



Development of a modified independent parallel reactions kinetic model and comparison with the distributed activation energy model for the pyrolysis of a wide variety of biomass fuels



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HIGHLIGHTS

- TGA pyrolysis of residual biomass samples from municipal and industrial sector.
- Development and assessment of a modified independent parallel reactions model (IPR).
- Development and assessment of DAEM model: comparison with IPR models.
- Better fitting and prediction results from the modified IPR model.
- Very good fitting to the experimental data from DAEM model.

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ABSTRACT

The pyrolysis of six waste biomass samples was studied and the fuels were kinetically evaluated. A modified independent parallel reactions scheme (IPR) and a distributed activation energy model (DAEM) were developed and their validity was assessed and compared by checking their accuracy of fitting the experimental results, as well as their prediction capability in different experimental conditions. The pyrolysis experiments were carried out in a thermogravimetric analyzer and a fitting procedure, based on least squares minimization, was performed simultaneously at different experimental conditions. A modification of the IPR model, considering dependence of the pre-exponential factor on heating rate, was proved to give better fit results for the same number of tuned kinetic parameters, comparing to the known IPR model and very good prediction results for stepwise experiments. Fit of calculated data to the experimental ones using the developed DAEM model was also proved to be very good.

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1. Introduction

The increased demand for fuel diversification in the fuels market and the environmental impact associated with the exploitation of fossil fuels worldwide, demonstrate the need for additional amounts of renewable energy sources. Biomass is the fourth largest primary energy resource in the world, accounting for at least 9% of the global final energy consumption (REN21 Steering Committee, 2015). At the same time it offers a remarkable potential reduction of greenhouse emissions (Berndes and Hansson, 2007; Damartzis et al., 2011; Vamvuka et al., 2009) and gains increasing interest as a source of useful products via thermochemical processes. In specific, agricultural and forestry residues is a form of biomass readily available and of high interest in Mediterranean countries,

which have a remarkably high potential of such residues. Furthermore, other types of biomass such as municipal solid wastes (MSW), sewage and animal sludges and other industrial by-products are becoming matter of public concern and importance, due to the potential environmental and human health impacts. As a consequence, nowadays, thermal treatment of these wastes becomes more attractive as a disposable option (Becidan et al., 2007; Vamvuka et al., 2009).

Regarding thermal treatment methods, pyrolysis has attracted significant attention as a fundamental thermochemical conversion process for transforming biomass directly into gaseous and liquid fuels (Biagini et al., 2008; Branca et al., 2005; Cai et al., 2014; Chen et al., 2015; Grønli et al., 2002; Kim et al., 2014; Ma et al., 2013; Meng et al., 2013; Vamvuka and Sfakiotakis, 2011; White et al., 2011). Pyrolysis is also the first step in other thermochemical conversion processes, such as combustion and gasification.

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Knowledge of the chemical composition, the thermal behaviour and the reactivity of biomass fuels during pyrolysis, is very important for the effective design and operation of the thermochemical conversion units (Di Blasi, 2008; Vamvuka et al., 2003). Thermogravimetric analysis (TGA/DTG) under isothermal or non-isothermal conditions is a simple, rapid, inexpensive and widely employed technique for studying thermal events, providing information on partial processes and estimating kinetic parameters for various decomposition reactions, at relatively low heating rates.

Since the chemical transformation of solid raw materials to numerous products is highly dependent on the kinetic rates of the pyrolysis reactions, it is evident that accurate kinetic models are needed in order to best design the pyrolysis process. The degradation of biomass is a very complex process, mainly due to the large number and the diverse nature of the occurring reactions. Biomass fuels contain a wide variety of pyrolyzing species. The phase transition from solid biomass to gaseous and liquid products raises difficulty and often complicates the interpretation of the kinetic analyses (Damartzis et al., 2011). Consequently, in order to explain mass loss associates to pyrolysis, biomass is considered as a sum of pseudo-components, a fraction of the sample that basically contains a biomass component, thermally degrades as a unit, but it is not a pure substance (Barneto et al., 2010).

For kinetic modeling purposes, many authors have analyzed dynamic data of various biomass fuels, considering different schemes of reactions for the kinetic evaluation i.e. single reaction, series of competing and/or consecutive, or parallel independent first/nth order reactions and combinations of them. Substantial differences are observed in the kinetic parameters reported, related to the experimental methods, operating conditions, data analysis, as well as the chemical composition of the raw materials examined in each study (Becidan et al., 2007; Grønli et al., 2002). Regarding models based on a multi-component devolatilization mechanism, some authors, focusing on the chemical complexity and heterogeneity of the biomass content, propose the adoption of the distributed activation energy model (DAEM). DAEM model assumes one or several irreversible first order parallel reactions with invariant pre-exponential factor and a continuous distribution function (usually a Gaussian), representing the activation energies from the various reactions (Gašparovic et al., 2012; Várhegyi et al., 2011).

