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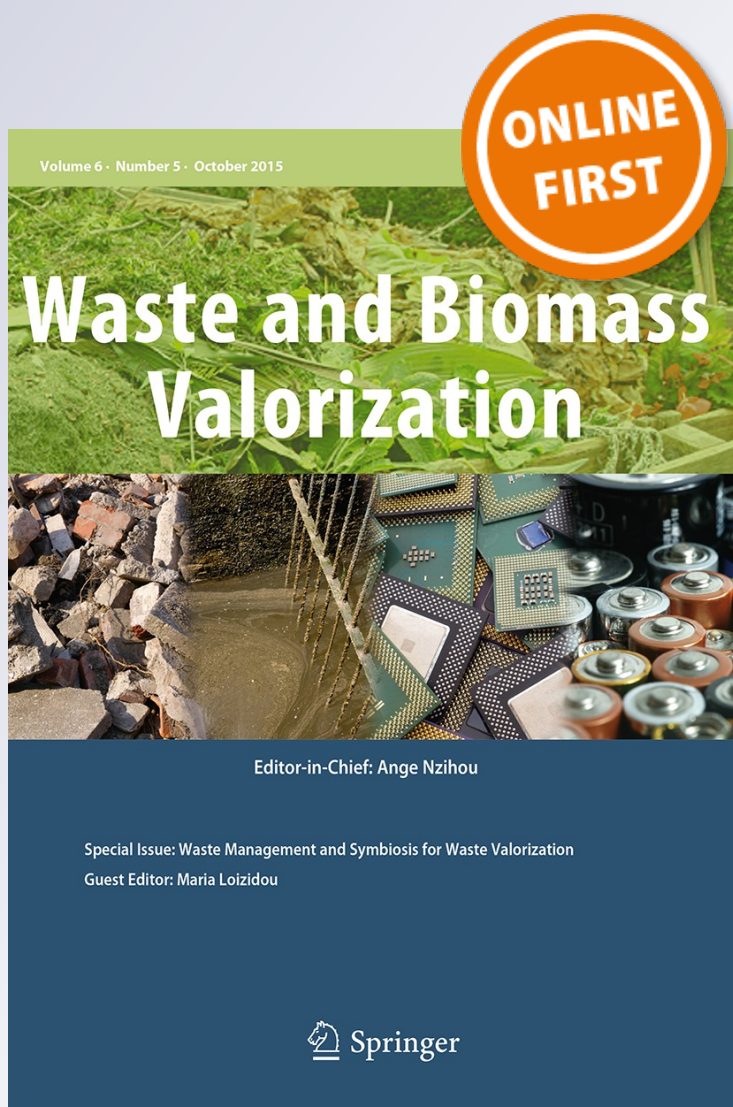
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Thermal Degradation of Household Solid Waste in the Town of Abomey-Calavi in Benin: Kinetic Study

Melhyas Kple^{1,2} · Pierre Girods¹ · Malahimi Anjorin² · Benoît Fagla² · Yann Rogeume¹

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Abstract Thermal behavior of household waste can be improved by knowing thermal degradation kinetics for the optimal design and operation of pyrolysis process. In the present study, Thermogravimetric analysis has been used for dynamic kinetic study of pyrolysis of waste cardboard, wood, and household waste of Abomey-Calavi city in Benin under Argon atmosphere at different heating rates 5–50 °C min⁻¹. For facilitating the laboratory study of household, a model waste (MW) based on wood (88 %), cardboard (7 %) and plastic (5 %) was developed. The kinetic of model waste was studied with Friedman iso-conversional method. The thermal degradation of MW is processed in two steps: the first step between 200 and 400 °C and second step between 400 and 600 °C. The difference of mass loss between experimental and theoretical ones (calculated as arithmetic sums of those from each separated component) was used as a criterion of synergetic effect. The experimental results indicated that a low synergetic effect existed between plastic and cellulosic materials during the pyrolysis of MW. Based on TG and DTG data with different heating rates, the kinetics parameters, especially activation energy were calculated using simple step kinetic model for reaction order $n = 1$. Reasonable fits of data to straight lines in kinetic study plot indicate that the reaction order $n = 1$ used for kinetic of

non-isothermal degradation of the household waste of Abomey-Calavi city in Benin is accepted.

Keywords Thermogravimetric analysis · Reaction kinetic · Activation energy · Household waste

Introduction

Choice of waste management systems depends on decisions by city leaders as well as strategic structures related to the nature, quality and quantity of waste produced [1, 2]. Waste management is a challenge that local authorities and researchers address using multidisciplinary approaches ranging from the humanities to exact sciences such as biology and engineering [1].

The level of development of a country has an impact on its waste management choices [1–3]. According to Riber et al. [4], developed countries utilize various methods for waste management which give way to renewable energy forms and the emergence of new products such as compost. In these countries, considerable investment is made to recycle waste for the benefit of agriculture [5, 6].

The development of African cities inevitably leads to the accumulation of waste quantities increasingly important and centralized. Moreover, the use of plastic bags made from PVC (or low density polyethylene: LDPE) is a scourge, these bags are not biodegradable, they accumulate in all locations of towns and in particular peripheries [7].

