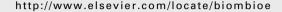


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Parametric study on the pyrolysis of manure and wood shavings

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ABSTRACT

In this work, a response surface methodology (RSM) was used to study the effects of temperature (A), feed rate (B) and gas flow rate (C) on the liquid yield, char yield and pH of the biocrude oil. Box—Behnken design was chosen and a total number of 15 experimental runs including 3 center runs were generated for the pyrolysis of a mixture of 50 wt.% layer manure and 50 wt.% loblolly pine wood shavings in a 50 mm bubbling fluidized bed reactor. The operational variables were as follows: temperature (400—550 °C), nitrogen gas flow rate (12—24 L/min), and feed rate (160—480 g/h). A second-order regression models were used to predict the responses. The analysis of variance (ANOVA) was performed with Minitab 16 software and the significant effect of the factors and their interaction effects were tested at 95% confidence interval. The biocrude yield was significantly influenced by temperature, feed rate and gas flow rate. Temperature was the only significant factor that influenced the char yield. Maximum biocrude yield (51.1 wt.%) was achieved at 475 °C with a feed rate of 480 g/h and a gas rate of 12 L/min. The lowest char yield (22.6 wt.%) was achieved at 550 °C, 320 g/h and 12 L/min and the biocrude had the highest pH (4.85) at 475 °C, 160 g/h and 24 L/min. The predictive models proposed agreed with the experimental values.

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1. Introduction

The potential of using poultry litter to produce biocrude oil and bio-char (fertilizer) is an attractive disposal technique. Due to the environmental problems associated with the traditional methods, the utilization of poultry litter as a source of biomass is a preferred approach. Pyrolysis technology converts poultry litter into biocrude oil, bio-char and gas [1–3]. The biocrude oil from poultry litter can be used as heating oil and the bio-char as an organic fertilizer. Among many factors and features that influence fast pyrolysis process, the choice of operating conditions affects the formation of the pyrolysis products mentioned above. Studies on the effect of operating conditions and reactor configurations on pyrolysis have been reported in literature [4–18]. Research on woody biomass

pyrolysis has shown that for a high liquid yield, high temperature, high heating rate, and short gas residence time are required and for high yield of char, low temperature and low heating rate are necessary. To maximize the yield of gas product, high temperature, low heating rate and long gas residence time are preferred [19–22].

Woody biomass is mainly composed of structural constituents (hemicellulose, cellulose, and lignin) and minor amounts of other organics and inorganics. In contrast, poultry litter has in addition to woody structural constituents, high amount of ash (over 22%) and protein (over 28%) which also accounts for the high amount of nitrogen (3–4.5%) [1–3,23,24]. As a result, woody biomass and poultry litter degrade at different rates, mechanisms and pathways [23–25]. When wood is completely pyrolyzed, the hemicellulose component breaks down first

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between 200 and 260 °C, and cellulose follows at 240-350 °C. with lignin being the last component to decompose over a wider temperature range of 280-500 °C [26-28]. Kim and Agblevor [23] studied the kinetic parameters during the pyrolysis of wood chips, broiler and flock litters. Among their findings, they establish from the thermogravimetric curves of the broiler and flock litters that, manure (protein) and lignin degraded between 375 and 500 °C. Another pyrolysis kinetic study on poultry litter by Singh et al. [24] found that the presence of inorganics such as sodium and potassium had catalytic effect on the thermal degradation of cellulose and hemicellulose. Additionally, the rate and extent of decomposition of cellulose, hemicellulose, lignin and protein (manure) depends on the pyrolysis process parameters [25]. Hence, the yields and chemical composition of pyrolytic products from a poultry litter mixture of manure and wood will be consequently affected by temperature and other pyrolytic conditions.

Although a lot of research has been carried out on the influence of various operating conditions on fast pyrolysis, most of the work has focused on woody biomass pyrolysis using the one-factor-at-a-time (OFAT) approach to study the effects of the pyrolytic conditions. This method (OFAT) allows only a variable in a multivariable system to be changed at a time. By this method it is difficult to develop an optimized formulation, as the method reveals nothing about the interactions among the variables. Design of Experiments (DOE) is a statistical technique that can be used for studying and optimizing such multivariable systems. The purpose of this study was to investigate the influence of temperature, gas flow rate, and feed rate on the total liquid and char yields and on the pH of the biocrude oils obtained from fast pyrolysis of a poultry litter mixture of 50 wt.% manure and 50 wt.% wood in a fluidized bed reactor.

