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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.

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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 C_2H_6 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

http://dx.doi.org/10.1016/j.fuel.2017.01.052 0016-2361/© 2017 Elsevier Ltd. All rights reserved. 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 MgObiochar and Mg oxyhydroxide composites, respectively, to remove phosphate from solution [11,12]. Zhang and Gao synthesized a selfassembled 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 pretreatment 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 $1.525 * 10^7$ 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 $2.333 * 10^7$ 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

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			Mango	[51.6

	Mango [51,52]	Pineapple [53]
Proximate analysis (dry basis)		
Volatile Matter	71.05	85.22
Fixed Carbon	24.32	6.85
Ash	4.63	7.93
Ultimate Analysis (dry basis)		
С	43.80	44.05
Н	6.79	5.81
N	1.13	0.87
0	45.18	49.27
Cellulose	14.50	12.93
Hemicellulose	52.40	35.49
Lignin	3.80	26.40

2.2. Thermogravimetric analysis (TGA) and kinetics analysis

The peak pyrolysis reactivity temperature in N₂ was determined via derivative thermogravimetric (DTG) curves. The raw and Fuller's Earth pre-treated biomass samples were placed into 70 µL alumina crucibles in a Mettler-Toledo TGA-DSC-1 for thermogravimetric analysis. Each sample was heated at 5 °C/min in 20 mL of high purity nitrogen up to 110 °C and held for 30 min to remove residual moisture, then was heated to 600 °C at 5 °C/min and held for 30 min under a constant 50 mL/min high purity nitrogen flow (with an additional 20 mL/min "balance protective gas" flow). The peak temperatures for the raw and impregnated biomass samples' decomposition rates were noted and used as the pyrolysis temperatures for bulk sample preparation. The heat flow requirements as a function of temperature were determined using differential scanning calorimetry (DSC). This analysis was performed on the TGA-DSC-1 at a heating rate of 5 °C/min. The DSC was calibrated using both NIST-traceable gold and indium at the same heating rate as analysis.

TGA was again employed to determine the activation energies of pyrolysis for the raw and treated samples. Each biomass was heated at 5, 10 and 15 °C/min in nitrogen up 600 °C, and the Distributed Activation Energy Model (DAEM) was applied to determine the activation energy of pyrolysis [26]. The use of this isoconversional method removes heating rate and transport dependencies on activation energy calculations, and is recommended by ICTAC Kinetics Committee [27]. Briefly, the extent of conversion at any time t, X(t), of a solid is assumed to take the form of a distribution function, f(E), such as:

$$X(t) = 1 - \int_0^\infty \exp\left(-A \int_0^t \exp\left(-\frac{E}{RT}\right) dt\right) f(E) dE$$
(1)

where A is the frequency (or pre-exponential) factor, E the activation energy, T the absolute temperature, and R is the universal gas constant. X(t) is calculated by the ratio of the mass of volatiles produced at any given time, and is equal to the initial solid sample mass, m_0 , minus the mass at time t, m_t , to the total mass remaining at the end of the pyrolysis reaction, m_f , as:

$$X(t) = \frac{m_0 - m_t}{m_0 - m_f}$$
(2)

f(E) is the distribution of the activation energy, normalized as:

$$\int_0^\infty f(E)dE = 1 \tag{3}$$

If the experiment is conducted nonisothermally at a constant temperature ramp rate, $\beta = dT/dt$, Eq. (1) can be rewritten as:

$$X(T) = 1 - \int_0^\infty \exp\left(-\frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT\right)f(E)dE$$
(4)

The frequency factor is often considered a constant for all reactions. Miura and Maki's integral method, as used here, includes a compensation effect between A and E [28].

The activation energy and frequency factor are calculated from TGA curves from at least three discrete heating rates at selected conversion values. Therefore, the activation energy obtained from the Arrhenius plots of Eq. (4) are across a range of decomposition levels. To achieve a 95% confidence in the Arrhenius parameters, if correlation coefficients, R^2 , were below 0.994, additional runs were performed at each ramp rate, and the data added to the plot to insure this statistical limit as put forth by the ICTAC Kinetics Committee was achieved [27].

TGA was also used for a proximate analysis. The moisture content was determined as the loss upon holding at 110 °C in nitrogen; proximate analysis (Table 1) is reported on a dry basis. Following water removal, the sample was heated to 910 °C at 100 °C/min under high purity nitrogen at 50 mL/min and held for 30 min to determine volatile matter. The sample was heated up to 950 °C under air and held for 30 min to determine fixed carbon. The remaining mass was attributed to ash.

2.3. Production and analysis of biochars and biofuels

The raw and Fuller's earth treated biomass samples were placed in a porcelain boat in a 2" MTI tube furnace. The samples were heated in 100 mL/min flowing high purity N₂ to the peak DTG temperatures (both raw and impregnated biomass sample temperatures) determined above at 5 °C/min and held for 1 h. During this time, evolved gas concentrations were monitored using a Quadrupole Mass Spectrometer (Extorr XT Series RGA XT300M) studying AMU signals of 2, 16, 26, 27, 30 and 44 (H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, CO₂, respectively (for more information on the use of these amu to monitor pyrolysis gas compounds, the reader is referred to Refs. [29,30]). Condensable gases were trapped in 5 mL dichloromethane (Acros Organics, HPLC grade) for further analysis. After pyrolysis, the solid samples were cooled to room temperature under N₂ and removed from the furnace.

