

THERMOGRAVIMETRIC ANALYSIS OF RICE HUSK AND COCONUT PULP FOR POTENTIAL BIOFUEL PRODUCTION BY FLASH PYROLYSIS

(Analisa Thermogravimetrik Sekam Padi dan Pulpa Kelapa Untuk Mengkaji Potensi Penghasilan Minyak Bio Melalui Pirolisis Pantas)

Noorhaza Alias¹, Norazana Ibrahim¹*, Mohd. Kamaruddin Abd. Hamid², Hasrinah Hasbullah³, Roshafima Rasit Ali⁴, Aziatul Niza Sadikin⁴, Umi Aisah Asli⁴

¹UTM-MPRC Institute for Oil and Gas, Faculty of Petroleum and Renewable Energy Engineering,

²Process Systems of Engineering Centre, Faculty of Chemical Engineering,

³AMTEC, Faculty of Petroleum and Renewable Energy Engineering,

⁴Faculty of Chemical Engineering,

Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Malaysia

*Corresponding author: norazana@petroleum.utm.my

Abstract

The purpose of this paper is to study the characteristics and thermal degradation behavior of rice husk and coconut pulp for biofuel production via flash pyrolysis technology. The elemental properties of the feedstock were characterized by an elemental analyzer while thermal properties were investigated using thermogravimetric analyzer (TGA). The pyrolysis processes were being out at room temperature up to 700° C in the presence of nitrogen gas flowing at 150 ml/min. The investigated parameters are particle sizes and heating rates. The particle sizes varied in the range of dp₁ < 0.30 mm and $0.30 \le dp_2 < 0.50$ mm. The heating rates applied were 50° C/min and 80° C/min. It was shown smaller particle size produces 2.11-3.59% less volatile product when pyrolized at 50° C/min compared to 80° C/min. Higher heating rates causes biomass degrades in a narrow temperature range by 25° C. It also increases the maximum peak rate by 0.01 mg/s for rice husk at dp₁ and 0.02 mg/s at dp₂. In case of coconut pulp, the change is not significant for dp₁ but for dp₂ a 0.02 mg/s changes was recorded.

Keywords: Rice husk, Coconut pulp, Thermogravimetric analyses, Flash pyrolysis, Biofuel

Abstrak

Tujuan kajian ini dijalankan adalah untuk mengenalpasti ciri-ciri serta corak degradasi therma sekam padi dan pulpa kelapa bagi tujuan penghasilan minyak bio melalui proses pirolisis pantas. Komposisi unsur ditentukan dengan menggunakan penganalisa unsur manakala ciri-ciri therma dikaji menggunakan penganalisa thermogravimetrik (TGA). Proses degradasi therma dijalankan pada suhu bilik sehingga mencapai 700°C, dengan aliran gas nitrogen pada kadar 150 ml/min. Dua pemboleh ubah telah dikenalpasti sebagai fokus kajian iaitu saiz partikel dan kadar pemanasan. Saiz partikel yang digunakan adalah dp $_1$ < 0.30 mm dan $0.30 \le dp_2 < 0.50$ mm manakala kadar pemanasan ditetapkan pada suhu 50°C/min dan 80°C/min. Hasil kajian mendapati bahawa saiz partikel yang lebih kecil menghasilkan kurang produk meruap sebanyak 2.11 - 3.59% apabila diproses pada suhu 50°C/min. Kadar pemanasan yang tinggi menyebabkan kedua-dua sampel lupus pada jangka suhu yang lebih cepat iaitu sebanyak 25°C. Kadar degradasi maxima bagi sekam padi turut meningkat sebanyak 0.01 mg/s pada dp $_1$ dan 0.02 mg/s pada dp $_2$. Pulpa kelapa tidak mencatat sebarang perubahan yang signifikan pada dp $_1$ tetapi pada dp $_2$ peningkatan sebanyak 0.02 mg/s telah direkodkan.

