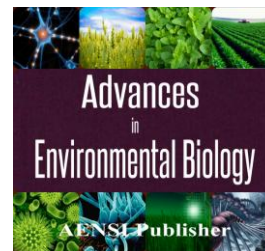




AENSI Journals

Advances in Environmental Biology

ISSN-1995-0756 EISSN-1998-1066

Journal home page: <http://www.aensiweb.com/AEB/>

Biomolecular Reaction and Heat Controlled in the Reactor for Synthesis of Charcoal and Bio-Oil Derived from Mixed Grass

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ARTICLE INFO

Article history:

Received 25 June 2014

Received in revised form

8 July 2014

Accepted 14 September 2014

Available online 27 September 2014

Keywords:

Cogongrass Manilagrass

Pyrolysis Bio-oil

Product yields

Chemical compound

ABSTRACT

Background: Charcoal and bio-oil derived from two substrates (Cogongrass [A] and Manilagrass [B]) were mixed during operated. This research was conducted by pyrolysis process in a continuous pyrolysis reactor under different thermal condition to determine the role of product yields and the quality of charcoal and bio-oil. The result has contributed to the opportunities not only in producing by-products [3-phases; solid (charcoal), liquid (bio-oil), and gas] of mixed grass (Cogongrass and Manilagrass) during pyrolysis but also physical and chemical properties and chemical compounds with temperatures condition in the range of 400 - 600 °C.

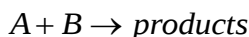
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To Cite This Article: Kittiphop Promdee, Chintana Sanvong, Somruedee Satitkune, Tharapong Vitidsant., Biomolecular Reaction and Heat Controlled in the Reactor for Synthesis of Charcoal and Bio-Oil Derived from Mixed Grass. *Adv. Environ. Biol.*, 8(14), 57-62, 2014

INTRODUCTION

The synthesis of charcoal and bio-oil from mixed grass by pyrolysis in a continuous reactor under standard conditions and controlled temperature balance in a continuous reactor. The utilization of this process could reduce waste dump areas in central Thailand. Bio-oil are now seen as holding promise as a future energy source from renewable natural resources. By itself, bio-oil may be used as fuel with high heat emission in special reactor units [1-5]. Many methods exist for the conversion of biomass into liquid, solid, and gaseous products. One such method holding the greatest promise for industrial application is pyrolysis, which can be used for the efficient conversion of biomass into fuel suitable both for internal combustion engines and heat generation [6-9]. The efficiency of the pyrolysis is determined by bimolecular reactions, the heating rate of the raw materials; the contact time between the raw material and the heat source should be in the range 0.5-5 seconds. The energy-containing components of the biomass are cellulose, hemicellulose, and lignin [10,11], consisting of sugars and polysaccharides.

Bimolecular reactions involve the collision between two species:



The rate of this bimolecular reaction should be proportional to the product of the concentration of A and B : $d[\text{products}]/dt = k[A][B]$. Consequently, bimolecular reactions follow second-order kinetics. Mechanism is a reaction that can proceed either in the forward or reverse direction. The differential rate law for the reaction is

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_{-1}[B]. \quad (1.1)$$

Although the principle of detailed balance is most powerful when applied to multiequation equilibrium, where it implies that at equilibrium $k_1A_e = k_{-1}B_e$ where A_e and B_e are the equilibrium concentrations. Hence, $d[A]/dt = d[B]/dt = 0$ when $[A]=A_e$ and $[B]=B_e$, so that the left-hand side of equation (1.1) is zero, and $k_1A_e = k_{-1}B_e$. We rewrite the equation in terms of the single variable x :

$$\frac{dx}{dt} = k_1([A(0)] - x - k_{-1}([B(0)] + x)). \quad (1.2)$$

However, since $A_e = [A(0)] - x_e$ and $B_e = [B(0)] + x_e$, we can rewrite equation (1.2) by substituting for $[A(0)]$ and $[B(0)]$:

$$\frac{dx}{dt} = k_1(A_e + x_e - x) - x - k_{-1}(B_e - x_e + x). \quad (1.3)$$

For this last equality, we have used the fact that $k_1A_e = k_{-1}B_e$, Rearrangement gives

$$\frac{dx}{x_e - x} = (k_1 + k_{-1})dt. \quad (1.4)$$

Integrating both sides, we find

$$-\int_0^x d \ln(x_e - x) = (k_1 + k_{-1}) \int_0^t dt, \quad (1.5)$$

or

$$-\ln \frac{x_e - x}{x_e} = (k_1 + k_{-1})t. \quad (1.6)$$

Exponentiation of both side gives

$$x = x_e \{1 - \exp[-(k_1 + k_{-1})t]\}. \quad (1.7)$$

Or, after subtracting both sides from $[A(0)]$,

$$[A(t)] = A_e + x_e \exp[-(k_1 + k_{-1})t]. \quad (1.8)$$

Thus, $[A(t)]$ start at $A_e + x_e = [A(0)]$ and decreases to A_e exponentially with a rate constant equal to the sum of the forward and reverse rates. Similarly, $[B(t)]$ start at $B_e + x_e = [B(0)]$ and increase to B_e exponentially with the same rate constant.

