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Thermogravimetric characteristic and kinetic of catalytic co-pyrolysis of biomass with low- and high-density polyethylenes

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Abstract The pyrolysis of wood fuel (WF) and polyethylenes (low-density polyethylene; LDPE and high-density polyethylene; HDPE) in a non-catalytic and catalytic co-pyrolysis over zeolite catalyst (ZSM-5) were studied via a thermogravimetric analysis. The result obtained for the biomass with LDPE and HDPE blends shows that the peak temperature decreases significantly only at blends with catalyst as compared to the peak temperature of isolated LDPE and HDPE materials. The peak temperature of WF/LDPE/ZSM-5 (390 °C) was lower than that of WF/HDPE/ZSM-5 (480 °C). The weight loss differences between experimental and theoretical values were greater than 1% at temperature higher than 500 °C in the various admixtures which depicts the occurrence of chemical interactions between the blends. After catalysts were added to the blend, the fuels became more reactive to thermal degradation. The results of the non-catalytic pyrolysis kinetics revealed activation energy values of 54.09 and 95.90 KJ/mol for WF/LDPE and WF/HDPE, respectively. However, with the presence of ZSM-5 activation, energy falls to 24.13 and 50.45 for WF/LDPE/ZSM-5 and WF/HDPE/ZSM-5, respectively. The findings in this work show that the kinetic of catalytic co-pyrolysis of biomass with plastic can be viewed as a potential thermochemical conversion method that can be effectively utilized for a marked reduction in energy requirement of the process.

Keywords Pyrolysis · Kinetics · TG/DTG · ZSM-5 · Biomass · LDPE · HDPE

1 Introduction

The continuous increase in the price of petroleum-derived fuels has led to need for an attractive and renewable based feedstock such as biomass for energy generation. Biomass is an environmentally benign, sustainable, and inexpensive feedstock derived from agricultural materials. Biomass can be converted into solid fuel and value-added chemical due to its abundant source of organic carbon and hydrogen [1]. It can be used directly as a solid fuel or converted into liquid or gaseous forms for generation of heat and electric power. Thermochemical conversion is an effective technique for transformation of biomass into these value-added products. This conversion process includes pyrolysis, gasification, or liquefaction. Fast pyrolysis, which is a rapid decomposition of biomass under inert atmosphere, is one of the most recent cost-effective thermochemical technique to convert solid biomass into bio-oil [2]. However, the resulting bio-oil cannot be used directly as a replacement for the petroleum-derived equivalent because of its high oxygen content (35–40 wt%), high acidity (pH of 2–3), poor volatility, low storage stability, and low heating value (17 MJ/kg); in order to upgrade its properties, it is often necessary to employ physical stabilization (fractionation, filtration, solvent addition) and/or thermochemical upgrading [3]. Thermochemical upgrading includes the use of either heterogeneous catalysts in the pyrolysis process (catalytic fast pyrolysis; CFP) or secondary

Highlights
• This work attempts the kinetics of catalytic co-pyrolysis with different plastics for the first time.
• Thermal behavior of catalytic co-pyrolysis of biomass with plastics was studied via TGA.
• Catalytic co-pyrolysis of biomass with plastics decreased activation energy.

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treatment of the liquid product in a catalytic process (hydrodeoxygenation). CFP is an effective method of converting biomass to value-added chemicals or transportation fuels [4]. The products obtained from this method are similar in chemical composition to current gasoline and diesel fuels than the conventional bio-oil [5, 6]. However, low product yields and high coke formation associated with the process are the major obstacles militating against the effectiveness of the process [7, 8]. In addition to the aforementioned drawbacks, the bio-oil obtained from catalytic pyrolysis is known to contain polycyclic aromatic hydrocarbons (PAH) such as phenanthrene, methylphenanthrenes, methyl fluorenes, chrysene, and the benzopyrenes [9]. Some of these compounds are known to cause gene mutation and cancer and therefore not environmentally safe for handling and utilization [9].