Kata kunci: Sekam padi, Pulpa kelapa, Analisa thermogravimetrik, Pirolysis pantas, Minyak bio

Introduction

Biomass is defined as the products fraction of biologically degradable waste from agriculture which includes animal and vegetable materials, forestry and biologically degradable fraction of industrial and household waste [1]. In Malaysia, the amount of biomass generated from agricultural waste is 72, 962 kton/year and holds an annual potential electricity generation of 5863 GWh [2]. The technology of converting biomass into energy is a right option

Noorhaza et al: THERMOGRAVIMETRIC ANALYSIS OF RICE HUSK AND COCONUT PULP FOR POTENTIAL BIOFUEL PRODUCTION BY FLASH PYROLYSIS

since it is a renewable type of energy source that could dramatically improve the environment, economy and energy security. Fast pyrolysis is one of the most promising technologies of biomass utilization, and it is also the first stage of biomass thermochemical conversion. Under this process, biomass is converted into liquid oil, char and gases. Up to 50-75% of biomass can be converted into liquid oils, which can be directly used in combustion application or upgraded for high-end chemical recovery. In the absence of oxygen, the yields and compositions of pyrolysis products depends on the type of biomass, operating temperature, heating rates, type of reactors, particles size and co-reactant [3]. The objective of this study is to investigate the characteristic and thermal degradation behavior of rice husk and coconut pulp by using thermogravimetric analysis (TGA). This study will provide important information for potential biofuels production from these two types of biomass.

Materials and Methods

Materials Preparation and Characterization

Rice husk was obtained from Bernas factory in Sabak Bernam, Selangor while coconut pulp was obtained from local coconut milk producer in Johor Bahru, Johor. All feedstock were first milled and sieved into smaller particle size of <0.50 mm. The characterizations of rice husk and coconut pulp were performed in order to obtain its ultimate, proximate and high heating value (HHV). The ultimate analysis was carried by out using elemental analyzer (The PerkinElmer 2400 Series II) to determine the amount of carbon, hydrogen, nitrogen and sulphur in the feedstock. The proximate analysis was conducted by using thermogravimetry analyzers (TGA) (TA Instruments Q500) to analyze volatile matter (VM), fixed carbon (FC), moisture content and ash content in all samples. The HHV of rice husk and coconut pulp were determined by using bomb calorimeter (Suprashesh ABC-123).

Experimental Procedures

TGA was carried out in the presence of nitrogen (N_2) at the flowing rate of 150 ml/min. Rice husk and coconut pulp samples between 0.5 and 1.0 g were pyrolyzed to a maximum temperature of $700^{\circ}C$. The samples were first heated to $110^{\circ}C$ and kept at that temperature for 30 minutes to remove any moisture. After that, the samples were heated at the rate of $50^{\circ}C$ /min and $80^{\circ}C$ /min individually until it reaches the maximum temperature. The experiment was repeated for each type of biomass at different particle size as follows: $dp_1 < 0.30$ mm and $0.30 \le dp_2 < 0.50$ mm.

Results and Discussion

Properties and Composition of Feedstock

From the analysis conducted, moisture contents for both types of biomass vary with 2.82%. Higher moisture content decreases the heating value of the coconut pulp, in this case by 0.88% because of some energy were needed to vaporize the moisture at the beginning of conversion process [4]. Rice husk contains high amount of ash due to the presence of silica that can constitute up to 90-97% in the final residue [5]. Coconut pulp contains higher volatile matter and fixed carbon content compared to rice husk by 5.22% and 7.37%, respectively. The elemental properties for both samples do not differ much as been reported. In general, coconut pulp contains higher amount of carbon and hydrogen but lower nitrogen and sulphur content. The properties of rice husk and coconut pulp used in this study are summarized in Table 1.

In general, the pyrolysis of any biomass can be divided into three phases which are drying and evaporation of light components (phase I), devolatilization of hemicellulose and cellulose (phase II) and decomposition of lignin (phase III). Phase I occurs at temperature below 150°C, phase II starts from 150°C to 450°C and finally phase III is attained at temperature above 450°C. From Fig. 1 (a), it was observed that the amount of residue left for dp₁ at higher heating rate (80°C/min) are 2.43% and 3.01% lower for rice husk and coconut pulp, respectively. When bigger particle size dp₂ is used however, the residue at higher heating rates is 1.99% and 1.18% more for rice husk and coconut pulp, respectively (see Fig.2 (a)). It is well agreed in the literature that larger particle sizes yields more residue because poor heat transfer to the inner surfaces leads to a low average particles temperature [6,7]. However, in this study it was shown that particle size does not provide a significant effect on thermal degradation of both rice husk and coconut pulp.

