

Thermal and Kinetic Behaviors of Corn Stover and Polyethylene in Catalytic Co-pyrolysis

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Thermal decomposition characteristics and kinetics of high-density polyethylene (HDPE), corn stover (CS), and their blended mixture (1:1 w/w ratio) during non-catalytic and catalytic co-pyrolysis were studied via thermogravimetric analysis (TGA). The results indicated synergetic interactions between the biomass and the plastics during co-pyrolysis as measured by weight loss (ΔW); this effect was attributed to radical interactions during co-pyrolysis. The pyrolysis catalysts with higher nickel loadings (5%, 10%, and 15%) appreciably diminished the solid residue. Kinetic studies indicated that the pyrolysis was a first-order reaction based on the fitted thermogravimetric data. The activation energy (E) and pre-exponential factor (A) ranged between 26.13 kJ/mol to 392.67 kJ/mol and between 156.24 min^{-1} to $9.19 \times 10^{23} \text{ min}^{-1}$, respectively. There was a kinetic compensation effect (KCE) observed among the two kinetic parameters. The activation energy (E) decreased for each pyrolysis stage with the presence of a catalyst. The results indicated that catalytic co-pyrolysis could provide great potential for reducing the pyrolysis energy input.

Keywords: Thermogravimetric analyzer (TGA); Synergistic effect; Kinetics; Coats and Redfern; Nickel catalysts; Kinetic compensation effect (KCE); Catalytic co-pyrolysis

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INTRODUCTION

Lignocellulosic biomass is one of the environmentally sustainable and renewable energy sources that is also carbon neutral during its lifecycles (Chattopadhyay *et al.* 2016). To help solve the global energy crisis, the production of liquid fuels and chemicals has become a promising conversion path (Yang *et al.* 2016). At present, numerous studies have been conducted to synthesize fine chemicals from the catalytic pyrolysis of lignocellulosic biomass. Dozens of microporous, mesoporous, and macroporous catalysts have been shown to be effective in converting biomass, such as ZSM-5, MCM-41, FCC, LOSA-1, SBA-15, CNT and their modified derivatives (Xia *et al.* 2015; Chagas *et al.* 2016; Hu *et al.* 2016; Kim *et al.* 2016; Zhang *et al.* 2016b). Among them, ZSM-5 zeolite has been proved to be one of the most effective catalysts because its strong acidity can be significant for removal of oxygenated organic compounds; at the same time, it can favor the production of aromatics due to its unique pore structure (Lin *et al.* 2015). However, coke formation has been found to be a main challenge in the catalytic pyrolysis of lignocellulose; coke formation leads to deactivation of the pyrolysis catalyst and to lower biomass conversion efficiency. This creates a bottleneck that restricts the development of catalytic pyrolysis technology (Li *et al.* 2014).

In this paper, the hydrogen to carbon effective ratio (H/C_{eff} ratio) is utilized to describe the characteristics of the feedstock (Zhang *et al.* 2015). The C , H , O , N and S in Eq. 1 are the moles of carbon, hydrogen, oxygen, nitrogen, and sulfur in the feedstock, respectively:

$$\frac{H}{C_{\text{eff}}} = \frac{H - 2O - 3N - 2S}{C} \quad (1)$$

However, the H/C_{eff} ratio of lignocellulose is very low (0 to 0.3), and this causes lower targeted petroleum chemicals (*e.g.*, aromatics, olefins, *etc.*) (Zhang *et al.* 2011). Hence, adding a material that has a higher H/C_{eff} ratio can improve the yields of targeted products. Grease (H/C_{eff} ratio of approximately 1.5), plastic (H/C_{eff} ratio of approximately 2), and saturated monohydric alcohols (H/C_{eff} ratio of 2) can be fed with lignocellulose to improve the overall H/C_{eff} ratio of feedstocks (Zhang *et al.* 2015a). Among such hydrogen-rich feedstocks, plastic waste is a recyclable resource, which is readily available in considerable amounts and at a low price with a high H/C_{eff} ratio (H/C_{eff} ratio of approximately 2). Moreover, current incineration and landfill of plastic wastes results in considerable environmental problems. Hence, plastic wastes can function as hydrogen sources during the catalytic co-pyrolysis process. Recently, several researchers (Zhang *et al.* 2012, 2015b; Dorado *et al.* 2015; Xue *et al.* 2015) have demonstrated that catalytic co-pyrolysis of lignocellulose with plastics could considerably enhance the hydrocarbons contents while reducing the coke formation. These reports indicated the existence of a synergistic effect when co-feeding biomass with hydrogen-rich feedstocks in the process of catalytic co-pyrolysis. Catalytic co-pyrolysis technology employs two materials as feedstock and an acidic catalyst for the production of bio-oils. The addition of catalysts plays an important role in the deoxygenation of bio-oil and in enhancing the target products in the process of catalytic co-cracking (Thangalazhy-Gopakumar *et al.* 2012; Rezaei *et al.* 2014; Zhang *et al.* 2015a). Aromatic and olefin yields increased from 27% to 80%, while coke yields decreased from 35% to 2% as the H/C_{eff} value increased with the provided feedstock. Moreover, the H/C_{eff} ratio of the feedstock has been found to be correlated with its hydrocarbon content (Zhang *et al.* 2011).

