

Thermal degradation of rice-bran with high density polyethylene: A kinetic study

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Abstract—Thermal degradation behavior of mixtures of rice bran (RB) and high density polyethylene (HDPE) was investigated by thermo-gravimetric analyses (TGA) under dynamic conditions in nitrogen atmosphere and was compared with that of individual materials. Experiments were carried out in the range of ambient temperature to 900 °C at two heating rates (5 and 20 °C per minute). Kinetic analysis indicated that activation energy for pyrolysis of RB, HDPE and those for RB-HDPE mixtures varied with rate of heating as well as with the three temperature ranges. This variation has been explained on the materials' decomposition behavior. Maximum difference between experimental and theoretical mass loss (Δm) was 26% at 475 °C and 34% at 489 °C at the heating rates of 5 and 20 °C per minute, respectively. These maxima indicate stronger interactions at corresponding temperature between RB and HDPE during copyrolysis. Reduction in activation energy for pyrolysis, lower temperatures at which rate of decomposition is highest, and negligible quantity of the residue suggest a synergism between thermal degradation of RB and HDPE.

Key words: Biomass/Plastic, Co-pyrolysis, Kinetic Study, Thermogravimetric Study, Rice Bran

INTRODUCTION

More than 100 million tons of plastics are produced worldwide every year and polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) amount to more than 65 percent of the plastics produced. Waste plastics contribute by 8-15 wt% and twice of that by volume to the municipal solid wastes (MSW) [1]. In India plastic waste increased from about 2.6 million tons per annum (MTPA) in 2003 to about 3.6 MTPA in 2007 [2]. From an environmental point of view, dumping plastics in landfills is not a desirable solution due to their non-biodegradability. Further, because of the release of toxic and greenhouse gases, incineration is also not a preferable solution. Incineration completely destroys the organic matter of plastics which could otherwise be utilized for valuable applications. In conjunction with that, certain industrial biomass residues, e.g., rice bran, an outer layer of rice, is a by-product from rice mills that is produced in large quantities in India as rice is one of the major crops there. Nearly one million tons of bran is produced every year in India consisting of 60-70 wt% starch along with proteins, fat, sugar, etc. [3] and becomes available for recovery of useful organic compounds. Biomass fuels contain cellulose, hemicelluloses and lignin. The first two of them form mainly volatile products during pyrolysis by the thermal decomposition of the sugar units. However, lignin molecules do not readily break and ultimately end up in char formation [4].

Energy contained in the biomass can be utilized by different methods starting from old direct burning to pyrolysis, gasification, and liquefaction. Production of syngas by pyrolysis and gasification of biomass is the most promising option [5]. Major products from biomass pyrolysis could be liquid oil, charcoal and gases in different

proportions depending on conditions applied during the process, e.g., temperature, particle size, heating rate, residence time, catalyst, atmospheres, biomass type, etc. [6]. The objective of widely reported literature on biomass pyrolysis has remained to maximize the yields of alternative liquid fuels [7,8]. Pyrolysis oil from biomass waste was found to be highly oxygenated and complex, and chemically unstable. Thus, the liquid products still need to be upgraded by lowering the oxygen content and removing residues. This problem can be partially overcome by cracking in presence of hydrogen. In case of RB, three distinct stages have been observed during its thermogravimetric (TG) characterization in an air at a heating rate of 10 °C/min [9]. Thermal stability was found to decrease in the order of rice>bran>husk. TG curve of rice bran exhibited two mass loss steps at 100 °C and between 175 and 500 °C due to evaporation of absorbed moisture and degradation of different constituents in it, namely starch, protein, sugar and fiber [3].

Many recent publications have dealt with the thermal- and catalytic-pyrolysis of waste polyethylene (PE), polystyrene (PS) and polypropylene (PP) generating products with further applications [10-13]. Moreover, pyrolysis of polystyrene has been optimized for reaction time and reaction energy using temperature profiles to establish the economic viability [14]. Performance of thermal and catalytic pyrolysis of various plastics and their pros and cons with reference to product distribution has been the subject of the recent reviews [e.g., 15]. Costs and rates of deactivation of the catalysts have been mentioned to be an impediment to wider applications of catalytic pyrolysis as a means to curb the menace of the waste plastics.

