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Influence of reactor and condensation system design on tyre pyrolysis products yields

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Abstract

This study investigates the effect the pyrolysis reactor and the condensing system type have on the tyre derived oil (TDO) and DL-limonene yield, as well as benzothiazole concentration in the TDO. All the experiments were performed at 475 ºC and three technologies were investigated, fixed bed reactor (FBR), bubbling fluidised bed reactor (BFBR) and conical spouted bed reactor (CSBR), with the latter being the reactor that provided the highest TDO yield (58.2 wt.%). Furthermore, the CSBR enhances DL-limonene production due to its excellent features (low residence time of volatiles and high heat and mass transfer rates), which minimize secondary cracking reactions. Moreover, in order to maximize the TDO retention efficiency and selectively and reduce the concentration of certain heteroaromatic species, two types of condensation systems were evaluated: tube-and-shell condenser (indirect contact) and a quenching condenser (direct contact). The quenching condenser not only promoted the condensation efficiency for DL-limonene, but also reduced the concentration of benzothiazole in the collected TDO. Indeed, the direct contact between water (fed into the quencher) and the hot volatile stream favours the dissolution of some polar heteroaromatic species, thus reducing the nitrogen and sulphur content in the TDO and increasing the applicability of TDO as fuel.

Keywords: Tyre pyrolysis; Pyrolysis oil; Condensation system; Pyrolysis reactor; Quenching condenser; Tube-and-shell-condenser.

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1. Introduction

Waste tyre pyrolysis, which is a thermal treatment of waste tyres under inert conditions to yield pyro-gas, tyre derived oil (TDO) and pyro-char [1,2], is one of the most attractive methods to eliminate the increasing waste tyre accumulation. Various strategies have been implemented to improve the pyrolysis process to be an effective conversion technique with reduced environmental emissions and improved waste tyre valorisation [3-6]. The rate by which waste tyre piles are increasing is higher than the rate of their elimination due to insufficient capacity of various techniques for waste tyre treatment and recycling [7-9]. This implies that waste tyre pyrolysis involves economic opportunities, in particular the TDO, which is a good source of valuable chemicals and liquid fuels alternative to petroleum-derived products. Thus, DL-Limonene, terpinolene and p-cymene are some of these valuable chemicals that can be recovered from the TDO. For example, DL-limonene has an estimated market price of 2 US$ /kg [10]. It should be noted that although the TDO physicochemical properties (density, viscosity and heating value) are similar to conventional petroleum-derived fuels, the presence of nitrogen and sulphur compounds hinders its direct application, and therefore they should be removed or their content reduced [5,6,11]. Typical methods employed to improve the quality of the crude TDO for fuel application are as follows, i) removal of the moisture, ii) desulphurisation, and iii) distillation [12-15]. Thus, in order to improve the viability of the tyre pyrolysis process and at the same time maximize the economic potential of TDO, the concentration of undesired compounds should be minimized, whereas the yield of TDO and, especially that of valuable chemicals, should be maximized.

Accordingly, the yield and the quality of the TDO are influenced by several operational factors. Temperature is the main factor influencing the distribution of gas, liquid, and solid phases in the pyrolysis products and their physical/chemical properties in the fast pyrolysis process [6,9,16] [9,16]. Other important influential factors, such as heating rate and residence time of hot volatiles in the reaction zone, will depend largely on the reactor configuration. The most common reactors for waste tyre pyrolysis include fixed bed reactors (FBR) and fluidized bed reactors [6,9,16,17]. The FBR is characterised by relatively low heating rates and long residence times of the volatiles, leading to lower TDO yields. Among the fluidized bed reactors, the bubbling fluidized bed reactor (BFBR) is the most developed technology for the fast pyrolysis process [18]. This reactor may operate at large scale under isothermal regime due to the good heat transfer rate between phases without segregation and low residence time of the volatiles (which minimizes gas formation).

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Nevertheless, it requires small particle sizes and high amounts of energy to heat the sand used to aid fluidization. An alternative to conventional fluidized beds is the conical spouted bed reactor (CSBR). This technology allows handling larger particles than those allowed in fluidized beds, particles of irregular texture, fine materials, and sticky solids with no agglomeration and segregation problems [19,20]. Moreover, the counter-current displacement of the solids in the annulus and the gas in the spout zone leads to high heat and mass transfer rates between phases [21]. In addition, very low gas residence times are attained (as low as milliseconds in the dilute spouted bed regime) [22], thereby minimizing gas formation. It is noteworthy that this reactor has a simple design (distributor plate is not required) and requires lower volumes than fluidized beds for the same capacity, simplifying the scaling up of the pyrolysis process.

