



Journal of Applied Sciences

ISSN 1812-5654

science
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Thermal Degradation Behaviour for Co-gasification of Rubber Seed Shell and High Density Polyethylene Mixtures using Thermogravimetric Analysis

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Abstract: The objective of this study is to investigate the thermal degradation behavior, degradation temperature and maximum degradation rate of rubber seed shell (RSS), high density polyethylene (HDPE) and binary mixture of RSS and HDPE in a weight ratio of 20/80 (HDPE/RSS) at different heating rates of 10, 20, 30 and 50 K min⁻¹ within temperature range of 323-1200 K under non-isothermal gasification conditions in argon atmosphere at flowrate of 100 mL min⁻¹ and steam flowrate of 300 μ L h⁻¹ using thermogravimetric (TGA) approach.

Key words: Thermal degradation behaviour, thermogravimetric analysis, polythene

INTRODUCTION

Co-gasification of plastic and biomass mixtures is an alternative to solid waste incineration and landfilling. Gasification of solid waste is considered as an extension of the well-known coal technology (Borgianni *et al.*, 2002). Although its feasibility has been demonstrated for several years, only recent studies have been carried out to develop processes for energy production (Borgianni *et al.*, 2002).

The understanding of the thermal decomposition or devolatilization occurring during the co-gasification of the biomass-plastic mixtures is important (Ebrahimi-Kahrizsangi and Abbasi, 2008). And also, it is vital to assess the feasibility of the design and scaling of industrial thermo-conversion applications (Raveendran *et al.*, 1996). Most publication reports on the thermal degradation behavior of individual components from Municipal Solid Waste (MSW) and binary mixtures of plastic and biomass waste specifically under pyrolysis condition (Saha and Ghoshal, 2006; Aboulkas *et al.*, 2008; Chin *et al.*, 2013). In contrast, limited studies carried out on thermal degradation of co-gasification of binary mixtures of plastic and biomass waste using Thermogravimetric Analyzer (TGA).

In this present study, the thermal degradation behavior, degradation temperature and maximum degradation rate for the Rubber Seed Shell (RSS), High Density Polyethylene (HDPE) and binary mixture of HDPE and RSS in weight ratio of 0.2/0.8 (HDPE/RSS) at different heating rates of 10, 20, 30 and 50 K/min within temperature range of 323-1200 K in argon atmosphere at flow rate of 100 mL min⁻¹ and steam flowrate of 300 μ L h⁻¹ under non-isothermal gasification condition using TGA are investigated.

MATERIALS AND METHODS

Materials and sample preparation: The raw materials used in this work are RSS from Vegpro Trading, Malaysia and HDPE plastic is from Shen Foong Plastic Industries Sdn Bhd, Malaysia. These materials are grounded and sieved to a particle size of = 710 μ m fractions. Homogenized RSS/HDPE blends in a weight ratio of 0.2:0.8 are prepared. The characteristics of the materials used in this study are presented in Table 1. The ultimate analysis and proximate analysis of the HDPE and RSS are conducted in LECO CHNS-932 elemental analyzer and thermogravimetry analyzer EXSTAR TG/DTA 6300 (Seiko Instrument Inc.), respectively.

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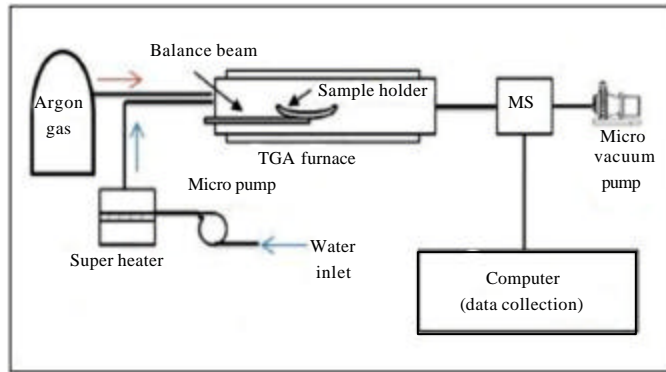


Fig. 1: Process flow diagram of TGA-MS

Table 1: Proximate and ultimate analysis for RSS and HDPE

Sample	Ultimate analysis (Weight %, dry basis)				
	C	H	N	S	O ^a
RSS	44.31	4.38	0.51	0.13	50.67
HDPE	81.45	12.06	0.34	0.79	5.36
Sample	Proximate analysis (Weight%, dry basis)				
	Moisture content	Volatile matter	Fixed carbon ^a	Ash	
RSS	8.59	80.98	6.62	3.81	
HDPE	0.00	99.46	0.00	0.34	