The condensable bio-oil components were analyzed using an Agilent 7890B gas chromatograph-mass spectrometer (GC–MS). Analysis was performed in split mode with a split ratio of 50:1 with an injection temperature of 250 °C using helium as a carrier gas. GC conditions started at 50 °C with a hold time of 2 min, followed by heating at 20 °C/min to 100 °C, then 5 °C/min to 300 °C, held for 7.5 min. Interface temperature was set at 325 °C. Mass spectra were recorded under electron ionization within three *m*/*z* ranges: (1) *m*/*z* 120–250 from 4 to 35 min, (2) *m*/*z* 120–400 from 35 to 40 min, (3) *m*/*z* 200–400 from 40 to 50 min. A semiquantitative analysis was performed by integrating the top (by area) 25 gas chromatogram peaks. Peaks are only reported if their NIST-library identification similarity was >90%. Five compounds (as listed in Table 2) were confirmed by injection with a pure standard to match retention time and mass spectra.

Surface area analysis was performed with a Quantachrome Autosorb-iQ analyzer using the N₂ Brunauer-Emmett-Teller (BET) adsorption method over a partial pressure range of 0.05–0.3. Samples were degassed at 180 °C for a minimum of 18 h, and subsequently weighed on a Sartorius semi-microbalance to ±0.1 mg. Scanning electron microscope (SEM) imaging of the biochar samples was conducted on a Zeiss Supra 55VP field emission scanning electron microscope. X-ray diffraction (XRD) analysis was performed using a Bruker Discovery D-8 X-ray diffractometer with Cu K α radiation in the 2 θ range of 10–50° at a 0.05° step with a sampling time of 2 s using a slit detector.

2.4. Evaluation of biochars' sorption capacity

Standard methylene blue (MB) adsorption kinetics and isotherm experiments were used to determine the impact of copyrolysis of bentonite clay and biomass on the relative adsorption capacities of each heterogeneous biochar. The MB sorption capacity of the biochars was examined using a 1:500 (0.01 g biochar in 5 mL solution) biochar:solution at room temperature (24.4– 26.3 °C). The dye concentrations for isotherm analysis ranged from 1 mg/L to 500 mg/L MB. The vials were agitated on an orbital shaker; at specified intervals samples were removed and the vial's contents were immediately filtered through 0.45 μ m pore size hydrophilic PTFE membrane filters to determine dye concentrations using a UV–Vis spectrophotometer (Shimadzu UV-1800) at 664 nm. The adsorption isotherms were determined with MB solution concentrations of: 1, 5, 10, 15, 20, 50, 100 mg/L for 48 h. Adsorption kinetics were examined using a 50 mg/L MB solution

Table 2

Bio-oil components from raw and impregnated biomasses analyzed by GC-MS.^a

Retention time (min)	Compound (min. 90% NIST library match)	M280	MF280	M350	MF 350	P300	PF300	P350	PF350
6.62	Maleamic acid						2.91		
6.95	2-Butyn-1-ol						1.46		
7.01	Maleic anhydride						2.86		
8.09	4-Methyl-2-pentyl acetate	4.58		5.70	4.98	4.24		2.72	
8.38	5-Hydroxymethylfurfural ^a	2.41	3.58	2.85	5.69			1.98	1.96
8.42	2-Ethoxyethyl acrylate			5.11					
8.42	3-Ethylphenol ^a				4.90				
9.11	5-Hydroxymethyl-2-oxotetrahydrofuran						2.86		
9.52	Methyl 3-methyl-2-furoate ^a	12.26	7.44	9.60	12.69	7.56		6.37	
10.06	1H-Indole, 7-methyl-					1.94			
11.41	Benzeneethanamine, N-methyl-							2.75	
12.19	2,6-Dimethoxyphenol	4.47	10.26		5.32			2.77	
14.31	1,1,3-Trimethyl-2-propylcyclohexane		4.54		9.51				
14.39	Eugenol	4.82	6.56						
16.10	1-Tridecene ^a		4.03						
16.21	4-Ethyl-2-methoxyphenol			4.02	5.04				
16.77	Quinoline ^a					2.65			
16.96	Ortho-Formylphenoxyacetic acid	4.10							
19.24	p-Hydroxybenzoic acid								5.98
19.60	Butanamide, N-(2-methoxyphenyl)-3-oxo								11.59

^a Compound identification confirmed by injection of pure standard.

and time intervals of 5,10, 20, 30 min, and 1, 2, 5, 10, 20, 30, 40 h. All experimental treatments were performed in duplicate and the average values are reported.