Table 1. Properties of rice husk and coconut pulp

Analysis		Rice husk	Coconut pulp
	Moisture content	6.73	9.55
	Ash content	17.06	0.45
Proximate analysis (db wt %)	Volatile matter	62.61	67.83
1 Toximate analysis (ub wt 76)	Fixed Carbon	14.96	22.30
	High heating value (HHV) (MJ/Kg)	17.91	17.03
	Carbon (C)	38.22	39.44
	Hydrogen(H)	5.88	6.14
Ultimate analysis (db wt %)	Nitrogen (N)	0.68	0.50
	Sulphur (S)	0.07	0.04

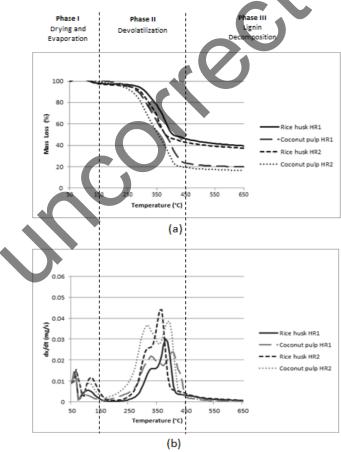


Figure 1. A plot of (a) TGA and (b) DTG for dp_1 at both heating rates, where $HR1 = 50^{\circ}C/min$ and $HR2 = 80^{\circ}C/min$

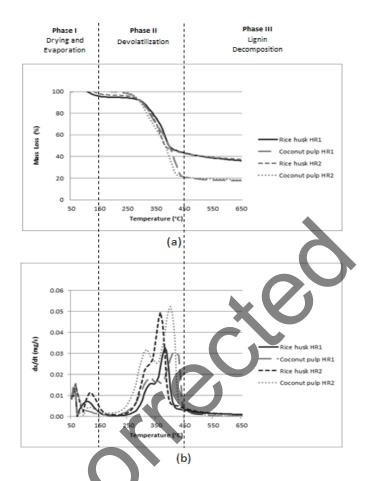


Figure 2. A plot of (a) TGA and (b) DTG for dp_2 at both heating rates, where HR1 = 50 °C/min and HR2 = 80 °C/min

Thermogravimetric Analysis

Thermogravimetric results for all eight samples are plotted as a function of temperature as shown in Figure 1 and 2. Fig. 1 (b) and Fig. 2 (b) illustrate the effects of heating rates and particle sizes on degradation peak rates. It was observed that higher heating rates speed up the degradation process by 0.01 mg/s (at 370°C) for rice husk samples in dp₁, while dp₂ recorded almost a 0.02 mg/s difference (at 355°C). The peak in phase I corresponds to the moisture released from the biomass feedstock. There are two peaks in phase II: the first peak shows the degradation of lower molecular weights components (hemicellulose) from 180°C to 310°C and second peaks indicates cellulose degradation which occurs between 320°C and 410°C. Lignin gradually degrades over a range of temperature from 380°C to 700°C. It is noted that when the temperature reaches 650°C, the degradation rates are no longer significant as most volatiles had already been pyrolysed and the rest were converted into char and gases. Lower heating rates causes the biomass to decompose under a wider temperature range from 225°C to 450°C compared to 250°C to 450°C.

The peaks pattern in phase II for coconut pulp is not similar at different particle size. In Fig. 1 (b), both peak rates does not changes that much (0.002 mg/s difference from 325-410°C) but in Fig. 2 (b) the difference is 0.02 mg/s (at 330-425°C). In this study, the pyrolysis behavior for coconut pulp is very unpredictable and is not well understood since not much research had been conducted before. However, it produced a very high amount of volatile and proves to be a very favorable feedstock for biofuel production via flash pyrolysis. Due to high composition of lignin

(24.4%) [8], the amount of volatiles for rice husk is lower compared to coconut pulp (10.0 % lignin) [9]. Biomass with more cellulose and hemicellulose contents (i.e. herbaceous biomass) will produces more volatiles compared to woody biomasses [10]. Table 2 summarized the product yields for both type of feedstock at different particle size and heating rates:

