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Wang, Z., Shen, D., Wu, C., & Gu, S. (2018). Thermal behavior and kinetics of co-pyrolysis of cellulose and polyethylene with the addition of transition metals. *Energy Conversion and Management*, 172, 32-38. <https://doi.org/10.1016/j.enconman.2018.07.010>

Published in:
Energy Conversion and Management

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

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Thermal behavior and kinetics of co-pyrolysis of cellulose and polyethylene with the addition of transition metals

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Abstract: The influence of the addition of transition metals involving nickel (Ni), cobalt (Co), iron (Fe) and manganese (Mn) on the thermal behavior and kinetic of co-pyrolysis of cellulose (CL) together with polyethylene (PE) was investigated according to thermogravimetric analysis (TGA). It is found that the involvement of transition metals acting as catalysts could promote the decomposition of individual component (CL and PE) in the mixture. The initial decomposition temperature of CL and PE in the mixture is reduced by 91-136°C and 8-15°C, respectively, after the addition of transition metals in comparison with that of the mixture of CL and PE. Meanwhile, transition

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metals could intensify the synergistic interactions between CL and PE, especially during the pyrolysis stage assigned to CL decomposition. The maximum difference of weight loss in this stage is -9.30%~-14.10% for transition metals treated-mixtures while that of the mixture without transition metal treatment is -2.99%. Kinetic results show that the co-pyrolysis of transition metal-involved CL/PE mixtures can be well described as two consecutive first order reactions. The activation energy (E) of CL and PE in the mixture is reduced by 53.21-80.53 kJ/mol and 8.23-12.36 kJ/mol, respectively, as transition metals were involved. In addition, the content of transition metal makes a large influence on the thermal behavior and kinetics of co-pyrolysis of CL/PE mixture.

Key words: Catalytic co-pyrolysis; Cellulose; Polyethylene; Transition metal; Thermal behavior

1 Introduction

Biomass is considered to be one of the most important renewable sources in nature. It is estimated that the world's annual biomass production is up to 146 billion tons [1]. At the same time, biomass is largely produced as a by-product of industry, agriculture and forestry such as bioethanol fermentation, pulp and paper manufacturing, grain planting, and forest mining [2]. For example, biomass waste derived from agricultural production is estimated to be as many as 30 billion tons per year and that from pulp and paper industry can reach 70 million tons per year as well [3]. On the other hand, plastics are extensively used in our daily lives to bring us considerable convenience. It is reported that the global annual production of plastics in 2015 was estimated to have come to 322 million tons [4]. As a consequence, large amount of plastic related wastes are generated causing serious environmental issues due to their high biochemical stability in environment. Although various conventional methods for the disposal of biomass and plastics have been developed, the management of these wastes is still challenging. Moreover, the technology to process these wastes such as incineration and landfill would bring about many potential secondary hazards to the health of human being and the environment [5, 6]. Accordingly, it appears much urgent to develop some green and available approaches to deal with the increasing production of biomass and plastic wastes.

Co-pyrolysis is a promising technique to simultaneously process biomass and plastic and produce high-value added products such as bio-oil and chemicals [7, 8]. It is

reported that the bio-oil directly derived from biomass generally presented a nature of high oxygen content, acidity, instability, viscosity and corrosion which highly restricted its applications [1, 9]. On the contrary, plastic contains high hydrogen content presenting a high effective hydrogen to carbon ratio [10]. Plastic can provide biomass with abundant hydrogen atoms (serving as hydrogen donor) to intensify the thermal decomposition of biomass and reduce the polycondensation of the intermediate products as it was employed to co-pyrolyze with biomass. Meanwhile, the oxygenated compounds originated from biomass during the co-pyrolysis process could promote the chain scission and cracking of plastic in return [11]. As a result, the quality and yield of targeted products (bio-oil or chemicals) were significantly improved. It is reported by Dorado et al. that the yield of alkyl benzenes from the catalytic fast pyrolysis of CL along with polyethylene terephthalate was greatly enhanced compared with CL alone [12]. Kositkanawuth et al. found that co-pyrolysis of biomass with polystyrene led to the improvement of the quality and quantity of the oil compared to pyrolysis of Sargassum alone [13]. Particularly, the oil quantity increased from 3% for Sargassum alone to 29% for the mixture of 67% Sargassum and 33% polystyrene.