3. Results and discussion

Though the use of minerals and clays in biomass pyrolysis system is known to produce higher quality biofuels, and heterogeneous biochars that result from co-pyrolysis of such materials are thought to possess high adsorption capacity, these are disparate fields in the literature. Thus, one goal of this paper was to demonstrate the use of TGA to identify lower pyrolysis temperatures that capitalize on peak reactivities while simultaneously producing biofuels and adsorbents for water treatment in a new integrated biorefinery concept.

3.1. Determination of pyrolysis temperature by TGA

Under a nitrogen atmosphere, TGA of Fuller's Earth impregnated and raw biomass samples was conducted with a heating rate of 5 °C/min from 110 °C to 800 °C to determine peak reactivity. Fig. 1 presents DTG curves of untreated and impregnated biomass samples; the Fuller's Earth pretreated biomass samples devolatilized at a higher peak rate, albeit at slightly higher peak temperature, than the raw biomass samples. This suggests that Fuller's Earth may improve the biomass's thermal properties in terms of rate of conversion. For the mango pits, the peak DTG temperatures occured at 280 °C for the raw biomass and at 350 °C for the claybiomass mixture. The peak temperatures for the raw and Fuller's Earth impregnated pineapple plant were 300 °C and 350 °C, respectively. The raw biomass DTG peaks determined here are within the literature range for various biomass samples such as cherry pits, brewer's spent grains and sawdust, among others [31–33].

While most studies seem to arbitrarily select a pyrolysis temperature – usually 450–650 °C depending on the product to be optimized (i.e. syngas production increases with temperature) [34] – here we used peak DTG temperatures for the pyrolysis. Reducing pyrolysis temperature, potentially improves the economic and environmental feasibility of biomass to biofuel conversions. As such, the biomass samples were pyrolyzed in a tube



Fig. 1. DTG curves of raw and Fuller's Earth impregnated biomass pyrolyzed at 5 °C/min: (a) mango pits; (b) pineapple plant.

furnace at the peak DTG temperatures determined above. Raw biochar and the Fuller's Earth impregnated biochar samples obtained at different pyrolysis temperatures were named as M (mango); MF (mango + fuller's earth); P (pineapple); PF (pineapple + fuller's earth) followed by the pyrolysis temperature in °C: M280, M350, MF280, MF350, P300, P350, PF300 and PF350, respectively.

3.2. Bio-gases evolved during pyrolysis

Fig. 2 illustrates the importance of both pyrolysis temperature and the inclusion of Fuller's Earth on the pyrolysis gases evolved from these two biomasses. Fig. 2a shows that the least amount of hydrogen was evolved for pyrolysis of raw pineapple plant at 300 °C; this increased threefold with the Fuller's Earth treatment, and still more hydrogen was evolved from raw pineapple at 350 °C, and even more for the impregnated pineapple at 350 °C. Fig. 2b shows that considerably higher methane was evolved from PF350 than either P300 or PF300, though the differences between P350 and PF350 were less pronounced, suggesting that temperature has a larger effect on methane yield than Fuller's Earth incorporation for this biomass. For all gases monitored (spectra available in Supplemental Information), both increasing temperature and pretreatment with Fuller's Earth resulted in higher quantities of pyrolysis gases, with the raw pineapple pyrolyzed at 300 °C having the least pyrolysis gas evolved than any other sample.

The results are less straightforward for the mango pit. In this case, increasing temperature from 280 °C to 350 °C for the untreated biomass yielded a consistent increase in pyrolysis gas yield. What is intriguing is that the Fuller's Earth treated mango pits pyrolyzed at 280 °C yielded the greatest amount of pyrolysis gases (for all species monitored) than another other biomass/temperature. In addition, the raw biomass pyrolyzed at 350 °C yielded consistently more pyrolysis gas than the Fuller's Earth impregnated samples at the same temperature, suggesting that the Fuller's Earth promoted volatilization at lower temperatures and constrained it at higher temperatures.

3.3. Bio-oils condensed from pyrolysis

The mango bio-oil was more heterogeneous than the pineapple pyrolysis liquids (assuming that each chromatogram peak corresponds to one compound), as shown in the chromatograms of the raw and impregnated biomasses pyrolyzed up to 350 °C in Fig. 3. The Fuller's earth appears to have suppressed some of the larger/higher molecular weight components (those with longer retention times) for the mango pit biofuels, and had the opposite effect on the pineapple plant pyrolysis liquids. These results were duplicated in two separate experiments of each sample for confirmation. Analyzing this data in the context of Garcia-Perez et al.'s characterization scheme [35], the mango bio-oils showed considerably more monolignols and semi-volatile polar compounds than the pineapple bio-oils. Given the large peaks at longer retention times for the impregnated pineapple (not observed in the raw pineapple), it appears that the Fuller's Earth promoted the formation and devolatilization of heavy non-polar compounds and extract-derived compounds with higher boiling points. Conversely, Fuller's Earth promoted formation of phenols and furans for the mango biofuels.