Studies on the characterization of African waste also show the presence of large amounts of organic matter, sand and various plastics in household waste. If organic materials can be used to produce compost under certain conditions, plastics are more difficult to manage because they are often contaminated and mixed with various inorganic

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materials (mainly sand), which does not allow for easy recycling.

Many researchers are widely being concerned with environmental friendly disposal of solid waste and biomass as a resource [8–11]. One of the promising ways for utilization of solid waste is pyrolysis. The pyrolysis process involves breaking down the molecular in the wastes under moderate pressure and temperature to produce liquid fuel [12]. Several authors have studied plastics pyrolysis and have demonstrated the potentialities of this technology to deal with the plastic wastes [13–16]. However, there are two constraints of the pyrolysis process [16]: first, recycled materials are not suitable for the whole range of applications; and second, different components of wastes are not easily separated from the post-consumer stream.

Another type of waste that raises some environmental questions is biomass-derived waste. They accumulate on forest ground and cause forestry fires; their organic and energetic potential are wasted in this manner [17]. Pyrolysis of biomass has been studied to produce a liquid product with adequate fuel properties (called “bio-oil”) [18]. However, some disadvantages of bio-oil obtained from biomass pyrolysis such as higher oxygen content, lower high-heat value (HHV), lower volatile, and delayed ignition time in engine severely hinder its use in practice [19, 20]. Thus, it is necessary to explore how to improve the quality of the bio-oil. At present, there are two main pathways to upgrade the bio-oil: (1) High-pressure hydrogenation processing and catalytic cracking [21]; (2) Co-pyrolysis for the mixture of synthetic polymers and biomass [13–16]. The latter have received much attention in recent years because it provides an alternative way to dispose and convert synthetic polymers and cellulose (or lignin)-derived materials into high-value feedstock and specific chemical [22]. At the same time, the co-pyrolysis need not bring in high-pressure hydrogenation, so the production process is more safe. In addition, the plastics and biomass often co-exist in the municipal solid waste (MSW), and there is no need to add other material into the co-pyrolysis process. Therefore, the co-pyrolysis process of plastics and biomass has the broad application prospect, and H-transfer may also be involved in the co-pyrolysis under ambient pressure conditions [23].

As we know, biomass energy is one of the most important renewable energy, and its application becomes more and more significant for environmental protection. Compared with the other renewable energies, biomass is abundant in annual production, with a geographically widespread distribution in the world [24]. The co-pyrolysis of plastics and biomass is a very promising method to reduce the volume of waste and allow the recovery of chemicals and replacement of fossil fuels [13, 25].

Pyrolysis characteristics of biomass fuels have been studied widely using thermoanalytical techniques. The

advantages of thermogravimetric analysis are its rapid assessment of the fuel value, the temperatures at which process starts and ends, and other characteristics such as maximum reactivity temperature, ash amount and total reaction time. Thermogravimetric analysis is very useful for studying the kinetics of pyrolysis processes [26–34]. Thermal methods such as TG, DTG and DTA have been used for studying a variety of areas of pyrolysis. Thermal analysis (TA) determines a set of methods for study of the selected physical properties of the substance under the influence of temperature. Sometimes, simultaneously, the environment (pressure, atmosphere chemical composition) can be changed. Thermogravimetry (TG) is a technique which monitors the sample mass as a function of temperature or time when the sample is subjected to a controlled temperature program. Derivative thermogravimetric (DTG) is based on the rate of mass loss. DTG profiles make it possible to know, for example, the mass loss which is taking place at a temperature during the reaction process.

In Benin (West Africa), few scientific studies have undertaken the management of household waste. The present study was undertaken as an extension of work of Topanou et al. [35] who characterized the typology and size of waste particles, their physico-chemical characteristics, organic matter content and contamination by metal trace element to better determine the amount of solid waste produced and collected at the source in the district of Abomey-Calavi, a city of Benin which doesn't get an effective system of waste management.

In this work it is studied the kinetics of the pyrolysis of the combustible household waste in the city of Abomey-Calavi using thermogravimetric analysis. Only the variations of the total mass of solid and of the cell temperature can be recorded in the course of time. Because a pure kinetic model is used, no mass or thermal transfer is taken into account. The solid sample is assumed homogeneous in temperature and composition. The initial mass of the sample, the flow rate and the properties of the gas have no influence with such a model. In conclusion, the only input available to improve the experimental conditions is the programmed profile of the cell temperature.

The heterogeneous nature of household waste not facilitating their laboratory study, it was developed a model waste based on wood, cardboard and plastic as recommended by ADEME [36].

Experimental Procedure

Materials

Plastic waste considered in the model waste of this study was the polyethylene (PE) because it is the only category of

plastic that found in domestic waste in the Abomey-Calavi city. Because of advanced recycling of high density polyethylene (HDPE), low density polyethylene (LDPE: plastic bag black color) was only plastic waste used in this study. The plastic waste was cut into small pieces (approx. 1 mm²) and used in the pyrolysis reaction.

The cardboard material used in this work is corrugated cardboard generally found in household waste from the city of Abomey-Calavi in Benin. The carton waste was also cut into small pieces (approx. 1 mm²) and used in the pyrolysis reaction.

The wood material used was waste chip and sawdust.

