done on what conditions optimize product yields from pyrolysis, there is less work done on optimizing product quality. Therefore, this paper presents a laboratory-based study on product quality optimization of a sample biomass to encourage researchers to holistically consider biorefinery product quality in their process feasibility analyses.

Compounding the need to develop renewable fuels is to do so in a sustainable manner; an integrated approach to food, water and energy security is necessary to address increasing global population, climate change, urbanization and overall increases in food consumption and standards of living [21]. Integrated systems – from small-scale bio-refineries to large-scale resource management integration – must be implemented to insure that our land, energy and water resources can sustain our global population [22]. Such integrated solutions are said to be key to addressing global climate management strategies [23]. The World Health Organization estimates that one-third of the world's population, across all continents, currently suffers from varying degrees of water scarcity. With the accumulation of pollutants such as pharmaceuticals, organics, metals and other potentially hazardous compounds in water, it is imperative to simultaneously develop a method to remove these contaminants that is inexpensive, effective, and easily implementable. Adsorption using activated carbon is one possible solution, the cost and environmental impact of which can be significantly reduced by using biomass waste as a precursor [24]. This integrated biorefinery proposed here produces high surface area activated carbons from the biochars resulting from pyrolytic fuel extraction. The goal of this work is to determine if there is a trade-off between optimal pyrolysis temperatures for fuel extraction versus activated carbon production.

The general method for the production of high surface area biochars via physical activation is well established [25]. Briefly, a mild oxidant, such as steam, air or carbon dioxide, can be used following pyrolysis to increase porosity and surface area. The preliminary pyrolysis step removes a majority of the hydrogen and carbon atoms incorporated into the biomass structure [25]. Given the abundance of carbon dioxide as a product of fuel combustion, its use as an activating agent represents a reasonably sustainable material choice [26]. In this process, CO_2 diffuses to the surface of the biochar's walls, where an oxygen atom dissociates from CO_2 and reacts with the carbon surface to form carbon monoxide [27]. The CO is subsequently desorbed from the surface, further developing the pore structure [28]. The rate of the carbon-carbon dioxide reaction is temperature-dependent [29]; the reaction is slow at temperatures below 800 °C, and temperatures exceeding 800 °C are generally required to achieve a sufficient rate of reaction [30].

Many groups have demonstrated the ability to activate biochars, including pistachio nutshells, using carbon dioxide. For example, Yang and Lua generated physically activated carbons from pistachio shells using carbon dioxide as the oxidizing gas [31]. They suggested that pyrolysis conditions, prior to activation, impacted the properties of the resulting chars. However, in another publication, this group found that the effect of pyrolysis temperature was minimal beyond 400 °C; at pyrolysis temperatures of 250 and 300 °C, the surface areas hovered around 350 m^2/g; all the surface areas at pyrolysis temperatures of 400–1000 °C ranged from 600 to 778 m^2/g, with the highest surface area achieved at 500 °C, and second highest (748.8 m^2/g) at 900 °C [32]. To upgrade carbonaceous biochar to an activated carbon, Acikalin et al. studied the pyrolysis of pistachio shells at various nitrogen flow rates, peak pyrolysis temperatures, hold times, and heating rates [33]. They found that conventional pyrolysis without activation yielded chars with relatively low surface areas (under 10 m^2/g), but postulated that physical or chemical activation could provide the additional surface area and porosity needed to make pistachio shells a suitable candidate for activated carbon applications. However, there is no systematic work that probes the true impact of pyrolysis and CO_2 activation conditions to determine the primary variables responsible for enhancing adsorptive surface areas of biochars. Furthermore, there is scant work that seeks to understand the balance between pyrolysis temperature on biofuel manufacture and its impact on biochar production.

Studies such as this are important to the economical production of biomass-based liquid and gaseous fuels, and activated carbons, in order to minimize energy, time, and materials requirements to produce such sustainable fuels and materials. The current work presents laboratory results from the pyrolysis and activation of pistachio shell biochars to develop an overall understanding of which processing conditions present the optimal route to biofuel and activated carbon production *in terms of product quality*. While other