To address the drawbacks attached with pyrolysis of plastics and biomass, their co-processing has been advanced as a practical solution. Potential benefits of co-processing include the volume reduction of waste, the recovery of various chemicals, and the replacement of fossil fuels [16]. In fact, a synergistic effect in terms of enhanced liquid yields and mechanistic explanations therefore has recently

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been reported [17-25].

Looking at the vast availability of two wastes, namely plastics and RB in India, our aim was to study their co-pyrolysis. Kinetics of this process has been reported in this communication, whereas the product analysis and characterization are the subject of the subsequent communication.

EXPERIMENTAL SECTION

1. Materials and Samples Preparation

RB used in this work was obtained from local rice mills and separated from physical impurities, ground, sieved to -60 to +120 BSS (British standard sieve) (120-250 μm) mesh size, oven dried overnight at 65 °C and stored in a desiccator. Granulated HDPE (200-500 micron particle size) with a density of 0.918 g/cm^3 (ASTM D792) and melt flow index of 7.7 g/min (ISO 1133) was kindly provided by Reliance Industries Limited, Dahej, India. Homogeneity of RB and HDPE (1 : 1 mass ratio) was achieved by mixing in a ball mill for 10 minutes. Typical analysis of RB and HDPE is presented in Table 1.

2. Procedure

Approximately 25 mg sample of HDPE, RB or their mixture with a specified size was placed in a quartz crucible of Perkin-Elmer Pyris 6 TGA. To measure loss of mass with temperature, experiments were conducted at two different heating rates, 5 and 20 °C/min, in the temperature range of 30 °C to 900 °C in flowing nitrogen (30 mL/min). Each run was conducted twice to check the reproducibility of results and the maximum variation in mass was $\pm 5\%$.

At this juncture it would be interesting to know the product characteristics to decide on their suitable applications. Condensed liquid products and un-condensed gas products obtained were quantified by GC-MS (gas chromatography-mass spectroscopy) and gas chromatograph with thermal conductivity detector, respectively. Calorific values and elemental and proximate compositions of the solid

residues have been obtained. These product characterizations are dealt with separately in the subsequent communication.

RESULTS AND DISCUSSION

1. Thermal Degradation of HDPE, RB and their Mixtures

In Figs. 1(a) and (b), it is seen that there are three stages of decomposition of the sample when RB was present unlike in the case of HDPE in which decomposition occurred in a single stage. A similar trend was observed during decomposition of deoiled cakes of jatropha or karanj alone, or with their mixtures with HDPE [18]. Typical nature of these curves remained unaltered with different rates of heating. However, both the curves shifted to the right at a higher rate of heating. HDPE degradation started at 400 °C and was complete by about 500 °C for a heating rate of 5 °C/min. The respective temperatures were 418 and 520 °C when the rate of heating was 20 °C/min. Such shifts have been also reported for pyrolysis of olive residue [26], oil-shale [27] and green river oil-shale kerogen [28]. Maximum rate of mass loss was found to increase with the rate of heating. Endothermicity of two stages, namely, melting of HDPE and its degradation, is responsible for such a shift. Due to absence of ash in HDPE (Table 1), its degradation occurs with minimal formation of residue for both the heating rates. A similar trend of nature during the analysis of HDPE decomposition by TG/DTG has been reported [26]. Though, a study with different shapes of the HDPE (rod, pellet, resin) is important from a practical point of view, it is the size and not the shape of the particles that determines the product distribution. With particle size, the difference in temperatures at the surface and the core increases. And this is known to lead to increased char formation [29]. Characteristic temperatures for various samples are summarized in Table 2.