Pyrolysis Tests

The experimental work was carried out on a computerized thermobalance (NETZSCH STA 449 F3 Jupiter) using a high speed furnace which allows a heating rate faster than 500 °C min⁻¹. The thermobalance configuration gives a sensitivity of ±0.4 µg. It allows us to use small sample mass (10–50 mg) which is needed to ensure isothermal conditions in samples. In order to establish an inert atmosphere during all experiments, a controlled argon flow (carrier gas) (fixed at 200 mL min⁻¹, 273 K, 1 atm) sweeps the measurement cell that is purged for 20 min before starting the heating program. During experiments, the argon flow is set to 20 mL min⁻¹. The initial dry mass of samples is about 30–50 mg.

Kinetic studies with TG instruments are typically conducted under isothermal conditions or non-isothermal conditions. Some experimental difficulties can exist with isothermal experiments i.e. a significant part of the reaction may occur during the setting of the experimental temperature at the beginning of the experiment; for instance, see [37] for more precision about this subject. One advantage of the isothermal conditions is the homogeneous sample temperature after the isothermal reaction temperature has been reached, whereas in non-isothermal mode, a temperature gradient in the sample can occur due to the resistance of heat conduction in the sample and the resistance of outer heat transfer [38]. A way for compensating for this effect is to use low heating rates. Isothermal and non-isothermal methods have been widely used in the literature but papers comparing the results obtained with the two methods are rare [39]. Furthermore, it is not easy to compare the scientific studies published for a given product: the experimental conditions (equipment, technologies, operating conditions, sample conditioning, etc.) are often different and not always well known; moreover, the models, the data treatments and the computational methods are never the same [37].

Only dynamic experiments were performed in this paper. For these tests, samples have been previously dried

in an oven at 103 °C for 48 h. The work under isothermal conditions allows studying the kinetic of reactions without being influenced by thermal effects caused by the temperature rise.

Raw materials sample were taken and heated from room temperature to a final temperature of 900 °C and a residence time of 30 min at 900 °C. TG was performed in Argon atmosphere at the heating rates of 5, 10, 20, 30, 40 and 50 °C min⁻¹ under 20 mL min⁻¹ gas flow rate. Thermogravimetric mass loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of waste materials takes place. This mass is high enough that even small temperature gradients are observed in the particles. However, this effect is limited due to the position of the thermocouple is as close to the center of the sample.

From these tests, the evolution with temperature of mass loss (TG) and the mass loss rate (DTG) were obtained for pyrolysis. The mass loss rate was calculated by the equation as follows:

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

where, W_0 is the original mass of the test sample; W_t is the mass at time t , respectively.

Results and Discussions

Model of Household Waste of Abomey-Calavi City

Household wastes have a variable composition depending on the season and the places of their production. In the case of a region or a city, find a representative composition of the waste requires campaigns characterization of the waste according to the seasons, to obtain a statistically valid model. The latest campaigns characterization waste from the city of Abomey-Calavi were performed by Topanou et al. [35]. Table 1 shows the results of these campaigns.

The composition of model waste reflects the fuel from household waste for the thermochemical treatment.

- fermentable and greens wastes are chemically treated as wood;
- cardboard, papers, textiles, and sanitary textiles are treated as cardboard;
- plastics and special wastes are treated as plastics;

On the basis of these assumptions, the model waste (MW) of the city of Abomey-Calavi is composed of 88 % wood, 7 % cardboard and 5 % plastic according to the mass fraction.

Table 1 Typological characterization of household solids waste in Abomey-Calavi

	Dry season	Rainy season	Average
Fermentable	48.64	53.50	51.07
Sand	34.50	19.64	27.07
Cardboard paper	1.14	1.76	1.45
Plastics	2.69	2.75	2.72
Glass	1.50	1.45	1.47
Metal	1.04	1.44	1.24
Textiles	2.28	2.79	2.54
Others	8.23	16.67	12.45

Fuel Analysis

Before thermogravimetric analysis, materials were analysed to determine the main properties affecting thermal conversion. The proximate and ultimate analyses of the studied samples were determined (Tables 2, 3). The properties including volatile matter, ash, and moisture content and chemical composition were tested in accordance with French standards (NF EN 14774, NF EN 1510, 14775, NF EN 15148 and NF EN 14918). The moisture content was determined by successive weighing of a sample placed in an oven at 103 °C until achieving constant mass. The proximate analyses were performed on the TG apparatus in described in “[Experimental Procedure](#)” section. The results, similar with those found in the literature are presented in Tables 2 and 3.

Table 3 shows the values of elemental analysis of model waste (MW) determined from elemental compositions of wood, plastic and cardboard found in this study and in agreement with the literature [40–42]. The analysis of Table 3 shows that the model waste of the city of Abomey-Calavi is mainly composed of Carbon, Hydrogen and Oxygen. However, there is the presence of traces of chlorine atoms which are linked to the process of manufacturing plastic bags and in particular the fact that additives are added. It also appears clearly that the composition of the waste model and the wood are very similar.

Pyrolysis of LDPE, Cardboard, Wood and MW

As has been stated in previous works on pyrolysis of lignocellulosic and polymeric materials [43–46], dynamic

experiments carried out with constant heating rates present some advantages over isothermal experiments. One of these advantages is the possibility of obtaining results in a larger temperature range and more representative of industrial process. Furthermore, these experiments allow the study of the influence of the heating rate β on the thermal decomposition process. Taking this into account, experiments at different β between 5 and 50 °C min⁻¹ have been carried out.

