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Torrefaction of oil palm kernel shell in the presence of oxygen and carbon dioxide

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HIGHLIGHTS

- Torrefaction of palm kernel shell was done under N_2, O_2 and CO_2 atmospheres.
- The severity of torrefaction was in the order of $O_2 > CO_2 > N_2$.
- The van Krevelen plots showed the common trend among the three different atmospheres.
- The oxidative torrefaction rate was extracted from the overall torrefaction rate.
- The morphological changes were distinctive among the three different atmospheres.

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ABSTRACT

Torrefaction of oil palm kernel shell (PKS), one of the biomass residues from the palm oil industry, was carried out in a fixed-bed tubular reactor in the presence of oxygen and carbon dioxide at concentrations ranging from 0 to 15 vol.% (nitrogen balance). The effects of oxygen and carbon dioxide concentrations (0, 3, 9, 12, and 15 vol.%), temperature (493, 523, and 573 K) and biomass size (0.375 mm and unground) on the solid phase conversion, the energy yield and properties of torrefied biomass were investigated. The solid phase conversion increased with increasing temperature and oxygen or carbon dioxide concentration, but was not significantly affected by biomass size. The energy yield decreased with increasing oxygen or carbon dioxide concentration, but was still more than 70%. The extent of torrefaction was in the order of oxygen > carbon dioxide > nitrogen. The 'oxidative torrefaction' rate was extracted from the overall reaction rate. The increase in the oxidative torrefaction rate caused by oxygen was higher than that caused by carbon dioxide. Scanning electron microscope observations of the morphology of the PKS showed distinctive differences for torrefaction in nitrogen, oxygen, and carbon dioxide.

1. Introduction

Lignocellulosic biomass is one of the most abundant biomass resources on earth and can be used as a feedstock for preparing fuels and chemicals. Some of these technologies are still under development. Because of its availability in Malaysia, oil palm residues are considered to be the best biomass source [1]. In 2013, Malaysia was the second largest producer of palm oil, producing 19.8 million tons, or 33.4% of the total world supply. Indonesia was the world's largest producer of palm oil, producing 31.0 million tons of oil, or 52.2% of the total world supply [2]. In 2013, productive oil palm plantations in Malaysia covered 5.23 million hectares, a 3.0% increase from 2012 when productive oil palm plantations covered 5.08 million hectares [3]. Types of biomass produced by the oil palm industry include empty fruit bunches (EFB), mesocarp fiber, palm kernel shells (PKS), fronds, and trunks. EFB, mesocarp fiber, and PKS are generated at palm oil mills, whereas fronds and trunks are generated at the plantations [4]. The total amount of this biomass produced annually is 17 Mtoe (million tons of oil equivalent) [1]. Since the current primary energy supply in Malaysia is approximately 70 Mtoe, the total oil palm biomass energy potential of 17 Mtoe may contribute considerably to decreasing the consumption of fossil fuels, such as natural gas, coal, and oil. However, to use biomass waste for energy efficiently, the following drawbacks, compared with the situation for fossil fuels, must be overcome.

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(1) Higher energy consumption during collection
(2) Heterogeneous and uneven composition
(3) Lower calorific value
(4) Higher cost of transportation due to its lower energy density
(5) High ash content
(6) Reduction in quality by biodegradation

A number of options exist to reduce these drawbacks. The most common techniques are pelletization, liquefaction, and gasification of the biomass. Pelletization involves drying, chipping, grinding, and pelletizing lignocellulosic biomass. Pelletization is the cheapest option, but its disadvantages include lower heat values and quality deterioration by moisture (pellet disintegration, moss growth, or bioorganic decomposition). Recently, treatment of biomass at a low temperature of 473–573 K under an inert atmosphere was found to improve the energy density and shelf life of the biomass. This treatment is called 'torrefaction' and has been widely researched for wood and grass biomass over the past few years [5–16]. Torrefaction studies have largely been conducted on wood and grass biomass, including wood dust [10–14,16], beech [6,7], eucalyptus [5,11], willow [6–9,13], larch [6,7], bamboo [13] and canary grass [8].

Although torrefaction is one of the most promising methods for improving lignocellulosic solid fuels, the procedure requires thermal energy and an inert atmosphere. Could flue gas from burners be used, inert gas and a considerable quantity of energy would be saved, making the process more economically viable. In light of this, we have examined the effect of an oxygen atmosphere on the solid and energy yields for EFB torrefaction [17]. Following the first study of oxidative torrefaction, several papers have been published on torrefaction under an oxygen atmosphere [18–22].