The varving impact of Fuller's Earth as a catalyst can be semiquantitatively analyzed using peak areas of the gas chromatograms; all analyses used the same starting fuel mass and were condensed into the same volume of dichloromethane over the same reaction time and gas flow rates. As such, under the assumption that peak chromatogram area is directly related to concentration, by comparing the relative chromatogram area of each component identified across starting fuel, it is possible to determine the relative impact (increase/decrease) in condensable biooil yield for each component. As shown in Table 2, for pineapple plant the Fuller's Earth suppressed the evolution of methyl 3methyl-2-furoate, a common product of glucose degradation [36]. However, chromatograms of mango pyrolysis oils displayed large and varying amounts of this component, comprising 12.26% of total chromatogram area for M280 to 7.44% for MF280. Interestingly, increasing the temperature decreased the relative amount of this product for the raw biomass (to 9.60%) and increased it with the incorporation of Fuller's Earth (12.69%). The incorporation of Fuller's earth improved the yield of 5-hydroxymethylfurfural, a key biorefinery intermediate, for both the mango bio-oils evolved at both temperatures. No 5-hvdroxymethylfurfural was detected for the pineapple samples at 300 °C, and there was relatively little impact on the amount detected for the raw versus impregnated pineapple pyrolyzed at 350°.

There was a varying effect of Fuller's Earth on different biomasses, including more phenols identified in the mango pyrolysis



Fig. 2. Mass spectra of (a) H₂ and (b) CH₄ evolved in pyrolysis gases from raw and Fuller's Earth impregnated biomasses (spectra of all monitored gases available in Supplemental Information).



Fig. 3. Gas chromatograms of raw and impregnated biomass oils collected after 350 °C pyrolysis; black line indicates raw biomass samples, red line is Fuller's Earth impregnated samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oils than pineapple oils, with the Fuller's Earth catalyzing the phenolic evolution. In particular, the evolution of 2,6dimethoxyphenol was two times higher for MF280 than M280. None was detected for M350, and the area for MF350 was similar to the M280. This was somewhat surprising given the higher oxygen content of the pineapple plant versus the mango pit (49.27% vs. 45.18%). The mango has a considerably higher volatile carbon and hemicellulose content with lower lignin content than the pineapple plant, and as such the ability to devolatilize more of the mango's oxygen at lower temperatures may explain this phenomenon. Such phenolic components can be hydrogenated and deoxygenated to form cyclic hexane and benzenes, and thus this represents a potential line of inquiry for future research on biofuel upgrading [39].

While exploring the effects of various catalysts to upgrade pyrolysis oils from *Alcea pallida* (commonly known as hollyhocks), Aysu found that the raw biomass evolved no methyl 2-furoate, nor did biomass pyrolyzed with calcium hydroxide, zinc chloride, alumina or ulexite (hydrated sodium calcium borate hydroxide), but the compound was detected with tincal (sodium borate) [37]. Similarly, Yang and co-workers detected no methy-2-furoate in the pyrolysis oil of raw corn stover, but after treatment with *P. ostreatus* (a white-rot fungi) trace amounts were detected [38].

3.4. Activation energy and heat required for thermal treatment

The average activation energy for the complete pyrolysis of each sample is given in Table 3 (activation energy determined at each fractional conversion level and a representative isoconversional plot available in Supplemental Information). The average activation energy for the raw mango pits $(173.2 \pm 4.8 \text{ kJ/mol})$ was moderately higher than the impregnated mango pits $(162.7 \pm 8.8 \text{ kJ/mol})$, though this was just within statistical significance using a 95% confidence interval. The average activation energy of the raw pineapple biomass $(169.1 \pm 24.0 \text{ kJ/mol})$ was almost equal to the impregnated biomass $(164.3 \pm 7.6 \text{ kJ/mol})$, and certainly within the 95% confidence interval. Thus, while the Fuller's Earth may "catalyze" the devolution of various pyrolysis gas and liquid components, the overall reaction energy barrier to pyrolyzed decomposition was not impacted in a statistically significant way.

There are conflicting results of the impact of various catalysts on biomass pyrolysis in the literature; Lu et al. find a modest decrease in the activation energy of pyrolysis of wheat straw with a series of solid acid, rare earth, and bifunctional catalysts (though statistical significance is not reported) [40]. Conversely, Nowakowski et al. find that potassium impregnated willow biomass shows higher activation energies (up to twice as high) for the "catalyzed" biomass; they note a similar increase in methane evolution from impregnated samples as we find here [41]. Micro- and nano-NiO catalyst demonstrated the ability to lower the activation energy by only 5-10% for the pyrolysis of cellulose and xylan, but showed little to no effect on lignin devolatilization, though this study was not done using ICTAC-recommended iso-conversional methods [42]. Though pyrolysis reactions can be "catalyzed" to produce different compounds and increase yields, the activation energy required to initiate the reactions may not decrease with inclusion of a catalyst.

DSC curves in Fig. 4 indicate that the heat required to initiative pyrolysis, as a function of total sample loading, may increase with

Table 3

Surface areas and thermal analysis of raw and impregnated samples (±one standard deviation).