Figure 1 shows thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of different wastes materials at 10 °C min⁻¹. The corrugated cardboard and the wood decompose thermally within relatively narrow temperature regions between 200 and 400 °C and causes a more important mass loss as found in the work of David et al. [47] and Han et al. [48] with a temperature range of degradation of 300–450 and 200–400 °C respectively. Moreover, the decomposition of plastic takes place between 400 and 600 °C as it has already been established in some work [49–51]. The DTG plot of MW shows two step of decomposition. The first decomposition is carried out between 200 and 400 °C as found for cardboard [52] and wood. The second decomposition takes place between 400 and 500 °C as found for LDPE [7]. These results show that there would no synergetic effects between biomass and PE blends. It would be nice to verify this assumption later in the study.

DTG curves of wood and MW at different heating rates (Fig. 2) were shifted to higher temperature due to the heat transfer enlarging with increasing heating rate as it was found in previous studies on LDPE [7] and cardboard [52]. Similar effect of various heating rates on DTG curves for HDPE pyrolysis has been obtained by Aboulkas et al. [53] and Kumar and Singh [51]. It is also the case for more authors who studied the thermal degradation of polyethylene and cellulosic materials [50, 54–57].

Study of Synergetic Effects of Plastic and Biomass Blend

To further illuminate the synergetic effect between the plastic and biomass (wood and cardboard) samples, we defined the difference of mass loss as (ΔW):

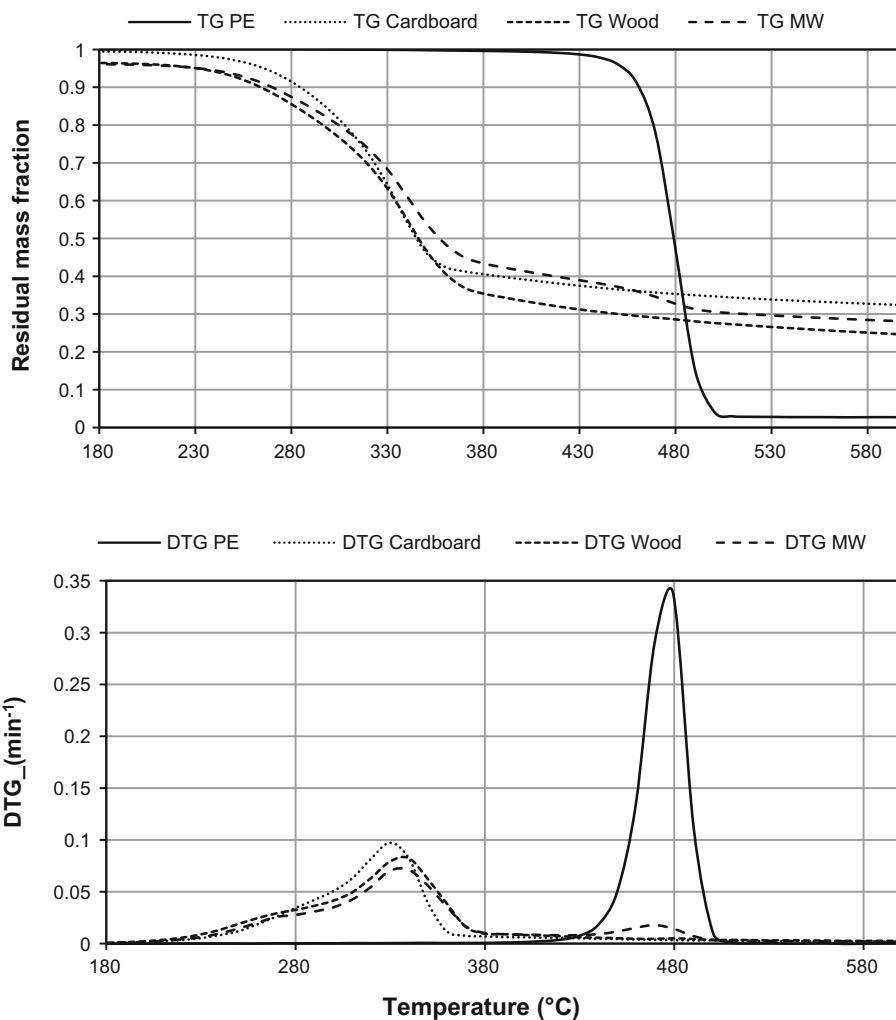
Table 2 Proximate analysis of LDPE, cardboard, wood and model waste (MW)

	Plastic	Cardboard	Wood	MW _{Experimental}	MW _{Calculated}
Volatile matter (%)	97.72	81.93	80.43	80.21	81.40
Fixed carbon (%)	0.71	7.45	14.2	13.72	13.05
Ash content (%)	1.57	10.62	5.37	6.07	5.55
Moisture content (%)	1	6.7	9.6		8.97

Table 3 Elemental analysis of model waste (MW)

Sample	C (%)	H (%)	N (%)	O (%)	S (%)	Cl (%)	Cendres (%)	Total (%)
Wood	44.79	5.07	0.18	37.05	0.04	0.00	0.88	88
Cardboard	3.06	0.40	0.01	3.15	0.01	0.00	0.37	7
Plastic	3.69	0.58	0.01	0.24	0.01	0.14	0.34	5
MW	51.54	6.04	0.19	40.43	0.06	0.14	1.59	100