It can also be observed from the TG curve that RB decomposes at lower temperature than HDPE does. Thermal degradation of RB started at about 70 °C and 100 °C for 5 and 20 °C/min, respectively.

Table 1. Chemical composition of HDPE and RB

Substance	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	C (%)	H (%)	N ^a (%)	O ^b (%)
RB	6.26	77.48	6.9	9.36	51.48	5.23	0.67	42.62
HDPE	0	100	0	0	84.95	14.30	0.55	0.2

^aDry, ash-free basis

^bBy difference

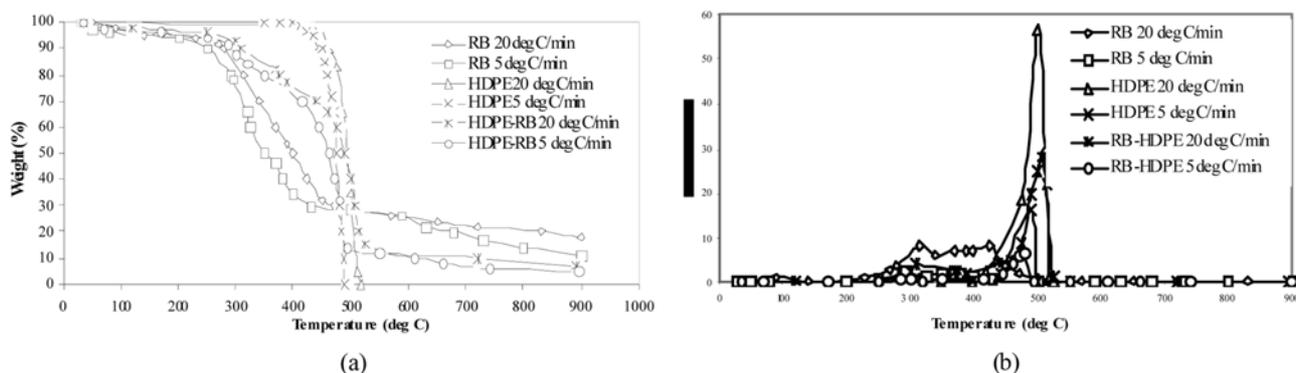


Fig. 1. (a) TG- and (b) DTG-curves of HDPE, RB and their mixture.

Table 2. Degradation temperatures of HDPE, RB and their mixture

	Heating rate, °C/min	First stage		Second stage		Third stage		Residue, wt%	Maximum % Degradation per min
		TR	PT	TR	PT	TR	PT		
HDPE	05			400-500; 490**				00	16
	20			418-520; 501**				00	57
RB	05	70-296	186	296-383	349			11	2.3
	20	100-316	187	316-418	370			18	8.27
HDPE : RB (1 : 1 Mass ratio)	5	70-310	225	310-475	400	475-505	481	5	6.5
	20	100-321	230	321-480	430	480-536	508	7	28

*TR: Temperature Range, °C; PT: Peak Temperature, °C

**TR and PT, respectively for entire range of degradation

Weight loss in the early stage may be attributed to the loss of moisture present. The DTG curve (Fig. 1(b)) for RB shows two major mass loss peaks due to degradation of different constituents, protein and sugar, at intermediate temperature and starch at higher temperature as reported earlier [25]. Peaks at still higher temperatures have been ascribed to degradation of crude fibers. Thus, peaks observed in Fig. 1(b) in the range of about 70 °C to 316 °C are due to degradation of protein and sugar, while those from 296 °C to 418 °C might be due to degradation of starch in RB.