O^a is by difference

Procedure: The experiments are performed using thermogravimetry analyzer EXSTAR TG/DTA 6300 (Seiko Instrument Inc.) as shown in Fig. 1. Approximately 5 mg of sample is placed on a ceramic crucible in TGA under an inert atmosphere of argon. A flow rate of 100 mL min⁻¹ of argon gas is fed into the system for 20 min at a temperature of 323 K. Subsequently, all samples are heated from 323-1173 K at respective heating rates and temperatures are kept constant for 10 min. During heating, the TGA is used to measure the mass of the materials and furnace temperature. Thermogravimetric curves are obtained at four heating rates (10, 20, 30 and 50 K min⁻¹) within the temperature range of 323-1173 K. Steam is generated by a super heater at 383 K and is injected into the TGA at a flow rate of 300 μL h⁻¹ when the temperature inside the TGA equipment reached to 383 K to avoid any occurrence of condensation within the system. All experiments are repeated two or three times.

RESULTS AND DISCUSSION

Thermal degradation of rubber seed shell (RSS): The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the RSS at four different heating rates are presented in Fig. 2 and 3, respectively. Table 2 shows the degradation temperatures for RSS, HDPE and binary

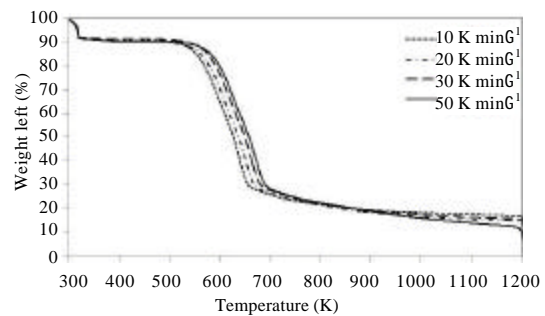


Fig. 2: TG curves for RSS at different heating rates for gasification process

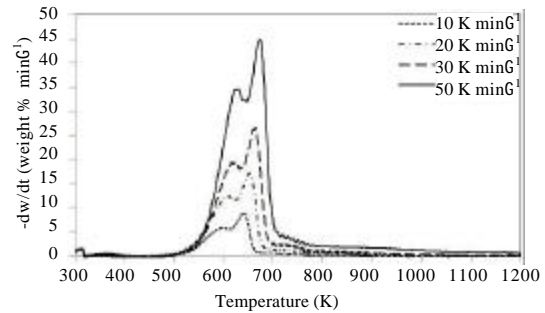


Fig. 3: DTG curves for RSS at different heating rates for gasification process

mixture of HDPE and RSS. Table 3 displays the remaining residue and maximum degradation rate for RSS, HDPE and binary mixture of RSS and HDPE. In Fig. 2, all the curves in TG shows an almost identical trend within the range of heating rates studied. It is also observed that the residual weight of the sample with temperature decreases as the

Table 2: Degradation temperatures for RSS, HDPE and binary mixture of HDPE and RSS

Sample	Heating rate (K min ⁻¹)	Degradation temperature, T _i /T _{max} /T _f ^b		
		1st stage	2nd stage	3rd stage
RSS	10	505/584/616	616/630/661	-
	20	516/598/618	618/646/693	-
	30	520/609/621	621/657/694	-
	50	523/618/636	636/668/701	-
HDPE	10	682/748/776	-	-
	20	691/761/794	-	-
	30	693/764/794	-	-
	50	694/776/811	-	-
HDPE:RSS (0.2:0.8 mass ratio)	10	499/584/606	606/632/661	661/735/764
	20	504/603/618	618/649/677	677/751/778
	30	514/607/623	623/655/683	683/756/788
	50	527/625/641	641/670/700	700/765/800

^bT_i, T_{max}, T_f is the initial, maximum and final temperature respectively of the main mass loss in each stage

Table 3: Remaining residue and maximum degradation rate for RSS, HDPE and binary mixture of RSS and HDPE

