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Conversion of cacao pod husks by pyrolysis and catalytic reaction to produce useful chemicals

Dieni Mansur [a,*], *Teruoki Tago* [b], *Takao Masuda* [b], *Haznan Abimanyu* [a]

[a] Research Center for Chemistry, Indonesian Institute of Sciences, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia

[b] Division of Chemical Process Engineering, Hokkaido University, N-13 W-8 Kita-Ku, Sapporo 060-8628, Japan

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ABSTRACT

Recently, much attention has been devoted the generation of useful chemicals from biomass. Cacao pod husks, a waste biomass, are one of the agricultural crop residues that can be utilized for this purpose. The husks were treated by pyrolysis to produce pyrolysis oil that contained several chemical compounds such as ketones, carboxylic acids, aldehydes, furans, heterocyclic aromatics, alkyl benzenes, phenols and benzenediols. Therefore, this biomass-derived pyrolysis oil is potentially a rich source of useful chemicals. The pyrolysis oil was upgraded over iron oxide catalysts. During the catalytic upgrade, ketonization, selective oxidation and demethoxylation reactions occurred and selectively produced aliphatic ketones (acetone, 2-butanone), phenol and alkyl phenols (cresol, xylenol, ethylphenol).

1. Introduction

The depletion of crude oil reserves and the effect of greenhouse gases on global warming call for the substitution of petrochemical processes with biomass-based processes for chemical production. Biomass as a renewable resource is considered to be the only raw material for sustainable production of chemicals [1]. It is different from other energy sources such as solar, hydropower, wind, nuclear, and geothermal energy.

Recently, biomass used for chemical production has been derived from waste biomass due to its lower cost than virgin biomass. In fact, it often has negative costs. Waste biomass includes municipal solid waste, livestock and poultry manure, agricultural crop residues, forestry residues and industrial waste [2]. In this study, we utilize an agricultural crop residue generated from a cacao plantation in Indonesia, which ranks third highest in the world in the production of cacao [3].

Cacao is an industrially important crop since cocoa beans and its processed products are the main ingredients of chocolate, one of the world's most popular foods. However, in the production of the beans, waste in the form of cacao pod husks is also generated. Every ton of dry cacao beans generates 10 tons of wet cacao husks. The cacao's pod, bean and husk are shown in Fig. 1 and the husk has composition as shown in Table 1. The husks are typically left to rot and decompose into organic manure on the cacao plantation. However, besides producing foul odors, rotting can propagate diseases such as black pod rot [6]. Proper usage of the husks could provide economic advantages and decrease their environmental impact. For example, the husks have been treated to produce pectin [6,7], a viable dietary supplement for fish [8] and pigs [9].

* *Corresponding author*. Tel.: +62 21 756 0929; fax: +62 21 756 0549.
E-mail addresses: dieni.mansur@lipi.go.id, dienilipi@gmail.com (D. Mansur).

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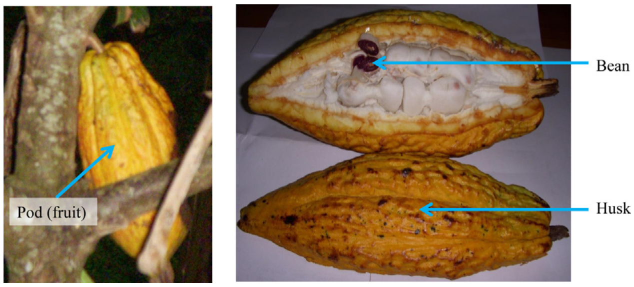

Fig. 1 – The cacao's pod (fruit), bean and husk.

The utilization of biomass to increase its added value and to develop clean and sustainable technologies involves physical, chemical and biological processing to convert agricultural and organic raw materials into chemical products [1]. Most processes begin with pyrolysis, followed by catalytic upgrading to produce low-cost and environmentally friendly compounds. Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion, which results in char, gas, and liquid products [10]. The char is a high quality solid fuel and fuel gas is used as a source of power generation [11,12]. The liquid product from biomass pyrolysis is known as tar or pyrolysis oil. The pyrolysis oil is a mixture of different molecules (alcohols, aldehydes, ketones, esters and phenolic compounds) derived from fragmentation of lignin, cellulose, hemicelluloses and extractives [1]. The yield and composition of biomass pyrolysis oil are dependent on the chemical and structural composition, particle size and species of the biomass used, as well as temperature, heating rate, and residence time of the pyrolysis [10,13]. Pyrolysis oil is a promising material for replacement of fossil oil for production of different chemicals from sustainable and renewable sources.

