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Determination of activation energy of pyrolysis of carton packaging wastes and its pure components using thermogravimetry

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ABSTRACT

Many processes have been used for recycling of carton packaging wastes. The pyrolysis highlights as a promising technology to be used for recovering the aluminum from polyethylene and generating products with high heating value. In this paper, a study on pyrolysis reactions of carton packaging wastes and its pure components was performed in order to estimate the kinetic parameters of these reactions. For this, dynamic thermogravimetric analyses were carried out and two different kinds of kinetic models were used: the isoconversional and Independent Parallel Reactions. Isoconversional models allowed to calculate the overall activation energy of the pyrolysis reaction, in according to their conversions. The IPR model, in turn, allowed the calculation of kinetic parameters of each one of the carton packaging and paperboard subcomponents. The carton packaging pyrolysis follows three separated stages of devolatilization. The first step is moisture loss. The second stage is perfectly correlated to devolatilization of cardboard. The third step is correlated to devolatilization of polyethylene.

1. Introduction

The carton packaging has been widely used all over the world as an efficient aseptic packaging material for conservation of liquid-food products. This type of packaging avoids contamination of food by microorganisms and bacteria, and has the ability to preserve them for months without the necessity of refrigeration and usage of chemicals (Zortea, 2001). The carton packaging consists of laminates composed of 75% paper, 20% polyethylene and 5% aluminum. The paper gives mechanical support to the packaging; polyethylene has the function to isolate the paper of moisture (external layer), prevent the aluminum contact with food (internal layer), and even act as an adhesion element between the components of the packaging; the aluminum creates a barrier against light and oxygen to avoid food spoilage (Tetra Pak, 2014).

The recycling of carton packaging waste has become increasingly important as it permits us to give solid wastes an appropriate destination instead of being disposed of in dumps and landfills. The recycling starts in the paper industry where recycling fibers can be recovered by repulping process. The polyethylene and aluminum separated in a hydropulper can be recovered in three different ways: energy generation from paraffinic oil, recovery of aluminum in pyrolysis ovens, reusing of polyethylene and aluminum by plasma technology, and the processing of the mixtures of polyethylene and metal to obtain high-end plastic lumber products (Lopes and Felisberti, 2006). Thus, pyrolysis can be considered a good alternative for carton packaging recycling, i.e., to separate aluminum from polyethylene or to generate products with high heating value. Most of the current interest associated with pyrolysis is focused on the environmental issue, since this process represents attractive ways of reusing of agricultural and forestry residues, but also in the reuse of great part of the components in municipal solid wastes.

The drying and pyrolysis of carton packaging wastes has aroused the interest of the scientific community (Bacelos et al., 2009; Bacelos and Freire, 2012; Alvarenga et al., 2012; Marques et al., 2012). Several studies have been investigated the pyrolysis mechanisms of the major components of carton packaging: cardboard (cellulose material) and polyethylene. Qu et al. (2011) conducted experimentally fast pyrolysis of cellulose, xylan, and lignin in a tube furnace between 350 and 650 °C. The authors investigated the effect of temperature on pyrolysis products (char, noncondensable gas, and bio-oil). Völker and Rieckmann (2002) performed microcrystalline cellulose pyrolysis in a thermogravimetric analyzer

Abbreviations: IPR, Independent Parallel Reactions; TGA, thermogravimetric analysis; DTG, differential thermogravimetric.

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Nomenclature

c	mass fraction
E_a	activation energy (kJ mol^{-1})
k_0	pre-exponential factor (s^{-1})
m	mass (mg)
n	order of reaction
R	universal gas constant (kJ mol^{-1} K^{-1})
RMSE	root-mean-square error
r^2	correlation coefficient
T	temperature (K)
t	time (min)
X	conversion

Greek symbols

β	heating rate (K min^{-1})

