



Combined model-free and model-based devolatilisation kinetics of tyre rubbers



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ABSTRACT

The pyrolytic devolatilisation behaviour of four rubbers, which are predominantly used in tyre manufacturing, has been studied using combined model-free and model-based kinetics. Natural rubber, synthetic polyisoprene, butadiene and styrene-butadiene rubbers were investigated experimentally using a TGA-DTA instrument. For all of these rubbers two distinct zones of weight loss (here termed as devolatilisation reactions) were observed, i.e., primary depolymerisation/condensation and secondary (consecutive) degradation of the condensed product. Moreover, the DTG and DTA results indicated that the two butadiene rubbers started to boil around 450 °C. Next, fixed values of the activation energy, derived from two different isoconversional methods, were implemented as fixed values in a model-based kinetic procedure. The values of the apparent activation energies for the rubber devolatilisation reactions were between 200 and 440 kJ mol⁻¹. This kinetic strategy resulted in a decrease of the degrees of freedom of the model-based multivariate nonlinear regression procedure. Therefore, the estimated kinetic parameters are less dependent on the initial guesses. Furthermore, the interdependence of the two consecutive devolatilisation reactions has also been successfully incorporated in the model, further improving the regression. This combined kinetic approach resulted in very accurate predictions of the experimental data.

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1. Introduction

Over the last decades more stringent legislation has boosted the scientific and industrial interests in waste treatment processes for end-of-life tyres in many countries [1]. Among many different processes, pyrolysis seems to be very promising, especially from a valuable chemicals recovery and materials recycling point of view [2]. Many laboratory-scale experimental studies have been performed using thermogravimetric analysis (TGA) in order to better understand the pyrolysis of a waste tyre [3–12]. These studies allow for a close investigation, including kinetic modelling, of the devolatilisation behaviour of the volatile matter of the tyre. This volatile matter mainly consists of rubbers, the most important being natural (polyisoprene) rubber (NR), synthetic polyisoprene (PI), butadiene rubber (BR) and styrene-butadiene rubber (SBR) [13]. Apart from these rubbers, a tyre additionally includes a plethora of processing oils, additives, fillers, vulcanisation accelerators/inhibitors, which are all added during either the rubber or tyre processing [2]. Due to this complexity of components, the

devolatilisation of the tyre is notoriously difficult to model kinetically. Moreover, the lack (in most cases) of exact individual rubber contents in the tyre, combined with very similar devolatilisation behaviour of some of the rubbers (mainly BR and SBR), further complicates the modelling [7,14–16,17]. Therefore, the assessment of the kinetic parameters of the individual tyre rubbers will ultimately facilitate the kinetic modelling of the entire tyre.

Model-free (or isoconversional) methods, while being widely applied for biomass kinetic modelling [18], have been implemented only sparsely for waste tyre (rubber) devolatilisation kinetics. The few examples include the kinetic modelling of styrene-butadiene rubber [19,20] and butadiene rubber [21] devolatilisation. On the other hand, model-based kinetics have been more widely applied for the kinetic modelling of the devolatilisation of waste tyres and tyre rubbers. Generally, a power-law function is assumed as the reaction model in these studies [5–8,10]. Seidelt et al. have modelled the devolatilisation of NR, BR and SBR, including an estimation of the reaction order [22]. As a different approach, Oh et al. modelled SBR devolatilisation using the sum of a zero-, first- and second-order reaction [23]. Conesa et al. focusing on PI, BR and SBR, and Yang et al. modelling NR, BR and SBR, have both used the sample weight in their model-based kinetic expressions, instead of the more generally used conversion (α) [17,24]. The results of all these

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studies will be discussed in more detail below, comparing them with the presently obtained results.

However, even the modelling of the devolatilisation kinetics of the individual rubbers is not a straightforward exercise. For example, the reported values for the activation energy for the tyre rubbers cover a wide range, between 150 and 250 kJ mol⁻¹, see Section 4.2. This can (at least partly) be attributed to the high dependence of the model-based kinetics on their initial guesses for the multivariate nonlinear regression. Indeed, Mui et al. showed that a higher/lower value of the pre-exponential factor (A) can be 'compensated' by a lower/higher value of the activation energy (E), and vice versa [5]. This dependence can be reduced by decreasing the degrees of freedom during the minimisation procedure. It is proposed here to use a combination of model-free and model-based kinetics to achieve this. Model-free and model-based kinetics have been used complementarily in previous studies. Khawam and Flanagan modelled the desolvation of drug solvates using model-based kinetics employing various reaction models [25]. For every reaction model the activation energy and pre-exponential factor were estimated. Then, the best reaction model was defined as that which accompanied an E with a value closest to the E determined using a model-free isoconversional method. Chrissafis studied the thermal degradation of poly(ethylene adipate) also using the two kinetic procedures complementarily [26]. Again, the best reaction model was chosen based on the agreement between the activation energies predicted by the two different kinetic procedures. Thus, as both the limitations of the separate usage of model-based kinetics have been recognised and the complementary usage of model-based and model-free kinetics have been explored, these two types of kinetics have not yet been integrated.