It is notable that the involvement of catalyst during the co-pyrolysis of biomass and plastic would further improve the quality of bio-oil compared to that without catalyst. The presence of catalyst can serve active sites for the decomposition of raw materials and the interaction of the intermediates. For example, the surface acid sites of HZSM-5 zeolite can promote the catalytic cracking and refining reactions of biomass and its

mixture together with plastic to de-oxygenate bio-oil, favoring the production of hydrocarbon products [14]. At the same time, the catalyst with unique porosity structure is efficient to enhance the selectivity of desired products. Kim et al. found that HY zeolite with a large pore size (7.4×7.4 Å) and cavities could be favorable for the diffusion of reactant molecules from the co-pyrolysis of CL and polypropylene into internal pores, resulting in the enhancement of the yields of aromatic hydrocarbons [15]. On the contrary, using a catalyst with pore size smaller than raw material (CL with a kinetic diameter of 8.6 Å) resulted in the reactions mainly occurred at external surface of the catalysts which greatly restricted the catalytic reaction [15]. Up to date, the catalysts employed are those with unique physicochemical characteristics mainly concerning zeolites and metal oxides [7, 16-18]. For example, LOSA-1, spent FCC and γ - Al_2O_3 were employed as catalysts during a catalytic co-pyrolysis of PE and black-liquor lignin for the production of petrochemicals and these catalysts were consequently proven to be effective in the catalytic conversion [17]. In the co-pyrolysis of CL and polypropylene, microporous zeolites (ZSM-5) was found to be more favorable in the formation of aromatic hydrocarbons in comparison with mesoporous Al-SBA-15 [16].

Transition metals especially for Ni, Co, Fe and Mn have been widely applied in various fields such as catalytic pyrolysis of biomass for the preparation of high quality bio-oil [19, 20]. It was found that the involvement of Ni and Fe could simultaneously catalyze rearrangement reactions and promote depolymerization of biomass which were favorable for the preparation of desired pyrolysis products such as fuels, chemicals [21].

Meanwhile, transition metals are the necessary minerals for the growth of plant, which are extensively dispersed in biomass [22, 23]. In this work, transition metals have been used for the co-pyrolysis of biomass and plastic. We aim to develop a new, low-cost and high-efficient catalyst for the catalytic co-pyrolysis of biomass and plastic blend, and assess the effect of natural biomass with intrinsic transition metals on its co-pyrolysis process. Particularly, CL and PE were employed as the representatives of biomass and plastic, respectively. The thermal behavior and kinetics of co-pyrolysis of the mixtures affected by the type of transition metals (Ni, Co, Fe and Mn) and the concentration of catalyst (Ni) were investigated according to TGA at ambient temperature to 750 °C under nitrogen atmosphere.

2 Materials and methods

2.1 Raw materials

Commercially available CL (CAS number 9004-34-6) in the form of microcrystalline powders was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). PE powder (CAS number 9002-88-4) with average M_w and M_n of ~4000 and ~1700 by GPC, respectively, was provided by Sigma-Aldrich Corporation (St. Louis, MO, USA). The detailed elemental composition and chemical structure of CL and PE are presented in Table S1 and Fig. S1. Transition metal nitrates including nickel nitrate hexahydrate (Ni), cobaltous nitrate hexahydrate (Co), iron nitrate nonahydrate (Fe) and manganese nitrate tetrahydrate (Mn) were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA).

2.2 Experimental procedure

2.2.1 Preparation of samples

For the preparation of Ni-involved CL/PE mixture, 1 g CL powder was immersed into a 20 mL of 0.1 mol/L Ni solution. The mixed suspension was stirred at 60 °C for 3h to evaporate and then dried at 105 °C. Afterward the dried powder was collected and mixed with 1 g PE powder in an agate mortar via manual grinding for 20 min. The as-grinded powder was the targeted mixture of CL and PE in a ratio of 1:1 with a Ni concentration of 1 mmol Ni/ g mixture, which was labeled as CL/PE-Ni-1. CL/PE mixture with different dosage of Ni (0, 0.25, 0.5, 0.75 and 1 mmol Ni/ g mixture) and different type of transition metals as catalysts (Ni, Co, Fe, Mn) were prepared in the similar process via regulating the concentration of Ni solution and catalyst solution type, respectively. For comparison, CL/PE mixture without catalyst and CL with 1 mmol/L transition catalyst (i.e., CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1) were also prepared.