Fig. 1 TG and DTG of wastes materials



$$\Delta W = W_{MW\ Experimental} - W_{MW\ Calculated} \tag{2}$$

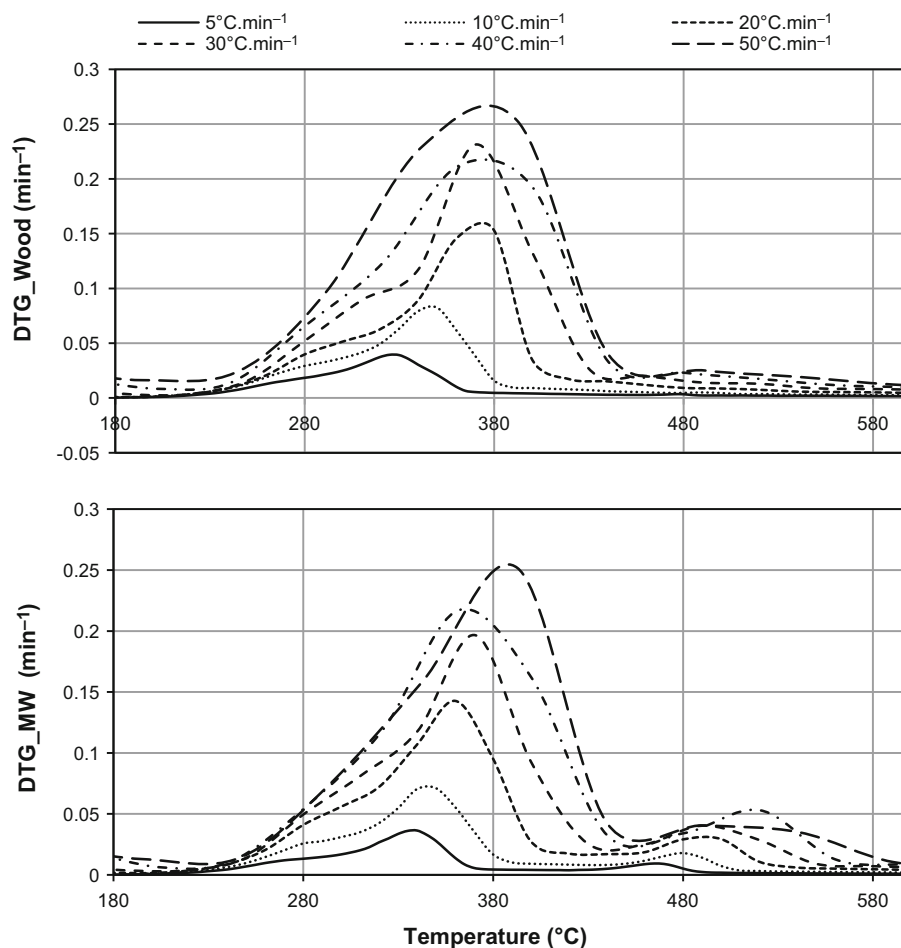
$$W_{MW\ Calculated} = (x_1 W_1 + x_2 W_2 + x_3 W_3) \tag{3}$$

x_i is the fraction of each material in the blend, and W_i is the mass loss of each material in the same operational conditions. Obviously, ΔW describes the “extent” of synergetic effect during the process of co-pyrolysis between plastic and cellulosic materials.

Figure 3 shows the significant interaction, i.e. the synergetic effect between PE and cellulosic materials. Before 300 °C, LDPE softened and had only a slight impact on the

decomposition of the blend in the first stage $\Delta W < 1\%$. ΔW becomes important after 300 °C and varies between 1 and 5 %. This behavior was probably due to the presence of chlorine atoms which are linked to the process of manufacturing plastic bags and in particular the fact that additives are added. Indeed, the HCl released from LPDE can act as an acid catalyst to promote dehydration and coke generation in biomass pyrolysis and inhibit the fracture of cellulose molecular chains [58–60]. These results show that the synergetic effect between cellulosic materials and plastic is very low.

Fig. 2 DTG plots of wood and MW at different heating rates



Kinetic Study

The first step of kinetic study consists in choosing the kinetic model i.e. the mathematical model describing the time evolution of the different mass fractions during the thermal degradation process. The complexity of the chosen model depends on the desired objectives. The thermal degradation of heterogeneous and complex materials, such as waste or biomass, cannot be expressed in detail. Simplified reaction schemes with pseudo-components are generally used. At this stage, a key question is to decide whether heat and mass transfer processes have to be taken into account. A large majority of the works assumes the regime of kinetic control: all influences of internal and external mass and thermal transfer are neglected and the sample is assumed to follow the programmed temperature of the thermobalance perfectly and to have a uniform temperature [38]. However, sources of error related to the temperature undoubtedly exist: the placement and the accuracy of the thermocouple, the thermal lag between the sensor and the sample, and the effect of heats of reaction

[61]. Some authors have demonstrated the influence of experimental conditions (for example [62, 63]).