Recently, biomass has been co-fed with plastics and alcohols in order to enrich the feedstock with hydrogen. This advancement is reported to provide an alternative pathway of solving the problems of low product yields and high coke formation [10]. The addition of plastic to biomass during catalytic pyrolysis has dual beneficial advantages; firstly, it serves as a way of reducing the menace of environmental pollution caused by this recalcitrant material, and secondly, it assists in energy recovery. Co-pyrolysis of catalytic biomass with plastic results in qualitative petrochemicals with high yield and minimizes the rate of coke formation. Numerous studies have documented the effect of plastic in catalytic biomass pyrolysis [11–14].

Pyrolysis of biomass is a complex process involving parallel and series reactions [15, 16]. The decomposition of biomass has been described by three-component independent reaction, each corresponding to the decomposition of hemicellulose, cellulose, and lignin, respectively. The knowledge of biomass pyrolysis kinetic is essential for the design and optimization of reactors. The weight loss kinetic model developed for biomass is of two types: the single component overall model (SOM), which considered the biomass as composed of a single component and uses its char–volatile reaction to describe the weight loss kinetics [16]. The second one is the multi-component overall model (MOM) considering biomass as being composed of hemicellulose, cellulose, and lignin [17, 18]. In this case, the components are modeled separately and the biomass decomposition is the summation of all the three components. Generally, the weight loss changes as the temperature increases. This weight loss is controlled mainly by lignocellulose decomposition. Since the weight loss depends on cellulose, hemicellulose, and lignin component, SOM cannot account for the possible change in weight loss.

Thermogravimetry analysis (TGA) is the most common thermo-analytical technique used in the analysis of biomass. TGA measured the changes in weight loss caused by devolatilization of biomass during thermal decomposition as a function of increasing temperature or time. Numerous studies have investigated the pyrolysis kinetics of different biomass materials using TGA method. The kinetic of catalytic biomass pyrolysis has been investigated for straw mixed with solid acid catalysts (ZSM-5 loaded on γ-Al$_2$O$_3$), bifunctional catalysts (Ni-Mo-ZSM-5 loaded on γ-Al$_2$O$_3$), and industrial catalysts (CIP) [19, 20]. Foster et al. [20] reported the pyrolysis of tobacco rob over two different catalysts (dolomite and NiO). While Iliopoulou et al. [21] carried out pyrolysis of beech wood with ZSM-5 modified with Ni and Co. Recently, Zhang et al. [12, 13] studied the thermal behavior of two kinds of biomass materials (cellulose/Douglas fir sawdust) mixed with plastic (LDPE) over ZSM-5 catalyst [12, 13].

In the present study, the devolatilization kinetic of non-catalytic and catalytic pyrolysis of biomass with different plastics (LDPE and HDPE) using a TGA was investigated. This is with the view of understanding of the synergistic effect of two admixtures for bio-fuel. Although catalytic kinetics of different biomass materials on plastic material (co-pyrolysis of cellulose and sawdust with LDPE) has been reported, the effect of catalytic co-pyrolysis of biomass on different plastics has never been documented. According to Miranda et al. [22], Chattopadhyay et al. [23, 24], and Xiong et al. [25], different plastics exhibit different thermal behavior depending on the kind of the polymer structure (linear or branch) and type of side groups attached to the macromolecular chain. The variation in structural arrangement is envisaged to exhibit different behaviors in pyrolysis product upgrade. However, there is no documented evidence in this regard. Therefore, the present study will be attempting for the very first time the thermogravimetric characteristic and kinetics of catalytic co-pyrolysis of tropical biomass (sawdust) with two different plastic (LDPE and HDPE) materials.

2 Materials and methods

2.1 Materials

The Iroko wood (*Chlorophora excelsa*) used was obtained from a Sawmill in Gidan Kwano, Minna, Nigeria. The sawdust was dried using an oven at 105 °C for 2 h. It was then crushed into smaller particle sizes using mortar and pestle. The sawdust was further sieved to obtain biomass of particle size 150 μm in diameter. LDPE and HDPE (Sigma-Aldrich Corporation, USA) were purchased from Minna Market Nigeria. ZSM-5 which was obtained from Zeolyst international has SiO$_2$/Al$_2$O$_3$ ratio of 80 and surface area of 425 m^2/g. LDPE and HDPE densities are 0.925 and 0.941 g/cm^3, respectively. Polymers were prepared by crushing, cutting, and

shredding. The crushed and sized material were heated to 100 °C and then cooled to atmospheric temperature.