2. Materials and methods

A prepared 50:50 w/w mixture of layer manure and loblolly pine wood shavings obtained from poultry growers in Shenandoah Valley, Virginia was used. The samples with moisture content of 8%—10 wt.% were ground in a Wiley mill to pass a 1 mm mesh screen. The ultimate analysis and the higher heating value (HHV) of the manure and pine wood shavings were performed by Galbraith Analytical Laboratory (Knoxville, TN, USA) and the data as shown in Table 1.

2.1. Response surface methodology (RSM)

Design of Experiments (DOE) is a statistical technique that can be used to study and optimize multivariable systems. A response surface methodology (RSM) was used to study the effects of temperature (A), feed rate (B), gas flow rate (C) on the liquid yield, char yield and pH of the biocrude oil. The RSM is a mathematical and statistical technique which seeks to optimize the response by finding the true relationship between the response and the set of independent variables. For three factors, the Box—Behnken design was chosen since it offers some advantage in requiring a fewer treatment combinations than a central composite design in cases involving 3 factors.

A total number of 15 experimental runs including 3 center runs were generated and analyzed using Minitab software. Table 2 shows the coded the units of each factor used in the Box—Behnken design. A second-order regression model was used to approximate the responses since it provides a sufficient basis for selecting optimal settings for a given process. The regression models were based on the generalized second-order Taylor series approximation of the form as follows:

$$\begin{split} Y_i &= \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \ldots + \beta_k x_{ik} + \beta_{11} x_{i1}^2 + \beta_{22} x_{i2}^2 + \ldots + \beta_{kk} x_{ik}^2 \\ &+ \beta_{12} x_{i1} x_{i2} + \beta_{13} x_{i1} x_{i3} + \ldots + \beta_{k-1,k} x_{i,k-1} x_{ik} + \epsilon_i \\ &= \beta_0 + \sum_{j=1}^k \beta_j x_{ij} + \sum_{j=1}^k \beta_{jj} x_{ij}^2 + \sum_{j=1}^{k-1} \sum_{j'>j}^k \beta'_{jj} x_{ij} x'_{ij} + \epsilon_i \end{split}$$

The experimental results for each response variable (A, B and C) were analyzed statistically using analysis of variance (ANOVA) at an alpha level of 0.05. The ANOVA analysis of the Box—Behnken design was used to find the statistically significant terms and also estimate the fitness of the regression models initially proposed in equations (1, 2 and 3).

Liquid yield =
$$\beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \beta_{12} A B + \beta_{13} A C + \beta_{23} B C + \varepsilon$$
 (1)

Char yield =
$$\beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \beta_{12} A B$$

 $+ \beta_{13} A C + \beta_{23} B C + \varepsilon$ (2)

pH of biocrude oil =
$$\beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \beta_{12} A B + \beta_{13} A C + \beta_{23} B C + \epsilon$$
 (3)

2.2. Fluidized bed pyrolysis

The parametric studies on the fast pyrolysis of the poultry litter mixture of 50 wt.% layer manure and 50 wt.% loblolly pine wood shavings were carried out in a bench-scale fluidized bed reactor unit located at the Biological System Engineering Department, Virginia Tech, U.S.A (Fig. 1). A detail description of the pyrolysis unit and process used was reported by Mante et al. (2010). The feedstock was pyrolyzed at

Table 1 $-$ Sample characterization (layer manure and pine wood shavings).		
Elemental composition (wt.%) ^b	Feedstock	
	Layer manure	Pine
С	29.15	48.53
Н	4.13	5.91
N	6.42	< 0.5
0	36.56	43.31
S	0.36	< 0.05
Cl	0.62	180 ppm
HHV(MJ/kg)	14.79	18.02
Ash (wt.%) ^a	23.53	1.95
Bulk density (kg/L)	0.41	0.24

- a ASTM E1755, Standard test method for ash in biomass.
- b Moisture free basis

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