The approach adopted by many researchers in kinetic analysis of *TG* data for solid fuel pyrolysis is to assume first order reaction for devolatilization [49, 51, 64, 65]. So the *n* order reaction of simple step of solid material with respect to the amount of undecomposed material states that,



The solid, noted *A*, is degraded by only one reaction. Gaseous products (*C*) and solid residue (*B*), called char are produced.

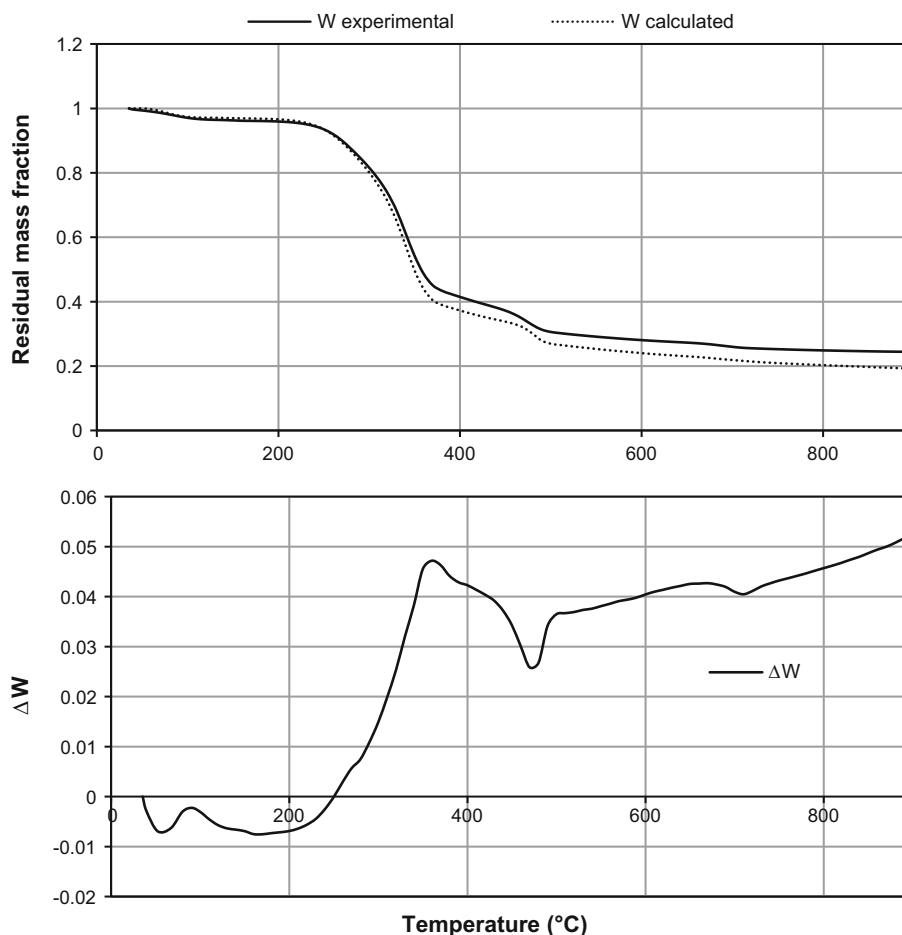
The kinetics calculation was based on the Arrhenius equation. At a constant heating rate:

$$\beta = \frac{dT}{dt} \tag{4}$$

The conversion α follows:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = K_0 f(\alpha) \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

Fig. 3 Curves of synergetic effects versus the temperature (°C)



$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (6)$$

K_0 is the pre-exponential factor, E_a (kJ mol^{-1}) is the activation energy, T (K) is the absolute temperature, and R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant. Many empirical formulas can be used in evaluating the kinetics parameters, including the most commonly used methods, the Friedman method. Compared with the other methods, the Friedman method has a simple calculation process which can skip over the assumptions of the reaction order (n) and achieve activation energy values conveniently. Therefore, the Friedman method was selected as the calculation process in the current paper. The data used in these calculations were obtained from the TG results, which include the mass loss curves at different heating rates. The Arrhenius formula was transformed into its integral form, $\ln(\beta d\alpha/dT) = \ln K_0 + \ln(1 - \alpha) - E_a/RT$. For the selected α , the series points were plotted as $\ln(d\alpha/dt)$ versus $1/T$. These points can be fitted into a straight line, and the slope of the line determines the activation energy values, the calculation results and Friedman plots of the LDPE and the model waste as shown in Figs. 4 and 5.

The activation energy (E_a) of plastic (LDPE), cardboard, wood, and their blends in the co-pyrolysis process are shown in Fig. 6. As can be seen from Fig. 6, the E_a of LDPE is very stable throughout the thermal degradation stage. The average value of E_a obtained is 248 kJ mol^{-1} . This E_a value is similar to those found by Kple et al. [7] in kinetic study on isothermal conditions. Table 4 recapitulates the results typically obtained from the literature. Indeed, these results are very close to those obtained by other authors who have worked on kinetic of pyrolysis of polyethylene.