Therefore, the objective of this study is to estimate the kinetic parameters for the devolatilisation of four rubbers (NR, PI, BR and SBR) using combined model-free and model-based kinetics. The present paper is structured as follows. First, the experimental results, comprising of the derivative thermogravimetric (DTG) and the differential thermal analysis (DTA) data, are presented for the four rubbers. Next, the activation energies are determined using two different model-free isoconversional techniques. The estimated values of the activation energy are then implemented as fixed values in the model-based kinetics. Finally, the more substantiated sets of estimated kinetic parameters thus obtained will be compared with previously reported values.

2. Experimental

Four different rubbers, which are widely used in tyre manufacturing, were studied. Synthetic 97% *cis*-1,4-polyisoprene was obtained from Sigma–Aldrich. Natural rubber (SMR 20) was sourced from Continental Tyre SA, while the 97% *cis*-polybutadiene rubber (Neodene 40) and the cold emulsion polymerised styrene-butadiene random copolymer (Afpol 1500, 23.5% styrene) were both procured from a local rubber manufacturer (Karbochem Pty Ltd). All of the rubbers were cryogenically milled in order to obtain a particle size below 1 mm, but other than that were used as received.

A Mettler Toledo TGA/DCS 1 analyser (equipped with a DTA sensor) was used for the kinetic experiments. For all experiments samples were prepared to be 10 ± 0.5 mg, to diminish sample size influences on the kinetics. Experiments have been performed in duplicates to verify reproducibility, with a standard deviation of the duplicates not exceeding 1.3%. The thermogravimetric programme consisted of a drying period of 5 min at 110 °C, followed by the kinetic experiment up to 600 °C with heating rates of 2, 5, 10, 15 or 20 °C min⁻¹ and a nitrogen flow of 100 mL min⁻¹. It is assumed that at these particle sizes and heating rates mass and heat transfer limitations will be negligible [27]. For the differential thermal analysis

Table 1
Proximate analysis of the four tyre rubbers (%wt).

| | NR | PI | BR | SBR |
|------------------|------|------|------|------|
| H ₂ O | 0.3 | 0.3 | 0.0 | 1.1 |
| Additives | 2.7 | 1.8 | 0.3 | 10.6 |
| Volatiles | 95.9 | 97.6 | 99.1 | 85.4 |
| Fixed carbon | 0.3 | 0.0 | 0.3 | 2.6 |
| Ash | 0.8 | 0.3 | 0.3 | 0.4 |

(DTA), as performed with the current equipment, the sample temperature was determined by a thermocouple directly beneath the crucible. The difference between this sample temperature and the furnace temperature, corrected for the sample temperature profile of a separate run with an empty crucible, was used for a qualitative estimation of the apparent heat of reaction.

Using the same apparatus, proximate analyses have been performed for the four tyre rubbers. These analyses were performed at a heating rate of 10 °C min⁻¹ and incorporated three isothermal segments in an inert N₂ atmosphere, at 110, 275 and 600 °C for the quantification of water, additives and volatiles, respectively. It was verified that at the end of all of these isothermal segments the sample weight was constant. The proximate analysis ended with an isothermal segment at 600 °C with pure oxygen, for the distinction between the fixed carbon and ash content. As can be observed in Table 1, the rubbers consist mostly of volatile matter, while the amount of fixed carbon is very low. Also, the water content is very low, while, especially for SBR, there are significant amounts of additives. All these results do agree well with previously published values for these types of rubbers [19,20,21,24,28].

3. Kinetic model

Kinetic modelling of devolatilisation is generally based on the conversion (α), which is defined as,

$$\alpha = \frac{(m_o - m)}{(m_o - m_f)} \quad (1)$$

where m is the mass at a specific reaction time, while m_o and m_f are the initial and final mass of the investigated temperature range, respectively. Next, devolatilisation is modelled according to the rate of change in the conversion,

$$\frac{d\alpha}{dt} = A \exp \left[-\frac{E}{RT} \right] f(\alpha) \quad (2)$$

where A represents the pre-exponential factor (s⁻¹), E is the activation energy (J mol⁻¹), R the universal gas constant (8.314 J mol⁻¹ K⁻¹), T the temperature (K) and $f(\alpha)$ is the reaction model. The experimental value of the change in conversion at time $t = k$ (s) is calculated with the following expression:

$$\frac{d\alpha_k}{dt} = \frac{(\alpha_{k+1} - \alpha_{k-1})}{(t_{k+1} - t_{k-1})} \quad (3)$$

3.1. Model-free isoconversional kinetics

Two different isoconversional methods have been applied in this study, i.e., the Friedman (differential) and Kissinger (integral) method. As pointed out by Budrugaec and Segal, for better predictions of the activation energy, experimental data at multiple heating rates are required [29]. Moreover, it is reported that, if the experimental data is accurate enough, differential isoconversional methods are preferable over integral methods for establishing the dependence of the activation energy on the degree of conversion [29,30]. Furthermore, Starink showed that, when using integral isoconversional methods, the approximation of the temperature integral mainly determines the precision of the model

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