Bioresource Technology xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

# Kinetic study of solid waste pyrolysis using distributed activation energy model

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## HIGHLIGHTS

- The proposed DAE model explained the solid waste pyrolysis process successfully.
- The activation energy of MSW significantly decreased with addition of agri-residues.
- The reactivity ($R_M$) of groundnut shell was higher compared to the other solid wastes.
- The pyrolysis process of MSW and MSW + agri-residues occurred in three stages.
- The maximum degradation was observed in the second stage, with all the solid wastes.

## ARTICLE INFO

*Article history:*
Received 31 July 2014
Received in revised form 5 October 2014
Accepted 7 October 2014
Available online xxxx

*Keywords:*
Municipal solid waste
Agricultural residues
Thermogravimetric analysis
Distributed activation energy model
Pyrolysis kinetics

## ABSTRACT

The pyrolysis characteristics of municipal solid waste, agricultural residues such as ground nut shell, cotton husk and their blends are investigated using non-isothermal thermogravimetric analysis (TGA) with in a temperature range of 30–900 °C at different heating rates of 10 °C, 30 °C and 50 °C/min in inert atmosphere. From the thermograms obtained from TGA, it is observed that the maximum rate of degradation occurred in the second stage of the pyrolysis process for all the solid wastes. The distributed activation energy model (DAEM) is used to study the pyrolysis kinetics of the solid wastes. The kinetic parameters $E$ (activation energy), $k_0$ (frequency factor) are calculated from this model. It is found that the range of activation energies for agricultural residues are lower than the municipal solid waste. The activation energies for the municipal solid waste pyrolysis process drastically decreased with addition of agricultural residues. The proposed DAEM is successfully validated with TGA experimental data.

## 1. Introduction

Rapid urbanization and increased population add large amount of municipal solid waste to our planet. Currently, world cities generate about 1.3 billion tonnes of solid waste per year and expected to increase to 2.2 billion tonnes by 2025 (Hoornweg and Bhada-Tata, 2012). This has significant impact on disposal area, economics of waste management and the environmental consequences. So, there is a growing interest in developing efficient biomass thermal modification technologies worldwide to combat climate change and to provide solutions for the current energy crisis. In recent years many investigations have been done for the possible use of solid waste biomass, such as combustion, pyrolysis and gasification. In all the thermochemical systems, pyrolysis is the first step taking place with consequent occurring of combustion and gasification. A better understanding of the pyrolysis will be of immense help in designing the gasifiers with better efficiency. The pyrolysis process can be understood thoroughly by knowing the kinetic parameters. Thermogravimetric analysis (TGA) is one of the most widely used techniques for studying the degradation mechanism and for the determination of the kinetics parameters of pyrolysis and other thermochemical conversion processes. By using the TGA data, researchers have developed different models such as single step model, two parallel reaction model, three-pseudo component model and distributed activation energy model (Li et al., 2009) for establishing the kinetic mechanism of pyrolysis process. Distributed activation energy model (DAEM) has been widely used for analyzing the complex reactions of coal and biomass pyrolysis. Cai et al. (2013) studied the pyrolysis behavior of lingo-cellulosic biomass samples by considering the three parallel reactions associated with the primary pyrolysis of hemicellulose, cellulose and lignin present in the lingo-cellulosic biomass. Kinetic study from DAEM revealed that the activation energy distribution for lignin

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http://dx.doi.org/10.1016/j.biortech.2014.10.028
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Please cite this article in press as: Bhavanam, A., Sastry, R.C. Kinetic study of solid waste pyrolysis using distributed activation energy model. Bioresour. Technol. (2014), http://dx.doi.org/10.1016/j.biortech.2014.10.028

is wide compared to cellulose, which has the narrowest distribution. From the DAEM, it was observed that the activation energy for pyrolysis of Pine pellets was low (in the range of 160–270 kJ/mol) compared to the activation energy of Sewage sludge samples, which was in the range of 170–400 kJ/mol (Soria-Verdugo et al., 2013). It also was observed that the activation energy distribution of bituminous, lean coals and biomass such as corn-stalk skins follow the approximate Gaussian distribution (Li et al., 2009). The complex reactions of typical medical waste pyrolysis and the evolution of various volatile species were successfully explained by DAEM model (Yan et al., 2009). This model was also used for studying the pyrolysis kinetics of fresh water algae, fungal pre-treated corn stover (Kirtania and Bhattacharya, 2012; Ma et al., 2013). DAEM model was also used to check the accuracy of other integral iso-conversional methods in estimating the activation energy of the pyrolysis process of various materials such as wood, algae, corn stalk skin, kerogen, cellulose, lignin and coal (Wu et al., 2013). It was known from this model that, the catalytic effects of alkali and alkali earth metals present in the biomass play a key role in the variation of activation energy during the pyrolysis process (Sonobe and Worasuwannarak, 2008). This model was used for knowing the combustion characteristic of wood and from the results it was observed that the DAEM was not suitable for knowing the combustion behavior (Shen et al., 2011). Till date, there is no reported work on pyrolysis of municipal solid waste, groundnut shell and cotton husk using DAEM. The present study is focused on understanding the pyrolysis characteristics of municipal solid waste, agricultural residues and their blends and provides the necessary information in filling the present knowledge gap on solid waste pyrolysis.

