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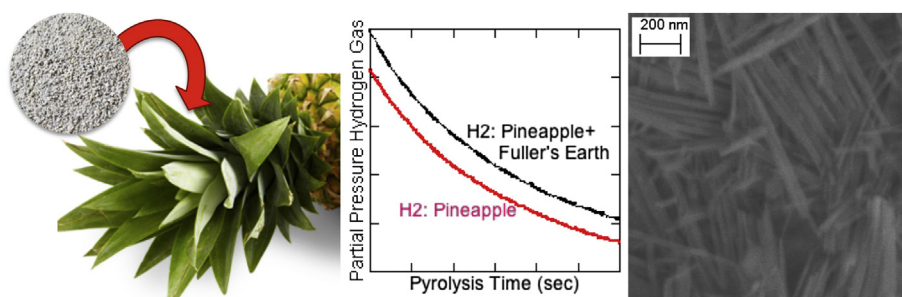
In situ upgrading of pyrolysis biofuels by bentonite clay with simultaneous production of heterogeneous adsorbents for water treatment

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HIGHLIGHTS

- Bentonite incorporated into biomass increases pyrolysis gas yield.
- Impact of pretreatment on bio-oil depends on biomass precursor, can increase furans.
- Despite catalytic effects on fuels, no change in overall activation energy.
- Pyrolysis of pretreated biomass yields heterogeneous char for water treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

The ability to *in situ* upgrade pyrolysis biofuels, together with the production of a value-added byproduct from the solid biomass residue, would reduce the economic and environmental costs of the integrated biorefinery. In the present work, biomass samples (mango pits and pineapple plants) were immersed in Fuller's Earth (bentonite clay) suspensions. Pyrolysis at low temperatures (290–350 °C) showed that the incorporation of Fuller's Earth into both biomasses increases the amount of H₂, CH₄, C₂H₂, C₂H₄, and C₂H₆ evolved as compared to raw biomass. The biomasses' behavior diverges in terms of bio-oil and biochar quality. For mango pit, pretreatment with Fuller's Earth increased desirable compounds such as furans and hexanes, whereas for pineapple plant oxygenated and high molecular weight compounds increased with pretreatment. While surface areas of both biomasses increased with incorporation of bentonite clay, the mango pit saw a significant increase in adsorption capacity and rate of methylene blue removal from water, whereas the pineapple plant adsorption rate decreased with pretreatment; capacity increased at low pyrolysis temperature and decreased at high temperature. While incorporation of Fuller's Earth increased the thermal energy required to heat the impregnated mixtures to pyrolysis temperature, a distributed activation energy model analysis shows that activation energy of pyrolysis was virtually the same for impregnated and raw biomass samples, suggesting that this may be either a thermally catalytic or chemically catalytic effect. Thus, incorporation of bentonite into some biomasses may represent positive benefits in terms of *in situ* upgrading bio-fuels and hybrid biochars produced at lower pyrolysis temperatures.

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1. Introduction

The use of biomass-based biofuels is steadily increasing; they currently comprise approximately 13% of the world's energy

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supply, and may represent the most important future global renewable energy source [1]. To convert biomass to energy, pyrolysis (heating in an inert atmosphere) can be used for power generation and the production of biochar, bio-oil and pyrolysis gas. However, pyrolysis bio-oils suffer high viscosity, low calorific value, and instability [2]. Many have explored the possible upgrading of pyrolysis bio-oils through chemical and/or thermal means, such as high pressure and catalytic transformations [3–5]. However, the extraordinarily heterogeneous nature of bio-oil (over 350 components), combined with the cost of upgrading (including catalyst degradation and recovery) currently limits the widespread adaptation of these biofuels [6,7].

Biochar, the carbonaceous solid produced from biomass via pyrolysis, is widely used as a soil amendment, carbon fixer and to remove various contaminants from water due to their cost effectiveness and proven sorption ability [8–10]. Biochars are often modified to enhance their sorption capacity for various chemical contaminants. For example, Zhang et al. and Yao et al. used MgO-biochar and Mg oxyhydroxide composites, respectively, to remove phosphate from solution [11,12]. Zhang and Gao synthesized a self-assembled biochar/AlOOH nanocomposite through slow pyrolysis of AlCl₃ pretreated biomass at 600 °C, and successfully removed arsenic, methylene blue and phosphate from solution [13]. A magnetic biochar/ γ -Fe₂O₃ composite with a highly efficient sorption capacity to remove arsenic from water was fabricated via pyrolysis of FeCl₃ pre-treated biomass at 600 °C [14]. Because of their lamellar structure, high surface area, and high ion exchange capacity, clay minerals are also used to improve the sorption capacity of biochar. An engineered biochar with montmorillonite and kaolinite on its porous carbon surfaces demonstrated higher sorption capacity for methylene blue than the original char [15]. To date, however, all the biochar-based composites synthesized via pyrolysis are obtained under a high fixed temperature (often 600 °C), for which little research into the optimal (or even simply lower) conversion temperature has been done. This is surprising as high temperatures are a primary reason for low net energy gains of pyrolysis systems. As such, it is interesting that the literature lacks studies on why a pretreated biomass, such as mineral and inorganic-impregnated biochars, are pyrolyzed at a fixed temperature. Therefore, one goal of the current work is to probe the possibility of using thermal analysis to lower pyrolysis temperatures of pre-treated biomasses.

