



Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire



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ABSTRACT

This study optimized the use of biomass waste to generate fuel through co-pyrolysis. In this paper, the effects of stepwise co-pyrolysis temperature and different ratios between palm shells and scrap tires in feedstock were studied to observe any improvements in the quantity and quality of the liquid yield and its byproduct. The ratio of palm shells and scrap tires varied at 100:0, 75:25, 50:50, 25:75, and 0:100. The experiment was conducted in a fixed-bed reactor. The study was divided into two scenarios. The first scenario was performed at the optimum temperature of 500 °C with a reaction time of 60 min. In the second scenario, the temperature was set at 500 °C for 60 min before the temperature was increased to 800 °C with a high heating rate. After the temperature reached 800 °C, the condition was maintained for approximately 45 min. Results showed that an increase in the liquid and gas yields was achieved when the temperature increased after optimum conditions. Increased yield was also obtained when the proportion of scrap tire was increased in the feedstock. Several other important findings are discussed in this paper, including the phases of pyrolysis oil, features of the liquid product, and characteristics of the byproducts. All products from both scenarios were analyzed by various methods to understand their fuel characteristics.

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1. Introduction

Lignocellulosic or wood-based biomass is a major renewable energy source available worldwide, which can be used to produce oil through pyrolysis. Oil from this process has potential use as fuel or feedstock for various commodity chemicals [1]. Numerous types of lignocellulosic biomass have been successfully pyrolyzed by researchers to obtain liquid fuel. However, the fuel characteristics of oil from lignocellulosic biomass remain lower than those of fossil fuel because the liquid product contains high levels of oxygenated compounds, which can lead to low calorific values, corrosion problems, and instability [2]. A large amount of oxygen content is present usually around 40–50 wt% in the pyrolysis liquid [3]. For quality improvement, the liquid needs to be upgraded by an additional upgrading process. Catalytic cracking and hydrodeoxygenation are the most commonly used upgrading processes [4]. The upgrading process involves the addition of a catalyst, solvent, and large amount of hydrogen [5], which potentially can cost more than the oil itself. Thus, a novel approach is necessary to overcome this

issue and make the oil from lignocellulosic biomass more competitive and reliable as a renewable fuel.

Co-pyrolysis is a technique with design and operation simplicity, which is suitable for the production of high-grade pyrolysis oil. This method can be run without the presence of any catalysts or solvents and with free hydrogen pressure. This process involves two or more different materials as feedstock. The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. Basically, the process is performed in a closed reactor system with moderate operating temperatures and the absence of oxygen. Most of the studies were performed using a fixed-bed reactor for the purpose of liquid production. According to Fei et al. [6], the extent of contact between the used feedstock is an important factor to achieve the synergistic effect; therefore, the synergistic effect is more favorable for the pyrolysis operation carried out on a fixed-bed reactor than on a fluidized-bed reactor. As a general rule, temperature in co-pyrolysis can be adjusted within the range of 400–600 °C to maximize liquid yield production. Compared with normal pyrolysis, co-pyrolysis can produce extra liquid yield, typically between 1.42 and 22 wt% [7]. Moreover, it is important to highlight the salient features of co-pyrolysis process being regarded as a promising, economic and environmental friendly technology for both the energy production and waste remediation [8].

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Nomenclature

BP	block polypropylene	N ₂	nitrogen flow rate (L/min)
C	carbon (wt%)	O	oxygen (wt%)
CH ₄	methane	PS	polystyrene
d	day	S	sulfur (wt%)
FTIR	Fourier transform infrared	s	second
h	hour	TGA	thermogravimetric analysis
H	hydrogen (wt%)	X ₁	mass of the desired product (g)
H ₂	hydrogen gas	X ₂	initial weight of the raw material (g)
HHV	high heating value (MJ/kg)	Y _p	product yield (wt%)
min	minute		
N	nitrogen (wt%)		

The research on co-pyrolysis process is generally focused on the study of synergistic effects or the interactive effects between the feedstock used. All improvements in oil quality and quantity during co-pyrolysis occurred through synergistic effects. The positive or negative synergy depends on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors [9]. However, the type of blending feedstock has a significant influence among these factors; thus, synergistic effects on co-pyrolysis can be complicatedly varied based on the feedstock [6]. Onal et al. [10] argued that the synergistic effect in co-pyrolysis is a complex phenomena because of various chemical species. According to the authors, several reaction radicals can be induced during co-pyrolysis of high density polyethylene and biomass, including initiation, formation of secondary radicals [depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffin and dienes), and isomerization via vinyl groups], and termination by disproportionation or recombination of radicals.