To further confirm the synergistic effect and the function of the catalyst during catalytic co-pyrolysis, thermogravimetric analysis (TGA) has been used to study the mechanism of the resulting blends. It can be concluded that co-pyrolytic characteristics are quite different from the individual feedstock alone, which implies synergistic interactions occur between plastic and biomass (Oyedun *et al.* 2014). A previously proposed distributed activation energy model (DAEM) described the co-pyrolysis of municipal solid waste (MSW) with agricultural residues (Bhavanam and Sastry 2015). It has been reported that the addition of agri-residues could significantly decrease the required activation energy of MSW. Most recent studies (Li *et al.* 2013; Abnisa and Wan Daud 2014; Zhang *et al.* 2015a; Fang *et al.* 2016; Hassan *et al.* 2016; Zhang *et al.* 2016a; Chen *et al.* 2017b) have focused on the catalytic co-pyrolysis of biomasses and plastics. However, the accurate mechanism for the effect of catalysts on the biomass/plastics co-pyrolysis is still unclear; thus more research works are needed to clarify this mechanism. The goal of the present work was to explore reaction process of corn stalks (as a typical agricultural waste in Northern of China) and polyethylene in catalytic co-pyrolysis, which

can be beneficial for the utilization of renewable agricultural waste biomass and for environmental sustainability.

In this paper, catalytic co-pyrolysis of corn stover and high-density polyethylene (HDPE) with a HZSM-5 and nickel-modified HZSM-5 catalyst was studied using TGA to determine the synergistic mechanism. With the obtained TGA data, kinetic parameters (*i.e.*, the activation energy and pre-exponential factor) were estimated using both the one-step and the multi-step integral methods. Moreover, the performance of the catalyst during catalytic co-pyrolysis was also explored. This study provides a theoretical basis to optimize the design and operation of lignocellulose and plastic co-conversion processes.

EXPERIMENTAL

Materials

In this study, a commercially available HDPE was used as the plastic feedstock (Shandong Petrochemical Company, Jinan, China). Corn stover was obtained from a local farm in the Zibo district in Shandong, China. Prior to the experiment, the corn stover was mechanically pulverized and sifted through a 40-mesh sieve. Subsequently, the biomass samples were dried at 110 °C for 24 h.

The standards ASTM D1102 (2013), ASTM E871 (2013), and ASTM E872 (2006) were used for determining the proximate and ultimate analyses of the samples. Ultimate analysis was conducted using an EA-3000 elemental analyzer (EuRo Vector, Milan, Italy). The higher heating value (HHV) was measured using a bomb calorimeter (C2000, IKA Werke GmbH & Co. KG, Staufen, Germany). To ensure reliability of analytic test results, all runs were performed in triplicate; the reported averages had standard deviations below 3%. The respective data for the samples are provided in Table 1. From Table 1, HDPE has high hydrogen contents and can provide hydrogen during co-pyrolysis with biomass, resulting in the increase of liquid production (Rutkowski and Kubacki 2006).

Table 1. Properties of the Samples

Sample	HDPE	Corn Stover
Proximate Analysis (db ^a)		
Moisture content (%)	0.27	8.42
Volatile matter (%)	98.93	67.58
Fixed carbon (%)	0.29	14.54
Ash (%)	0.51	9.46
Ultimate Analysis (wt.% daf ^b)		
C	85.60	50.07
H	14.40	6.03
O ^c	n.d ^d	42.60
N	n.d	1.30
<i>H/C_{eff}</i>	2.02	0.17
HMV (MJ/kg)	43.78	16.65

^a Dry base; ^b dried and ash-free base; ^c calculated *via* difference; ^d not detected

Impregnation was used to prepare Ni/HZSM-5 catalysts, and HZSM-5(Si/Al = 25) was used as the support; these catalysts were obtained from the Catalyst Company of Nankai University (Tianjin, China). The Ni source was from nickel nitrate

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, St. Louis, USA), which was purified *via* recrystallization from water. Finally, Ni species were evenly distributed onto the support surface. Three modified-catalysts with Ni contents of 5%, 10%, and 15% were synthesized, and they were designated as $\text{Ni}_5/\text{HZSM-5}$, $\text{Ni}_{10}/\text{HZSM-5}$, and $\text{Ni}_{15}/\text{HZSM-5}$, respectively. The modified HZSM-5 catalysts were air-dried at 120 °C overnight and then calcined at 550 °C for 5 h. Subsequently, the catalysts were crushed and sieved to a particle size between 40 to 60 mesh; the sieved material was then dried at 105 °C for 24 h in an automatic drying oven.

Biomass (corn stover) and HDPE powder were uniformly blended at a mass ratio of 1:1 in a micro rotary mixer. To prepare the samples for catalytic co-pyrolysis, the catalyst was thoroughly mixed with a particular reactant (corn stover and HDPE) in a catalyst-to-reactant ratio of 1:4. Finally, the blended samples were placed in a vacuum plastic bag until needed.

