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Characteristics of products from the pyrolysis of oil palm fiber and its pellets in nitrogen and carbon dioxide atmospheres

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The present study focuses on the pyrolysis characteristics of OPF (oil palm fiber) and OPFP (oil palm fiber pellet) in N_2 and CO_2 to evaluate the impacts of biomass pattern and carrier gas on the three-phase products. Three different reaction temperatures of 400, 450, and 500 °C along with 30 min pyrolysis are considered. The results indicate that OPFP pyrolysis gives a higher liquid yield when compared to OPF pyrolysis, and the liquid yield using CO_2 as a carrier gas is higher than that using N_2. The influences of carrier gas and biomass pattern on the components in bio-oils are not profound. The deoxygenation and dehydrogenation mechanisms on solid biomass are obviously exhibited, and the latter is more pronounced than the former. The higher heating values of OPF and OPFP from pyrolysis are intensified up to 39 and 24%, respectively. The CO_2 and CO concentration distributions suggest that the most drastic pyrolysis reaction develops at 7–9 min. On account of more energy required for breaking methoxyl groups, CH_4 formation is later than CO and CO_2 formations. In summary, OPFP pyrolyzed in a CO_2 environment is a feasible operation for producing bio-oils, thereby saving facility space and achieving CO_2 utilization.

1. Introduction

The development of renewable and alternative fuels has attracted much attention lately because it is considered as a crucial remedy of decreasing fossil fuel reserves and deteriorating atmospheric greenhouse effect [1]. During the last three decades, more than half of the global renewable energy research has been focused on bioenergy (56%), followed by solar energy (26%), wind power (11%), geothermal energy (5%), and hydropower (2%) [2,3]. This clearly elucidates the potential of bioenergy development. Biomass can be consumed for the production of heat, power, and transportation fuels [4]. However, biomass is relatively difficult to be handled, transported, stored, and utilized in its original form because of its high moisture content, low grindability, irregular shape and size, and low bulk and energy density [5,6].

Biomass pelletization is a process applying a mechanical force to compact biomass residues or wastes into uniformly sized solid particles [6]. Biomass pellets possess the merits of lower moisture content, higher calorific value, uniform shape, and clear burning. In addition, the bulk density of biomass pellets is larger than its raw biomass by factors of 4–10, rendering the easier handling and transport of the pellets [5,7]. However, pelletization is an expensive process. In the United States, it costs about $50 for producing one tonne wood pellets, excluding raw material cost [8]. The main reason for pellets widely used in industry is due to its high bulk density and low moisture content. The savings from long distance transportation of pellets can offset the high pelletization cost.

Pyrolysis is a thermal conversion process in which biomass is thermally degraded at the temperature range of 400–800 °C [9] and in the absence of oxidants or in a nitrogen environment [10,11]. Both slow pyrolysis and fast pyrolysis have been widely applied in industry. Compared to fast pyrolysis which is featured by a high heating rate (10–600 °C s^{-1}) and a short residence time of hot vapor (1–3 s), slow pyrolysis is characterized by a low heating rate (5–10 °C min^{-1}) and a long residence time of hot vapor (10–30 s) [3]. Due to the low heating rate in slow pyrolysis, the reaction rate of biomass is also slow. In contrast to fast pyrolysis, a longer residence time of hot vapor in slow pyrolysis results in larger portions of char and non-condensable gas in the products. After undergoing pyrolysis, biomass is converted into bio-oils, biochar, and non-condensable gases. Pyrolysis has been considered as a promising technology to develop bioenergy from biomass in an

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eco-friendly and cost-effective manner. Bio-oils, which potentially present valuable liquid fuels, are the main product in pyrolysis. Alkanes, aromatic hydrocarbons, phenol derivatives, and little amounts of ketones, esters, ethers, sugars, amines, and alcohols are contained in bio-oils [2]. Bio-oils can be utilized as the sources of chemical production such as phenols, organic acids, oxygenates, etc., and in boilers and engines for heat and power production [1]. They can also be used as the transportation fuels [12], and even be upgraded by catalysts (e.g., zeolites) to produce high-performance fuels such as motor fuels and jet fuels [13,14]. With regard to biochar, it can be burned directly as a solid fuel. Biochar in soils can be considered as an “electron shuttle” which facilitates the transfer of electrons to soils denitrifying microorganisms, and promotes the reduction of N_2O to N_2 [15]. Therefore, its addition into soils can increase nutrient and water retention, and thereby help improve the growth of crops [16]. Alternatively, biochar can be employed as a feedstock to produce activated carbon, fertilizers for carbon sequestration, and reducing agents for ironmaking [17].