Sample	Heating rate (K min ⁻¹)	Residue (weight%)	Maximum degradation rate at 1200 K (Weight% min ⁻¹)
RSS	10	15.3	7.9
	20	15.2	15.0
	30	12.2	25.4
	50	11.9	43.7
HDPE	10	2.7	26.7
	20	0.4	47.3
	30	2.8	73.5
	50	2.8	116.7
HDPE:RSS (0.2:0.8 mass ratio)	10	12.2	6.2
	20	12.1	13.4
	30	8.1	18.7
	50	7.3	32.6

heating rate increases. A similar behavior is seen when compared to other published literature data on pyrolysis of biomass (Aboulkas *et al.*, 2008; Rotliwala and Parikh, 2011; Luangkiattikhun *et al.*, 2008; Khan *et al.*, 2011b). Findings by Rotliwala and Parikh (2011), Bilbao *et al.* (1997) and Sampath and Babu (2006) stated that the thermal hysteresis is influenced by the heating rate hence the increase of the heating rate will increase the thermal hysteresis which will result in both TG and DTG curves to be shifted to a higher temperature. In addition, higher heating rate will lead to an increase of mass volatilization at the core of the sample which will transform the solid residue structure with an increased yield of the liquid and gaseous fractions.

Results in Fig. 2 show that a slow increment of mass loss for RSS from room temperature to 513 K indicates that the water present in the RSS is generally removed through evaporation. Thereafter, a significant increased of mass loss from temperature of 524-665 K which shows that the RSS undergoes main devolatilization phase where volatiles and carbon are released. A moderate increased of mass loss from temperature of 666-1054 K is observed followed by a constant mass loss to temperature of 1200 K. At non-isothermal temperature of 1200 K, the solid

residue left and maximum degradation rate is in the range of 11.9-15.3 weight% and 7.9-43.7 weight%/min respectively.

In Fig. 3, it is observed that there are two peaks in the DTG thermogram. The two peaks gradually become more distinct as the heating rate increases from 10 to 50 K min⁻¹. This behavior is consistent with the results reported by Aboulkas *et al.* (2008) and this phenomenon is speculated to be resulted from the slow decomposition of lignin in the RSS. This can be further elaborated that the two peaks is said to be associated with two group of main reactions involving the main components in the biomass which are cellulose, hemicellulose and lignin occurring at different temperature during the decomposition process (Luangkiattikhun *et al.*, 2008). From the literature, the first peak is linked to the decomposition of hemicellulose and some of the lignin and meanwhile the second peak is associated to the decomposition of cellulose in the biomass (Bilbao *et al.*, 1997). It is reported by Becidan *et al.* (2007) that hemicellulose decomposed at temperatures between 473 and 648 K, cellulose decomposed at temperatures between 548 and 653 K and lignin is decomposed gradually in a wider range of temperatures between 453-823 K. The analysis of the temperature range of thermal degradation of hemicellulose, cellulose and lignin carried out in this present study falls closely with the aforementioned studies of Khan *et al.* (2011a).

From the DTG curves, it is also observed that an increment of lateral shift in temperature of T_{max1} and T_{max2} occurs when the heating rate increases for RSS. This behavior is due to the thermal lag in the decomposition from the combined effects of the heat transfer at different heating rates, kinetics of the decomposition and heat conductive property of the biomass particles (Aboulkas *et al.*, 2008; Khan *et al.*, 2011a; Zhang *et al.*, 2009).

Thermal degradation of high density polyethylene (HDPE):

The TG and DTG thermograms of the thermal decomposition for HDPE at four different heating rates are illustrated in Fig. 4 and 5, respectively. All the curves in both TG and DTG thermograms show an almost identical trend in the range of heating rates studied. However, it is seen in Fig. 4 that the weight loss increases with heating rates.

In TG thermogram shown in Fig. 4, it is observed that the thermal degradation for HDPE starts at 682-694 K and is almost complete at 776-811 K. It is worth noting that the thermal degradation takes place at a much higher temperature compared to RSS. In DTG thermogram (Fig. 5), it is observed that there is only one peak

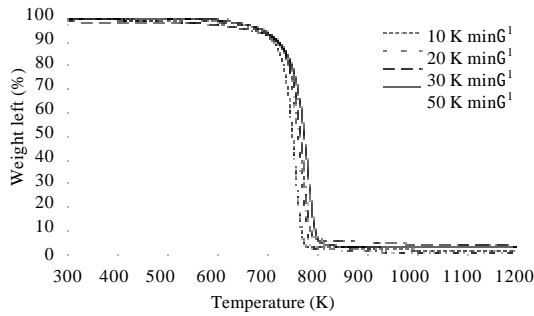


Fig. 4: TG curves for HDPE at different heating rates for gasification process

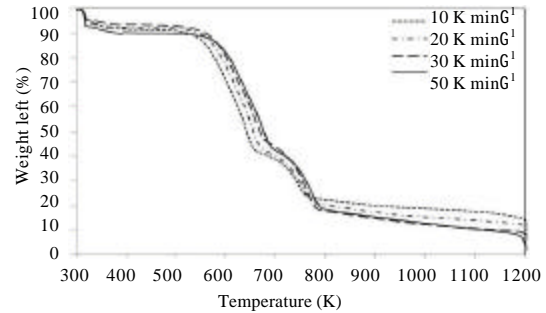


Fig. 6: TG curves for binary mixtures of RSS and HDPE at different heating rates for gasification process