Methods

TGA

The thermal behaviors of the samples were characterized using a thermogravimetric analyzer (Netzsch STA449C, Selb, Germany). Prior to the analysis, approximately 5 mg of the sample was placed in an alumina crucible and heated at a rate of 10 °C/min. Afterwards, the sample was heated from 30 °C to 800 °C under a nitrogen atmosphere that was supplied at a rate of 30 mL/min. Residual weights and derivative weights of the samples were recorded with respect to time and temperature. From these assays, the evolution of weight loss (TG) with temperature and the weight loss rate (DTG) were obtained for co-pyrolysis (Miranda *et al.* 2007; Zhou *et al.* 2009; Çepelioğullar and Pütün 2013; Oyedun *et al.* 2014; Zhang *et al.* 2016a). The weight loss rate was calculated:

$$\frac{dW}{dt} = -\frac{1}{W_0} \left(\frac{dW_t}{dt} \right) \quad (2)$$

The weight loss rate (W) was used to evaluate the synergistic effect of plastic and lignocellulose biomass, which was calculated with Eq. 3. The difference in weight loss (ΔW) has previously been defined by the synergistic effect of each component during pyrolysis (Zhang *et al.* 2016a),

$$W(\%) = \frac{W_0 - W_t}{W_0} \times 100 \quad (3)$$

$$\Delta W = W_{blend} - (x_1 W_1 + x_2 W_2) \quad (4)$$

where W_0 is the initial (at 383 K) mass of the test sample, W_t is the mass at instantaneous t , W_{blend} is the weight loss of CS/HDPE blends, x_i is the weight fraction of CS and HDPE in the blends and W_i is the weight loss for the pyrolysis of the CS and HDPE alone in the same conditions.

Kinetic study

The activation energy and pre-exponential factor of the co-pyrolysis of biomass with polymers were determined by the integral method. It was assumed that the co-pyrolysis was a first-order reaction (Zhou *et al.* 2009; Çepelioğullar and Pütün 2013;

Oyedun *et al.* 2014; Zhang *et al.* 2016a). Generally, the rate of solid decomposition is described by Eq. 5,

$$\frac{d\chi}{dt} = kf(\chi) \quad (5)$$

where χ is a co-pyrolysis conversion, which can be calculated *via* Eq. 6,

$$\chi(\%) = \frac{W_0 - W_t}{W_0 - W_f} \times 100 \quad (6)$$

where W_f represent the final mass of the sample. The reaction rate constant, k , was expressed according to the Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Equation 5 can be further rearranged to yield Eq. 8,

$$\frac{d\chi}{dt} = A \exp\left(-\frac{E}{RT}\right)(1 - \chi) \quad (8)$$

where A is the pre-exponential factor and E is the activation energy. Supposing that the heating rate H ($H = dT / dt$) is constant during co-pyrolysis, then Eq. 8 can be integrated using the Coats and Redfern integration method, which has also been recently used by several investigators (Zhou *et al.* 2009; Çepelioğullar and Pütün 2013; Oyedun *et al.* 2014; Liu *et al.* 2016; Zhang *et al.* 2016a). Rearranging Eq. 8 results in Eq. 9:

$$\ln\left[\frac{-\ln(1 - \chi)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (9)$$

In most cases, $2RT/E$ is very small (Oyedun *et al.* 2014), and therefore, Eq. 9 can be approximated by the following expression:

$$\ln\left[\frac{-\ln(1 - \chi)}{T^2}\right] = \ln\left[\frac{AR}{HE}\right] - \frac{E}{RT} \quad (10)$$

In general, the value of $\ln(AR/HE)$ in Eq. 10 is a constant. The left-hand side of Eq. 10 can be plotted *versus* $1000/T$, which can be analyzed by linear regression. Activation energy and pre-exponential factor can be obtained from the linear regression from the slope and intercept values, respectively.

Kinetic compensation effect (KCE)

The KCE means that the alteration in E values will prompt a complementary compensating response in A (Chornet and Roy 1980), which can also be used to test the experimental results. The KCE proves a strong linearity of $\ln(A_n)$ *versus* E_n (Xu *et al.* 2017),

$$\ln A_n = \omega \cdot E_n + \nu \quad (11)$$

where subscript n represents reaction order, ω and ν are the slope and intercept of the regression line, respectively.

RESULTS AND DISCUSSION

Thermal Decomposition of Raw Materials and their Blends

Thermogravimetric analysis has commonly been used as a tool to quantify the weight loss of a sample during pyrolysis; it can be used to examine the thermal behavior and decomposition kinetics of organic materials during thermal decomposition. The TGA results of the raw materials are shown Fig. 1a. The major pyrolytic interval for cellulose occurred at 300 °C to 400 °C. The cellulose was decomposed to small molecules of gas and condensable volatile compounds, which caused substantial weight loss. Simultaneously, a dehydration reaction took place during this process, which resulted in polymerization and char formation in the absence of hydrogen atoms. The thermogravimetric (TG) curve of corn stover was extremely similar to that of cellulose. Likewise, corn stover mainly decomposed between 300 °C to 400 °C. In general, corn stover has three major pyrolytic stages. The first stage (25 °C to 200 °C) is a result of the initial evaporation of water contained in the material. The second stage (300 °C to 400 °C) is where the main weight loss occurs as a result of pyrolysis volatilization of the organics. Most organic compounds in the corn stover (cellulose, hemicellulose, and lignin) were degraded at this stage. The third stage (above 400 °C) corresponds to continuous volatilization of the remaining lignin (over 455 °C) and its reduction during its decomposition (exceeding 600 °C). However, HDPE had a very narrow pyrolysis interval (470 °C to 510 °C) with an approximate 97% conversion rate (Chen *et al.* 2017a).