The decomposition temperature of the hemicellulose and cellulose in wood takes place between 0 and 50 % of conversion rate (Fig. 6). The E_a of wood pyrolysis in this stage was $150\text{--}200 \text{ kJ mol}^{-1}$. When the conversion rate was above 60–70 %, the E_a of wood pyrolysis was $200\text{--}300 \text{ kJ mol}^{-1}$, which may be caused by the coking of lignin. Comparing these results with those of some authors for kinetic of poplar wood pyrolysis in dynamic study, Slopiecka et al. found for activation energy values 154 kJ mol^{-1} for Kissinger method, 159 kJ mol^{-1} for FWO method and 157 kJ mol^{-1} for KAS method. Han

Fig. 4 Friedman plots of the LDPE and activation energy calculated from the fitting curves

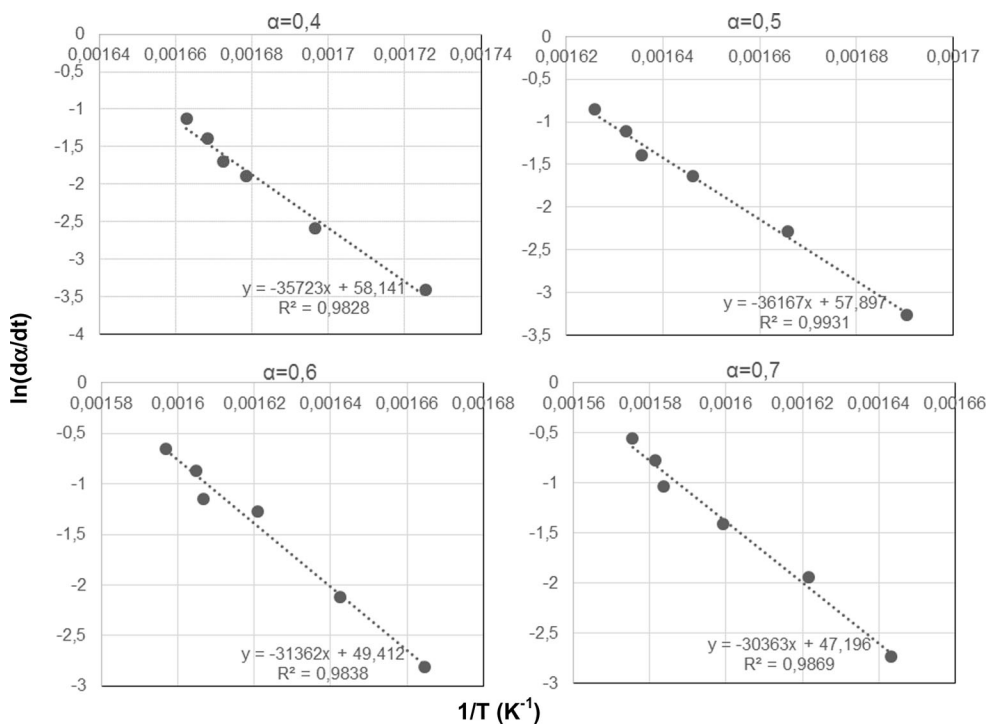
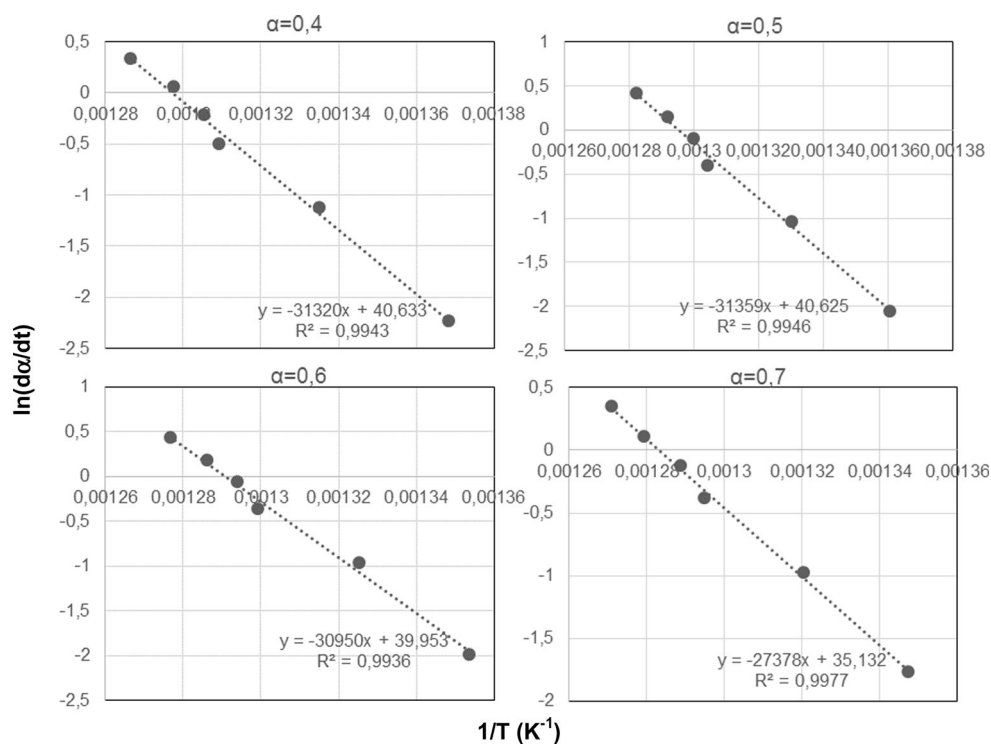


Fig. 5 Friedman plots of the MW_200–400 °C and activation energy calculated from the fitting curves

et al. [48] proposed E_a values between 150 and 350 kJ mol^{-1} and Sorum et al. [72] found E_a value of 110 kJ mol^{-1} for kinetic study of cellulosic materials in municipal waste.