Biochar	BET surface area (m²/g)	Heat required for pyrolysis (J/g)	Heat required for full pyrolytic decomposition (up to 800 °C) (J/g)	Average activation energy (kJ/mol)
M280	7.39 ± 0.42	27.32 ± 4.52	2.28E+03 ± 3.82E+01	173.21 ± 4.81
M350	6.01 ± 0.14	46.49 ± 7.70		
MF280	12.15 ± 0.14	41.19 ± 8.85	1.54E+03 ± 3.39E+01	162.65 ± 8.82
MF350	105.57 ± 1.64	60.81 ± 13.07		
P300	12.67 ± 0.20	22.21 ± 2.13	4.21E+03 ± 4.03E+01	169.15 ± 24.04
P350	4.20 ± 0.11	22.02 ± 2.11		
PF300	61.08 ± 0.63	14.25 ± 4.02	9.41E+02 ± 2.76E+01	164.30 ± 7.64
PF350	65.22 ± 0.70	18.64 ± 5.26		
Fulller's Earth	77.29 ± 0.06			



Fig. 4. DSC curves of raw and impregnated biomass samples heated at 5 °C/min.

clay presence. Though a comprehensive energy balance is beyond the scope of the present work, analysis of the heat flow required to pyrolyze the biomass samples offers insight into the differences in energy required between pyrolysis temperature and resulting product (readers are referred to van de Velden et al. [43] for a review on the endothermicity of pyrolysis). Shown in Fig. 4, the pyrolysis of biomass was *almost* entirely endothermic, with the noted exception of the Fuller's Earth impregnated samples above 560 °C. Overall, as temperature increases (up to 560°), by extension the heat (and energy input) required to pyrolyze the sample at higher temperatures also increases.

The heat required for pyrolysis of a given sample mass can be determined by integrating the area under the curves up to each pyrolysis temperature; results are reported in Table 3. The heat required to pyrolyze raw mango pits at 280 °C versus 350 °C represented an increase of 70%; for the impregnated samples the increase in temperature represented an increase in heat flow of 48%. Conversely, pyrolyzing the pineapple at 300 °C versus 350 °C was statistically indistinguishable in terms of the amount heat required (22.20 ± 2.13 J/g versus 22.02 ± 2.11 J/g for the 350 °C). For the Fuller's Earth impregnated pineapple, increasing the temperature by 50 °C increased the heat required by 31%. However, the impregnated samples had considerably higher heat requirements than the raw samples; to pyrolyze the impregnated mango at 280 °C required 51% more heat than the raw, and 31% more was required to pyrolyze the impregnated samples at 350 °C. The opposite was noted for the pineapple samples; pyrolysis of the impregnated samples required 36% and 15% less heat at 300 °C and 350 °C, respectively, over the raw samples. However, by integrating the DSC curves from 110 to 800 °C, one finds that the impregnation of mango pits lowered the overall heat requirement by 33%, and of the pineapple by 78%. This is due to the exothermic nature of the impregnated samples above \sim 510 °C. At this point, it is likely that some of the carbonate minerals in the Fuller's Earth decompose and partially oxidize the sample.

3.5. Characterization of resulting biochars

For both raw biomass samples, the lower temperature samples had higher BET surface areas than their higher temperature counterpoints (19% for mango, 67% for pineapple plant), as shown in Table 3. While high (>600 °C) pyrolysis temperatures have been shown to increase BET surface areas due to enhanced volatilization

opening porous voids [44], low temperatures often result in the recondensation of volatilized species into the solid matrix as the heat is not sufficient to remove them from the matrix [45]. Both biomass samples treated with Fuller's Earth yielded higher surface areas than the biochars alone, though there were substantial differences between the Fuller's Earth mango and pineapple samples. Specifically, MF280 showed a surface area of $12.15 \pm 0.14 \text{ m}^2/\text{g}$, and MF350 of $105.57 \pm 1.64 \text{ m}^2/\text{g}$, which were higher than both the raw biomass samples. However, the difference between PF300 and PF350 was considerably lower; $61.08 \pm 0.63 \text{ m}^2/\text{g}$ versus $65.22 \pm 0.70 \text{ m}^2/\text{g}$ for the 300 and 350 samples, respectively, though again both of these were considerably higher than the raw biomass samples.

The improvement in surface area as a function of Fuller's Earth addition is not likely due to the surface area contribution of the Fuller's Earth alone, whose BET surface area was measured at $77.29 \pm 0.06 \text{ m}^2/\text{g}$. The biomass:bentonite ratio was initially 4:1. but the surface areas of MF and PF do not increase by a factor of 25%. For example, if the Fuller's Earth did not interact with the biomass to open pores, one might expect the resulting MF280 surface area (SA) to be $\sim 24 \text{ m}^2/\text{g}$ [if $(SA_{predict} = (0.75)(SA_{M280}) + (0.25)$ (SA_{Fuller's})], yet it is half of this value. It might be expected that MF350 would have a surface area of \sim 24 m²/g, yet the actual surface area was almost four and a half times this value. One explanation for the improved surface area of the biomass is that the Fuller's Earth promotes devolatilization and removal of the pyrolysis products from the solid, opening porous voids in the material. This is likely accomplished by (1) improving the heat transfer within the solid matrix as the bentonite clay minerals have a higher specific heat capacity than biomass [46] and (2) possible oxygenated groups on the bentonite clay devolatilizing and partially oxidizing the char.