The TG curves of the blended components fell within the curve of the individual components. For the co-pyrolysis of biomass with a plastic blend, the first stage mainly corresponded to the decomposition of biomass, which had minimum impact on the decomposition of plastic materials. In the second stage of the HDPE and biomass co-pyrolysis, HDPE played a bridging role in blends, which was conducive to both the heat and mass transfer of samples, and thus benefited the release of volatiles during the pyrolysis of blends. Additionally, blends also led to the maximum weight loss rate (0.142 %/min) at 485.9 °C, as shown in Fig. 1b and Table 2. In the process of thermal degradation, the biomass first decomposed and produced free radicals, which initiated the decomposition of the polyolefin chain. Hydrogen atoms in plastic are relatively abundant (Table 1), which can supply hydrogen to the biomass to stabilize the free radicals during the co-pyrolytic process. As shown in Fig. 1, there was a reduction in coke residues between experimental and calculated results (the theoretical values of the respective pyrolysis calculations) during co-pyrolysis of CS and HDPE, which indicated that there was a positive interaction during thermal decomposition of CS and HDPE.

Table 2. Characteristic Temperature and Maximum Weight Loss Rates of Samples Determined *via* TGA

Sample	Pyrolysis Range (°C)		Peak Temperatures (°C)		(dW/dt) max (min ⁻¹)		Residue (wt.%)
	T _I	T _F	T _{P1}	T _{P2}	W ₁	W ₂	
Cellulose	275.4	441.2	338.1		0.238		14.62
Corn Stover (CS)	92.4	715	326.7		0.083		32.61
HDPE	467.5	511.7	484.9		0.266		3.61
CS-HDPE	192.1	643.2	330.7	485.9	0.033	0.142	15.60
CS-HDPE-HZSM-5	185.4	645.3	330.1	466.5	0.022	0.078	40.31
CS-HDPE-Ni ₅ HZSM-5	184.3	646.2	330.0	478.4	0.024	0.102	32.66
CS-HDPE-Ni ₁₀ HZSM-5	184.1	647.1	330.7	478.0	0.026	0.106	28.08
CS-HDPE-Ni ₁₅ HZSM-5	185.3	645.7	330.6	473.8	0.025	0.110	36.50

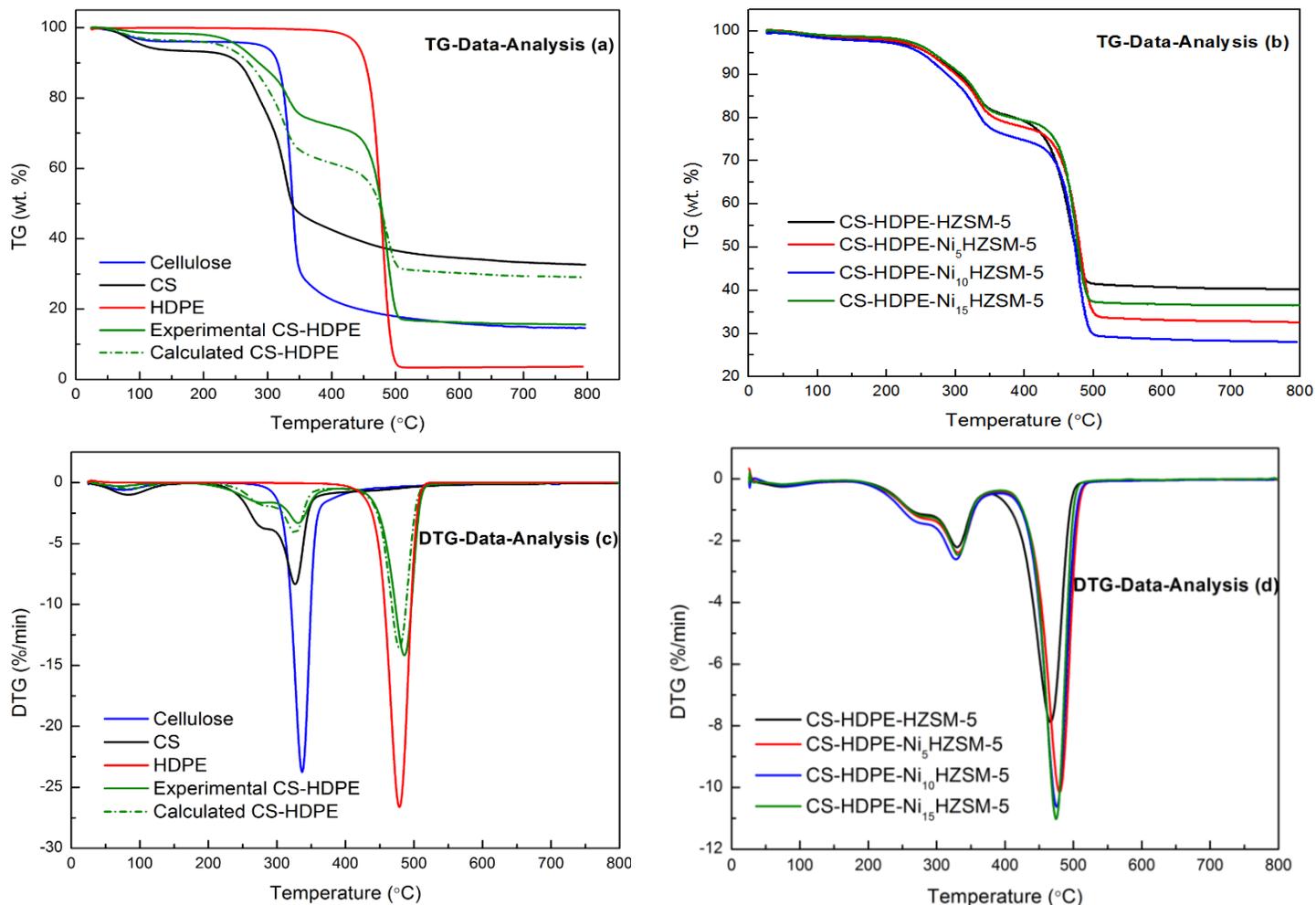
**Fig. 1.** Weight loss versus temperature of cellulose, corn stover (CS) with HDPE (a), and catalyst-treated CS/HDPE blends (b); DTG of cellulose, corn stover (CS) with HDPE (c), and catalyst-treated CS/HDPE blends (d)