2.2 Catalyst preparation

The ZSM-5 zeolite was impregnated via wet impregnation method [26]. About 100 g of ZSM-5 was added to solution of ammonium hydroxide slowly. The mixture was stirred continuously for 30 min, filtered, and washed with deionized water. The filtered ZSM-5 was oven dried at 105 °C for 6 h and calcined in a muffle furnace at 550 °C for 5 h in air atmosphere to convert it to its protonated form, H-ZSM-5. The H-ZSM-5 obtained solid was sieved to 150 μm.

2.3 Thermogravimetric analysis

The thermal decomposition of the samples (WF, LDPE and HDPE) was carried out using PerkinElmer thermogravimentric analyzer (Perkin ElmerTGA-4000). TGA equipment was purged with nitrogen gas at a heating rate of 283.15 K min^{-1} where the temperature ranged from room temperature to 900 °C. About 5 g of individual sample with particle size of <150 μm was placed inside the crucible and heated with nitrogen flow rate of 50 ml/min. Biomass and plastics were blended in a mass ratio of 4:1 for non-catalytic co-pyrolysis. While for the catalytic co-pyrolysis, the biomass/plastic blends were mixed with ZSM-5 powder in a mass ratio of 4:1. For each run, 5 g was loaded into the crucible to perform the TGA experiment.

2.4 Experimental and theoretical weight loss calculation approach

The decomposition of solid sample is expressed by two important thermographs: differential thermogravimetric (TG)/differential TG (DTG) curves. While TG curve expresses the features of weight loss against temperature or time, DTG magnified the small changes in these features. The interaction between biomass and plastic would be highlighted by DTG that is calculated based on the following expression [12, 25].

$$W_{exp} = \frac{W_o - W_t}{W_o} \times 100\% \tag{1}$$

where W_o and W_t represent the weight of the initial sample and at temperature T, respectively. Meanwhile, the theoretical weight loss (W_{cal}) of the blend is defined by Eq. (2):

$$W_{cal} = x_1 W_1 + x_2 W_2 \tag{2}$$

where W_1 and W_2 are the weight loss of pure different materials at the same experimental conditions, and X_1 and X_2 are the mass fraction of each material in the blend.

The ΔW, which is the difference in weight loss, is defined as Eq. (3):

$$\Delta W = \left(W_{exp} - W_{cal}\right) \tag{3}$$

2.5 Kinetic study

The decomposition rate of solid material can be expressed as

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E_a}{RT}\right)} f(\alpha) \tag{4}$$

where α is the conversion factor, A is the pre-exponential (frequency) factor, E_a is the activation energy, T is the absolute temperature, R is the gas constant, and $f(\alpha)$ is the reaction model. Gravimetrically, α is defined by

$$\alpha = \frac{mo - mt}{mo - mf} \tag{5}$$

where m_o is the initial mass of sample, m_t and m_f refer to the mass at temperature T and at the final pyrolysis temperature, respectively. Many researchers have assumed first-order reaction in describing solid fuel pyrolysis [27, 28]; therefore, the pyrolysis reaction equation of waste plastic transformed into Eq. (6):

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E_a}{RT}\right)}(1-\alpha) \tag{6}$$

Under non-isothermal conditions in which the sample is heated at a constant rate, rearranging and integrating Eq. (6) gives

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right]\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \tag{7}$$

where $\beta = dT/dt$ is the heating rate. It has been shown that for most value of E and for the temperature range of pyrolysis, $E/RT \gg 1$, thus the expression $\ln[(AR/\beta E) \times (1-2RT/E)]$ in Eq. (7) is a constant, which gives

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = -\frac{E_a}{RT} \times \frac{1}{T} + \ln\left(\frac{AR}{\beta E_a}\right) \tag{8}$$

The plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$ gives a straight line of slope $-E_a/R$. From this slope and intercept, the E_a and pre-exponential factor A can be determined, respectively.