2.2.2 Thermogravimetric analysis

The pyrolysis experiments were carried out in a thermogravimetric analyzer (Mettler Toledo 188 TGA/SDTA 851, Switzerland) to investigate the thermal decomposition profiles of CL and PE and their mixtures with or without catalysts. About 10 mg of sample was pyrolyzed under 0.1 m³/min N₂ flow at a heating rate of 10 °C/min from room temperature to 750 °C. More than two parallel runs were carried out for all the experiments to ensure low relative errors (below 5%).

145

146 2.3 Kinetic study

147 Kinetic parameters such as activation energy (E) and pre-exponential factor (A) can be
148 employed to qualitatively describe the pyrolysis characteristics of reactant which can
149 be calculated according to DTG data. It is assumed that the pyrolysis of solid fuel such
150 as coal, plastic and biomass belongs to a first order reaction and can be expressed as
151 following equation (Eq. 1):

$$152 \quad \frac{dx}{dt} = A \exp\left[\left(\frac{-E}{RT}\right)(1-x)\right] \quad (1)$$

153 where E is activation energy (kJ/mol), A is pre-exponential factor (1/min), T is
154 temperature (K), t is time (min), R is a universal gas constant (J/mol K), χ is conversion
155 of raw material which can be obtained from the following equation (Eq. 2)

$$156 \quad x = \frac{W_0 - W_{time}}{W_0 - W_{final}} \quad (2)$$

157 where W_0 is the initial mass of sample (mg), W_{time} and W_{final} are the mass of sample at
158 time t and at the end of pyrolysis, respectively. For a constant heating rate H ($H=dT/dt$)
159 during pyrolysis, Eq. 1 can be integrated as following equation (Eq. 3):

$$160 \quad \ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (3)$$

161 Based on most E values and temperature range during pyrolysis, $RT/E \ll 1$, thus the
162 expression $\ln[AR/HE(1-2RT/E)]$ can be considered as a constant. The slope and the
163 intercept of the plots of $\ln[-\ln(1-\chi)/T^2]$ versus $1/T$ according to Eq. 3 are E and A,
164 respectively.

3 Results and discussion

3.1 Pyrolysis characteristics

3.1.1 CL with or without transition metals, PE and CL/PE mixture

Fig. 1 shows TG and DTG curves of pyrolysis of CL with or without transition metals catalysts (CL, CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1), PE and CL/PE mixture under N₂ atmosphere from ambient temperature to 750 °C at a heating rate of 10 °C/min. Corresponding pyrolysis parameters are showed in Table S2.

It can be seen that CL showed a good thermal stability before 300 °C with only 2.83wt.% weight loss which can be attributed to its high crystallinity. After that, CL underwent a fast weight loss stage taking place at 314-373 °C (see TG curve in Fig. 1a) with 78.37wt.% weight loss. This result was well in agreement with a previous study where the same feedstock (CAS number 9004-34-6) was investigated [24]. It is reported that the great weight loss of CL in this stage was mainly related to the fast decomposition of CL into volatile matters involving liquid products (tar and H₂O) and permanent gases (CO, CO₂, H₂ and CH₄) [25, 26]. With the further increase of reaction temperature, the pyrolysis of CL came into a slow carbonization stage (373-750 °C). In this stage, CL continued to lose weight in a slight extent resulting from the release of small molecular gases from the rearrangement of solid phase [21]. 10.67wt.% solid residue (char) was obtained at the end of the experiment. The DTG curve in Fig. 1b illustrated that the main decomposition stage of CL exhibited a narrow weight loss peak with a maximum weight lost rate of -26.89 wt.%/min at 349°C.

