



Effect of temperature and heating rate on limonene production from waste tyre pyrolysis



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ABSTRACT

The effect of pyrolysis temperature and heating rate on limonene production during waste tyre pyrolysis was investigated using gram-scale (fixed-bed) and microgram-scale (TGA) pyrolysis reactors. The investigation was carried out with final pyrolysis temperatures between 350 and 550 °C and heating rates in the range of 5–25 °C/min. Only the effect of the pyrolysis temperature was significant on the tyre derived oil (TDO) yield, while the effects of both pyrolysis temperature and heating rate were significant on the chemical composition of the TDO, i.e., limonene yield. In the gram-scale reactor, a maximum limonene yield was obtained at a pyrolysis temperature of 475 °C and a heating rate of 20 °C/min, with a value of 7.62 wt.% (based on the steel- and fabric-free tyre) or 22 wt.% (based on the polyisoprene content of the tyre). DTG curves showed that increasing the heating rate led to (1) a decrease in secondary degradation reactions, and (2) an increased temperature at the maximum depolymerisation rate. At the same heating rate, MS ion current signals showed that limonene formation occurred at slightly higher temperatures compared to isoprene formation, indicating a slight higher activation energy for the former reaction. Since a higher activation energy indicates a stronger temperature dependency for a reaction, it implies, in combination with the observation of higher temperatures at maximum limonene production rate in the MS ion current signal, an improvement of the selectivity of polyisoprene depolymerisation towards limonene.

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1. Introduction

The development of waste tyres recycling using pyrolysis has encountered various legislative barriers due to its classification as incineration in most regions [1]. Moreover, the markets for both the liquid (tyre derived oil or TDO) and solid (char) pyrolysis products are not yet fully established. The TDO cannot, at the current relatively low oil prices, compete with fossil fuels, while the char is characterised by relatively high levels of impurities (e.g. ash and sulphur contents) [1]. To improve the economic feasibility of waste tyre pyrolysis, recovery of valuable chemicals from the TDO, while using the remainder as a fuel, has been proposed [2–5]. These valuable chemicals include rubber monomers (isoprene, butadiene, styrene), some of their dimers (DL-limonene, 4-vinyl-cyclohexene), as well as a variety of aromatics [6–8]. The present study focusses on the production of limonene (C₁₀H₁₆) from waste tyre pyrolysis. Limonene is derived from the polyisoprene (natural rubber or NR) fraction of a tyre and is typically the most abundant compound in

the TDO [9,10]. Limonene is an important starting material in several industrial formulations for e.g. solvents, resins, or adhesives, with an estimated price of 2 USD/kg [11–13].

In previous studies [7,9] the influence of the pyrolysis temperature (i.e. the final/highest temperature of the heating programme) on the chemical composition of the TDO was predominantly investigated. It has been reported that limonene yields are highest for temperatures between 400 and 500 °C [10]. The maximum limonene concentration in the TDO reported by Cunliffe and Williams was at a temperature of 450 °C [14]. Islam et al. obtained highest limonene concentration in the TDO at a temperature of 475 °C [15]. The influence of the heating rate on limonene yields has received considerably less attention. It is nevertheless known that the heating rate has a significant effect on rubber devolatilisation during waste tyre pyrolysis [16–21]. A study by Banar et al. indicated that, at a final pyrolysis temperature of 400 °C, limonene concentration in the TDO decreases from 17,062 to 219 ppm, as the heating rate was increased from 5 to 35 °C/min [20]. However, a study carried out by Brazier and Schwartz reported a higher combined butadiene and vinylcyclohexene yield (95%) at a higher heating rate (100 °C/min) compared to 66% at a heating rate of 5 °C/min, for polybutadiene depolymerisation [21]. They also indi-