XRD spectra of the Fuller's Earth-biochar hybrid fabricated at different temperatures (presented in Supplemental Information) show distinct peaks for quartz and palygorskite, common components of Fuller's earth and bentonite clays in general [22]. Though this is a qualitative analysis, we note that MF 350 appears to have stronger peaks for palygorskite as compared to the other three samples. Though the Fuller's earth we used was a finely ground, "homogenized" powder, it is feasible to have heterogeneities in the mineral samples.

Fig. 5 shows selected SEM images of the pyrolyzed samples, used to note morphological changes. The Fuller's Earth impregnated samples' surfaces were widely covered by acicular structures as compared with raw biochar samples, which are representative of a more amorphous carbon.

3.6. Methylene blue adsorption onto biochars

The ability of the biochars to adsorb pollutants from water was tested using the removal of methylene blue (MB) from aqueous solution as a model compound.

3.6.1. Equilibrium adsorption isotherms

Equilibrium isotherm experiments were conducted at concentrations ranging from 1 to 100 mg/L of methylene blue, with 5 mL of solution and 0.01 g of biochar. Four isotherm models, Langmuir (Eq. (5)), Freundlich (Eq. (6)), Langmuir-Freundlich (Eq. (7)), and Redlich-Peterson (Eq. (8)) models were used to fit the adsorption data according to the following equations:

Langmuir :
$$q_e = \frac{KQC_e}{1 + KC_e}$$
 (5)

Freundlich :
$$q_e = K_f C_e^n$$
 (6)





c. P300

b. MF280

d. PF300



Fig. 5. SEM images of pyrolyzed Fuller's earth impregnated biomass samples.

$$Langmuir-Freundlich: q_e = \frac{K_{lf}QC_e^n}{1 + K_{lf}C_e^n}$$
(7)

Redlich-Peterson:
$$q_e = \frac{K_r C_e}{1 + a C_e^n}$$
 (8)

In these equations, C_e is the equilibrium concentration in mg dye per gram of biochar, K, K_f, K_{lf}, and K_r are the isotherm constants of Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson moderls respectively, Q is the maximum adsorption capacity, and n and a are constants for each model. Plots are available in the Supplemental Information; isotherm parameters are given in Table 4 with their corresponding correlation coefficients values (R^2).

The Freundlich isotherm model fitted the experimental data well for M280 with an R^2 of 0.918, whereas the Langmuir-Freundlich model fitted well for M350 and MF350 with R^2 values of 0.916 and 0.910, respectively. The MF280 adsorption data was not as well represented by any of these models, though the closest "best fit" was the Redlich-Peterson model with an R^2 of 0.882. This suggests that MB adsorption onto M280, M350 and MF350 may be monolayer adsorption onto a heterogeneous surface. The application of the Redlich-Peterson model for the MF280 sample suggests that the mechanism may be multiple layer adsorption onto heterogeneous surfaces, though there is no concrete reason to explain why this one sample would be multi-layer versus the mono-layer coverage likely observed for the other samples. The Fuller's Earth impregnated mango pit biochars have higher adsorption capacities than the raw mango biochars, with MF350 having the highest maximum adsorption capacity of up to 110.56 mg_{MB}/g_{biochar}. This is indeed higher than raw Fuller's Earth itself, which was measured to be 93.13 mg_{MB}/g_{Fuller's}, similar to the capacity of ~80 mg_{MB}/g_{sorbent} measured by Kahr and Madsen for an Arizona bentonite clay [47]. The Fuller's Earth enhanced the adsorption capacity of the mango pits biochars, and again beyond what one might predict using a weighted average of the M350 and Fuller's Earth as $[(Q_{predict} = (0.75)(Q_{MF350}) + (0.25) (Q_{Fuller's})]$, which would lead to a "predicted" adsorption capacity of 82.4 mg_{MB}/g_{biochar}, less than the 110.2 mg_{MB}/g_{biochar} observed.

The adsorption isotherm behavior of the pineapple plant biochars was substantially different from that of mango pits biochars. For the P350, PF300 and PF350 samples, the Redlich-Peterson model fitted the experimental data best for P350, PF300 and PF350 with R² values of 0.999, 0.984 and 0.958, respectively. The Langmuir isotherm model fitted the experimental data "best" for P300, with an R² of 0.930, though the R² of the Redlich-Peterson was 0.913, such that it is difficult to distinguish between the model fits. As for the mango samples, these biochar samples likely have heterogeneous surfaces and the adsorption process is likely of multiple mechanisms. The biochar for Fuller's Earth impregnated pineapple plant pyrolyzed at 300 °C (PF300) had the highest maximum adsorption capacity (137.72 mg_{MB}/g_{biochar}) of all biochars, indicating that Fuller's Earth enhances the adsorption capacity of pineapple plant biochars at lower temperatures only,

Table 4 Isotherm model parameters for MB adsorption onto biochar samples.