Fig. 1 Pyrolytic behavior of CL with or without transition metals catalysts, PE and

CL/PE mixture: a) TG curves, b) DTG curves

The decomposition of CL with transition metals treatment (CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1) was composed of three stages. The first stage occurred at 80-170 °C referring to 3.26wt. %-4.75wt. % weight loss, which resulted from the loss of water and low volatile compounds [27]. The weight loss of CL with transition metals treatment at this stage was slightly higher than that of the pure CL, revealing that the introduction of transition metals can improve the hydrophilicity of CL. Collard et al. proposed that the introduction of transition metals such as Fe and Ni would weaken some hydrogen bonds of CL and partly promote the transformation of crystalline CL to amorphous phase one [25]. As a consequence, more water content was involved during the pyrolysis of the transition metal-treated CL. At the same time, the involvement of transition metals was also found to be effective in catalyzing the formation of condensable products and incondensable gas in this stage, resulting in a larger mass loss compared to pure CL [26]. The decomposition of CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1 at about 179-350 °C and 350-750 °C were assigned to the main decomposition stage and carbonization stage, respectively. The decomposition of CL-

Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1 started at 219, 210, 179 and 223 °C, respectively, which was 91-135 °C lower than that of pure CL. It was reported that transition metal ions could serve as Lewis acid sites to promote the dehydration and other depolymerization of CL [25]. The initial decomposition temperature of the transition metal-treated CLs was negatively related to the Lewis acidity intensity of the transition metal employed, yielding to an order of Mn > Ni > Co > Fe.

DTG curves in relation to the transition metal-treated CL are shown in Fig. 1b. It can be found that CL-Ni-1 and CL-Fe-1 presented a sole weight loss peak while two weight loss peaks were observed in CL-Co-1 and CL-Mn-1, respectively. The maximum weight loss rate of CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1 was located at 327, 327, 318 and 313 °C, respectively. These temperatures have been shifted to lower temperature compared to pure CL (349°C). It further confirmed that the involvement of transition metals was favorable for the catalytic decomposition of CL. The shoulder peak in CL-Co-1 and CL-Mn-1 was believed to be related to the decomposition of amorphous CL, which rose from the transformation of crystalline CL into amorphous CL under the presence of certain catalyst [28]. Similar results can be found in previous studies [28, 29].

The weight loss of PE shown in Fig. 1a was negligible before 300 °C due to its crystal structure having high thermal stability. PE started to gradually decompose after 335°C and emerged a sharp weight loss at 424-490 °C. During this decomposition period, PE

was totally decomposed without solid residue which was coincided with its low fixed carbon content (Table S1). DTG curve further reveals that PE showed a maximum weight loss rate of -19.63 wt.%/min at 466 °C.

For blending CL together with PE, the as-obtained mixture showed two successive weight loss stages at 314-385 °C and 422-511 °C which were assigned to the weight loss of CL and PE, respectively. CL and PE were mostly decomposed in their corresponding stage showing two narrow weight loss peaks (Fig. 1b). The temperature of the maximum weight loss rate of the mixture of CL and PE is 342 and 467 °C, respectively, which is slightly different from those of raw materials (pure CL and PE), indicating that interactions were occurred in the pyrolysis of the mixture. The solid residue after decomposition (Fig. 1a) was 8.35wt.% which was much higher than the theoretical one (5.33wt.%) calculated in terms of the mixture ratio of CL and PE, further demonstrating that there was an interactions existed in CL/PE mixture. Matsuzawa et al. suggested that the presence of plastic can fascinate the dehydration, decarbonylation and decarboxylation of CL inhibiting the depolymerization process [26].

3.1.2 CL/PE mixture with transition metal catalyst

Fig. 2 shows the TG and DTG curves of CL/PE mixture with or without transition metals catalysts (CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1) at a heating rate of 10 °C/min from room temperature to 750 °C. The weight loss of transition metal treated-CL/PE mixture was mainly composed of three stages, i.e., 73-206 °C, 178-

319 °C, and 406-509 °C, which were assigned to the loss of water and the decomposition of CL and PE, respectively (Fig. 2a). It is worth noting that the decomposition temperature of CL significantly decreased during the pyrolysis of the mixture of CL and PE after the introduction of transition metals. For example, the initial decomposition temperature decreased from 314 °C to 223 °C when the sample was changed from CL/PE to CL/PE-Ni-1. The initial decomposition temperature was reduced to 211 °C for CL/PE-Co-1, 178 °C for CL/PE-Fe-1 and 216 °C for CL/PE-Mn-1, respectively (Table S2).