MATERIALS AND METHODS

A sample of mixed grass was ground and dried at 105 °C for 2 h. The moisture content in the resultant sample did not exceed 5%. The fraction with particle diameter 0.1-1.0 mm was taken for the pyrolysis. The ground raw material was placed into the continuous reactor at a feeding rate of 2 kg/h using a twin screw rotating at 150 rpm. Figure 1 shows a scheme for the apparatus used for pyrolysis at 400-600 °C with coarse sand and rounded rocks as the support (Fig 1.). The bio-oil was analyzed to determine moisture, ash content, volatile matter, and fixed carbon; elemental analysis was also carried out. Proximate analysis of the biomass was carried out according to ATSM D3173, D3174, D3175. Moisture, volatiles, fixed carbon, and ash were determined in the biomass, as well as carbon, hydrogen and nitrogen [12-17]. Analysis of the chemical compounds in the biofuel was carried out by GC/MS [18]. The gas chromatograph was equipped with a thermal detector and mass spectrometric detector. The pyrolysis products were entered directly into the gas chromatograph. The split inlet for Agilent GC/MS (criteria) instrumentation and setup-points for organic compounds analyzed; 1) Inlet Temperature = 300°C, 2) Split ratio = 50:1, 3) Column = 20m x 0.18 mm x 1µm, 4) Carrier gas = Helium at 1.0 ml/min constant flow, 5) Inlet = Split, 6) Inlet liner = Singer taper. Both aliphatic and aromatic compounds were detected and identified in the resultant biofuel. The pyrolysis vapor containing condensable gases, i.e., bio-oil, acetic acid, and water, gave the liquid product [19,20]. More than 100 compounds were found among the pyrolysis products.



Fig. 1: Schematic diagram of experimental setup: 1) control panel and switchboard 2) biomass hopper 3) catalysts hopper 4) motor screw I 5) pyrolysis reactor 6) burner 7) charcoal outlet slit 8) motor screw II 9) condenser 10) bio-oil stock 11) gases storage and recovering in the system.

RESULTS AND DISCUSSION

The mixed grass is composed of major components and other minor components including organic extractives (fats, waxes, terpenes, resins, etc.) and inorganic minerals. The analysis of tissue components of mixed grass, shown in Table 1, reveals that it mainly composed of Holocellulose and lignin. The tissue

composition of mixed grass was as follows (wt.%): lignin, 42.55; holocellulose, 57.45, including α -cellulose 26.98 and hemicellulose 30.47. Table 1 also gives the results of the proximate and ultimate analysis (elemental analysis). As we see, mixed grass is characterized by low moisture content and low ash, moderate fixed carbon, and high volatiles, which indicates that it might be used as raw material for obtaining bio-oil. The elemental composition of mixed grass is close to that of Hazelnut cupulae and Napier grass [21,22]. The higher oxygen content in the mixed grass leads to obtaining bio-oil with lower heating value.

The elemental (or ultimate) analysis of the mixed grass showed that the raw material contained 48.58 wt.% carbon, 8.51 wt.% hydrogen, 3.97 wt.% nitrogen, and 38.94 wt.% oxygen (Table 1). Such composition of the biomass used was similar to the composition of hazelnut cupulae: 51.15 wt.% carbon, 5.89 wt.% hydrogen, 2.12 wt.% nitrogen, and 40.84 wt.% oxygen [21]. Comparison of data presented bears witness to the fact that bio-oil obtained from mixed grass can be used as a renewable fuel and raw materials for the chemical industry.

Table 1: The tissue components of mixed grass.

Tissue components	(wt.%)
Holocellulose	57.45
Alfa-Cellulose	26.98
Hemicellulose	30.47
Lignin	42.55

Table 2: Proximate analysis and ultimate analysis of mixed grass.