Rousset et al. [18] torrefied a large piece ($10 \times 40 \times 80$ mm) of eucalyptus under 2–21 vol.% oxygen at 513 and 553 K in a fixed bed reactor, and reported that the solid and energy yields decreased considerably only at 553 K. They did not report results for torrefaction under a nitrogen atmosphere. Lu et al. [19] torrefied oil palm fiber and eucalyptus in nitrogen and air at 523–623 K in a fixed bed reactor, and found that torrefaction in air resulted in lower solid and energy yields than in nitrogen. Wang et al. [20] carried out torrefaction experiments using spruce sawdust in 0–21 vol.% oxygen at 533–573 K using a thermogravimetric analyzer and a fluidized bed, and concluded that the presence of oxygen results in slightly poorer torrefaction. Chen et al. [21] torrefied five types of biomass, oil palm fiber (<30 mm), coconut fiber (<30 mm), eucalyptus ($15 \times 10 \times 5$ mm) and *Cryptomeria japonica* ($15 \times 10 \times 5$ mm), in 0–21 vol.% oxygen at 573 K in a fixed bed reactor and drew a similar conclusion to Wang et al. [20]; that is, non-oxidative torrefaction produces better results than oxidative torrefaction. Chen et al. also investigated the effect of the superficial velocity of the torrefaction gas on the performance of oxidative torrefaction [22].

All of the findings of the above-mentioned studies were reported in relatively quick succession. However, knowledge of torrefaction of agricultural residues under an oxygen atmosphere is still insufficient. There has also been no comprehensive study of torrefaction under oxygen and carbon dioxide, which are the two major components in flue gases. Therefore, oxidative torrefaction must be studied further to find out whether burner flue gases can be used for torrefaction of biomass from the palm oil industry. Investigating how carbon dioxide affects the torrefaction process is of particular importance. Only one paper has been published on torrefaction under carbon dioxide to date and only pure carbon dioxide was used [23], whereas concentrations of carbon dioxide in burner flue gases typically range from 6 to 14 vol.% [24].

In this paper, torrefaction of PKS was carried out in a fixed-bed tubular reactor in the presence of oxygen and carbon dioxide from 0 to 15 vol.%. The effects of oxygen and carbon dioxide concentrations, temperature, and biomass size on the solid phase conversion, energy yield, and properties of torrefied biomass were investigated.

2. Experimental

2.1. Biomass samples

PKS was collected from an oil palm plantation at Bota in Perak, Malaysia. After drying at 378 K for 24 h, the PKS was ground using a mechanical grinder. The ground powders were sieved into 0.25–0.50 mm powder, which has a nominal average diameter of 0.375 mm. The dried unground and ground sieved particles were used in the present study. The fundamental properties of the PKS are summarized in Table 1.

The ground and sieved particles (0.375 mm in average diameter) were used to examine torrefaction in a biomass size range free from heat and mass transfer effects. By comparing the results from unground and 0.375 mm particles, the extent of the heat and mass transfer effects can be determined.

2.2. Torrefaction experiment

Torrefaction of the PKS biomass samples was carried out at an ambient pressure using a vertical tubular reactor made of stainless steel, with an internal diameter of 0.028 m. Approximately 3 g of PKS was placed in the reactor. After flushing the reactor with torrefaction gas for 15 min, the temperature of the reactor was increased to the desired level (493, 523, or 573 K), at a constant rate of 10°/min, using an electric furnace surrounding the reactor. The temperature range of 493–573 K was chosen because the selective decomposition of hemicelluloses occurs between 473 and 573 K. The minimum temperature of 493 K was selected because the torrefaction rate below 493 K would be too low. After torrefaction for 30 min, the heater was turned off and the reactor was left to cool to ambient temperature. The torrefied sample was then recovered, weighed, and stored in an airtight vessel until it was characterized. Throughout the procedure, 30 mL/min of torrefaction gas was passed through the reactor. The concentration of oxygen or carbon dioxide in the gas was adjusted to 0, 3, 9, 12, or 15 vol.%, to investigate the effect of oxygen or carbon dioxide concentration on torrefaction. The concentration ranges of oxygen and carbon dioxide were chosen because flue gases from burners and boilers contain 6–14 vol.% oxygen and 1–13 vol.% carbon dioxide [24]. The torrefaction gas was prepared by mixing nitrogen and compressed air or carbon dioxide under ambient pressure.

Table 1
Proximate, elemental, calorific and fiber analyses of palm kernel shell used in this study.

Proximate analysis (wt.%)	
Moisture	10.0
Volatile matter	70.5
Fixed carbon	18.7
Ash	0.84
Elemental analysis (wt.%)	
C	50.62
H	6.02
N	0.37
O	42.15
HHV [MJ/kg]	20.1
Chemical composition analysis (wt.%)	
Hemicellulose	18.2
Cellulose	33.2
Lignin	48.6