Many researchers have studied co-pyrolysis for producing pyrolysis oil, and their results are encouraging. Most of them focused on the co-pyrolysis of lignocellulosic biomass mixed with plastic. The addition of plastic during the pyrolysis of lignocellulosic biomass can improve the quantity and quality of the oil product. Abnisa et al. [11] studied the co-pyrolysis of palm shells and polystyrene (PS) to obtain high-grade pyrolysis oil. Their results showed that by adding the same weight ratio of PS during the pyrolysis of palm shell, the oil yield increased to approximately 61.63 wt%, whereas the pyrolysis of palm shell alone yielded oil at approximately 46.13 wt%. The high heating value (HHV) of the oil product was obtained (i.e., approximately 11.94 MJ/kg) for the pyrolysis of palm shells alone. However, the pyrolysis of palm shells mixed with PS raised the HHV of oil to 38.01 MJ/kg. Jeon et al. [12] studied the co-pyrolysis of wood chips with block polypropylene (BP). Their study was conducted in a fixed-bed reactor, and the temperature was set at 500 °C for the pyrolysis of the wood chip and BP mixture. The results of their experiment showed that the liquid yield reached 39.30 and 63.10 wt% when the BP mass was 0% and 50% of the mixture, respectively. The authors also noted that the liquid produced from wood chips alone had an HHV of 19.90 MJ/kg, whereas this value increased to 45 MJ/kg when BP mass accounted for 50% of the mixture. In addition, Cornelissen et al. [13] reported the reduction of water content in pyrolysis oil produced via the flash co-pyrolysis of biomass with polylactic acid. Berruoco et al. [14] studied the co-pyrolysis of high density polyethylene mixed with sawdust in a fluidized bed reactor. The authors found a decrease in the concentration of oxygenated and aliphatic compounds in liquid fraction.

Tires are another material with characteristics similar to those of plastics. This material can be added during the pyrolysis of lignocellulosic biomass to obtain high-grade pyrolysis oil. Pyrolysis of tires alone can produce the liquid yield of up to 63 wt%, depending upon the operating conditions applied [15]. A large majority of oils produced have energy values in the range of 28–46 MJ/kg [16]. Oil containing very low levels of oxygen has a high H/C atomic ratio (approximately 1.5) and consists of aliphatic and aromatic compounds [17]. Consequently, the presence of tires during the pyrolysis of lignocellulosic biomass can have a positive contribution to the heating value through synergy. However, studies that focus on the pyrolysis of lignocellulosic biomass/waste tire blends are currently limited [7]. Therefore, some effort should be made to obtain a clear overview of synergistic effects during the co-pyrolysis of lignocellulosic biomass and waste tires.

Limited examples of the co-pyrolysis study of biomass and waste tires can be found in the literature. Martínez et al. [18] studied the co-pyrolysis of pine wood chips with scrap tires in a fixed bed reactor and a continuous auger reactor, while Uçar and Karagöz [19] performed the co-pyrolysis of pine nut shells with scrap tires at different blend ratios. Both studies applied the same procedure of pyrolysis process, where the samples were placed into the reactor and the reactor was subsequently heated from ambient temperature to 500 °C. The studies were emphasized on the product distribution and characterization of all pyrolysis products at reaction temperature of 500 °C. However, no literature was reported about the possibility of fuel recovery after optimum temperature achieved. This issue is interesting to investigate since the co-pyrolysis process uses two materials as feedstock which have different characteristics of thermal properties. Hence, the use of stepwise temperature technique in the co-pyrolysis process seems reasonable to achieve this objective.

This study also tried to investigate the production of organic and aqueous phases during the co-pyrolysis. A study performed by Martínez et al. [18] found that a single liquid phase was obtained for all the biomass/waste tire blends. The authors assumed that radical interaction during the pyrolysis reaction leads to a new bio-oil that avoids phase separation. In another study, Cao et al. [20] reported that the liquid produced from co-pyrolysis of biomass and tire contained two layers: an aqueous layer and an oil layer, which is also observed in the present study. However, there was no detailed discussion provided in their report. In order to obtain a clear insight, the phenomenon on the phase separation of liquid product is covered in this paper. Furthermore, the byproducts produced during this process were quantified. To evaluate the fuel quality, all the products were characterized by several analytic approaches.

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