Table 2. Pyrolysis product	veilds for rice husk and	coconut pulp at heating rate	50° C/min and 80° C/min

Types of biomass	Product yields (%)	Heating rate (50°C/min)		Heating rate (80°C/min)	
	(13)	dp_1	dp_2	dp_1	dp_2
Rice husk	Char	39.09	35.50	37.47	37.49
	Volatile matter	60.91	64.50	62.53	62.51
Coconut pulp	Char	19.57	17.46	16.56	18.64
	Volatile matter	80.43	82.54	83.44	81.36

Conclusion

There are many factors influencing the pyrolysis process. The main factors discussed in this research are the effect of particle size, heating rate and the properties of biomass itself. Smaller particle size produces 2.11-3.59% less volatile product when pyrolized at 50° C/min. At higher heating rate however, the amount of volatiles is 2.08% higher for dp₁. As such, it can be concluded that particle size has insignificant effect on pyrolysis of rice husk and coconut pulp. Higher heating rate however causes biomass to be degraded under a narrow temperature range by 25° C. It also increases the maximum peak rate by 0.01 mg/s for rice husk at dp₁ and 0.02 mg/s at dp₂. In case of coconut pulp, the change is not significant for dp₁ but for dp₂ a 0.02 mg/s changes were recorded. High lignin content in rice husk lowers the amount of volatiles produces which is in accordance to literature findings. Further studies need to be conducted to understand more on the behavior of coconut pulp pyrolysis since it provides a promising potential feedstock for biofuel production.

Acknowledgement

The authors gratefully acknowledge the financial support from Universiti Teknologi Malaysia and Ministry of Higher Education (MOHE) of Malaysia (Q.J130000.2542.07H10 and R.J130000.7842.4L128).

References

- 1. Patel, B. and Gami, B. (2012). Biomass Characterization and its Use as Solid for Combustion. *Iranica Journal of Energy and Environment*, 123-128.
- 2. Zafar, S., (2014). Bioenergy Developments in Malaysia. Retrieved from http://www.bioenergyconsult.com/tag/biomass-resources-in-malaysia/
- 3. Jahirul, M. I., Rasul, M. G., Chowdhury, A. A. & Ashwath, N. (2012). Biofuels Production through Biomass Pyrolysis A Technological Review. *Energies 5: 4952-5001*.
- 4. Mansaray, K. G. and Ghaly, A. E. (1997). Physical and Thermochemical Properties of Rice Husk. *Energy Sources*, 27: 989-1004.
- 5. Chuayjuljit, S., Eiumnoh, S. and Potiyaraj, P. (2001). Using Silica from Rice Husk as a Reinforcing Filler In Natural Rubber. *Journal of Scientific Research Chulalongkorn University*, 26: 127-137.
- 6. Stenseng, M., Jensen, A. and Dam-Johansen, K. (2001). Investigation of Biomass Pyrolysis by Thermogravimetric Analysis and Differential Scanning Calorimetry. *Journal of Analytical and Applied Pyrolysis* 58-59: 765-780.

Noorhaza et al: THERMOGRAVIMETRIC ANALYSIS OF RICE HUSK AND COCONUT PULP FOR POTENTIAL BIOFUEL PRODUCTION BY FLASH PYROLYSIS

- 7. Stresov, V., Moghtaderi, B. and Lucas, J. (2003). Thermal Study of Decomposition of Selected Biomass Samples. *Journal of Thermal Analysis and Calorimetry*, 72: 1041-1048.
- 8. Wannapeera, J., Worasuwannarak, N. and Pipatmanomai, S. (2008). Product Yields and Characteristics of Rice Husk, Rice Straw and Corncob During Fast Pyrolysis in a Drop-Tube/Fixed-Bed Reactor. *Songklanakarin J. Sci. Technol.* 30 (3): 393-404.
- 9. Ho, Y.S., and Ofomaja, A.E. (2006). Biosorption Thermodynamics of Cadmium on Coconut Copra Meal as Biosorbent. *Biochemical Engineering Journal*, 30: 117–123.
- 10. Burhennea, L., Messmer, J., Aicher, T. and Laborie, M. (2013). The Effect of The Biomass Components Lignin, Cellulose and Hemicellulose on TGA and Fixed Bed Pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 101: 177–184.

