

Pyrolysis of natural, butadiene, styrene–butadiene rubber and tyre components: Modelling kinetics and transport phenomena at different heating rates and formulations

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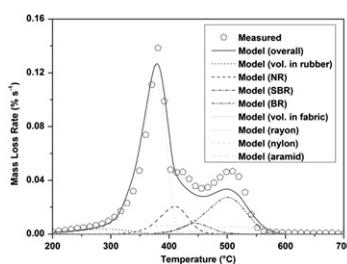
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HIGHLIGHTS

- ▶ Pyrolysis of scrap rubber, other tyre components (fabric, etc.) and composites.
- ▶ Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements.
- ▶ Influence of volumetric flow rate and heating rate on rubber pyrolysis process.
- ▶ Modelling chemical reaction kinetics, external and internal mass and heat transfer.
- ▶ Evaluation of pyrolysis with sensitivity analysis (differing waste compositions).

GRAPHICAL ABSTRACT



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ABSTRACT

A model acknowledging reaction kinetics and thermal conduction during waste end-of-life (ELT) tyre pyrolysis was developed based on the individual consideration of elastomers, namely natural (NR), butadiene (BR) and styrene–butadiene (SBR) rubber; fabric, that is rayon, nylon and aramid; and wire. External diffusional and thermal film resistances proved to be negligible during the thermal cracking. An algorithm was developed to extract pre-exponential factors, activation energies, the orders of reactions, the enthalpies of reactions, and transport parameters. The pyrolysis of various formulations at different volumetric flow rates and heating rates was monitored by thermogravimetry (TG) and differential scanning calorimetry (DSC), whereas the pertinent thermodynamic properties (density, specific heat capacity, and thermal conductivity and diffusivity) were determined separately. The un-decomposable weight fraction containing carbon black, char and ash was 39% for the investigated rubber and 13% for the fabric formulation. The sensitivity analysis of the pyrolysis on compound and process (operating) conditions was performed. The obtained results (taking into account their drawbacks) with the additional measurements and modelling may be used for the thermochemical treatment reactor scale-up and optimization, and consequently, a suitable design of energy and products recovery instead of disposal or landfilling, thus minimizing hazardous waste and contamination to soil and water resources.

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1. Introduction

Pyrolysis is performed in the absence of oxygen (de-polymerization under an inert atmosphere) and at relatively low temperatures up to 500–700 °C. Compared with other technologies, it is a more sustainable option with the high recovery rate of products with minimal contaminants discharge management (Al-Salem et al., 2009). The pyrolysis reactive processes can be attributed to complex reaction mechanisms such as random chain scission, end-chain scission, chain-stripping, cross-linking, and coke formation (Al-Salem et al., 2009; Chen et al., 2001; Rofiqul Islam et al., 2009).

The main problem of the process is the choice of optimal operating conditions, for example maximum temperature, heating rate, and pressure. The operating conditions are closely related to process parameters, such as heat capacity, enthalpy of reactions, kinetic parameters, heat transfer coefficients, thermal diffusivity, etc. The kinetic parameters (activation energies and pre-exponential factors) of the decomposition of main tyre components are considered to be dependent on the heating rate and pressure (Charpenay et al., 1998; Chen et al., 2001; Galvagno et al., 2007; Gonzales et al., 2001; Koreňová et al., 2006; Leung and Wang, 1998, 1999; Lin et al., 1998; Lopez et al., 2009; Murena et al., 1996; Murena, 2000; Olazar et al., 2005; Rofiqul Islam et al., 2009). Only Quek and Balasubramanian (2009) considered the kinetic parameters as constant (except for the pre-exponential factor) and that heat transfer plays an important role.