The mean activation energy E_m of co-pyrolysis of blend was calculated using the following equation proposed by Cumming [29]:

$$E_m = \sum E_i F_i \tag{9}$$

3 Results and discussion

## 3.1 Thermogravimetric analysis of individual materials and their blends

Thermogravimetric analysis (TGA) is a thermal analytical technique which is extensively used to understand the pyrolysis characteristics and reaction mechanism of a fuel prior to its actual utilization in energy production [30]. Information on multiple pyrolysis indices such as onset temperature and peak temperature can be rapidly extracted from the TGA thermograph. Figure 1a, b shows TG curves of sample of biomass with individual polymers investigated in this study. It can be observed that the WF had started decomposing at a lower temperature (178 °C) than the HDPE (465 °C) and LDPE (370 °C); however, rapid degradation of WF begins at 250 °C and end at 350 °C. The thermal degradation of HDPE and LDPE occurred within the temperature range of 370–550 °C. The residual biomass after degradation was obtained at a temperature of 904 °C, while complete decomposition of the polymers was achieved at final temperature of 600 °C. It is obvious that the order of reactivity of the isolated materials studied is WF (315 °C) > LDPE (440 °C) > HDPE (530 °C), as evidenced by the decomposition peak temperature in Fig. 2a, b, since low decomposition peak temperature means high reactivity of the sample, respectively [31]. The residual mass of the biomass case significantly diminished in comparison to the biomass/plastic cases shown Fig. 1a, b. This residual variation may be attributed to high liquid yield by hydrogen supplied from the plastics materials during pyrolysis. Vasile and Brebu [32] reported that plastics act as source of hydrogen in thermal co-pyrolysis with biomass which is associated with limited hydrogen content.