DTG results in Fig. 2b showed that the maximum weight loss rate of CL in CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1 was at 268, 223, 233 and 236 °C, respectively, which was 47-118 °C lower than that of CL/PE (342 °C). The corresponding maximum weight loss temperature of CL in transition metals treated-mixtures followed the order of CL/PE-Mn-1 $\approx$ CL/PE-Co-1 $>$ CL/PE-Ni-1 $\approx$ CL/PE-Fe-1. Moreover, the weight loss peak of CL/PE-Ni-1 and CL/PE-Fe-1 was broader than that of CL/PE-Mn-1 and CL/PE-Co-1. These observations indicated that the involvement of transition metals would significantly influence the pyrolysis behavior of CL in mixture. And this influence varied with the type of catalyst [25]. On the other hand, the initial decomposition temperature of PE in CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1 was 409, 410, 407 and 414 °C, respectively, which was slightly lower than that of CL/PE (422 °C), indicating that transition metal based-catalysts were effective to promote the thermal decomposition of PE. The other reason to explain this

phenomenon is that the oxygenated compounds (oxygen-containing free radicals) originated from the decomposition of CL under a relatively low temperature can effectively interact with PE molecular to make contributions to PE decomposition [24]. The maximum weight loss rate of all samples in Fig. 2b were located at about 466 °C and followed an order of CL/PE-Ni-1 < CL/PE-Fe-1 < CL/PE-Co-1 < CL/PE < CL/PE-Mn-1.

Fig. 2 Pyrolytic behavior of CL/PE mixture with or without transition metals

catalysts: a) TG curves, b) DTG curves

3.1.3 CL/PE mixture with different content of Ni catalyst

Fig. 3 shows TG and DTG curves of the CL/PE mixture with different content of Ni (CL/PE-Ni-0 (CL/PE), CL/PE-Ni-0.25, CL/PE-Ni-0.5, CL/PE-Ni-0.75 and CL/PE-Ni-1 represents 1 g CL/PE mixture containing 0, 0.25, 0.5, 0.75 and 1 mmol Ni catalyst, respectively) during pyrolysis under N₂ atmosphere from ambient temperature to 750 °C at a heating rate of 10 °C/min. It is indicated that the weight loss of CL/PE with different content of Ni content can be divided into three stages (Fig. 3a). At the first stage,

CL/PE-Ni-25, CL/PE-Ni-0.5, CL/PE-Ni-0.75 and CL/PE-Ni-1 lost 0.69wt.%, 1.52wt.%, 1.57wt.% and 4.14wt.% of total weight, respectively, which was attributed to the loss of water content. The decomposition of CL in the mixture mainly emerged at the second stage. It started at 215 °C for CL/PE-Ni-0.25, 207 °C for CL/PE-Ni-0.5, 200 °C for CL/PE-Ni-0.75 and 222 °C for CL/PE-Ni-1, respectively. The initial decomposition temperature decreased with the increase of Ni content and reached a minimum value as the Ni content in mixture was 0.75 mmol/g.

At the same time, DTG results in Fig. 3b reveal that the temperature of the maximum weight loss rate of CL in CL/PE-Ni-0.25, CL/PE-Ni-0.5, CL/PE-Ni-0.75 and CL/PE-Ni-1 is 280, 273, 271 and 268 °C, respectively. The temperature showed a negative relationship with the Ni content involved in mixture. The maximum weight loss rate of CL/PE-Ni-25 was -4.71 wt.%/min which was obviously higher than those derived from relative high Ni content (0.5-1 mmol/g), indicating that the increase of Ni content resulted in the reduction of the intensity of weight loss. The third weight loss stage was assigned to the decomposition of PE in the mixture. It can be seen that the initial decomposition of PE is at 422 °C for CL/PE, 419 °C for CL/PE-Ni-0.25, 406 °C for CL/PE-Ni-0.5, 408 °C for CL/PE-Ni-0.75 and 409 °C for CL/PE-Ni-1, respectively (Fig. 3a). This observation may reveal that the increase of Ni content can provide more active catalytic sites for PE decomposition and produce more oxygenated compounds to promote the decomposition of the chains of PE [30]. On the other hand, the temperature of the maximum weight loss of PE in CL/PE-Ni-25, CL/PE-Ni-0.5, CL/PE-Ni-0.75 and

CL/PE-Ni-1 is close to that of CL/PE, at around 465 °C (Fig. 3b).