Figure 1 (c and d) presents the TGA curves for the blended mixture (CS and HDPE) in the presence and absence of various Ni-based catalysts. The main characteristic parameters are summarized in Table 2. The blended mixture thermal decomposition mostly occurred in the 450 °C to 500 °C temperature range, which was identical to that of HDPE alone. In this degradation, the decomposition peak temperature shifted to lower values in the presence of the HZSM-5 catalyst. These results of the mixture clarified that the amount of char decreased during the catalytic co-pyrolysis process. As revealed by Table 2, the catalyst with the greater Ni loading (5%, 10%, and 15%) resulted in lower solid residue than HZSM-5 alone. Here, the modified Ni₁₀HZSM-5 reduced the coke content of pyrolysis to only 8.08% without regard for the mass loss of the catalyst. These results indicated that the presence of both HDPE and catalyst had a positive effect on the degradation temperature. Moreover, other research demonstrated that there was an apparent synergistic effect between corn stalk and FW during co-CFP process, which promoted the production of aromatics significantly (Zhang *et al.* 2015b). Hence, the catalyst used could be beneficial to the decomposition of CS and HDPE.

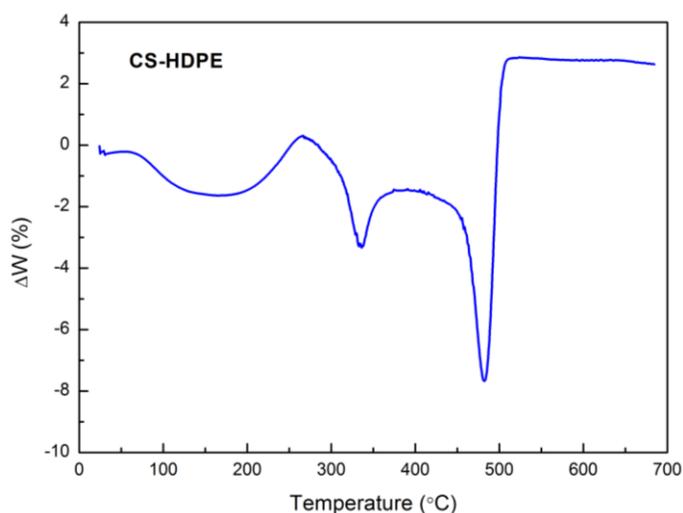


Fig. 2. Variation of ΔW for CS and HDPE blended mixture

Figure 2 shows the variation of ΔW with the pyrolytic temperature of the CS/HDPE blends. It can be clearly seen that ΔW ranged less than $\pm 3.5\%$ before 400 °C, which indicated no obvious interaction between the CS and HDPE. This observation may have been because the temperature was too low for HDPE to decompose. However, ΔW of the blends first declined and then sharply increased at 400 °C to 500 °C, with a peak at 482 °C. The different degradation behavior was mainly attributable to the HDPE beginning to quickly decompose with a strong interaction between the CS and HDPE. Above 500 °C, the HDPE was mostly depleted, with only a negligible amount of lignin taking part in the decomposition behavior. Therefore, the devolatilization reaction of blends had essentially went to completion, which indicated a gradually decreasing interaction between the CS and HDPE (Han *et al.* 2014; Özsin and Pütün 2017; Xiang *et al.* 2017).

The synergetic effects of plastics and biomass on co-pyrolysis were attributed to the radical interactions that occurred during co-pyrolysis. During the co-pyrolysis process, the biomass first produced free radicals, which formed polymer-chain generated

primary radicals at random (Sharypov *et al.* 2002; Zhou *et al.* 2009; Haykiri *et al.* 2010). Through intermolecular hydrogen transfer *via* β -scission reaction, more stable free radicals appeared. Simultaneously, synthetic polymers of HDPE provided hydrogen for biomass; this promoted the precipitation of volatile matter, which further increased the conversion rate of the blends.

Kinetics Analysis

Figure 3 shows the plots of $(\ln(1-\chi)/T^2)$ *versus* $1000/T$ using the one-step integral method. The pyrolytic process of cellulose and HDPE can be described as a first-order reaction. However, for CS and CS-HDPE blends, this process can be described as two and four consecutive first-order reactions, respectively. Hence, the pyrolytic process was also calculated using the multi-step integral method, as shown in Fig. 4. The kinetic parameters of all samples were determined with this method, and are presented in Table 3. Due to the good correlation coefficient (≥ 0.93) of the linear models, this was revealed as a first-order reaction mechanism that fitted the thermogravimetric data well.