As shown in Table 2, degradation of RB at a heating rate of 5 °C/min generates residue unconverted at 900 °C which increased by 38% upon increasing the heating rate to 20 °C/min. It is a common phenomenon observed in the literature pertaining to the kinetics of biomass pyrolysis. Slower heat transfer from exterior to interior would lead to a temperature gradient at higher heating rates, i.e., lower temperature at the core. This further leads to reduced volatilization of the mass at the core. Also, at higher temperatures diffusional rates of the cracked products out of the particles would be slower than the chemical reaction rate. A similar argument was advanced by Sarvana and Babu [30]. Further, Table 2 also shows that maximum rate of mass loss in RB degradation increases with heating rate. This can be explained on the basis of endothermic nature of decomposition of the constituents, i.e., protein, sugar, fiber and starch. Conversions in endothermic reactions increase with temperature. Hence, at a higher rate of heating, the rate of mass loss too would increase. A shift in the TGA curve to the right at increased heating rate can be seen in Fig. 1.

Table 2 also depicts the pyrolysis behavior of the HDPE-RB mixture. As can be expected, due to the presence of biomass, mass loss starts occurring at lower temperatures also. However, it can be seen that rate of mass loss increases in the case of mixtures as compared to that of pure biomass. For example, the maximum rate of mass loss at 5 °C/min for RB is 2.3. This increases to 6.5 in the presence of HDPE. In the case of biomass, major mass loss occurs at about 300 °C to 400 °C and that for HDPE at 400 °C to 500 °C. Thus, it can be concluded that decomposition of biomass accelerates in the presence of HDPE. Further, pyrolysis of only biomass leaves behind a larger quantity of residue (about 10 to 20%). In biomass-HDPE pyrolysis, very little quantities of residue form (about 5 to 7%). Thermal degradation of RB occurs at lower temperature than that for HDPE. During the early stage of degradation of RB, a wide range of products, such as char, CO₂, CO, H₂O, volatiles, etc., form. At

higher temperatures, CO₂, CO, bio-oil and char are produced due to depolymerization of protein, etc. Char formation during RB degradation at relatively lower temperatures (about 380 to 420 °C) is considered to be responsible for alteration of HDPE degradation behavior, e.g., reduced peak temperature (PT), shift of PT to lower values. Jakab et al. [19] also made similar observations in thermal decomposition of polypropylene (PP) in the presence of wood flour, lignin, cellulose and charcoal in a thermogravimetric analysis. Further, pyrolysis of only biomass leaves behind a larger quantity of residue. In biomass-HDPE pyrolysis, very little quantities of residue form. During the early stage of HDPE-RB degradation, formed bio-oils interact with HDPE leading to increased production of volatiles, and hence carbonization (to residue formation) of the bio-products is suppressed. Similar reasoning was advanced by Zhou et al. [17] also to explain lower residue formation in co-pyrolysis of Chinese pine wood sawdust with HDPE, LDPE and PP. As is evident in Fig. 1(a), the location of the TGA curves for the mixture is in between that of HDPE and the biomass. This indicates that HDPE too starts losing mass at temperatures lower than 400 °C (at which pure HDPE decomposition starts). Thus, enhanced rate of mass loss of biomass, reduced residue formation and earlier degradation of HDPE bespeak for the synergistic effect of co-pyrolysis of HDPE-biomass.

In contrast to HDPE, structures of PP with tertiary carbon atoms have considerably lower resistance against degradation. Thus, higher conversions to volatiles (higher yield of liquids) can be achieved in PP pyrolysis [31]. Degradation of polystyrene occurs at lower temperature [32] and involves two steps: cracking of polymer chain mainly into monomer, ethylbenzene and oligomers, and splitting-off substituents from the aromatic rings [33]. Differential thermogravimetry (DTG) curves for HDPE, PP and PS contain only one peak, while more peaks have been observed in case of PVC due to more degradation steps. [34]. Though pyrolysis of individual polymers has attracted much attention, studies on pyrolysis behavior, particularly of mixed plastics, are rather scarce. Still, from the study reported by Chattopadhyay, et al. [35] it can be deduced that the mixture of HDPE, PP and PET starts decomposing at about 250 °C against 477 °C for pure HDPE [17]. The decomposition of these two plastic samples ends at 521 °C and 700 °C, respectively. In the latter case, solid residue seems to have formed due the presence of PET. The addition of PP in HDPE has been reported [36] to improve the liquid yield during the degradation in supercritical acetone (450 °C