When biomass pellets are pyrolyzed, one of the potential benefits is the savings by increasing in-plant equipment throughput. For example, the high bulk density of pellet allows a larger single train pyrolyzer design where the feeding system and reactor could be the bottleneck using low bulk density biomass. In this case, the equipment cost will be reduced significantly due to the economy of scale [8]. In the last decade, a number of studies concerning the thermal behaviors, reaction mechanisms, and kinetics of biomass pellet pyrolysis have been conducted. Jong et al. [18] studied the pyrolysis behaviors of wood and Dutch MG pellets using a thermogravimetric analyzer accompanied by a Fourier transform infrared spectroscopy (TG-FTIR). They found that tar release appeared to increase with increasing heating rate, but light gaseous species, mostly CO, CO_2, and CH_3CHO, showed an adverse dependence on the heating rate. The yields of char, CH_4, CH_2O and CH_3OCH_3 were independent of the heating rates; HCN and HNCO were the major N-products, and the NH_3 fraction was minor. Chandrasekaran and Hopke [19] utilized a TG (thermogravimetric) to investigate the thermal degradation of grass pellets in inert and oxidative atmospheres. They found that the biomass decomposition with 40–75% conversion occurred during pyrolysis, and the activation energy was 314 kJ mol^{-1}. The conversion in air was between 30 and 55% and the activation energy was 556 kJ mol^{-1}. They also pointed out that the heating rate had a substantial effect on mass loss and mass loss rate; specifically, the decomposition curve shifted toward higher temperature ranges when the heating rate increased.

Erlich et al. [20] discussed the effects of sugarcane bagasse pellet size and origin on the thermal characteristics of pellets at various temperatures (600, 750, and 900 °C), gas flow rates (4, 7, and 10 L min^{-1}), and O_2 concentrations (5, 10, and 15 vol%) in N_2. They reported that the char yield of larger pellets with high ash content was independent of the treatment conditions; smaller pellets gave better mechanical stability of char, but lower reactivity. They [21] further studied the pyrolysis of sugarcane bagasse and wood pellets, and described that the char density decreased during pyrolysis to a minimum at around 450 °C, followed by increase with continued heating. Zhou et al. [22] investigated the pyrolysis of pelletized municipal solid wastes, and showed that the char yield of the pellets dropped significantly with increasing temperatures, especially at 450–700 °C, due to the high content of plastics with high decomposition temperatures. Liu et al. [23] focused on the effects of carbonization temperature and time upon the properties of bamboo pellets. Their results showed that the effect of carbonization temperature on mass loss, pellet absorption, bulk density, pellet density, gross calorific value, and combustion rate were significant at certain conditions, whereas the influence of carbonization time on all the properties was slight. The above reviewed literature of biomass pellet pyrolysis was performed under conventional heating. A number of studies of biomass pellet pyrolysis along with microwave-assisted heating have also been reported [24–27]. The relevant literature of biomass pellet pyrolysis at various operating conditions is summarized in Table 1.

Despite numerous studies conducted on the thermal pyrolysis behaviors of biomass pellet, available data on the difference of the pyrolyses of raw biomass and its pellets and the influence of reaction atmosphere (or carrier gas) on pyrolysis remain insufficient. OPF (Oil palm fiber) is a common and abundant agricultural waste [28]. When OPF is pelletized to OPF pellets OPFP (oil palm fiber pellet), the usage of the pellets in pyrolysis can significantly reduce the reactor volume and thereby the facility cost. In recent years, research on pyrolysis processes has been conducted using several types of reactors heated by conventional or microwave-assisted heating sources (e.g., electric, gas, or microwave heaters), namely, fluidized bed reactors, rotating cone reactors, melting vessels, blast furnaces, tubular or fixed bed reactors [29,30]. In

Table 1
A list of literature concerning the pyrolysis of biomass pellets.

Biomass	Reactor	Carrier gas	Temp. (°C)	Objective	Reference
Miscanthus Giganteus and wood	TG-FTIR	He	80–900	Pyrolysis of Miscanthus Gigcanteus and wood pellets by TG-FTIR, including product yields and kinetic analysis.	[18]
Bagasse	Fixed bed	N_2/O_2	600–900	Effects different conditions (various temperatures and gas flow rates with different N_2/O_2 ratio) on thermochemical characteristics of bagasse pellets during pyrolysis.	[20]
Switch grass	TGA	N_2/Air	40–800	Thermal decomposition behaviors of switch grass pellets, including the activation energy and pre-exponential factors under volatilization, burning and slow oxidation.	[19]
RDF	Fixed bed	N_2	450–900	Pyrolysis behaviors of RDF, including the devolatilization rate, heat transfer properties, char properties, and swelling/shrinkage properties.	[22]
Bamboo	Microwave reactor	Air	180–220	Effect of carbonization conditions (temperature and reaction time) on the properties of bamboo pellets and to evaluate product properties.	[23]
Oil palm empty fruit bunch	Microwave reactor	N_2	110–790	Pyrolysis behaviors of the biomass in a multimode microwave (MW) system with and without the MW absorber, activated carbon.	[24]
Douglas fir sawdust	Microwave reactor	N_2	300–481	Direct catalytic cracking of biomass pyrolysis vapor into aromatics derived from Douglas fir sawdust pellets under microwave heating.	[26]
Torrefied Douglas fir sawdust	Microwave reactor	–	450	Effects of torrefaction conditions on biofuel production during pyrolysis of Douglas fir sawdust pellet under microwave heating.	[25]
Douglas fir sawdust	Microwave reactor	N_2	400	Effects of different activated carbon catalysts on product yield and chemical compositions of upgraded pyrolysis oils during microwave pyrolysis of Douglas fir sawdust pellets.	[27]