Table 3 shows that the biomass was gradually decomposed at the lower temperature with a long interval at 203 °C to 694 °C. Here, the conversion of CS was almost completed by 10% to 75% during the first step. The HDPE had almost no weight loss at the lower temperature; however, the conversion rate of HDPE was completed at approximately 96% at the 450 °C to 500 °C range. Simultaneously, the apparent activation energy (E) of HDPE was 253 kJ/mol, which showed that the plastic required more energy to breakdown inner bonds in the structure of polymers than the cellulose and CS.

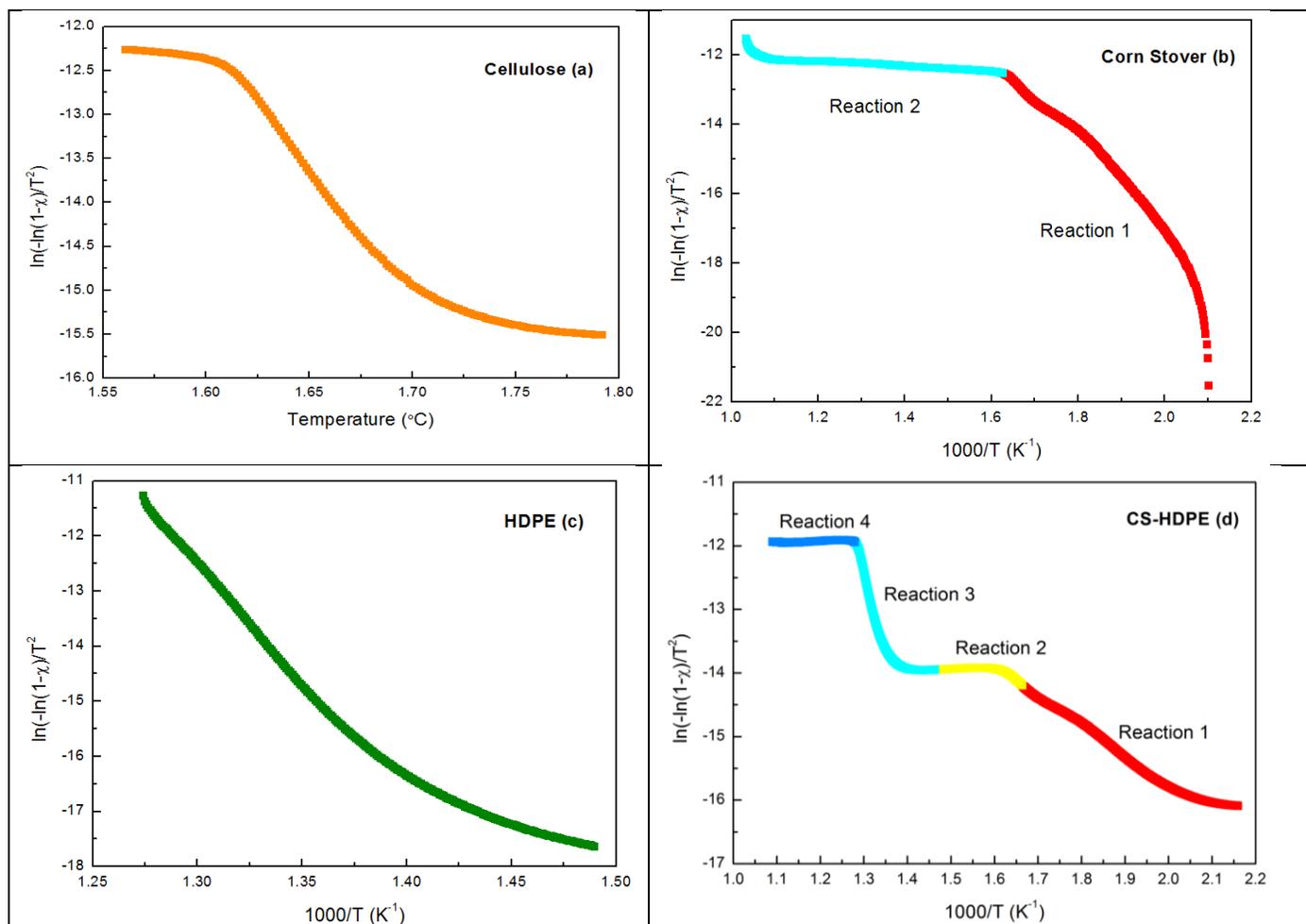


Fig. 3. Plots of $\ln(1 - \chi)/T^2$ versus $1000/T$ of: cellulose (a), CS (b), HDPE (c), and CS-HDPE (d) pyrolysis calculated with the one-step integral method

Kinetic parameters of CS-HDPE blends were different from those of each individual component alone. It is striking that the activation energy of CS at 203 °C to 341 °C showed less difference to the initial pyrolytic reaction of CS-HDPE blends, which indicated that CS mainly participated in the reaction at this temperature interval. However, beyond 450 °C, the activation energy changed appreciably, which indicated that the HDPE began to participate in the reaction. As a result, the conversion of blends completed at the third step was approximately 35% to 98%. The free radicals produced by CS were involved in the decomposition of HDPE, and their interaction was related to these reactions. Simultaneously, the reaction with high activation energy (393 kJ/mol) required more energy to initiate the reaction.