For 20 wt% LDPE blended with 80 wt% WF, the degradation occurred at temperature range of 380–460 °C which lie between the curves of the individual materials. However, the decomposition of the blend over catalyst occurred at lower temperature (365–410 °C) than that without catalyst. This result demonstrated that the catalyst exerts significantly influence on the decomposition of WF, LDPE, and HDPE which seriously lower the peak decomposition temperature. WF/LDPE blends exhibit lower degradation than WF/HDPE blends. This could be due to the fact that the degree of polymerization of LDPE is normally lower than that of HDPE.
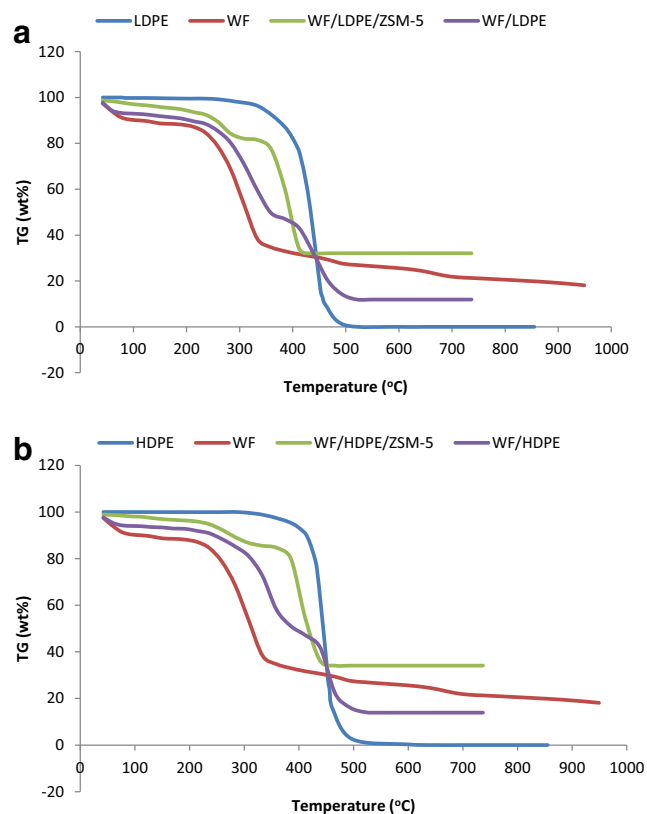
Fig. 1 **a** TG curves for pyrolysis of individual materials (WF and LDPE) and various blends (WF/LDPE) and (WF/LDPE/ZSM-5). **b** TG curves for pyrolysis of individual materials (WF and HDPE) and various blends (WF/HDPE) and (WF/HDPE/ZSM-5)
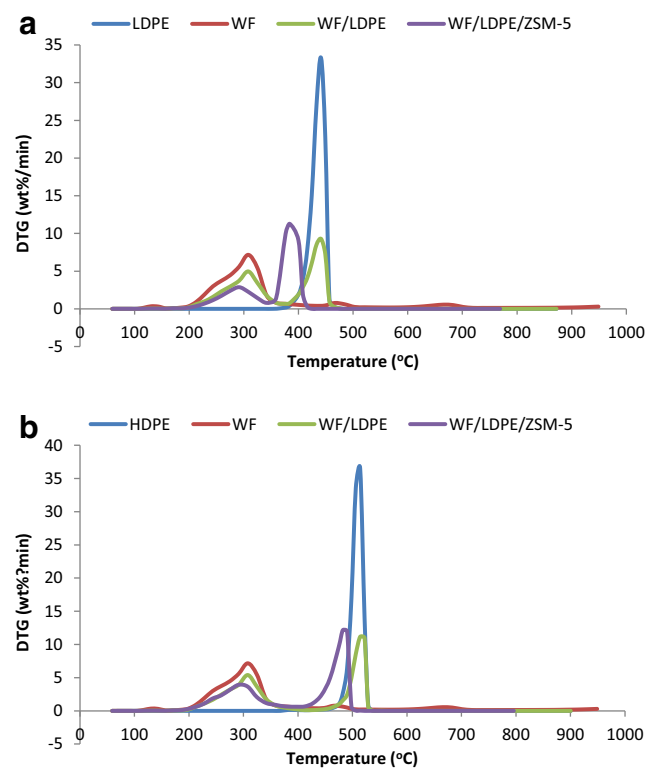
Fig. 2 **a** DTG curves for pyrolysis of individual materials (WF and LDPE) and various blends (WF/LDPE) and (WF/LDPE/ZSM-5). **b** DTG curves for pyrolysis of individual materials (WF and HDPE) and various blends (WF/HDPE) and (WF/HDPE/ZSM-5)

LDPE has a lot of branches with less compact structure as against the linear closely packed structure associated with HDPE. This is the obvious reason why HDPE is more stable against degradation than LDPE [33, 34].

The pyrolysis process of WF can be divided into three stages (dehydration, main devolatilization and continuous slight devolatilization) based on the slope change of the DTG curve. During the first stage, the TG curves of WF exhibited slight degradation between 29 and 178 °C due to the physical loss of water. The second stage took place between 178 and 378 °C with major weight loss resulting from the main devolatilization via the decomposition of most lignocelluloses components (hemicelluloses, cellulose, and lignin). In this stage, the hemicelluloses, cellulose, and lignin exhibited different peaks at different temperature as shown on the DTG curve of WF (Fig. 2a, b). Hemicellulose decomposition on the DTG curve of WF shows a minor peak at about 270 °C as depicted in Fig. 2a, b). The main peak on the DTG of WF decomposition emerged at about 305 °C, corresponding to the decomposition of cellulose. However, the thermal degradation of lignin run in parallel with that of hemicellulose and cellulose and as a result covered a wide temperature range between 178 and 500 °C. Similar results for the thermal behavior of biomass have been reported [24, 25, 41]. The TG and DTG curves for each blend were found to lie between the curves of isolated materials and the final weight losses of blends corresponding to type of blending. For non-catalytic pyrolysis, the final weight loss was lower than that of catalytic pyrolysis as shown in Fig. 1a, b. According to the open literature, coke formation on the catalyst is the main reason for the reduction of weight loss, which actually is the obstacle militating against the effectiveness of the catalytic process [7, 8]. The course of thermal degradation and product composition was reported in many articles [35, 36]. The study of biomass pyrolysis process has revealed that bio-oils are produced via free radical generation by thermal bond cleavage with oxygenated compounds [37]. During this process, hydrogen is removed from carbohydrate unit, and this resulted to high char formation. However, the presence of hydrogen atmosphere during co-pyrolysis of biomass with plastic produces a higher yield of bio-oils as char formation is inhibited and recondensation of the volatiles takes place. In our case, this hydrogen is donated by LDPE and HDPE both of which has hydrogen content of approximately 14 wt%. Consequently, bio-oil production is enhanced and less amount of char is produced. During co-pyrolysis of biomass with plastic, biomass can initiate the radical formation that lead to scission of plastic chain. This likelihood has been reported by Sharypov et al. [38] while explaining the course of degradation of biomass which occurred at lower temperature than those of polyolefines during the co-pyrolysis process of biomass with plastic materials.