When modeling biomass pyrolysis kinetics according to a devolatilization mechanism, there is a wide consensus that the methodology of deriving kinetic parameters by force-fitting models to a single heating rate is simplified and mainly useful for comparison, or similarity test purposes (Várhegyi et al., 2011). Kinetic parameters, derived according to this methodology, often fail to predict the dynamics at different experimental conditions, especially when the sample is more complex and inhomogeneous. The incorporation of such a model in large scale heat transport models, for the description of biomass conversion systems, must often be avoided or carried out with care (Di Blasi, 2008). Furthermore, an ill-conditionality of such models, due to the so-called mathematical compensation effect between the kinetic parameters, has also been widely acknowledged (Garn, 1976). The effect is more severe when DAEM models are applied, as more parameters have to be simultaneously adjusted and the fit has more degrees of freedom, depending also on the variety of experimental data. The wide variations among kinetic parameters of similar samples, observed in the literature, have also been attributed to a thermal compensation effect, that is, dependence of the kinetic triplet on the heating rate, when the effects of heat transfer phenomena are not negligible, especially at high heating rates (White et al., 2011).

The fuels examined in this work are of strong interest in many countries for their exploitation at biomass systems of small or

industrial scale. However, to propose their conversion to energy and/or useful products, a detailed investigation on the properties and the thermal behaviour of each specific raw material is required, since these kinds of fuels present diverse nature and complexity. Most of the previous studies have focused on woody residues (Branca et al., 2005; Cai et al., 2014; Chen et al., 2015; Gašparovic et al., 2012; Kim et al., 2014; Ma et al., 2013; Várhegyi et al., 2011; White et al., 2011). However, to the authors' knowledge, there is no kinetic analysis for non-woody residues such as animal sludges in literature, while investigations for meat and bone meal (MBM) are rare last decade (Ayllon et al., 2005; Skodras et al., 2007) and report different kinetic parameters for each heating rate.

Furthermore, there is lack of information or little information on DAEM and IPR models, respectively, using simultaneous data fitting at multiple heating rates (Barneto et al., 2010; Branca et al., 2005; Quek and Balasubramanian, 2009; Wu et al., 2009; Várhegyi et al., 2011). Most of the studies, adopting simultaneous data fitting at multiple heating rates, use a greater number of parameters to be tuned (as compared to the single heating rate fitting method) for a satisfactory fitting result. This results mainly from (a) the more complex mathematical equation utilized, including more physical or empirical parameters in the basic kinetic equation of these investigations, or (b) a greater number of adopted pseudo-components or (c) a greater number of basic kinetic parameters to be tuned, by keeping some of them invariant and some to vary with the heating rate.

The present study aimed at (a) developing and assessing a modified IPR (Independent Parallel Reactions) pyrolysis kinetic model at linear and stepwise temperature programs, in order to eliminate as far as possible the aforementioned drawbacks of previous investigations, (b) assess the effectiveness of modified IPR model against existing IPR models for a wide variety of biomass fuels, presenting heterogeneous structures and (c) compare the modified IPR model with DAEM model, when simultaneous fitting at multiple heating rates is applied to describe the pyrolysis of biomass fuels.

2. Methods

2.1. Materials and characterization

The samples used in this study were three woody and three non-woody biomass residues, all taken from the municipality areas of Chania and Rethymno, in the island of Crete in South Greece. The three woody biomass samples were the agricultural residues olive tree pruning (OP), olive kernel (OK) and vine shoots (VS). The non-woody samples included an undigested sewage sludge from a waste water treatment plant (SS), a sludge coming from the primary sector of a biological animal waste treatment unit (CFS), as well as a sample of animal by-products (MBM) from an industry producing deli meats.

After air drying, homogenization and riffing, the biomass samples were milled and sieved to a particle size of <200 µm. Representative samples were characterized in terms of proximate analysis using programmable laboratory furnaces according to the EN14774, EN15148, EN14775 standards, ultimate analysis using a Thermo Scientific CHNS Flash 2000 type analyzer (EN15104, EN15289) and calorific value using a Leco AC-300 type calorimeter (EN14918).

2.2. Thermogravimetric analysis

Pyrolysis tests were performed in a differential thermogravimetric analyzer with microbalance sensitivity below 10 µg. From a series of replicate measurements using a woody biomass sample,

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