Fig. 3 Pyrolytic behavior of CL/PE mixture with different content of Ni catalyst: a) TG curves, b) DTG curves

3.2 Evaluation of the interaction during co-pyrolysis of CL and PE

In order to elucidate the interaction between the individual fractions in the mixture, the difference of weight loss (ΔW) between the experimental values and the estimated ones was calculated according to the following equation (Eq. 4).

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

where, $W_{mixture}$ is the weight loss of CL/PE mixture with or without transition metals catalysts; x_1 and x_2 is the weight fraction of CL and PE in the mixtures, respectively; W_1 and W_2 is the weight loss of the transition metals-treated CL and PE alone.

The variation of ΔW with the function of temperature for the CL/PE mixtures with or without transition metals catalysts is presented in Fig. 4. It can be seen that the variation of ΔW of CL/PE was lower than $\pm 1.5\%$ under 300 °C. The reason for this observation was that both CL and PE possess relative high thermal stabilities. As a result, almost no

interaction between CL and PE occurred at this temperature period. With the continuing increment of reaction temperature, the co-pyrolysis of the CL/PE mixture showed a slight decrease of ΔW at the temperature range of 300~330 °C with the maximum ΔW value of -2.99% at 322 °C. At this stage, CL in the mixture started to decompose and PE was greatly melted (see Scheme S1). The softened PE coated on the surface of CL inhibiting the evolution of volatile matter [24]. Afterwards, the ΔW of CL/PE drastically rose and kept a positive value at a wide temperature range (330~480 °C). Two overlapping peaks are observed and the corresponding maximum ΔW values of these two peaks are 7.62% at 348 °C and 14.42% at 446 °C, respectively. The considerable increase of ΔW value was accounted for the drastic decompose of CL and PE (see Scheme S1). Thereafter, the variation of ΔW of CL/PE reduces to below 3% as temperature was increased above 480 °C. In particular, the variation of ΔW could be considered as a result of the synergistic interaction between CL and PE. In other words, there was a strongly synergistic interaction in the decomposition of CL and PE.

Fig. 4 Variation of ΔW for samples as a function of temperature

After the pretreatment with transition metals (1 mmol/g), the variation ΔW shows a little different trend in comparison with that of non-transition metal treated one (CL/PE) depending on the type of transition metals. After a slight variation of ΔW (-0.44%~-2.72%) at relatively lower temperature, the transition metals-treated CL/PE mixtures underwent a significant process in ΔW decrease at temperature 145~325 °C. In particular, the maximum ΔW value of CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1 is -9.30% at 279 °C, -11.72% at 238 °C, -14.10% at 258 °C and -12.89% at 244 °C, respectively. These values are much higher than that of CL/PE (-2.99%) under the similar stage. The results indicate that the involvement of transition metals during the co-pyrolysis of CL and PE could greatly intensify the synergistic effect of PE on CL via inhibiting the release of volatile compounds.

With the increase of pyrolysis temperature from 325 °C, CL/PE-Ni-1, CL/PE-Co-1, and CL/PE-Mn-1 encountered a remarked rise of ΔW value while ΔW of CL/PE-Fe-1 was slightly changed ($\pm 1.3\%$). This observation implies that the synergistic interaction between CL and PE in the presence of transition metals-catalyst occurred in the whole pyrolysis process for the mixture. It is worth noting that the maximum ΔW value of CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1 in this stage is 12.10% at 456 °C, 6.23% at 468 °C, 1.30% at 453 °C and 8.35% at 447 °C, respectively. These values are all lower than that of CL/PE (14.41%). It hence can be concluded that the introduction of transition metals into CL/PE mixture during pyrolysis process was more effective in intensifying the influence of PE on CL rather than that of CL on PE.

363

364 Moreover, ΔW value of CL/PE-Ni-1, CL/PE-Co-1, CL/PE-Fe-1 and CL/PE-Mn-1 at the
365 end of pyrolysis were 6.91%, -2.72%, 0.12% and 4.95%, respectively. It may result
366 from the different catalytic performance of transition metals. The effect of Ni content
367 on the variation of ΔW was employed to interpret the influence of catalyst concentration
368 on the interaction of mixture samples (Fig. 4). Although the variation of ΔW of CL/PE-
369 Ni-0.5 exhibits a similar trend with CL/PE-Ni-1, the intensity of CL/PE-Ni-0.5 around
370 the maximum ΔW value is stronger than that of CL/PE-Ni-1. Therefore, the
371 concentration of transition metal also plays an important role in catalyzing the
372 decomposition of the CL/PE mixture.