Disparate studies in the literature suggest that incorporating inorganic nanomaterials and/or minerals into biomasses as a pre-treatment can catalytically upgrade the resulting pyrolysis biofuels. For example, nano-SnO₂ particles were shown to catalyze the pyrolysis of hazelnut shell biomass, producing greater amounts of biogas [16]. Nano-NiO on γ -Al₂O₃ was used to catalyze the removal of tar and upgrade pyrolysis gases [17]. Several studies demonstrate the ability to upgrade pyrolysis biofuels using various clays in the reactor. For example, pyrolysis of sludge with heterogeneous clays from the Venice lagoon showed a catalytic effect leading to decreased coke formation and enhanced gasification reactions from water present in the clay [18]. Alkaline spent drilling mud (a byproduct of bauxite refining) was used to upgrade the waste stream of a biodiesel plant [19]. Hick et al. demonstrated the ability to use bentonite as a mechanocatalyst to convert cellulose to glucose and other products [20].

What has yet to be demonstrated in the literature is an integrated biorefinery concept of upgrading biofuels during pyrolysis by simultaneously producing biochar-based hybrid adsorbents with enhanced sorption capacity. In this work, we investigate the feasibility of using Fuller's Earth, a bentonite clay, as an *in situ* catalyst to upgrade pyrolysis fuels while producing biochar-clay adsorbents for water treatment.

2. Materials and methods

Identifying biomass sources that do not compete with food supply/arable land or strain our water system is critical to addressing global needs at the Food-Energy-Water nexus [21]. The current work uses two biomasses that are otherwise discarded after their fruit is harvested or consumed: mango stones and pineapple plant. In addition, Fuller's earth is a naturally occurring material abundant in the U.S. with a high absorption capacity, comprised of bentonite, clay minerals of the smectite group. It is commonly used as an absorbent, bleaching liquid, for drilling mud, and a binder in pelletizing iron ore among other uses [22].

2.1. Materials

Mangos are a stone fruit of the genus *Mangifera*; the pit is an inedible waste product. Mangos are grown worldwide, with India as the largest producer of 1.525 * 10⁷ metric tons in 2012, representing 36% of global production [23]. Ten mangos of the Tommy Atkins cultivar were purchased at different local grocery stores in Boston, MA, USA. The fruit was separated from the stone, and the stones were washed, dried, and stored in airtight containers.

The pineapple plant (*Ananas comosus*) is an herbaceous perennial that yields a single fruit after 18 months of cultivation, though the mother plant will make several offshoots to cultivate as a second, and up to third generation [24]. The worldwide production of pineapples reached 2.333 * 10⁷ metric tons in 2012 [23]. Pineapples have a higher energy demand, stress-weighted water footprint, human and ecosystem toxicity and carbon footprint than tree fruits [25], making the ability to convert the vast quantities of plant waste to a useable byproduct essential to improving the environmental burden of this fruit crop. Pineapple plant fronds were harvested from a plant cultivated from the shoot of a previously harvested fruit in North Port, FL, USA.

Samples of both biomasses were dried in an oven at 80 °C (to prevent molding before use) and milled into powders of 125–250 μ m prior to use. Fuller's Earth (bentonite clay) was purchased from Fisher Scientific. Carbonaceous and elemental compositions of the raw biomasses are available in Table 1.

A stable clay suspension was prepared by adding 0.5 g Fuller's Earth powder to 100 mL deionized (DI) water followed by stirring of the mixture for 60 min. This clay suspension was then contacted with either 2.0 g of the ground mango pits or pineapple plants and stirred for 1 h. The impregnated biomasses were filtered and oven dried at 80 °C. Finally, the samples were stored in desiccators until treated or for further analysis.

Table 1
Characteristics of raw biomass samples.

	Mango [51,52]	Pineapple [53]
<i>Proximate analysis (dry basis)</i>		
Volatile Matter	71.05	85.22
Fixed Carbon	24.32	6.85
Ash	4.63	7.93
<i>Ultimate Analysis (dry basis)</i>		
C	43.80	44.05
H	6.79	5.81
N	1.13	0.87
O	45.18	49.27
Cellulose	14.50	12.93
Hemicellulose	52.40	35.49
Lignin	3.80	26.40

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