Proximate analysis	(wt.%)	Ultimate analysis	(wt.%)
Moisture	3.13	C	48.58
Ash	21.83	H	8.51
Volatiles	51.54	N	3.97
Fixed carbon	23.50	O	38.94

The result of product yields [3-phases; solid (charcoal), liquid (bio-oil), and gas] of mixed grass during pyrolysis, with temperatures between 400 - 600 °C, to compare the product yields from mixed grass. Fig. 4 shows the temperature dependence of the yield of liquid, solid, and gaseous pyrolysis products. As we see, the maximum solid yield (42.75 %) is observed at a temperature of 400°C. The liquid yield increases with temperature, and is maximum (39.42 %) at 600°C. This can be explained by enhancement of the reactions of thermal decomposition of lignin and holocellulose as the temperature rises. In the studied pyrolysis temperature range, the liquid yield is in the range 40-60 %. The gas yield is not very temperature dependent, and is in the range 18%-25%. According to the classification proposed in [21-23], biomass producing a liquid yield of 30%-40% when pyrolyzed is classified as in the moderate bio-oil yield range. In the liquid phase, optimum bio-oil could be separated at 30.47 %. Mixed grass yielded bio-oil more than 30 % which it was considered to be a moderate result. Also, other products were better in solid and gaseous phases.

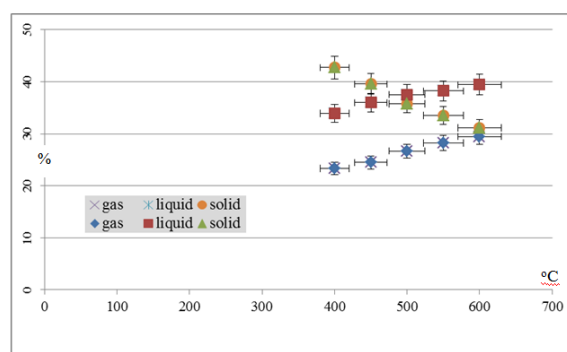


Fig. 2: Gas, liquid and Solid average of mixed grass by pyrolysis at 400-600 °C.

The heating value of charcoal and bio-oil were analyzed in manometer and reported in Mega joule per kilogram (MJ/Kg) at temperatures of 400, 450, 500, 550 and 600 °C. Charcoal and bio-oil have a highest heating rate as same result at 400 °C, 27.45 and 33.45 MJ/Kg, respectively., The HV average of charcoal and bio-oil in a range of 400 – 600 °C were 26.72 and 22.05 MJ/Kg., respectively., according to the research of Melligan *et al*, 2012 he has pyrolysis of Miscanthus at 400-500 °C [23], this result show that the average of HV in charcoal was 23.25 MJ/Kg and the average of HV in bio-oil was 20.57. In this research, Miscanthus tree gave a HV as good as HV from mixed grass (Table 3.).

Table 3: Heating value of Bio-oil and Charcoal

Temperature (C°) (MJ/Kg)	HV of Bio-Oil	HV of Charcoal (MJ/Kg)
400	33.45	27.45
450	29.13	24.00
500	26.56	21.56
550	23.38	19.75
600	21.12	17.53
Average	26.72	22.05

In works various authors [19-23], biomass producing between 20-40 % yield of liquid are often classified as producing a moderate yield of bio-oil. Mixed grass with a liquid yield of 30.49 wt.% can also be classified as producing a moderate amount of bio-oil. Gas yield of mixed grass during pyrolysis were slightly increasing 23.34, 24.47, 26.67, 28.24 and 29.45 % respectively., The main gases produced were H₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆ (Table 3.). The formation of these gaseous compounds is a consequence of the reactions between the species formed during pyrolysis. The origin of CO₂ mainly depends on the carboxyl groups. CO is mainly formed from the secondary of volatiles and the reduction of CO₂ [22]. The formation of methane is due to the release of methoxy groups. On the other hand, the higher hydrogen content is most probably caused by the polycondensation of free radicals generated during the pyrolysis and by dehydrogenation reactions in the char (such as the dehydrogenation of ethane to ethylene) and in the bio-oils, such as aromatization, condensation and alkene formation [23,24]. If the results obtained for the gas fraction are compared, it can be seen that the produces a gas with lower CO₂, CH₄, C₂H₆ and C₂H₄ contents than the conventional furnace as well as a higher content in H₂ and CO. This finding is very important as it shows that pyrolysis contributes to an increase in the production of syngas (H₂ + CO) [23,24].

