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Supercritical water gasification of empty fruit bunches from oil palm for hydrogen production

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HIGHLIGHTS

- Utilization of palm wastes in supercritical water gasification to produce hydrogen.
- Biomass model compounds degradation on product gas composition of SCWG.
- The effect of EFB water ratio on hydrogen production was investigated.
- The effect of reaction time on hydrogen production was investigated.
- Potential of palm oil mill effluent (POME) was studied as a reaction medium.

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ABSTRACT

Empty fruit bunches (EFBs) from the palm plantation sector are abundant agricultural waste products in Malaysia. Supercritical water gasification (SCWG) is a prominent way to convert high-moisture-content biomass such as EFBs into valuable end products. This investigation is focused on EFB conversion into hydrogen-rich products using SCWG (temperature = 380 °C and pressure ≈ 240 bar). Lignocellulosic model compounds (xylan, cellulose, and lignin) were used to study the degradation patterns and gas compositions under similar reaction conditions. The effect of the EFB/water ratio and the SCWG reaction time on the composition of the product gas was examined. Carbon gasification does not improve with increasing EFB/water ratio as well as with increasing reaction time caused by the thermally stable tar formation during reaction. The hydrogen concentration was found to be increased with reaction time along with raising the EFB/water ratio to 0.3 g (3.75 wt%). In addition, the possibility of using palm oil mill effluent as a reaction medium in comparison to deionized water was analyzed.

1. Introduction

Biomass is the fourth largest primary energy resource available after coal, crude oil, and natural gas that can be used as an alternative in the current energy crisis [1]. In conjunction with environment deterioration and fluctuating crude oil price, the development of cheap and clean energy sources as sustainable energy resources are prioritized to overcome fossil-fuel dependency. Agricultural residues are potential biomass wastes that can be used for energy conversion based on advantages such as they are cheap, sustainable, and could solve waste disposal problems. Palms are among the most successful commercial crops in the Southeast Asian region (Malaysia, Indonesia, and Thailand), where the tropical climate and fertile land support vast plantation areas for palm cultivation and high oil production. A growing demand for palm oil utilization, mainly as edible oil, and other oil-related industries such as oleochemical and biodiesel production boost commercial oil production. Malaysia is the second largest palm oil producer in the world with an overall production capacity of 18.8 million tonnes of crude palm oil from its 5.08 million hectares of cultivation [2]. The growing palm oil industry produces a large amount of byproducts from the extraction mills including empty palm fruit bunches (EFBs), fibers, shells, and palm oil mill effluents (POMEs). Generally, solid wastes are used as a boiler fuel to produce electricity and the required steam for the oil extraction process [3]. The high moisture content of EFBs (65%) is a major drawback of the material for downstream processes (combustion, gasification, and pyrolysis), and dry-

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ing is essential in order to achieve a minimum moisture level <10% [4,5]. POME is the effluent water discarded from oil extraction mills, which contains about 95–96% water with suspended solids, oils, and grease [6]. EFBs are rich in inorganic content, such as K_2O, SO_3, CaO, SiO_2, Cl, Fe_2O_3, P_2O_3, MgO, and some trace elements that are returned to the soil as organic fertilizer through the mulching process [3]. However, high transportation costs from the mills to the plantation fields, distribution hurdles on uneven field's topography, and lower benefits compared to the cost of mulching makes the process inefficient [7]. Conventionally, in Malaysia, POME is treated through a ponding system, which comprises a de-oiling tank, acidification ponds, as well as anaerobic and aerobic ponds, in which the quantities of ponds are based on the capacity of the mill [8,9]. Anaerobic degradation of POME under bacterial digestion releases a huge amount of biogas (CH_4 and CO_2) to the atmosphere, which contributes to global warming [8]. In Malaysia, almost 50% of POME treatment plants fail to capture the biogas, owing to inadequate implied systems. There are several technical barriers that have been identified in upgrading the current systems, such as high investment cost, inefficient technology, lack of law enforcement, and the uncertainty surrounding the biogas composition, as the POME properties vary seasonally [10]. Thus, our investigation focused on hydrogen production using palm waste materials through supercritical water gasification (SCWG). SCWG is an emerging technique that is a suitable for the conversion of high-moisture-content biomass into hydrogen-rich product gases [11]. There are specific characteristics of water under supercritical conditions ($T \geqslant 374$ °C and $P \geqslant 220$ bar), such as a low dielectric constant, thermal conductivity, ion product, viscosity, and density, making it an excellent reaction medium for biomass conversion [12]. Furthermore, Kelly-Yong et al. [13] have postulated the potential of palm biomass utilization in SCWG and have theoretically proven the feasibility of the process to obtain hydrogen as a renewable energy source. Hence, EFBs have been selected as a feedstock, and we are unaware of any similar studies of its utilization in combination with the SCWG reaction. In addition, we investigate the possibilities of POME conversion through SCWG as feedstock in comparison to water for EFB gasification.