Biochar	Langmuir			Langmuir-Freundlich				
	K (L/mg)	Q	R ²	K _{lf}	$Q(L^n/mg^n)$	n	R ²	
M280	1.40E-01	40.64	0.849	1.50E-01	83.48	0.39	0.905	
M350	8.00E-02	43.48	0.888	1.80E-01	66.46	0.43	0.916	
MF280	9.00E-01	58.79	0.874	4.60E-01	71.97	0.61	0.870	
MF350	9.70E-01	97.37	0.878	7.40E-01	110.56	0.55	0.910	
P300	3.00E-01	117.84	0.930	4.60E-01	113.21	1.95	0.905	
P350	6.10E-01	105.97	0.994	7.00E-01	104.53	1.23	0.994	
PF300	1.70E-01	72.77	0.949	1.40E-01	137.72	0.39	0.984	
PF350	2.00E-02	53.71	0.943	1.00E-02	51.32	1.10	0.930	
Biochar	Freundlich			Redlich-Petersor	Redlich-Peterson			
	$K_{f}(mg^{1-n}L^{n}/g)$	n	R ²	$K_r (L/g)$	a (L ⁿ /mg ⁿ)	n	R ²	
M280	1.13E+01	0.27	0.918	1.02E+02	7.76	0.76	0.906	
M350	1.19E+01	0.25	0.915	8.78E+01	6.31	0.79	0.908	
MF280	2.07E+01	0.26	0.852	7.60E+01	2.02	0.88	0.882	
MF350	4.03E+01	0.20	0.862	3.83E+02	6.30	0.89	0.909	
P300	2.86E+01	0.29	0.806	3.14E+01	0.15	1.13	0.913	
P350	3.14E+01	0.26	0.880	5.67E+01	0.36	1.09	0.999	
PF300	1.81E+01	0.26	0.981	4.40E+01	1.76	0.80	0.984	
PF350	3.92E+00	0.43	0.892	3.40E-01	0.00	2.52	0.958	

Table 5

Kinetics models parameters for MB adsorption onto biochar samples.

Biochar $q_{e,exp} (mg/g)$		Pseudo first order			Pseudo second order			Elovich		
	k ₁ (1/h)	$q_{e,cal} (mg/g)$	R ²	k ₂ (g/mg h)	$q_{e,cal} (mg/g)$	R ²	a (mg/g h)	b (g/mg)	R ²	
M280	68.6	6.00E-03	60.3	0.901	9.89E-05	67.2	0.922	9.06E-01	7.80E-02	0.900
M350	50.1	8.00E-03	46.5	0.908	1.87E-04	50.8	0.879	1.13E+00	1.11E-01	0.783
MF280	104.3	6.00E-03	91.2	0.913	7.00E-05	100.9	0.943	1.63E+00	5.40E-02	0.933
MF350	110.2	1.20E-02	101.2	0.913	1.65E-04	107.9	0.941	1.11E+01	6.70E-02	0.883
P300	68.1	5.00E-03	63.8	0.851	1.30E-04	66.8	0.934	2.43E+00	9.90E-02	0.997
P350	62.2	3.00E-03	55.6	0.942	7.21E-05	60.9	0.976	6.66E-01	9.00E-02	0.996
PF300	48.6	5.26E-04	53.0	0.951	7.23E-06	69.2	0.959	4.70E-02	5.10E-02	0.969
PF350	36.7	2.92E-04	48.1	0.892	3.86E-06	65.0	0.897	2.30E-02	5.80E-02	0.907

as the maximum adsorption capacity of the PF350 was only $51.32\;mg_{MB}/g_{biochar}$

Overall, all eight samples showed Freundlich exponents between 0.20 and 0.43, indicating favorable adsorption, for which 0 < n < 1 [48]. The adsorption isotherm data compared favorably to the removal of methylene blue from aqueous solutions for a variety of biochars. For example, Shi et al. probed the capacity of a sewage sludge-ZnCl₂ composite pyrolyzed at 650 °C and found a maximum adsorption capacity of 90–100 mg_{MB}/g_{sorbent}, though their Freundlich constants were all n > 2, suggesting unfavorable adsorption [49]. The present work achieves similar loadings, though with pyrolyzing these composite biochar samples at a considerably lower temperature. Furthermore, the adsorption capacities measured here were considerably higher than the MB adsorption onto a bagasse-montmorillonite composite pyrolyzed at 600 °C, which showed an equilibrium capacity of only 11.9-15 mg_{MB}/g_{sorbent} [15]. In this instance, the clay-biochar composites pyrolyzed at lower temperatures had significantly higher capacities for MB adsorption.