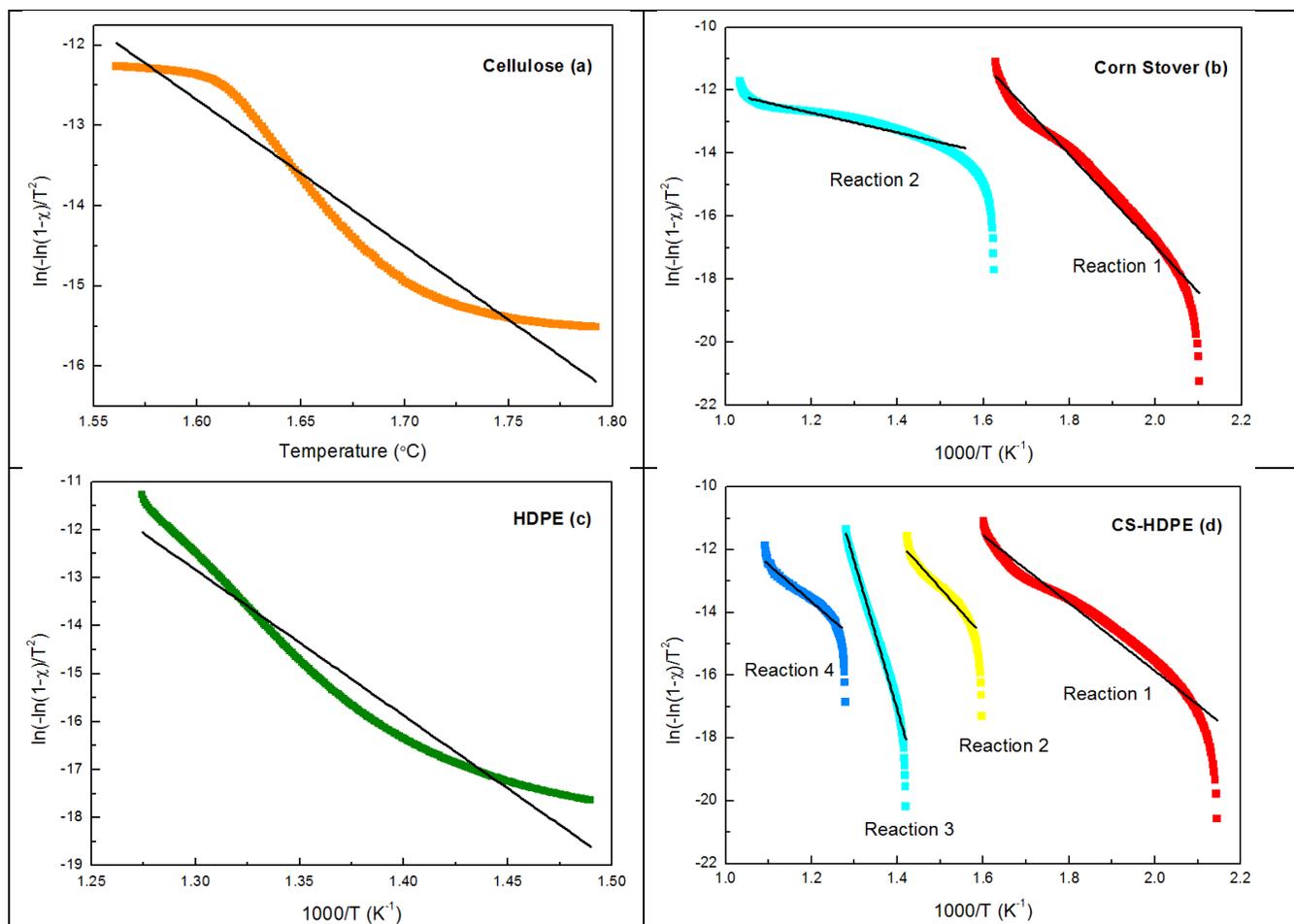


Fig. 4. Plots of $\ln(-\ln(1-\chi)/T^2)$ versus $1000/T$ of: cellulose (a), CS (b), HDPE (c), and CS-HDPE (d) pyrolysis recalculated via multi-step integral method

Additionally, for CS-HDPE-HZSM-5, CS-HDPE-Ni₅HZSM-5, CS-HDPE-Ni₁₀HZSM-5, and CS-HDPE-Ni₁₅HZSM-5 samples, multi-step integral methods were also used to describe the catalytic co-pyrolysis process (Table 3). The catalyst caused a decreasing trend for E and A values in the second and third reaction stages. However, no obvious change trend for E and A values could be found in the first and fourth stages. The catalyst could catalyze the co-pyrolysis reaction for the CS/HDPE blends, and this may be an important reason for the decrease of E (and A) values for the second and third reaction stages. In addition, the third stage had higher variation of E and A compared to other reaction stages, which indicated the catalyst had a great influence on the pyrolysis reactivity for CS/HDPE blends at different reaction stages. Meanwhile, there was approximately 60% conversion for the third stage, which affirmed that the third stage is the main decomposition region. Therefore, the plastic and the CS biomass might imply the synergetic effects, and the catalyst played a vital part for the observed decrease of E , which thus reduces the energy input cost of co-pyrolysis.