2. Materials and methods

2.1. Materials

The EFBs were obtained from local palm oil extraction mills in Johor, Malaysia. The EFBs were dried and ground to particle sizes <250 μm. All lignocellulosic model compounds (xylan-X4252, cellulose-C6288, and lignin-370959) were purchased from Sigma Aldrich. Xylan was used as a model compound to replicate hemicellulose. The POME was collected from a ponding tank that stores liquid wastes discarded from the mill sites. Demineralized EFBs were prepared by washing with deionized water for 20 h before they were dried overnight in oven [14].

2.2. Methods

The SCWG reactions were performed in a custom-made reactor system (Fig. 1) using stainless-steel tubing (SS-810-6-2, outside diameter = 1/8 in.) connected with one-way valves. The reactor cells for the experiments were made from stainless-steel tubing (SS-t8-049-6ME) with an outside diameter of 1/2 in. and a total volume of 13 mL. The reactor system was fixed with a Swagelok transducer (limitation 0–400 atm) in order to measure the pressure inside the reactor cell. The product gases were trapped and collected using a 1 mL luer lock gas-tight syringe. The collected gas was injected into a gas chromatograph with a thermal conductivity detector (GC-TCD) equipped with Porapak Q and Mole Sieve columns for CO_2, H_2, CH_4, and CO detection.

2.3. Experimental

The experiments were carried out using 0.3 g of the feedstock (EFBs/lignocellulosic model compounds) loaded into the reactor cell followed by 8 mL of deionized water. The cell was connected to the reactor system and placed inside the GC oven. The oven temperature was increased from 30 to 380 °C, ramping at 10 °C min^{-1}, and the reaction time was fixed at 8 min. After completion of the reaction, the reactor was cooled and both valves were opened intermittently to release the product gas for collection in a gas-tight syringe. Then, the residues from the reactor cell were collected and dried for Fourier transform infrared (FTIR) analysis. A PerkinElmer FTIR spectrometer, model 100 series, was used (sample preparation UATR-Universal Attenuated Total Reflectance Sensor) to study the functional-group cleavages of the feedstock before and after the SCWG reaction. The lignocellulosic model compounds were used as a feedstock for the SCWG reaction in order to imitate the individual components of real biomass, so that we could study the decomposition patterns under our experimental setup. The effects of EFB loading and the reaction time on the product gas composition and carbon concentration in gas phase is studied. In addition, the possibility of using POME as a reactant medium was studied in terms of the SCWG reaction in comparison to deionized water.

3. Results and discussion

3.1. SCWG of EFBs and lignocellulosic model compounds

EFBs are lignocellulosic compounds that are composed of hemicellulose, cellulose, and lignin, with small amount inorganic substances. The behavior of each constituent under SCWG conditions was studied using pure hemicellulose (xylan), cellulose, and lignin. The product gas (H_2, CO_2, CH_4, CO) distributions of the reactions enabled us to predict the decomposition patterns and possible reaction mechanism of the model compounds. Xu and Donald [15] postulated that the biomass decomposition under supercritical water involved in a series of complex reaction pathways, as stated in Eq. (1):

$$\text{Biomass} \xrightarrow[\text{Hydrolysis}]{\text{Solvolysis}} \text{Intermediates} \xrightarrow[\text{Fragmentation}]{\text{Cracking}} \text{Gaseous products} \quad (1)$$

Intermediate compound degradations were predicted based on following reactions mechanisms, such as decarboxylation (Eq. (2)), decarbonylation (Eq. (3)), and fragmentation/cracking (Eq. (4)):

$$\begin{aligned} &R-C(O)OH \text{ or } R-C(O)O-R' \\ &\leftrightarrow R-H+CO_2 \text{ or } R-R'+CO_2 \end{aligned} \quad (2)$$

$$\begin{aligned} &R-C(O)H \text{ or } R-C(O)O-R' \\ &\leftrightarrow R-H+CO \text{ or } R-R'+CO \end{aligned} \quad (3)$$

$$\begin{aligned} R-CH_2-CH_2-CH_3 \quad &\leftrightarrow R-H+C_3H_6 \text{ or } R-CH_3 \\ &+C_2H_4 \text{ or } R-CH_2 \end{aligned} \quad (4)$$

*where R and R' are possible functional groups.

The results of the ultimate analysis and the calculated theoretical moles of feedstock used in the experiments are given in Table 1. The product gas concentrations for each compound after the SCWG reaction are presented in Fig. 2. Variation in the product gas concentration shows that intrinsic properties such as the thermal stability, functional groups, and chemical linkages in the model