Since the thermal degradation process was much faster in biomass than plastic, the devolatilization of different components can be easily separated. In this case, two main stages were found in both TG/DTG curves for the blends. The first stage was attributed of the decomposition of WF, temperature ranges from approximately 200 to 360 °C, and the second stage occurred in the temperature range of 380–570 and 400–560 °C, which corresponded to the decomposition of LDPE and HDPE, respectively.

For the biomass/plastic blends, the decomposition is characterized by two main stages unlike the single decomposition stage that was observed when individual materials were thermally degraded. The first peak displayed decomposition characteristic of WF material. The effect of plastics is negligible at this stage since the decomposition temperature of WF is less than the onset temperature (300 °C) for plastic decomposition. According to Han et al. [39], at temperature less than 300 °C, polymers only soften but do not decompose. This phenomenon leads to a reduction in the heat transfer to the biomass during thermal decomposition. In comparison to pure WF material, the amount of WF on the second decomposition peak is marginal and overlaid by plastic decomposition. Consequently, the peak temperature decreases significantly for all the blends (see Fig. 2a, b). The DTG curves of WF/LDPE and WF/HDPE show independent peak at 435 and 515 °C, respectively. With the presence of catalyst, the peak shifted to 390 and 480 °C for WF/LDPE/ZSM-5 and WF/HDPE/ZSM-5, respectively.

3.2 Interaction effects between biomass and polymers

In order to provide in-depth insight into the interaction between biomass and polymers, the weight loss difference, ΔW, was considered [12, 13, 25, 40]. The weight loss, ΔW, for WF and different polyethylene blends is shown in Fig. 3. It can be observed that ΔW varies with temperature; however, this variation was lower than ±1% between room temperature and 250 °C for all the two blend cases. This is due to the fact that both LDPE and HDPE resist decomposition at these temperatures; hence, there was no observable interaction between
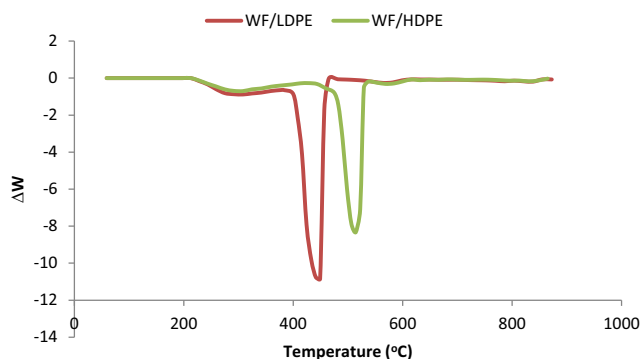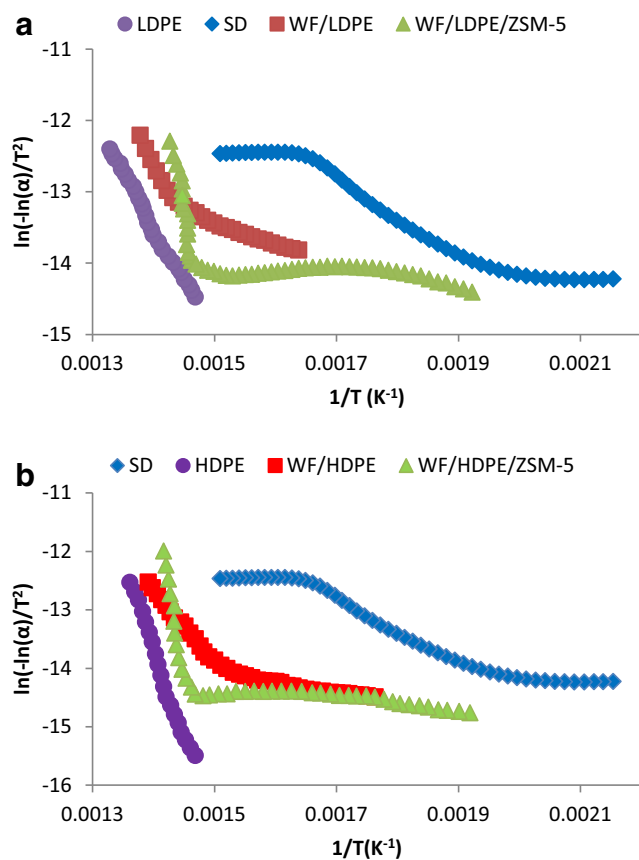