373

374 3.3 Kinetic analysis

375 The kinetic analysis of all samples focuses on the main decomposition stage based on
376 first-order reaction model. As a result, kinetic parameters, E and A, were obtained. The
377 fitting results of $\ln[-\ln(1-x)/T^2]$ versus $1/T$ of all samples are shown in Fig. 5 and
378 corresponding parameters are summarized in Table 1. It is found that correlation
379 coefficient (R^2) of all samples fitted by first-order reaction model are larger than 0.94,
380 indicating that the employed reaction model can describe all pyrolysis process very well.
381 The pyrolysis of PE and CL with or without transition metals could be described by a
382 single first-order reaction while the mixture of CL and PE with or without transition
383 metals could be described by two successive first-order reactions. Particularly, the first
384 stage and second stage pyrolysis of the mixture of CL and PE are mainly attributed to

the decomposition of CL and PE, respectively.

Fig. 5 Plots of $\ln(-\ln(1-x)/T^2)$ versus $1/T$ of samples, a) CL with or without transition metals, PE and CL/PE mixture; b) CL/ PE mixture with or without transition metals; c) CL/ PE mixture with different content of Ni catalyst

As shown in Table 1, E value of CL and PE is 208.76 and 241.24 kJ/mol, respectively.

The results are similar to other works [24]. PE shows higher E value compared to CL on account of its higher thermal stability. It is found that the activation energy of CL become significantly lower as it was blended with PE (CL/PE). The activation energy assigned to CL in CL/PE was decreased by about 2 folds in comparison with that of CL.

Meanwhile, the E of PE in CL/PE was decreased by 3 folds compared to that of PE

alone as well. This result may indicate that there was a positively synergistic interaction between CL and PE when they were co-pyrolyzed. On the other hand, apart from the blending with PE, the pretreatment with transition metals also resulted in the reduction of the E value of CL. Cellard et al. confirmed that the presence of transition metal could partly destroy the crystalline structure of cellulose which was favorable for its degradation [25]. Amongst the transition metals employed (Ni, Co, Fe and Mn), Fe seems to be the most efficient one reducing the E value of CL to 32.02 kJ/mol (CL-Fe-1). In this case, the E value of CL was reduced by more than 5 folds.

Table 1 Kinetic parameters for pyrolysis of samples including CL with or without catalyst, PE, and CL/PE mixture with or without catalyst

Material	Temperature	Conversion range (x_1 , %)	E(kJ/mol)	A(min ⁻¹)	R ²
CL	314-379	5.06-91.67	208.76	1.34×10 ¹⁷	0.9732
PE	357-390	8.07-85.46	154.24	3.82×10 ¹⁰	0.9981
CL/PE	318-384	5.43-43.36	120.41	1.22×10 ⁹	0.9411
	422-505	46.36-94.09	80.75	1.19×10 ⁵	0.9675
CL-Ni-1	262-349	16.75-68.78	52.43	4.99×10 ³	0.9963
CL-Co-1	220-347	6.50-68.20	44.70	1.01×10 ³	0.9825
CL-Fe-1	203-360	9.65-70.49	32.02	5.24×10 ¹	0.9925
CL-Mn-1	226-350	9.47-70.30	41.84	5.65×10 ²	0.9800
CL/PE-Ni-1	223-319	5.08-30.31	41.63	3.04×10 ²	0.9615
	409-509	40.14-94.16	71.52	2.40×10 ⁴	0.9782
CL/PE-Co-1	211-253	5.05-20.16	67.20	3.81×10 ⁵	0.9457
	416-484	38.92-79.64	72.52	2.45×10 ⁴	0.9558
CL/PE-Fe-1	178-271	5.78-25.55	29.88	2.99×10 ¹	0.9909
	406-499	39.89-90.15	67.39	1.09×10 ⁴	0.9513
CL/PE-Mn-1	216-267	7.86-26.93	52.14	8.88×10 ³	0.9583
	429-492	45.33-93.23	71.80	4.82×10 ⁶	0.9647
CL/PE-Ni-0.25	226-336	1.50-34.62	69.78	1.45×10 ⁵	0.9438
	419-496	44.72-95.96	64.55	2.54×10 ⁶	0.9524
CL/PE-Ni-0.5	207-332	1.68-32.08	51.68	2.81×10 ³	0.9491