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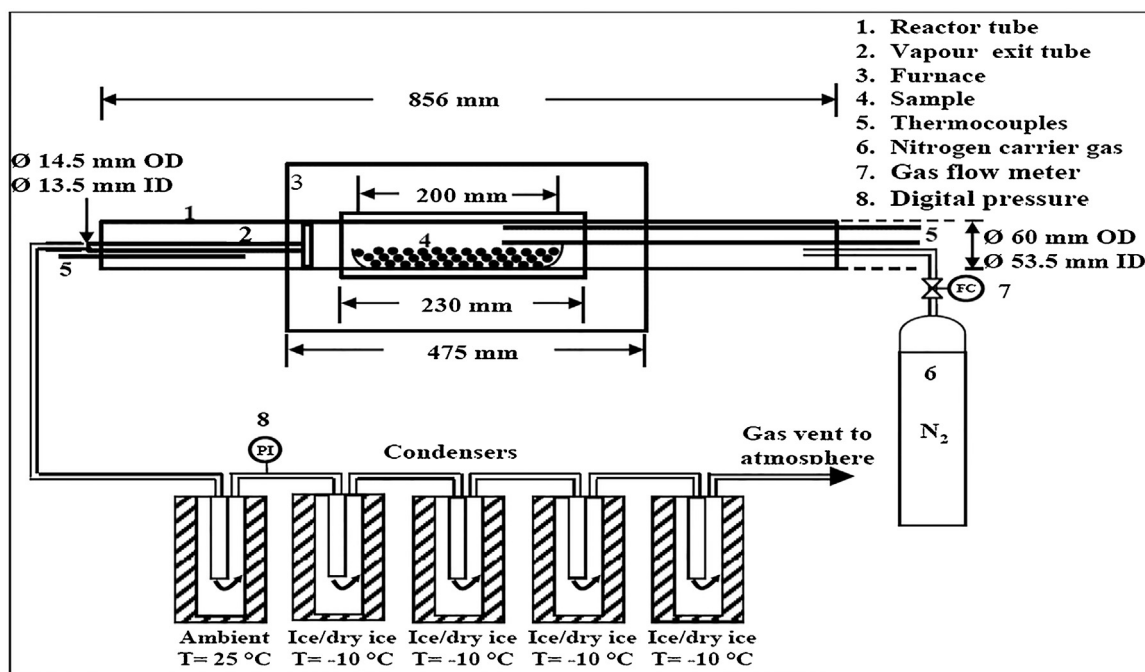


Fig. 1. Fixed-bed slow pyrolysis reactor.

Table 1

Proximate analysis and rubber composition of the crumb.

Proximate analysis (wt.%)	Moisture	Oils	Volatile matter	Fixed carbon	Ash
	0.6	5.6	56.0	30.0	7.8
Rubber composition/volatile matter (wt.%)	Polyisoprene (natural rubber)		Synthetic rubber (SBR and BR) ^a		
	64		36		

^a By difference.

cated that the depolymerisation of polybutadiene is analogous to that of polyisoprene. Therefore, it remains unclear how the heating rate affects the production of limonene.

Some studies [16,19,22] investigated the effect of heating rate on the pyrolysis of the different components of waste tyre, such as, processing additives and rubbers. Cheung et al. pointed out that, when the heating rate was increased, the processing additives in the tyre were more readily devolatilised, while the fraction of the tyre that devolatilises via depolymerisation was increased at the expense of the fraction devolatilising via degradation [16]. A similar observation was reported by Leung and Wang [22]. Lam et al. observed that lower heating rates required a lower energy input for the pyrolysis of tyres, while reaction times and heat losses were increased [19].

The main objective of this study is to investigate the effect of the pyrolysis temperature and the heating rate on the limonene yield from waste tyres pyrolysis. A central composite design of gram-scale experiments (in a fixed-bed reactor) was used to investigate the influences of these two variables. Additionally, experiments on microgram-scale, using a thermogravimetric analyser (TGA), which could be combined with a mass spectrometer (TGA-MS), were performed to further elucidate the effect of the heating rate.

2. Materials and methods

A bulk sample of approximately 500 kg crumbed (steel- and fabric-free) waste truck tyres, consisting of particle sizes up to 5 mm, was supplied by a local waste tyre recycler. Subsampling

was carried out to ensure feedstock homogeneity. Subsequently, the sample was sieved to obtain two samples with particle size ranges of 0.6–0.8 mm and 2.8–3.4 mm. All experiments in the gram-scale reactor were performed with the larger particle size sample, while for the microgram-scale experiments both particle sizes were employed. Preliminary experiments indicated that the effect of particle size between 0.6 and 3.4 mm on pyrolysis oil yield and its chemical composition was insignificant, which is also supported by previous studies [16,19,23]. Proximate analysis on the larger particles was conducted using a slightly adjusted version of ASTM E1131-08 (with X = 275 °C). Additionally, kinetics experiments were carried out (using the smaller particle size) to determine the rubber composition of the crumb using a procedure described by Danon and Görgens [24]. The results of the proximate analysis and rubber composition are shown in Table 1.

For the gram-scale experiments a fixed-bed slow pyrolysis reactor was used, see Fig. 1. The sample size used in these experiments was 40 g. The hot volatiles were purged with nitrogen gas (99.5% purity, Afrox, South Africa) at a constant flow rate of 1 l/min. A two-level full factorial design with two replicates and augmented with 3 centre points, i.e. a central composite design (CCD), was employed. All the design and response factors are overviewed in Table 2. The pyrolysis temperature range, heating rate range and centre points were selected based on the operability range of the existing setup and typical values reported in the literature [3,25,26]. Moreover, statistical analysis of variance (ANOVA) was employed to study the effects of the individual factors and their interactions. Additionally, a response surface model was fitted to determine optimal operat-

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