## 2. Methods

### 2.1. Materials

The solid waste biomasses of different origin such as Municipal solid waste (MSW), Agricultural Residues (AR) are chosen in the present study. The municipal solid waste is collected from the dump sites of Warangal city. The agricultural residue, particularly cotton husk (CH) is collected from the cotton fields and groundnut shell (GS) is collected from oil processing mills. The collected municipal solid waste contains combustible organic materials (paper waste, food waste, used plastic, cloth waste, yard waste etc.) along with soil, mud, sand and other inert materials that are not separated manually. The recyclable materials like glass, metals and most of the plastic are separated from the collected MSW.

### 2.2. Sample preparation

About 2 kg of material is taken from the collected municipal solid waste and agricultural residues. These collected samples of MSW, CH, and GS are grounded thoroughly using lab scale grinding mill and sieve analysis is carried out using sieves with ASTM mesh numbers of 30, 40, 50, 60 and 70 to obtain uniform particle size of 250 μm for the preparation of samples. In total, four samples are prepared using MSW, CH, GS and MSW + AR. The MSW + AR sample is prepared by mixing 70% of MSW, 15% of CH and 15% of GS. Finally the samples are stored in air-tight plastic containers for further analysis.

### 2.3. Material characterization

The proximate and ultimate analysis of MSW, CH and GS samples are presented in Table 1. The proximate analysis is done according to ASTM standards of D 1102, E871 and E872 for ash, moisture content and volatile matter respectively. The fixed carbon is calculated as a difference. The ultimate analysis is done using CHNS analyzer (Elementar Vario EL III, Elementar Analysensysteme GmbH, Germany). The higher heating values (HHV) are calculated by using the correlation proposed by Parikh et al. (2005), based on the proximate analysis, considering the entire spectrum of solid carbonaceous materials like coals, lignite and all types of biomass material.

**Table 1**
Proximate and ultimate analysis of selected solid waste biomass.

| Biomass | Cotton husk | Groundnut shell | Municipal solid waste |
|---|---|---|---|
| *Proximate analysis (wt.%)* | | | |
| Moisture content | 7.9 | 4.9 | 6 |
| Volatile matter | 66.0 | 70.2 | 29 |
| Fixed carbon | 20.1 | 19.0 | 10 |
| Ash | 6.0 | 5.9 | 55 |
| *Ultimate analysis (wt.%)* | | | |
| Carbon | 46.88 | 48.2 | 16.14 |
| Hydrogen | 4.83 | 5.7 | 1.79 |
| Nitrogen | 0.93 | 0.80 | 1.36 |
| Sulfur | 0.36 | 0.33 | 0.26 |
| [a]Oxygen | 41 | 39.07 | 25.45 |
| HHV (MJ/kg) | 17.34 | 17.58 | 6.46 |

[a] By difference.

$$\mathrm{HHV} = 0.3536\mathrm{FC} + 0.1559\mathrm{VM} - 0.0078\mathrm{ASH}\ (\mathrm{MJ/kg}).$$

### 2.4. Methods

#### 2.4.1. Thermogravimetry

Thermogravimetric analysis (TGA) is carried out for studying the thermal degradation behavior of municipal solid waste, agriculture residues and their blends using Perkin Elmer, Diamond TG/DTA analyser. Non-isothermal TGA analysis is conducted at different heating rates of 10, 30 and 50 °C/min in inert (Nitrogen) atmosphere from 30 to 850 °C. The purge flowrate of nitrgen is maintained constantly at 100 ml/min. For analysis, 5–10 mg of biomass sample is taken in the pan of TGA microbalance. The residual weights and derivative weights are recorded with respect to time and temperature.

#### 2.4.2. Distributed activation energy model

The distributed activation energy model (DAEM), originally developed by Vand (1943), has been extensively used for analyzing the complex reactions occurring during the pyrolysis of fossil fuels. Later this model is successfully applied to different biomass fuels for understanding the reaction kinetics of pyrolysis process (Sonobe and Worasuwannarak, 2008; Wang et al., 2008; Shen et al., 2011; Navarro et al., 2009). This model assumes that number of parallel irreversible first order reactions that have different kinetic parameters occur simultaneously. The change in total volatiles at time $t$, is given by

$$1 - V/V^{*} = \int_{0}^{\infty} \exp\left(-k_0 \int_{0}^{t} e^{-E/RT} dt\right) f(E) dE \tag{1}$$

where $V^{*}$ is the effective volatile content, $V$ is the volatile content at temperature $T$, $f(E)$ is the distribution curve of activation energy that represents the difference in the activation energies of all the reactions and $k_0$ is the frequency factor corresponding to $E$ value. In this study, the integral method proposed by Miura and Maki (1998) is used for estimating the kinetic parameters.

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