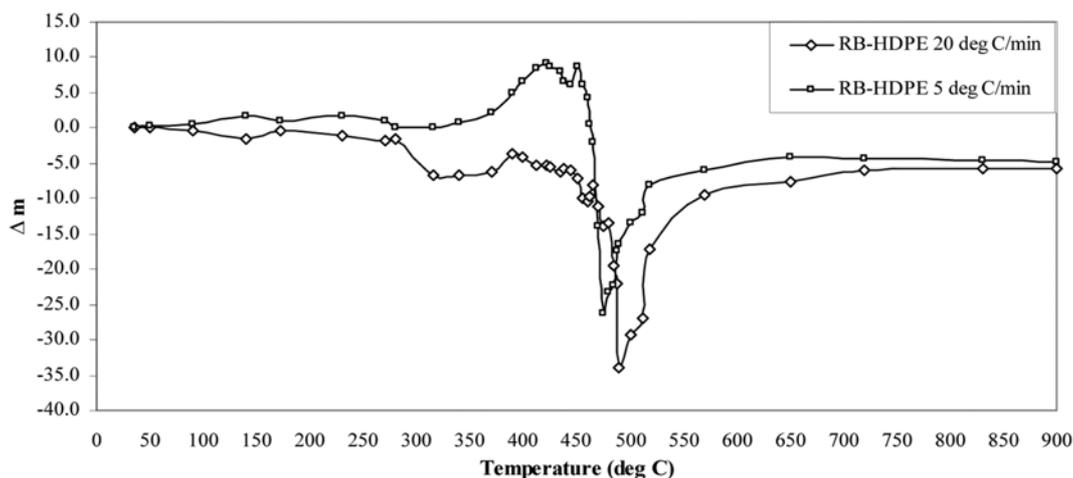


Fig. 2. Variation of Δm for RB, HDPE and their mixtures at different heating rates.

to 470 °C, and 60 atm to 100 atm). In case of catalytic decomposition, a reduction of 20 °C was reported [37] when LDPE, PP and PS were present along with HDPE.

To investigate whether interactions existed between RB and HDPE, we defined the difference of weight loss (Δm), $\Delta m = m_{mixture} - (y_1 m_1 + y_2 m_2)$, where $m_{mixture}$ is the weight loss of mixture, y_i is the weight fraction of each material in the mixture and m_i is the weight loss of each material in the same operating conditions. Finally, m describes the extent of synergistic effect during co-pyrolysis. It was found that for the RB-HDPE mixture m was less than $\pm 11\%$ at temperatures lower than 470 °C, indicating poor interactions between RB and HDPE. After 470 °C, the value of m declines first and then increases up to 650 °C. The value reached a maximum of about 26% at 475 °C and 34% at 489 °C for a different heating rate of 5 °C per minute and 20 °C per minute, respectively. The positivity of the values and their extent imply the interactions between RB and HDPE co-pyrolysis. Thus, at a higher rate significant synergistic effect could be achieved. Above 650 °C, the devolatilization process of the mixture was complete and hence m becomes stable at this stage (Fig. 2).

2. Kinetics of Thermal Degradation

Thermal degradation of cellulosic compounds involves a large number of parallel and series reactions, and thermogravimetry study of such compounds provides information on the ‘overall’ reaction kinetics. Many researchers have studied the kinetics of biopolymer cracking [e.g., 24,26]. The general observation from these reports is that kinetics of bio- and synthetic polymers follows the first order. Further, pyrolysis of different combinations of petroleum vacuum residue with PP, coal or biomass also can be represented by the first order kinetics [24].