Another important stage in the fast pyrolysis process, typically viewed as secondary compared to reactor configuration, is the liquid collection system. While reactor conditions are the main drivers in oil yield and quality, the condenser design impacts the oil quality with respect to composition [23]. The product stream exiting the reactor is a combination of vapours, aerosols and polar molecules [24]. Besides, the high nitrogen flow rates (used as fluidization agent) [25], as well as the formation of non-condensable gases, pose significant heat and mass transfer resistance, as well as low partial pressures, which significantly limit the efficient collection of the liquid product [26]. Currently, there are a few different options available in the literature for liquid collection [23,27], which can be divided into two major categories: spray towers and heat exchangers, or in other words, direct and indirect contact between hot volatiles and the cooling liquid, respectively. Heat exchangers utilize a cool surface to cool the gases and condense hot volatiles, with the most typical ones being those of tube-and-shell type [28]. These systems permit using a serial condenser train, instead of a single condenser, thus creating the chance of separating the oil into different fractions depending on the dew point of the oil components [23,29,30]. However, the mass transfer resistance of the gases forces the conventional indirect contact heat exchangers to larger sizes [27]. On the other hand, spray tower or spray quench systems utilize a re-circulated spray of water/pyrolysis liquid in counter-current manner to cool and collect all of the liquid at once [28,31-34], and is usually employed at larger scale units. It is noteworthy that direct contact heat exchangers have a number of advantages over the indirect ones, as are simpler design, lower capital and maintenance costs, higher specific heat transfer areas, and higher heat transfer rates [35]. The

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main drawback facing the direct contact condenser (quenching condenser) is that involved by the mixture of the condensate product with the cooling fluid, whose separation may require high cost and/or a special piece of equipment [36]. However, given the non-polar nature of most hydrocarbons in the TDO, the use of water as cooling agent will facilitate the full decantation of the collected oil. Furthermore, as TDO also contains (at lower extent) heteroaromatic species of polar nature (formed by nitrogen and sulphur compounds) [37], they could be selectively removed with the quenching condensation system [28].

These heteroaromatic compounds stem from the processing additives and vulcanization agents during the devolatilization of the tyre. Previous works in the literature revealed that one of the main nitro-sulphurated compound was benzothiazole, whose yield increased with temperature [11,38-40]. Choi et al. [41] proposed a combination of an auger and a fluidized bed reactor in order to reduce the concentration of benzothiazole. They observed that when the two-step pyrolysis (firstly in an auger reactor and then in a fluidised bed reactor) was compared to a one-step auger reactor pyrolysis, the concentrations of heteroatomic compounds in the TDO were reduced. Recently, reduction of the heteroatomic compound concentration in the TDO was reported by Mkhize et al. [28] when the tube-and-shell condenser was replaced with the quenching condenser.

The aim of this work is to study different reactor configurations and condensation systems in order to improve the quantity and quality of the TDO by increasing the concentration of DL-limonene and lowering that of heteroaromatic compounds (with the reference one being benzothiazole) in the waste tyre fast pyrolysis. This approach entails comparison of the TDO yields and the concentrations of DL-limonene and benzothiazole in those TDOs produced in a fixed bed reactor (FBR), a bubbling fluidised bed reactor (BFBR) and a conical spouted bed reactor (CSBR), each equipped with either a tube-and-shell condenser (indirect contact between cooling liquid and hot volatiles) or a quenching condenser (direct contact between the cooling water and the hot volatiles). The three different types of pyrolysis reactors were operated at the same temperature, fed with the same waste tyre crumb, and combined with the two alternative methods to condense the hot volatiles. It should be noted that the novelty of the work lies in the joint comparison of reactor configuration and condenser type, which has hardly been approached in the literature, even though these pieces of equipment are essential for the fast pyrolysis of wastes tyres.

