



Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel

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HIGHLIGHTS

- The pyrolysis of palm shell mixed with polystyrene was performed.
- The maximum of pyrolytic liquid obtained was 68.3 wt% at an optimum process condition.
- The polynomial model fits well to predict the response with high determination coefficients of R^2 (0.972) and Q^2 (0.610).
- The HHV and composition of the pyrolytic liquid were very close to those of conventional fuel oil.

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ABSTRACT

The mixtures of palm shell and polystyrene waste were pyrolyzed to obtain a high-grade of pyrolytic liquid that potentially could be used as a fuel. Three effective parameters were chosen: temperature, feed ratio, and reaction time. The first phase of the study was a screening test to select the range point of each parameter that resulted in high production of liquid. The selected points were then used as reference data for an optimization study using response surface methodology. The maximum liquid yield of approximately 68.3% was obtained under optimum conditions, which were shown to be a temperature of 600 °C, a palm shell/polystyrene ratio of 40:60, and a reaction time of 45 min. The characterization results showed that the high heating value of the liquid obtained was 40.34 MJ/kg with a water content of 1.9 wt% and an oxygen content 4.24 wt%. The liquid mainly consisted of aliphatic and aromatic hydrocarbons.

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1. Introduction

The use of palm shell and polystyrene wastes for recovery of liquid fuel by co-pyrolysis is the key to overcoming environmental problems stemming from the high volume of palm shell waste generated by the oil palm industry. In 2007, a study reported that the amount is about 4.7 million tons [1] and then sharply increased up to 5.2 million tons in 2009 as reported by Mohammed et al. [2]. Most often it is left to decompose naturally, with only a fraction of it used to cover road surfaces in the plantation area or burned for steam generation [3,4].

Furthermore, a study estimated that well over 280,000 Tons of waste polystyrene is produced annually in Malaysia, most of it by food packagers [5]. The volume of polyethylene waste has increased as the product gets wider use because of its light weight, durability, and low cost [6]. Currently most of this waste is dumped in landfill sites, which will pose environmental and social problems as volumes accumulate [7]. Because polystyrene waste is not biodegradable, dumping in the landfill site is not an environ-

mentally friendly option. This study investigates the possibility of producing liquid fuel by co-pyrolysis of this waste material with the palm shell waste that is also causing environmental concerns.

Pyrolysis is one method used to recover potential energy in biomass and plastic wastes. This method is useful to break down the waste materials into three products; char, liquid, and gas in an inert environment. Pyrolysis is known to be an environmentally friendly method because no wastes are produced during the process.

The liquid is attractive because its properties show its potential for use as chemical feedstock or fuel. A number of studies of liquid fuel production have been reported at various scales and with varying success [8–10].

The yield of liquid from co-pyrolysis depends on the relationship of parameters set in the process. An optimization study was needed to adjust the parameters to maximize the production of liquid. One of the methods used to solve the optimization problem is to apply response surface methodology (RSM). The method is a statistical approach to analysis of the relationship between several selected variables and one or more defined responses [11]. RSM can include designing experiments from the collection of statistical techniques, building models, evaluating the effects of variables, and searching for the optimum conditions of variables for desirable

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responses [12]. The RSM has been widely used in optimization of pyrolysis process variables for several purposes [3,13–16].

In general, plastic has been recognized by many researchers as a good material to produce liquid fuel. Some studies showed that the pyrolysis of plastic resulted in high oil yield, particularly with polystyrene [17–21]. The authors also reported that the quality of the oil was acceptable for use as a fuel. It mainly consisted of aliphatic and aromatic hydrocarbons. Aliphatic hydrocarbons include alkanes, alkenes (paraffin, olefins) and alkanes (methane, ethane, heptane, octane, propane). Aromatic hydrocarbons include styrene, toluene, benzene, cumene, ethylbenzene, monocyclic aromatics (alkyl benzenes, alkyl toluene) and polycyclic aromatics (naphthalene, methylnaphthalene and ethylnaphthalene). On the other hand, the oil produced from biomass is found to contain high amounts of oxygen (35–40 wt%) and water (15–50 wt%) [22], which causes the liquid to have a low high heating value (HHV). Typically, the HHV of oil from biomass has been approximately 17 MJ/kg. In comparison, the oil produced from plastics has shown a HHV in the range of 37–40 MJ/kg [23].

In this work, co-pyrolysis of palm shell mixed with polystyrene waste was carried out to evaluate the yield and quality of liquid produced. The mass ratio between palm shell and polystyrene waste, temperature, and reaction time were chosen as independent variables. The process was optimized by using response surface methodology with the aim of maximizing liquid yield. The liquid obtained was tested for pH, density, viscosity, water content, elemental analysis, and Fourier transform infrared (FTIR).