The process maybe represented by the following reaction:



The method of determining activation energy from the TG/DTG data was described in detail earlier [18]. The resultant equation for this is as follows:

$$\ln[-\ln(1-x)] = \ln(A RT^2/\beta E) - E/RT \quad (1)$$

The activation energy, E , can be calculated from the slope of $\ln[-\ln(1-x)]$ versus $1/T$ plot. Results of this exercise are exemplified in

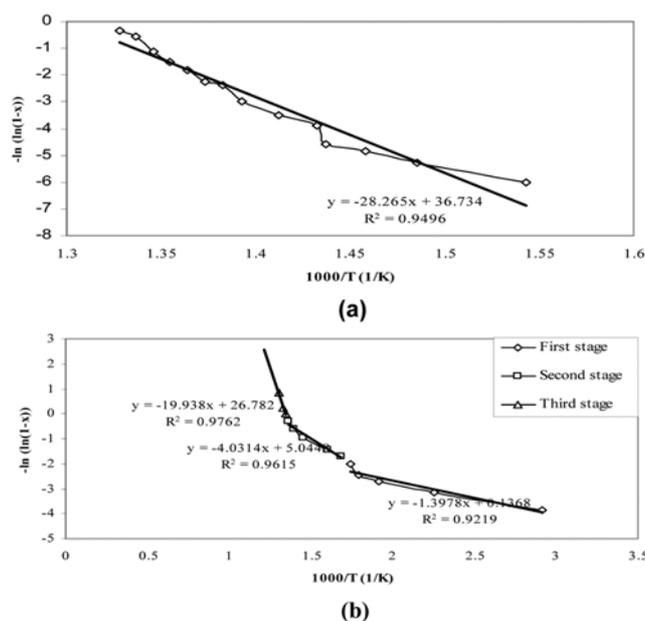


Fig. 3. Arrhenius plot for (a) HDPE (b) RB-HDPE degradation at 5 °C per minute.

Fig. 3 for degradation of HDPE and RB-HDPE at a heating rate of 5 °C/min. Similarly, values of activation energy for other cases were determined.

Table 3 shows the activation energy of all samples that were determined by this method. Degradation of RB-HDPE occurred in three subintervals resulting in three different values of activation energy for the entire range, while HDPE degradation occurred in a single stage. It is easy to notice that the values of activation energy are less for the mixture than those for individual species. The presence of RB reduces the activation energy for the mixture containing 50 wt% HDPE at both the rates of heating. Here it is required to mention that HDPE decomposes between 400 and 500 °C. At higher rate as well as at higher temperatures the activation energy is higher. This can be explained on the basis of predominating diffusional resistance at those conditions. Similar behaviors have been reported by Aboulkas et al. [26] and Ahmaruzzaman and Sharma

Table 3. Activation Energy for thermal decomposition of HDPE, RB and their mixture

Substance	Heating rate, °C/min	Activation Energy, kJ/mol		
		First stage	Second stage	Third stage
HDPE	5	234.99*		
	20	257.80*		
RB	5	13.08	44.78	--
	20	15.49	46.33	--
HDPE:RB	5	11.62	33.51	165.76
	20	14.54	33.57	174.96

*Entire range

[24] for olive residue-HDPE and calotropis procera-PP mixtures, respectively. Free radicals formed during the polymer's cracking have been proposed [24] to react with the degradation products from the biomass, which in turn leads to reduced overall activation energy.

CONCLUSIONS

Thermogravimetry analysis provides useful information on thermal decomposition characteristics of RB, HDPE and their mixture at different heating rates. Results show that heating rate has a significant effect on degradation pattern. Co-pyrolysis of RB with HDPE offers reduction in yield of residue. Synergistic pyrolysis of biomass and a polymer (HDPE) is reflected in difference of weight loss (m) between experimental and theoretical ones, reduced overall activation energy, lower peak temperatures and negligible quantity of the residue left behind.

NOMENCLATURE

HDPE: high density polyethylene

RB : rice bran

 β : heating rate [°C/min]

E : activation energy [kJ/mol]

R : gas constant [8.314 J/gmol K]

T : pyrolysis temperature [K]

x : conversion

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