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Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana

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ABSTRACT

Bio-Oils derived from biomass pyrolysis are promising feedstock for the direct production of valuable platform chemicals, fuels and energy from renewable and sustainable resources. Among the numerous technologies utilized for biomass pyrolysis, fast pyrolysis technologies are chosen for liquid products yield maximization, and characterized by short residence times for solids and vapors, operating temperatures in above ≥500 °C and very high heating rates. Inspired by the vast potential of biomass pyrolysis bio-oils, a thermochemical conversion (fast pyrolysis) and characterization of cocoa pod husks, an abundant agricultural biomass waste from Ghana, West Africa, has been investigated and their potential as renewable feedstock for the production of high-value added chemicals determined by analyzing chemical components of the derived bio-oil. GC–MS analysis of the bio-oil indicated that major constituents were 9, 12-octadecadienoic acid and hexadecanoic acid". Product distributions revealed 58%wt. of bio-oil, 30%wt. of bio-char and 12%wt. of Non-condensable gas (obtained by difference). Ultimate, proximate, structural composition, calorific value and thermogravimetry analyses were also performed on the cocoa pod husks. Elemental analysis showed that the recovered milled cocoa pod husks contained about 7 elements potentially essential for plant growth.

1. Introduction

The rapid depletion of fossil fuel coupled with the quest to reduce greenhouse gas emission has brought into focus the potential utilization of renewable biomass as a sustainable energy feedstock, and for the synthesis of "green" valuable platform chemicals (Amaniampong et al., 2014, 2015; An et al., 2012). Biomass can be converted to bio-fuel and bio-chemicals *via* different transformation routes, including physical, biochemical and thermochemical transformation routes (Bridgwater et al., 2002; McKendry, 2002; Tsai et al., 2017). Among these biomass conversion processes, pyrolysis has attracted more interest particularly to liquid fuel products due to its enormous advantages in transportation and versatility in application such as turbines, boilers and combustion engines, etc. (Bridgewater, 2004). The crude bio-oil can also be directly used in boilers and turbines for heat and electricity generation and as feedstock for the synthesis of platform chemicals (resins), fine chemicals such as levoglucosan and fertilizers. Alternatively, they can be upgraded either via chemical or physical means to more valuable products. The production of biomass derived bio-oils and other products (char and gas) *via* pyrolysis of different biomass feedstock's has been extensively investigated, typically including woody biomass (Demiral and Şensöz, 2008; Mohan et al., 2007), baggase (Asadullah et al., 2007), beech wood (Demirbas, 2005), straws (Aho et al., 2008) and municipal solid waste (MSW) (Asadullah et al., 2007; Jensen et al., 2001; Pütün et al., 2006). Pyrolysis technology has the potential to produce high value bio-oil capable of competing with and consequently replacing non-renewable fossil fuels. The composition of the bio-oil thereof produced, greatly depends on the conversion process utilized, as well as the biomass source used. When pyrolysis bio-oils are the target of production, the development of technologies based on fast pyrolysis is sought in order to maximize the liquid fraction and to obtain bio-oils of high quality. Fast pyrolysis technologies possess significant advantages over other biomass and waste processing technologies. Classical examples of the numerous advantages of fast pyrolysis are; easy and cost-competitive storage and transportation of biomass and waste, greater energy efficiency achieved in combustion processes, raw

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material processing can be decoupled from the final use of products and facilitates the valorisation of delocalised biomass resources in small scale autonomous installations, etc. (Bimbela et al., 2014). Reactor types such as vacuum pyrolysis reactors, ablative pyrolysis reactors, entrained flow reactors, fluidised bed, circulating bed and fixed bed reactors, with varying configurations has also been reported for fast pyrolysis technologies (Aho et al., 2008; Asadullah et al., 2007; Bridgwater et al., 2002; Demirbas, 2005). Composition of the bio-oil thereof produced, greatly depends on the conversion process utilized, as well as the biomass source used.

In this study, we employed an abundant agricultural crop residue generated from a cocoa plantation in Ghana as the sole biomass source for fast pyrolysis upgrading. Cocoa makes a very important contribution to the economy of Ghana with it, being the most important single export product in Ghana (Duku et al., 2011). The husk which is the main residue generated during processing using the method of drying, when compressed, can provide a source of alternative energy in the form of bio-fuel. With an objective of reducing dependency on crude oil and other related non-renewable energy sources, there have been a lot of interests and investments in numerous renewable energy projects in Ghana. Therefore, the onward transformation of cocoa pod husks, a notable agricultural waste generated in huge amounts annually in Ghana, into valuable chemicals and bio fuels, is particularly of enviable interest. Cocoa pod husk, similar to other plant biomass, contains a mixture of cellulose, hemicellulose, lignin, pectin and crude fibre, and therefore serves as a potential source of biomass substrates for biochemical production. The upgrading of cocoa pod husks to pyrolysis oil is expected to contain several compounds such as ketones, carboxylic acid, aldehydes, furans and phenols. Hence, the proper usage of the husks could effectively provide economic advantages and decrease their environmental impact. It is envisaged that, knowledge of the components of the fast pyrolysis products from cocoa pod husk will serve as a basis for the possible catalytic upgrading to produce other useful platform chemicals in subsequent studies.