Fig. 3 Variation of ΔW for WF with LDPE and HDPE blends

Fig. 4 **a** Pyrolysis kinetic curves of individual materials (WF and LDPE) and various blends (WF/LDPE) and (WF/LDPE/ZSM-5). **b** Pyrolysis kinetic curves of individual materials (WF and HDPE) and various blends (WF/HDPE) and (WF/HDPE/ZSM-5)

WF and different polyethylene blends, and ΔW is ideally equal zero. But in this study, ΔW was not equal to zero. Xiong et al. [25] and Zhang et al. [12] reported similar results during co-pyrolysis of potato/HDPE and cellulose/LDPE mixtures. Both researchers attributed the changes (<1%) in ΔW to experimental error caused by the thermal conductive

conditions and the different initial weight of the two samples. This pyrolysis behavior of the blends is attributed to the fact that LDPE/HDPE soften at about 300 °C but does not decompose. At higher temperature (>400 °C), WF/LDPE and WF/HDPE blend rapidly decompose; therefore, ΔW increased significantly. The change in ΔW points to the occurrence of chemical reaction during WF/LDPE and WF/HDPE blends. This finding contradicted previous research *findings* indicating the lack of synergy between biomass and plastic during co-pyrolysis but confirmed more recent reports of Xiong et al. [25] and Zhang et al. [10]. The exact mechanism by which synergy between plastic and biomass causes chemical reaction during co-pyrolysis is not very clear.

3.3 Kinetic analysis

To determine the kinetic parameters (apparent activation energy (E), the correlation coefficient (R), and pre-exponential factor (A)), $\ln[-\ln(1-x)T^2]$ is plotted against $1/T$ for pyrolysis of individual biomass, LDPE, and HDPE, and the various blends were utilized as shown in Fig. 4a, b. The R of all the fitting straight lines was above 0.9 suggesting that all the experimental data were fitted by first-order reaction model. Thus, the pure pyrolysis of WF and plastic can be described as a first-order reaction, whereas the co-pyrolysis process of WF and plastics blends can be described as two successive first-order reactions.

The α is the difference of conversions at final and initial temperature of each pyrolysis stage, which shows the degree of conversion in different stages. For pure materials of WF, LDPE and HDPE were about 15–90, 1–100, and 1–99%, respectively. In the case of non-catalytic and catalytic blends, value of α the values of α was within the temperature ranges as shown in Table 1. These results indicated that the volatile release from WF pyrolysis was inhibited by the melting plastic samples, which translate to the fact that only physical effect has taken place during primary pyrolysis of WF and plastic

Table 1 Kinetic parameters for the pyrolysis and co-pyrolysis of WF with LDPE and HDPE