Pyrolysis oil exhibits two main problems as a source of useful chemicals: its high water content and its instabilities, such as viscosity increase and phase separation. The instabilities result from a breakdown in the stabilized microemulsion and chemical reactions, which continue to occur in the oil. Stabilization of pyrolysis oil can be achieved by upgrading over catalysts [10,14]. Adam et al. investigated catalytic upgrading of pyrolysis vapor using mesoporous molecular sieves (MCM-41), FCC, and SBA-15 catalysts. All of the catalysts reduced the undesirable product yield, while the desirable product yield remained the same or increased [14].

Table 1 – Composition of cacao pod husk.

Composition	Amount (g. kg^{-1} dry matter)
Cellulose	350[a]
Hemicellulose	108[b] – 110[a]
Lignin	146[a]
Pectin	61[a]
Crude fiber	226[a] – 325[b]
Crude protein	59[a] – 76.6[b]
Ash	91[a] – 101[b]

[a] The values were according to Ref. [4].
[b] The values were according to Ref. [5].

Adjaye et al. studied the catalytic upgrading of pyrolysis oil into hydrocarbons using HZSM-5, silicalite, H-mordenite, H–Y and silica–alumina [15]. Moreover, Jackson et al. reported that ketonization of carboxylic acid into ketone over a mixed oxide of Fe, Ce, and Al is another approach to stabilize and upgrade pyrolysis oil [16,17].

In catalytic upgrading of pyrolysis oil, the high water content should be considered because water will deactivate the catalysts [18]. In our previous studies, iron oxide based catalysts selectively produced ketones from sewage sludge, woodchips and ethanol fermentation stillage, and phenols from lignin. These catalysts have been successfully utilized to upgrade oxygen-containing tars derived from thermochemical conversion of biomass [19–22]. Activity iron oxide catalyst also investigated by Taimoor et al. for ketonization of acetic acid and its activity increased by introducing H_2 in carrier gas [23]. In this study, the cacao pod husk waste from a cacao plantation, was subjected to pyrolysis to produce pyrolysis oil, and the pyrolysis oil was then upgraded over zirconia–iron oxide catalysts for production of useful chemicals such as ketones and phenols.

2. Material and methods

2.1. *Material*

The cacao pod husks were obtained from a cacao plantation in West Sumatera province, located in western Indonesia. The husks were separated from the beans, and then sun-dried for a week. Before being fed into the pyrolyzer, the husks were reduced in size using a size reducer (MF10, IKA-Werke GmbH & Co. KG) operating at 3500 rpm min^{-1}. The cut husks were sieved to obtain chips between 0.84 and 4 mm in length. Moisture content (water content) of the cacao pod husk chips was analyzed using moisture analyzer (MB45, Ohaus) at 105 °C for 10 min and found that the moisture content was 14.93%. The samples were stored at 2 °C to discourage the growth of fungi. The cacao pod husks contained 42.78 wt% carbon based on elemental analysis. This value was used as the basis for calculation of the total carbon yield of products after the pyrolysis process.

2.2. *Pyrolysis process of the cacao pod husks*

The pyrolysis experiments were carried out in a fixed-bed quartz reactor. The length and inner diameter of the pyrolyzer were 0.5969 m and 0.0254 m, respectively. About 20 g of cacao pod husk chips were placed in the pyrolyzer. Nitrogen as a sweeping gas was passed through the pyrolyzer to remove air/oxygen. The nitrogen flow rate was set to 20 cc. min^{-1}, the temperature of the pyrolyzer was increased from room temperature (approximately 25 °C) to 500 °C for 9 min, and then the temperature was maintained at 500 °C until pyrolysis had occurred for 50 min. Process pyrolysis of cacao pod husk can be classified into slow pyrolysis due to low heating rate as well as pyrolysis of pistachio shell that conducted by Apaydin-Varol [24].

The temperature was measured using a thermocouple located just below the bed. A condenser (0 °C) and cold trap

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