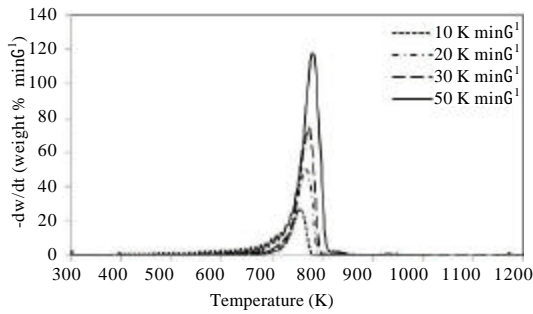


Fig. 5: DTG curves for HDPE at different heating rates for gasification process

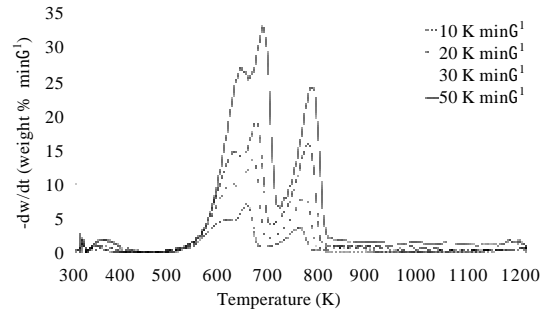


Fig. 7: DTG curves for binary mixtures of RSS and HDPE at different heating rates for gasification process

occurring in the range of heating rate studied. Hence, this indicates the thermal degradation of the HDPE occurred in a single stage. Several studies also reported similar trend observed from the thermal decomposition of HDPE from the DTG curves (Rotliwala and Parikh, 2011; Aboulkas *et al.*, 2009). The solid residue attained after the gasification process for HDPE is 0.4-2.8 weight% in the range of heating rate studied. The maximum degradation rate increased from 26.7 weight%/min at 10 K min⁻¹ to 116.7 weight%/min at 50 K min⁻¹.

Thermal degradation for RSS and HDPE mixtures: The TG and DTG thermograms of the thermal decomposition for binary mixtures of HDPE and RSS (0.2:0.8 weight ratio) at four different heating rates are depicted in Fig. 6 and 7 respectively. It is observed that the DTG curves show three stages of thermal decomposition. A similar behavior is observed when the binary mixture undergoes pyrolysis (Chin *et al.*, 2013). The first step occurs between 499 K and 641 K and is attributed to the decomposition of hemicellulose. The second step occurs between 606 and 700 K and is attributed to the decomposition of cellulose.

The third step occurs between 661 and 800 K and is attributed to the decomposition of lignin and HDPE. The solid residue attained after gasification process at 1200 K for the binary mixtures is 7.3-12.2 weight% within the range of heating rate studied. The maximum degradation rate increased from 6.2 weight% min⁻¹ at 10 K min⁻¹ to 32.6 weight% min⁻¹ at 50 K min⁻¹.

CONCLUSION

The co-gasification behavior of Rubber Seed Shell (RSS), High Density Polyethylene (HDPE) and binary mixture of HDPE and RSS mixture at weight ratio of 0.2: 0.8 was investigated. The degradation temperature, remaining residue and maximum degradation rate are presented. It is observed from the DTG (derivative thermogravimetric) curves that HDPE, RSS and binary mixture of RSS and HDPE shows one, two and three stages of thermal decomposition. The remaining solid residue after the gasification process for RSS, HDPE and binary mixture of RSS and HDPE respectively are in the range of 11.9-15.3, 0.4-2.8 and 7.3-12.2 weight%. The maximum degradation

rate achieved by the RSS, HDPE and binary mixture of RSS and HDPE respectively are in the range of 7.9-43.7, 26.7-116.7 and 6.2-32.6 weight%/min.

ACKNOWLEDGMENTS

This study is carried under financial support of Petroleum Institute, United Arab Emirates and UNIVERSITI TEKNOLOGI PETRONAS, Malaysia. The authors would also like to thank Shen Foong Plastic Industries Sdn Bhd, Malaysia for sponsoring HDPE waste samples for this research.

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