Figure 6 shows that the E_a values of cardboard which is composed mainly by cellulose material, are higher than those found in the case of wood. This behavior was probably due to the presence of added chemical elements linked

Fig. 6 Activation energy values of plastics, cardboard, wood, and their blends during pyrolysis

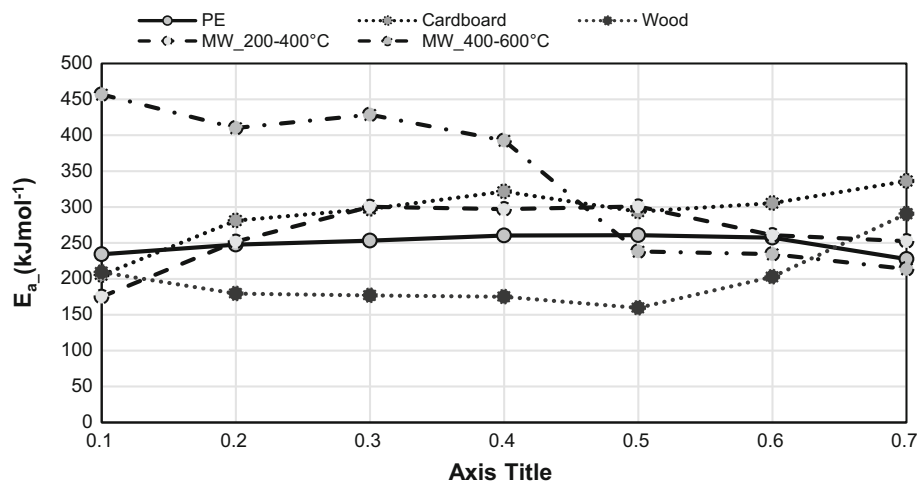


Table 4 Comparison of results with literature

References	Material	Order n	T (°C)	Ea (kJ mol ⁻¹)
Kple et al. [7]	LDPE	1	400–500	251
		0.667	400–500	244
Kim and Kim [50]	HDPE	0.5	440–470	190
Westerhout et al. [66]	HDPE	1	400–450	220
	LDPE1	1	400–450	241
	LDPE2	1	400–450	201
Bockhorn and Knumann [67]	PE	0.81	200–600	259
Klose [68]	PE	1	385–520	275
Madorsky [69]	PE		385–405	284
Wu et al. [70]	HDPE	0.74	327–487	234
		0.63	327–487	206
Bockhorn et al. [71]	HDPE	0.8–1.4	400–470	268
Ceamanos et al. [55]	HDPE	1	390–470	249

to the process of manufacturing of cardboard and which act as catalyst at high heating rates and promote coke generation in biomass. These values of E_a (209–350) kJ mol^{-1} are higher than those found by Alvarenga et al. [64]: 14,489 kJ mol^{-1} for cardboard, 121 kJ mol^{-1} for carton packaging, Zhou et al. [73]: 101 kJ mol^{-1} for cardboard, 94 kJ mol^{-1} for printing paper, Wu and Chang [74]: 150 kJ mol^{-1} for carton packaging. Moreover, these values are in agreement with result of Völker and Rieckmann [63]: 244 kJ mol^{-1} for cardboard in kinetic study with non-isothermal conditions. It is clear that these results are acceptable. The differences observed may be due to the raw material used and the experimental conditions (equipments, technologies, operating conditions, samples conditioning, etc...) in each case.

The results of the dynamic study of the MW showed two areas of thermal decomposition (Fig. 2). Kinetic studies were therefore conducted in both temperature range of degradation: 200–400 and 400–600 °C. The E_a of the first

and second temperature ranges of the model waste were 175–350 and 200–450 kJ mol^{-1} , respectively. These E_a values of model waste between 200–400 and 400–600 °C are higher compared to values found to cardboard and wood. This behavior is caused by the synergy between the various components of the model waste. Between 400 and 600 °C and from 50 % of conversion rate, the E_a values of MW are close to those found for the plastic. LDPE is the main material which degrades from this conversion value.

Conclusion

The pyrolysis kinetics parameters of waste LDPE, cardboard, wood and model waste of Abomey-Calavi City in Benin under non-isothermal conditions using TG were determined for reaction order $n = 1$. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum pyrolysis

regimes. Dynamic experiment showed that the pyrolysis of model waste of the city of Abomey-Calavi takes place in two temperature ranges: 200–400 and 400–500 °C for the cellulosic materials (wood and cardboard) and plastic (LDPE bag used in Benin) respectively. The synergetic study confirm this assumption and show that the HCL from LDPE has not a significant effect on the thermal decomposition of wood and cardboard. The activation energy values were determined by Friedman isoconversional method. Reasonable fits of data to straight line in kinetic study plot indicate that the reaction order $n = 1$ used for kinetic of dynamic degradation of model waste is acceptable.

In conclusion, these results show that the pyrolysis of household waste of Abomey-Calavi and other waste composed of cellulosic materials and LDPE is not feasible at the temperatures below 400 °C. Slow pyrolysis could be achieved above 400–500 °C and a flash pyrolysis from 600 °C.

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