Subscripts

0	initial
i	component
f	final

applying constant heating rates between 0.14 and 105 K min^{-1}. They used a software module for the evaluation of thermokinetic experiments and the calculation of kinetic parameters by analyzing single experiments as well as by applying the multivariate regression technique. Paik and Kar (2009) carried out thermogravimetric analysis (TGA) in a range of temperatures from 25 to 600 °C in N_2 atmosphere and heating rates of 5, 10 and 15 °C min^{-1}. The authors studied the degradation behavior of polyethylene particles of different diameters and calculated activation energy of reaction using techniques such as Friedman, Freeman–Carroll, second Kissinger, first Kissinger, Kim–Park and Flynn–Wall kinetic models. Aguado et al. (2002) analyzed the polyolefin (low-density polyethylene, high-density polyethylene, and polypropylene) pyrolysis in a conical spouted bed reactor under nitrogen atmosphere. The temperatures studied were 500, 550 e 600 °C and the reaction times were between 1 and 1080 s. The data obtained in the kinetic study have been carried out by feeding 1 g of plastic (with a particle size of approximately 1 mm) and using 30 g of sand (with a size between 0.63 and 1 mm). They stated that a conical spouted bed reactor may be an alternative to the fluidized bed reactor for obtaining olefins by polyolefin pyrolysis. Korkmaz et al. (2009) investigated the carton packaging pyrolysis in a semi-batch fixed bed reactor using inert atmosphere. They quantified the yield of pyrolysis products (coal, liquid and gas) and pointed out that carton packaging waste are useful resources for recycling as the wastes conversion into solid carbon and waxes generate products with high heating value which can be used in power generation.

The pyrolysis process is complex. It is comprised of many primary and secondary parallel reactions as well as competitive reactions. According Órfão et al. (1999), it is difficult to propose mechanisms to accurately characterize the thermal degradation of biomass. However, for practical engineering applications, consider only simplified mechanisms, such as primary thermal decomposition, may be sufficient (Gronli et al., 2002).

The most widely used models in the modeling of primary thermal degradation kinetics are one-step, isoconversional, consecutive reaction (CR) and Independent Parallel Reactions (IPR). Santos et al. (2012a) and Hu et al. (2007) makes a comparison between these four models. One-step model, which considers a single global reaction, although widely used, is extremely simplified and may be unsuitable for describing the last stages of the pyrolysis process. In the CR model, each peak in the DTG (differential thermogravimetric) curve corresponds to an individual and sequential decomposition of the components of material, as through no interactions occur between them. In most cases, there are three components or zones that coincide with hemicellulose, cellulose, and lignin. Hemicelluloses decompose at 498–598 K, cellulose at 598–648 K, and lignin decomposes gradually in the temperature range of 523–773 K (Di Blasi, 2008). Thus, the assumption that the degradation of lignin occurs after that of hemicellulose may lead to an inaccurate estimate of its kinetic parameters. In isoconversional methods, the estimation of activation energy is based on the premise that temperature change, which occurs due to change of heating rate, is a function of activation energy when comparing two or more curves in a conversion point equal. In isoconversional method, the global activation energy is obtained from a simple linear regression. In IPR model, each component of material is degraded individually in the same temperature range, ensuring the possibility of simultaneous decomposition. The total rate of weight loss is calculated considering the individual reaction rates and their respective mass fraction. IPR model requires more sophisticated algorithms, but provides an activation energy estimate for each component.

Although there are some plants operating on industrial scale, it can be said that the pyrolysis process is recent, presenting many challenges that must be overcome such as determining optimal operating conditions. Knowledge of the kinetics of pyrolysis is essential to predict the process behavior and design of suitable reactor. This information could be used to support future studies in the area.

In spite of all these studies on pyrolysis of pure components of carton packaging, only few have been done on pyrolysis of carton packaging waste. Thus, in order to contribute to a greater understanding of the reaction kinetics of carton packaging pyrolysis, this work aims to analyze two different kinds of kinetic models (the isoconversional models and Independent Parallel Reactions (IPR) model) to calculate the global activation energy of pyrolysis reaction of carton packaging, as well as of pure components, using data obtained from thermogravimetric analyses. It was not found in literature any application of these models for pyrolysis of carton packaging. Thus, it is presented here as a novelty.

2. Materials and methods

2.1. Materials

Carton packaging and its pure components, cardboard and polyethylene, were used to obtain thermogravimetric analyses data. Initial samples particles were analyzed in a photo-optical particle analyzer (HAVER CPA 2-1). The data of particles size and specific surface are shown in Table 1.

Table 1
Size characterization of carton packaging, cardboard and polyethylene particles used in this paper.

Material	Carton packaging	Cardboard	Polyethylene
Particle count (total)	5086	4735	4036
d5 (mm)	0.396	0.477	0.616
d50 (mm)	0.85	0.744	0.985
d95 (mm)	1.188	1.045	1.225
Specific surface (cm^2 cm^{-3})	81.535	84.759	65.55

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