	406-517	40.28-96.64	67.58	1.45×10^4	0.9861
CL/PE-Ni-0.75	216-327	2.62-30.77	50.95	3.90×10^3	0.9456
	408-499	39.93-94.19	68.16	2.33×10^5	0.9512

Note: CL-metal-X or CL/PE-metal-X represents the metal content in 1 g CL or CL/PE is X mmol.

407

408 It is well-established that the introduction of catalyst during the co-pyrolysis of biomass
409 and plastic was favorable for lowering the activation energy of the mixture [24]. For
410 example, the E value of co-pyrolysis of CL and low density polyethylene was decreased
411 from 201.57 kJ/mol to 168.81 kJ/mol after the employment of HZSM-5 [31]. As shown
412 in Table 1, when transition metals were involved into the mixture CL and PE, E values
413 assigned to CL and PE in the mixture were lower than that derived from using the sole
414 feedstock (CL or PE) and that in CL/PE mixture without transition metal treatment.
415 This reveals that the presence of transition metals could promote the decomposition of
416 pure component (CL and PE) and intensify the synergistic interaction between CL and
417 PE in mixture. In particular, the E value of CL in mixture is reduced by 53.21-80.53
418 kJ/mol while that of PE is decreased by 8.23-12.36 kJ/mol.

419

420 The reduction of E in CL is larger compared to that of PE indicating that there was a
421 strong interaction between CL and transition metals. The influence of transition metals
422 on E values of CL and PE in the mixture are both subjected to the order of $Fe < Ni <$
423 $Mn < Co$. Moreover, it is suggested that the content of transition metal also made
424 significant influence on the E value of CL/PE mixture (see Table 1). With the increase
425 of Ni content, the E value of the mixture assigned to CL is gradually reduced from 69.78
426 kJ/mol for CL/PE-Ni-0.25 to 41.63 kJ/mol for CL/PE-Ni-1 while that of PE in mixture

exhibits a positive relationship with Ni content. It is indicated that high catalyst content is beneficial in promoting the decomposition of CL in mixture rather than PE in terms of the activation energy.

4 Conclusions

TGA was employed to investigate the thermal behavior and kinetics of co-pyrolysis of CL/PE mixture. Different types of transition metals (Ni, Co, Fe and Mn) as well as different content of Ni as catalysts have been studied. It is found that the initial decomposition temperature of CL and PE in the mixture is decreased by 91-136°C and 8-15°C, respectively, after the mixture was pre-treated with 1 mmol/g Ni, Co, Fe or Mn. The increase of Ni content resulted in the reduction of initial decomposition temperature of CL in CL/PE. This influence is maximized with a Ni content of 0.75 mmol/g Ni. The presence of transition metals could intensify the synergistic interactions between CL and PE. The maximum difference of weight loss of CL and PE in transition metal treated-mixtures are -2.99%~-14.10% and 1.30~14.41%, respectively. The co-pyrolysis of transition metals-pretreated CL/PE mixtures can be well fitted using two consecutive first order reactions. The E value of CL and PE in the mixture is reduced by 53.21-80.53 kJ/mol and 8.23-12.36 kJ/mol, respectively, as 1 mmol/g Ni, Co, Fe or Mn were involved. With the increase of Ni content, the E value of CL in CL/PE is gradually reduced while the activation energy of PE exhibits a proportional relationship with Ni content.

449 **Declarations of interest:**

450 None.

452 **Acknowledgement:**

453 The authors greatly acknowledge the funding support from the projects supported by
454 *National Natural Science Foundation of China* (Grant no. 51476034 and 51628601),
455 *The Fundamental Research Funds for the Central Universities* and *Postgraduate*
456 *Research & Practice Innovation Program of Jiangsu Province* from the Education
457 Department of Jiangsu (KYCX17_0153) and *Royal Society International Exchange*
458 *Scheme* (IE150760). The authors gratefully acknowledge financial support from *China*
459 *Scholarship Council*.

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