2. Materials and methods

2.1. Biomass material

Cocoa pod husks were the main biomass agricultural wastes samples investigated in this study. Samples (Fig. 1a) were obtained from an agricultural farm at Effigyase, a town in the Ashanti Region of Ghana and were sun-dried for approximately 1–2 weeks. The husks were then reduced into smaller chips (Fig. 1b), ground with a mechanical grinder and sieved to a fine size of less than 1 mm, precisely using a BS mesh (Fig. 1c). The samples were then stored in sample bags and labelled prior to further analysis.

2.2. Characterisation methods

2.2.1. Proximate analysis

In an effort to obtain information about the moisture, volatile, ash and fixed carbon contents of the cocoa pod husks samples, proximate analysis was performed following the British and European Standards respectively. The fixed carbon contents were calculated by simple difference. The moisture content was determined as a constant weight loss in a drying oven between 105 °C and 110 °C. Ash contents were also determined as the residue after burning to constant weight at 600 °C within 4 h, volatile contents were measured as weight loss after exposing the sample to 900 °C within 10 min.

2.2.2. Ultimate analysis

Basic elemental compositions of the cocoa pod husks samples were determined via an ultimate analysis. Typically, carbon, hydrogen, nitrogen and sulphur contents were determined by various analytical methods and oxygen contents were obtained by difference.

2.3. Pyrolysis of cocoa pod husks

The pyrolysis experiments were carried out in a kiln reactor. Scheme 1 explains that the system design for the pyrolysis of cocoa pod husks in a kiln reactor. The feedstock was the same but the feed rate was approximately 110 g/h. The temperature of the pyrolyzer was set between 550 °C and 600 °C, with a heating rate of 400 °C/min and a

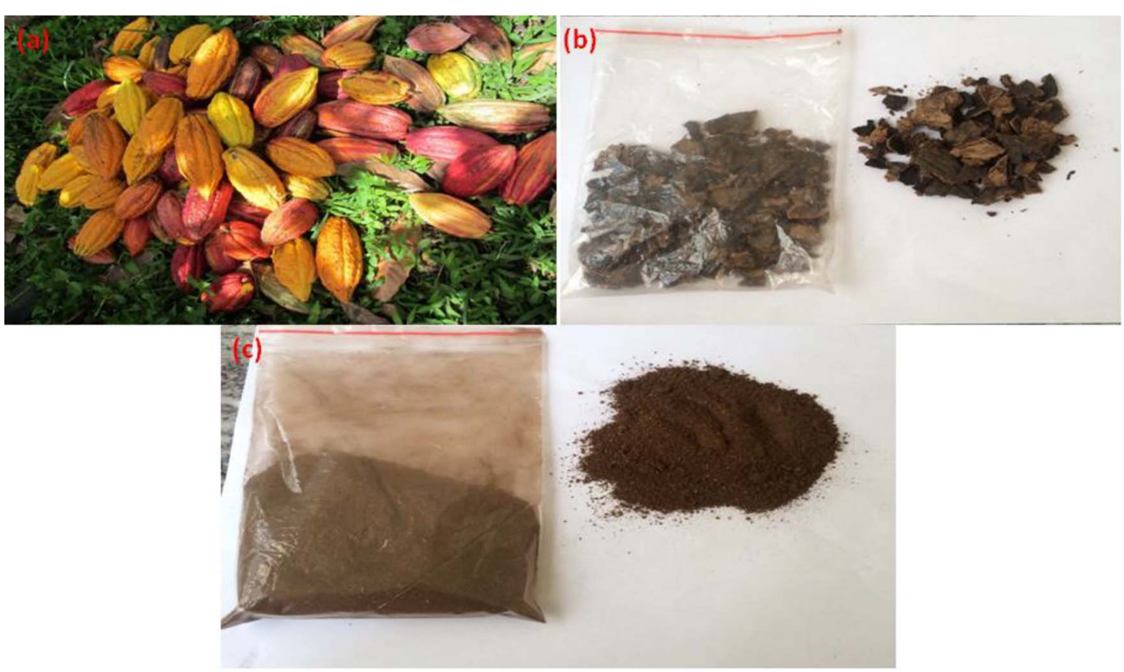

Fig. 1. (a) samples of cocoa pods, (b) dried cocoa pod husks, (c) milled cocoa pod husks.