Sample	Temperature (°C)	Conversion (%)	E (KJ/mol)	E_m (KJ/mol)	A (min^{-1})	R^2
WF	200–370	15–90	24.59		2.67×10^5	0.9744
LDPE	400–520	1–100	147.47		3.81×10^{14}	0.959
HDPE	415–550	1–99	250.39		1.83×10^{16}	0.9967
WF/LDPE	219–381	17–64	29.11		2.84×10^5	0.9841
	381–472	64–81	137.11	36.93	3.79×10^{14}	0.973
WF/ HDPE	400–550	17–67	29.90		2.871×10^5	0.9763
		67–88	188.73	95.90	1.83×10^{16}	0.951
WF/LDPE/ZSM-5	370–440	8–95	24.13		1.44×10^5	0.935
			108.12	24.13	1.92×10^{14}	0.973
WFH/HDPE/ZSM-5	400–500	17–59	21.90		1.711×10^5	0.966
		59–86	173.14	55.95	7.37×10^{15}	0.958

blends. The E_a value for WF is much lower than that of plastic samples, established that the thermal reactivity of WF was higher than those of plastic samples, which resulted into two distinct temperature intervals for the two tested materials. In the case of blends, the activation energies of stage I, corresponding to the devolatilization of WF, were quite close to the value obtained from the pyrolysis of pure WF. These results confirmed that since there is a large difference in initial temperature of the two materials, the presence of HDPE did not visibly affect the pyrolysis behavior of WF. Some researchers have drawn similar conclusions [24, 25]. Conversely, the activation energies of second stage were lower than the value obtained from the pyrolysis of pure HDPE. This inconsistency has been explained by previous researchers [24, 25]. They argued that the activation energy obtained from the TGA experiment is not a true one, and the experimental value of plastic was larger than the TGA experiment due to the delay in the release of volatiles, which give rise to in a lower apparent activation energy observed in the second stage.

The kinetic parameters include apparent activation energy (E) and pre-exponential factor (A) for WF, LDPE, HDPE, WF/LDPE, WF/HDPE, WF/LDPE/ZSM-5, and WF/HDPE/ZSM-5 during pyrolysis as obtained from Fig. 4a, b. The complementary data is also presented in Table 1.

The apparent activation energy (E_a) for WF, LDPE, and HDPE degradation was 24.59, 147.47, and 250.39 KJ/mol, respectively. The E_a of WF is lower than that of polyethylene, while the E_a of HDPE is 66 KJ/mol higher than that of LDPE. The difference in E_a value can be attributed to the difference in polymer structure. Wall et al. [41] reported that the variation in E_a between polyethylenes is dependent on the number and length of the branches. LDPE has lower degree of branching than HDPE. Miranda et al. [27] reported significant variation in E_a values between LDPE (230–163 kJ/mol) and HDPE (271–269 kJ/mol).

The E_a value of 54.09 KJ/mol for WF/LDPE blend is lower than that of E_a values of LDPE (147.47 KJ/mol). Consequently, the result shows that there was a positive synergy between WF and LDPE that led to lowering the E_a value. Blending WF/LDPE with ZSM-5 further lowers E_a value of WF/LDPE blend. Higher activation energy means slower reaction, and catalyst reduces the E_a value, thereby resulting in faster reaction. The E_a of HDPE and WF are 250.39 and 24.59 KJ/mol, respectively, while the E_a of WF and HDPE mixture is only 95.90 KJ/mol, which is both less than that of HDPE. Additionally, with the presence of catalyst, the E_a decreased to 50.45 KJ/mol. It was reaffirmed that the catalyst had an important influence in the decrease of E_a.

4 Conclusions

From thermogravimetric analysis of biomass/polyethylene blends in a non-catalytic and catalytic pyrolysis, the following conclusions are drawn. The ΔW variation can be attributed to occurrence of chemical reaction. The decomposition peak of WF/LDPE/ZSM-5 was higher than of WF/HDPE/ZSM-5. After catalysts were added to the blend, the fuels became more reactive to thermal degradation. The result of the kinetic evaluation for the biomass/plastic blends shows lower activation energy when compared to the individual plastics, while the kinetic evaluation of catalytic blends shows an appreciable reduction in the activation energy of the process in comparison to the non-catalytic blend process.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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