Any (A and E) change in one of these calculated quantities necessarily demands a compensatory change in the other. It was also argued that the KCE could be attributed to the reciprocal relationship between A and $\exp(-E_a/RT)$ in the Arrhenius equation (Chornet and Roy 1980). The linearity of $\ln(A)$ versus E (see Fig. 5) was perfect with the

correlation coefficient ($R^2 = 0.95056$). The KCE also provided a clue to recognize whether or not the obtained parameter set (E , A) fit the same mass loss kinetics.

Table 3. Kinetic Parameters for Pyrolysis of Corn Stover (CS), Plastic (HDPE), and Their Blended Mixture

Sample	Temperature (°C)	Conversion Range (%)	E (kJ/mol)	A (min ⁻¹)	$-R^a$
Cellulose	285 to 387	5 to 90	151.73	2.72×10^9	0.94202
HDPE	398 to 512	1 to 96	252.52	1.14×10^{14}	0.9518
CS	203 to 341	10 to 75	120.97	2.76×10^7	0.9659
	341 to 694	75 to 98	26.13	2.39×10^5	0.9396
CS-HDPE	192 to 352	2 to 29	89.66	3.26×10^4	0.9456
	352 to 430	29 to 35	127.28	2.62×10^6	0.9709
	430 to 508	35 to 98	392.67	9.19×10^{23}	0.9755
	508 to 643	98 to 99	98.35	204.31	0.9577
CS-HDPE-HZSM-5	192 to 343	3 to 28	82.74	2.91×10^4	0.93903
	343 to 421	28 to 38	104.37	1.07×10^5	0.94014
	421 to 504	38 to 97	322.88	9.50×10^{19}	0.95754
	504 to 645	97 to 99	96.24	311.88	0.98171
CS-HDPE-Ni ₅ HZSM-5	191 to 342	3 to 27	88.90	3.27×10^4	0.94715
	342 to 418	27 to 34	100.89	3.34×10^4	0.97166
	418 to 507	34 to 98	333.55	1.08×10^{20}	0.97244
	507 to 646	98 to 99	99.20	233.64	0.98757
CS-HDPE-Ni ₁₀ HZSM-5	190 to 341	3 to 28	90.48	4.71×10^4	0.94932
	341 to 427	28 to 37	90.03	3.39×10^3	0.95166
	427 to 509	37 to 98	365.80	1.82×10^{22}	0.97202
	509 to 646	98 to 99	98.03	317.82	0.97311
CS-HDPE-Ni ₁₅ HZSM-5	191 to 343	2 to 27	91.14	5.03×10^4	0.94432
	343 to 420	27 to 34	103.68	4.88×10^4	0.97124
	420 to 505	34 to 98	368.37	4.17×10^{22}	0.97725
	505 to 646	98 to 99	92.69	156.24	0.94140

^a R = correlation coefficient

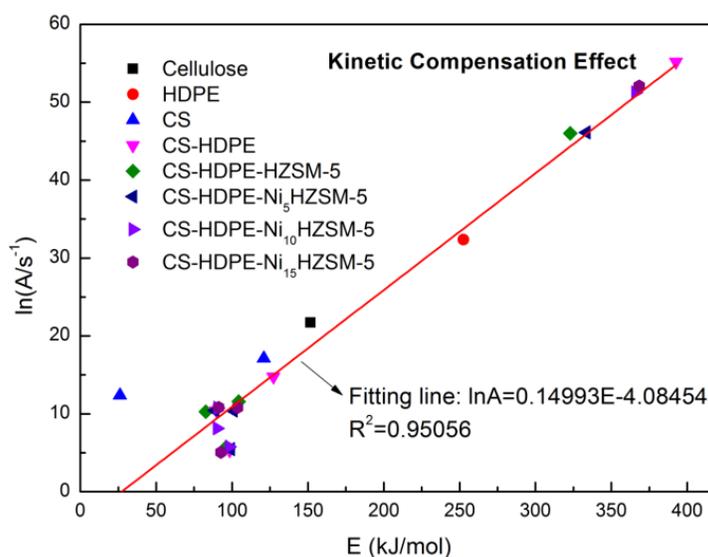


Fig. 5. Kinetic compensation effect of all tested samples

CONCLUSIONS

1. The co-pyrolysis behavior of the corn stover/high density polyethylene (CS/HDPE) blends were different from those of the individual materials. The maximum ΔW value for CS/HDPE blends was 7.83% at a peak of 482 °C. Hence, there was a positive interaction during thermal decomposition of CS and HDPE.
2. The catalyst had a strong catalytic effect on the co-pyrolysis of the CS/HDPE blends, leading to the decrease of the char yields. The modified Ni₁₀HZSM-5 catalyst reduced the coke content of pyrolysis to only 8.08% without regard for the mass loss of the catalyst. The results from kinetic analysis indicate that the presence of the catalyst led to a decreasing trend for E and A values in the second and third reaction stages. Meanwhile, there was an approximate 60% conversion for the third stages, which affirmed that the third stage was the main decomposition region.
3. Multi-step integration can be well validated with TGA experimental data to clarify the changes in the kinetic parameters of each reaction stage. In addition, the remarkably linear relationship between $\ln(A)$ and E in each reaction of all test samples seems to imply the existence of a kinetic compensation effect.

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