Table 4: Gases produced from pyrolysis at 400 – 600 °C

Gases produced from pyrolysis	(%)
H ₂	31.67
CH ₄	14.79
CO	20.08
CO ₂	18.52
C ₂ H ₆	1.65
C ₂ H ₄	1.23
C ₂ H ₄ /C ₂ H ₆	0.74
H ₂ + CO	51.75
H ₂ /CO	33.24

The compounds of Bio-oils derived from mixed grass are very complex mixtures of hundreds of organic oxygen-containing components (carboxylic acids, phenols, alcohols, aldehydes, ketones, ethers, esters, furans, sugars, and water). It have classified in the following classes and subclasses (between parenthesis): phenols (phenols, methoxy phenols, cresols, and phenolic diols), ketones (C5- and C6-cyclic ketone, furanones, aliphatic ketones, aromatic ketone, furan ketones), acids (aliphatic acids, furan acids, benzoic acids, ketonic acids), ethers (aromatic ether, benzofuranone ethers, furan ether), aldehydes (aliphatic aldehydes, benzaldehydes, cinnamaldehydes), and other.

The formation of aromatic structures is typical during the pyrolysis of biomass with the selective production of bio-oil depending on several key factors, such as characteristic of biomass feedstock, pyrolysis temperature, rotation of screw feeder and residence time. Bio-oil obtained from mixed grass is a complex mixture with a great amount of large-size molecules, which nearly involve all species of hydrocarbon compounds, such as phenols, esters, aldehydes, ketones, alcohols, and organic acids. The use of this raw material (mixed grass) provided for a moderate yield of biofuel (38.49 mass %), containing 25.67% phenols, 16.34% Phenol, 2,6-dimethoxy, 3.87% Phenol, 2-methoxy-, 4.52% Phenol, 3-methyl-, 4.12% Phenol, 2-methyl-, 3.15% Benzene, 1-ethyl-4-methoxy-, as well as various alcohols and ketones (Fig 5).

All of compounds can be detected in bio-oil derived from mixed grass showed the main groups of hydrocarbon compounds, there are composed of hydroxyl and carboxyl groups. These compounds showed that the investigating molecular compositions. It's have been detected compounds of bio-oil from several biomass [25-29], the results shown a good samples of molecular compositions detected.

Conclusions:

In this study, the product yields, physical and chemical properties and chemical compounds of charcoal and bio-oil derived from mixed grass by pyrolysis in continuous reactor had a good result because of high heating value and good various of functional groups. The raising temperature of the biomass pyrolysis leads to an enhanced yield of bio-oil. Conversely, The raising temperature of the biomass pyrolysis not leads to an enhanced yield of charcoal. Analysis of the content of the resultant bio-oil indicated the possibility of using this product as a renewable hydrocarbon fuel. The liquid pyrolysis product value can be used as chemical feedstock

or as fuel after upgrading in thermal or catalytic cracking processes. It is advisable to study the effect of the quality of the liquid pyrolysis product on its further processing and also to study the behavior of aromatic compound formation under pyrolysis conditions at different temperatures and in different media.

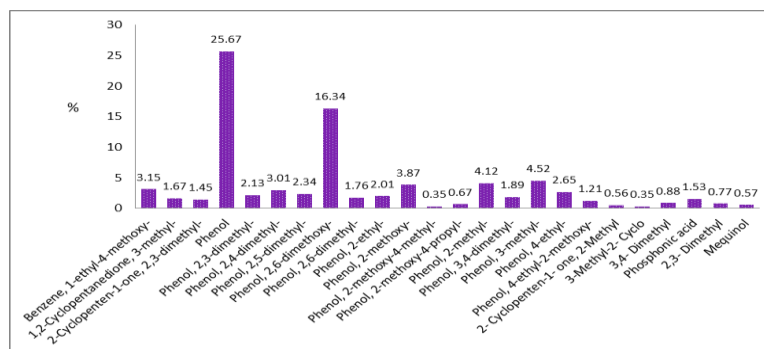


Fig. 3: The amount of some molecule compounds bio-oil obtained from mixed grass.

In addition; besides the biomass origin, the chemical composition of bio-oils depends upon other factors such as feedstock pretreatment (particle size and shape, moisture, and ash content), conditions of the pyrolysis process (temperature, heating rate, residence time, and pressure), vapor filtration, and condensation (filter type, condensing method and medium, cooling rate).

ACKNOWLEDGMENT

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (EN 272 A), Ratchadaphiseksomphot Endowment Fund (CU-CLUSTER-FUND), the Thai Government Stimulus Package 2 (TKK2555) under the Project for Promotion of bio and biomass utilization potential for fuel production and exporting technology, and Chulalongkorn University and Research Program on Materials for Future Energy, Center of Excellence on Petrochemical and Materials Technology.

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