2. Materials and experimental

2.1. Materials

The palm shell was collected from a local processing plant in Kuala Lumpur. The polystyrene waste was obtained from a local rubbish collection point. The palm shells were oven-dried at 105 °C for 24 h; the polystyrene was dried under the sun for several days. Then, both materials were ground to the desired size of 1–2 mm.

2.2. Experimental

The experiment was carried out by charging 100 g of feed into a stainless steel tubular reactor with an internal diameter of 5.0 cm and a length of 127 cm. The reactor was heated by an external vertical furnace. The temperature was monitored using a K-type thermocouple located inside the reactor. To minimize secondary reactions during the process, 2 L/min of nitrogen flow was applied for all experiments. The process flow of experimental work was presented in Fig. 1.

2.2.1. Screening point of parameters

The aims of the screening study were to obtain the reference data that were used later for the optimization study and also to observe the effect of each parameter on production of the liquid during co-pyrolysis. Three effective parameters were applied in this study with each parameter being evaluated at five different points. Each point was investigated to select the points that produced the largest volume of pyrolytic liquid.

The study was divided into several parts. The first part was to study the influence of reaction time on co-pyrolysis yields by applying the fixed parameters of feed ratio (50:50) and temperature (400 °C). The reaction times were varied from 15 to 75 min.

The second stage was to obtain the temperature effect. With the feed ratio fixed at 50:50 and reaction time constant at 30 min, the temperatures were varied in 100 °C increments from 300 to 700 °C.

The same procedure was followed to study the effect of feed ratio. The ratios of palm shell waste to polystyrene chosen were 80:20, 70:30, 60:40, 50:50 and 40:60. The yields of pyrolytic liquid, char, and non-condensable gas for all the experiments were calculated using the following equation:

$$\text{Yield of product} = \frac{\text{Desired product}}{\text{Total feed}} \times 100\% \quad (1)$$

2.2.2. Optimization study

The three points of each parameter that produced the highest yield of pyrolytic liquid were chosen for the optimization study. This study was designed to identify the variables that have the largest influence on the process and then develop the variables in the polynomial model. Therefore, RSM was used to determine the optimum and experimental design matrix in this study specified according to the central composite design (CCD) method. The variables and the experimental domain in this design are specified in Table 1. The CCD consists of axial points ($2n$), the number of independent variables (2^n) and replications of center points (n_c). Thus, the CCD in this study consists of $2n = 6$, $2^n = 8$ and $n_c = 6$, resulting in 20 experiments. The CCD matrix for varying three variables was constructed in Table 2. All experiments were performed randomly to reduce the effect of unexplainable variance in the observed response caused by unrelated variables. After running the experiments, the results were fitted to a quadratic polynomial model to predict the system response as given in the following equation:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i \times X_i + \sum_{i=1}^n \beta_{ii} \times X_i^2 + \sum_{i=1}^n \sum_{j>1}^n \beta_{ij} \times X_i X_j \quad (2)$$

where Y is the predicted response; n is the number of experiments; β_0 , β_i , β_{ii} and β_{ij} are regression coefficients for the constant, linear, quadratic and interaction coefficients, respectively; and X_i and X_j are the coded independent factors.

In this study, Design Expert software Version 8.0.0 (Stat-Ease, Inc., Minneapolis, USA) was used to design the experiments, do the analysis of variance (ANOVA) which includes the development of the quadratic model, and do the regression analysis and graphical analysis (three-dimensional response surface).

2.2.3. Characterization of pyrolytic liquid

The liquid products were produced with the optimum parameters conditions were characterized for viscosity, density, pH, water content, elemental analysis, and FTIR.

Viscosity is an important property in chemical process design. Viscosity data are essential for various heat transfer considerations, calculating pressure drop, distillation calculations and mixing system considerations. For fuels, viscosity data are used to evaluate the effect on pumping and injecting. In this study, measurement of viscosity was determined using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer model DV-II+Pro EXTRA). The measurement was taken at 50 °C with about 7 ml of sample required for the test.

One of the important physical characteristic of a material is density. Density describes the quantity of mass material divided by its volume. In this study, a 25 ml pycnometer was used to determine the density of the pyrolytic liquid. The measurement was started by carefully filling the liquid into the pycnometer and then measuring the mass. The density was determined by dividing the mass of pyrolytic liquid by the empty volume of the pycnometer. The analysis were conducted at 24 °C. The density calculation can be expressed by Eq. (3) where ρ is density, m is the mass of sample, and V is the volume.

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