3.6.2. Adsorption kinetics

Three kinetic models, pseudo first order (Eq. (9)), pseudo second order (Eq. (10)), and Elovich (Eq. (11)) models were applied to describe the MB adsorption kinetics onto the biochar samples using an initial solution concentration of 50 mg/L.

Pseudo first order :
$$q_t = q_e(1 - e^{-k_1 t})$$
 (9)

$$\label{eq:Pseudosecond} \text{Pseudosecond order}: \textbf{q}_t = \frac{\textbf{q}_e^2 k_2 t}{1 + \textbf{q}_e k_2 t} \tag{10}$$

$$Elovich: q_t = \frac{1}{\beta} ln(1+\alpha\beta t) \eqno(11)$$

In the pseudo first order and pseudo second order equations, k_1 and k_2 are the kinetic rate constants, q_t and q_e represent the amounts of MB adsorbed to the biochar at equilibrium and at time (t), respectively. In the Elovich kinetic model, α is the initial adsorption rate and $1/\beta$ is related to the number of sites available for adsorption. The values of the kinetics parameters of MB adsorption onto the biochar samples were calculated based on the kinetic plots (available in Supplemental Information) and are given in Table 5 with corresponding correlation coefficients.

As in Table 5, for M280, MF280 and MF350, the values of R² of the pseudo second order model were found to be the highest, indicating that the MB adsorption onto M280, MF280 and MF350 is controlled by chemisorption. In addition, the calculated qe values of the pseudo second order model were closer to the experimental q_e values. For M350, the R² value of the pseudo first order model was the highest, however, the pseudo second order q_e value of 50.787 mg/g was closer to the experimental qe value (50.076 mg/ g) than the value of the pseudo first order model. Thus, the pseudo first order kinetic model does not accurately describe the adsorption kinetics of MB onto M350 for the entire adsorption process. Compared with mango pits, the kinetic data of P300 and P350 indicated that MB adsorption was fitted better by the pseudo second order and Elovich model with higher R² values, implying that MB sorption onto P300 and P350 biochar could be governed by either pseudo second order or the Elovich model. The calculated q_e values of pseudo first order model for PF300 and PF350 are closer to the experimental q_e than the other two models. As such, MB sorption

Table	6
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Overall	results	summary
Ovcian	results	summary.

	Pyrolysis gas	Bio-oil	Surface area biochar	MB capacity bio-char	Adsorption rate bio-char	Activation energy			
Mango	Increases H ₂ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , CO ₂	Increases furans, phenols, hexanes	Increases surface area, especially at slightly higher temperature	Increase MB capacity	Increases rate of adsorption, especially at higher temperature	No significant impact on			
Pineapple		Increases high molecular weight, oxygenated compounds (organic acids)	Increases surface area at both temperatures	Increase MB capacity at low temperature, decreases at high temperature	Decreases rate of adsorption	E _a			

onto both PF300 and PF350 biochars is more likely controlled by pseudo first order or Elovich models, rather than pseudo-second order. These findings are in strong agreement with other biocharclay sorbent composites investigated in the literature and support a chemical adsorption mechanism [15], which we is often seen for biochar and clay sorbent materials that participate in cationexchange mechanisms [47,49,50].

One explanation for the differences among these results is the biomass precursor: mango pits are a dense, highly hemicellulosic biomass with more fixed carbon and less ash than the pineapple, which has a higher lignin content and more volatile carbon, as well as a higher oxygen:carbon ratio. While volatile matter represents the "pyrolyzable" content of the biomass, the fixed carbon is an integral "backbone" for an activated carbon support. As noted by previous researchers, activated carbons from biomass with lower lignin contents tend to remove more organic dyes from water [54]. This may explain both the higher surface area and adsorption capacity of the mango pit biomasses, and the lower amount of heat required for full pyrolytic decomposition as measured by DSC (see Table 6).

4. Conclusions

Incorporation of Fuller's Earth into biomass is not a "one-sizefits-all" solution to upgrading biofuels and producing heterogeneous biochars. For pineapple and mango pit biomasses, the incorporation of bentonite clay into raw biomass significantly increases the hydrogen and methane produced during pyrolysis, even at low temperatures. The incorporation of Fuller's Earth into the mango pit biomass improved pyrolysis gas yield, bio-oil quality, surface area of the resulting biochar, and adsorption capacity and rate of adsorption, without significantly impacting the activation energy required to pyrolyze the sample. The results are mixed for the pineapple plant biomass; while pyrolysis gases and surface area increased with the Fuller's Earth pre-treatment, the bio-oil was hampered with high molecular weight, polar, oxygenated compounds. The adsorption capacity of the impregnated pineapple plant pyrolyzed at the lower temperature (300 °C) was the highest of all the samples, whereas the higher temperature (350 °C) resulted in a biochar with low adsorption capacity. The incorporation of Fuller's Earth into the raw biomasses requires more thermal energy to reach pyrolysis temperatures, but does not impact the activation energy. Thus, the Fuller's Earth "catalyzes" the evolution of biogas components at low temperatures, and impacts the resulting bio-oil and biochar quality, but does not change the activation energy barrier to devolatilization.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.01.052.

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