Some researchers (Chen et al., 2001; Gonzales et al., 2001; Kim et al., 1995; Koreňová et al., 2006; Leung and Wang, 1999; Lopez et al., 2009; Olazar et al., 2005; Quek and Balasubramanian, 2009; Rofiqul Islam et al., 2009; Yang et al., 1995) assumed that the thermal decomposition of components, like natural rubber (NR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR), fabric, and oil, proceed as first-order reactions, which is not necessarily true, as the reaction orders may differ. The order of reaction in any rate equation may be directly related to the stoichiometry of the reaction equation, if the reaction is elementary. The non-integer orders of reaction are realistic, since the pyrolysis reactions are composed of several elementary steps, which upon the use of quasi-steady-state approximations and the definition of rate-determining steps yield the orders of reaction, which are not unity or two. One thus has to be careful in the application of reaction rate models in evaluating reactions. The result should at least come from *n*th-order kinetic model, which accommodates the possibility of several elementary steps, but preferably from a firm theoretical basis or reaction scheme, such as the one presented by Al-Salem et al. (2009), and be realistic so that it can be used for the improvements in actual pyrolysis reactors. On the other hand, a group of researchers (Charpenay et al., 1998; Chen et al., 2001; Galvagno et al., 2007; Gonzales et al., 2001; Kim et al., 1995; Leung and Wang, 1998, 1999; Lin and Chang, 1996; Lin et al., 1998; Murena et al., 1996) looked at the effect of the heating rate from the viewpoint of process efficiency. They investigated to which extent a larger heating rate speeded up the process and how much greater the energy consumption was. In the literature, two basic kinetic models occur most frequently. The first is called the “Three (or more)-component simulation model” (TCSM) (Al-Salem et al., 2009; Chen et al., 2001; Galvagno et al., 2007; Gonzales et al., 2001; Kim and Chun, 1995; Kim et al., 1995; Koreňová et al., 2006; Leung and Wang, 1998, 1999; Lin and Chang, 1996; Lopez et al., 2009; Olazar et al., 2005; Rofiqul Islam et al., 2009), in which waste rubber is considered as a composite made of oil, fabric, elastomer, and other components. However, the components of the model are seldom described or defined with regard to their nature or chemical composition. The second model is called the “Three-elastomer simulation model” (TESM)

(Charpenay et al., 1998; Leung and Wang, 1998, 1999; Yang et al., 1995), in which only elastomers in the tyre material are treated. The state of the art of the mathematical modelling of rubber tyre pyrolysis, presented above, was recently reviewed by Quek and Balasubramanian (2012); nonetheless, other tyre components are not thoroughly covered.

It was noticed that in almost all studies a tyre was looked upon only as a composite of rubbery materials. Only two took into account fabric, oil and additives (De Marco Rodriguez et al., 2001; Leung and Wang, 1999). Additionally, some studies presented specific kinetic models, which were a combination of the first two models (Lin et al., 1998), and some or interpreted the chemical reaction kinetics of tyre pyrolysis in their own way (Al-Salem et al., 2009; Murena et al., 1996; Murena, 2000).

In the present work, thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis of all important tyre components and their composites was done. Beside NR, SBR and BR, volatiles, fabric and other additives, as essential components of waste tyres, were included in the model. The advantages of the proposed model are simultaneous the acknowledgement of rubber, fabric and wire in the model (tyre formulation), the separate treatment of chemical kinetics and heat transfer (kinetic parameters are independent of heating rate), and the use of *n*th-order kinetic model (the orders of reaction, different from unity, may arise due to pyrolysis reactions not being simple monomolecular decompositions).

2. Materials and methods

2.1. Materials

Scrap tyres (provided by Albin Promotion d.o.o., Majšperk, Slovenia) were cut into five different neat and composite samples; specifically, neat rubber, neat wire and neat fabric, and rubber/fabric and rubber/fabric/wire composites. Neat rubber in average (rubber from different tyres was sampled) consisted of 6 wt% volatile compounds, 17 wt% NR, 31 wt% BR, and 7 wt% SBR (degradable parts).

2.2. Density determination

Scrap tyres were chopped to pieces with a mean size of 3 × 3 cm and a thickness of 1–3 cm, and weighed. An 800 mL graduated cylinder was filled with 500 mL of distilled water and previously weighed samples of scrap tyre. The measured initial temperature was 20 °C. The layer of tyre samples was then heated to 30, 40, 50, 60, and 70 °C. At each temperature the volume on the graduated cylinder was determined. The temperature dependence of water density was taken into account.

2.3. Heat capacity determination

Rubber heat capacities were determined by differential scanning calorimetry (DSC) on HP DSC 1 instrument from Mettler Toledo (Greifensee, Switzerland) in nitrogen atmosphere (50 mL min⁻¹). Samples were prepared by weighing 7–8 mg of rubber (with the dimensions of 4 × 4 × 1 mm) in 40 μL aluminium crucibles with a pin and hole in their lid. Samples, the sapphire standard and empty crucibles were subjected to the heating/cooling program described in our previous work (Likozar and Krajnc, 2008, 2011). Indium and zinc standards were used for temperature calibration and for the determination of the instrument's time constant.

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