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2. Material and methods

2.1. Waste tyre crumb characterization

The same waste tyre crumb as in previous works [10,28] was used, i.e., waste truck tyre with a particle size range between 2.80 and 3.30 mm sieved from a bulk of approximately 500 kg crumbed (steel- and fabric-free) waste tyre. The ultimate and proximate analyses have been carried out in a LECO CHNS-932 elemental analyser and in a TGA Q500IR thermogravimetric analyser, respectively. The higher heating value (HHV) has been determined in a Parr 1356 isoperibolic bomb calorimeter. The results are shown in Table 1. The chemical composition of the rubber has been obtained from the thermogravimetric analysis. The differential thermogravimetric (DTG) curve has been fitted to a multi-component model that describes the rubber degradation by considering the volatile formation by means of three concurrent independent and parallel reactions. The pseudo-components considered are the additives and the rubbers typically contained in the truck tyres, i.e., natural (NR) and synthetic rubbers. More information about the procedure followed can be found elsewhere [38]. The synthetic rubber commonly used in tyre formulation is styrene-butadiene rubber (SBR) followed by polybutadiene rubber (BR). However, given their similar thermal stability (their decomposition usually occur between 360 and 500 ºC) [42], their quantification by thermogravimetric analysis technique is not straightforward, and therefore all the synthetic rubber has been grouped into the SBR polymer.

Table 1. Proximate and ultimate analysis and rubber composition of the crumb.

Elemental analysis	
C (wt. %)	84.3
H (wt. %)	7.7
N (wt. %)	0.8
S (wt. %)	2.5
O (wt. %)*	4.7
Proximate Analysis**	
Volatiles (wt. %)	65.1
Fixed Carbon (wt.%)	29.9
Ash (wt.%)	4.9
Chemical composition (wt. %)***	
NR	49.6
SBR	32.1
Additives	18.3
Moisture (wt. %)	0.6
HHV (MJ kg^{-1})	38.2

* By difference

** On a dry basis

*** On a carbon black and ash free basis

2.2. Pyrolysis reactors and experimental procedure

This section describes the different reactors and heat exchangers evaluated in this study, as well as the experimental procedure followed in each equipment. It should be noted that the operating conditions selected in each case are the optimum ones for working under stable conditions and attaining the highest TDO yields.

2.2.1. Fixed bed reactor

A sample size of 40 g waste tyre crumb was fed into the fixed bed pyrolysis reactor. Figure 1a shows the FBR, which consists of a long horizontal quartz tube pyrolysis reactor (850 mm long, 60 mm OD), a heating furnace, and Figure 2a the five tube-and-shell condensers connected in series. The pyrolysis reactor furnace is heated at a rate of 20 °C min^{-1} to 475 °C by six well-insulated heating elements. The hot volatiles were purged out from the reactor with nitrogen gas (99.5% purity, Afrox, South Africa) at a constant flow rate of 1 NL min^{-1} resulting in a residence time of approximately 41 s.

Initially, the FBR was connected to five tube-and-shell condensers arranged in series to investigate an indirect contact between the cooling liquid (on the shell side) and hot volatile stream (on the tube side) (Figure 2a). Due to the complex nature of the volatiles formed in the pyrolysis process, the use of multiple condensation trains pursues to maximize the recovery of the liquids in the indirect contact condensation system. In the case of indirect condensers, the extent of the temperature effect is intimately linked to the dew point of the vapour and its composition. Thus, the temperature in the first condenser was ambient one, whereas the temperature in the subsequent condensers (two to five) was maintained at −10 °C using ~~dry-ice~~ a slurry of ice and dry-ice. Then, the TDO collected is weighed and analysed in order to determine the collection efficiency and DL-limonene and benzothiazole concentrations.

In order to study the effect of the direct contact condensation system, the tube-and-shell condenser was replaced with the quenching one specifically used for the FBR, as shown in Figure 2d. The quenching liquid is injected through a spraying nozzle. The hot volatiles from the pyrolysis reactor are introduced at the lower half of the quenching tower through an inlet pipe connected to the

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pyrolysis reactor. To prevent condensation of the hot volatiles before they are introduced into the quenching tower, the inlet pipe is maintained at a temperature of 200 °C. The quenching liquid (demineralised water) was introduced at the top of the quenching tower. The nozzle, supplied by Spraying Systems Company, South Africa, is a standard type, 0.635 cm NPT removable cap male, made of stainless steel (316SS). Maximum contact between the quenching water spray and the hot volatiles rising upward in the quenching tower was achieved by forming a full cone-spray profile, which covered the whole cross-sectional area of the quenching tower. As the condensable gases are contacted with the quenching water spray, the condensed TDO and quenching water flow downward. A mixture of the TDO and quenching water is collected in the collecting tank at the bottom of the quenching tower. The non-condensable gases exit the quenching tower via the top exit point above the nozzle. Finally, TDO and quenching water are separated by decantation and, according to the polar nature of some heteroaromatic compounds, such as benzothiazole [37], they could be partially dissolved in the water used for cooling. Therefore, apart from the product distribution obtained for different condenser types and the DL-limonene content in each TDO, benzothiazole concentration in the TDO will be also determined for each condensation device.
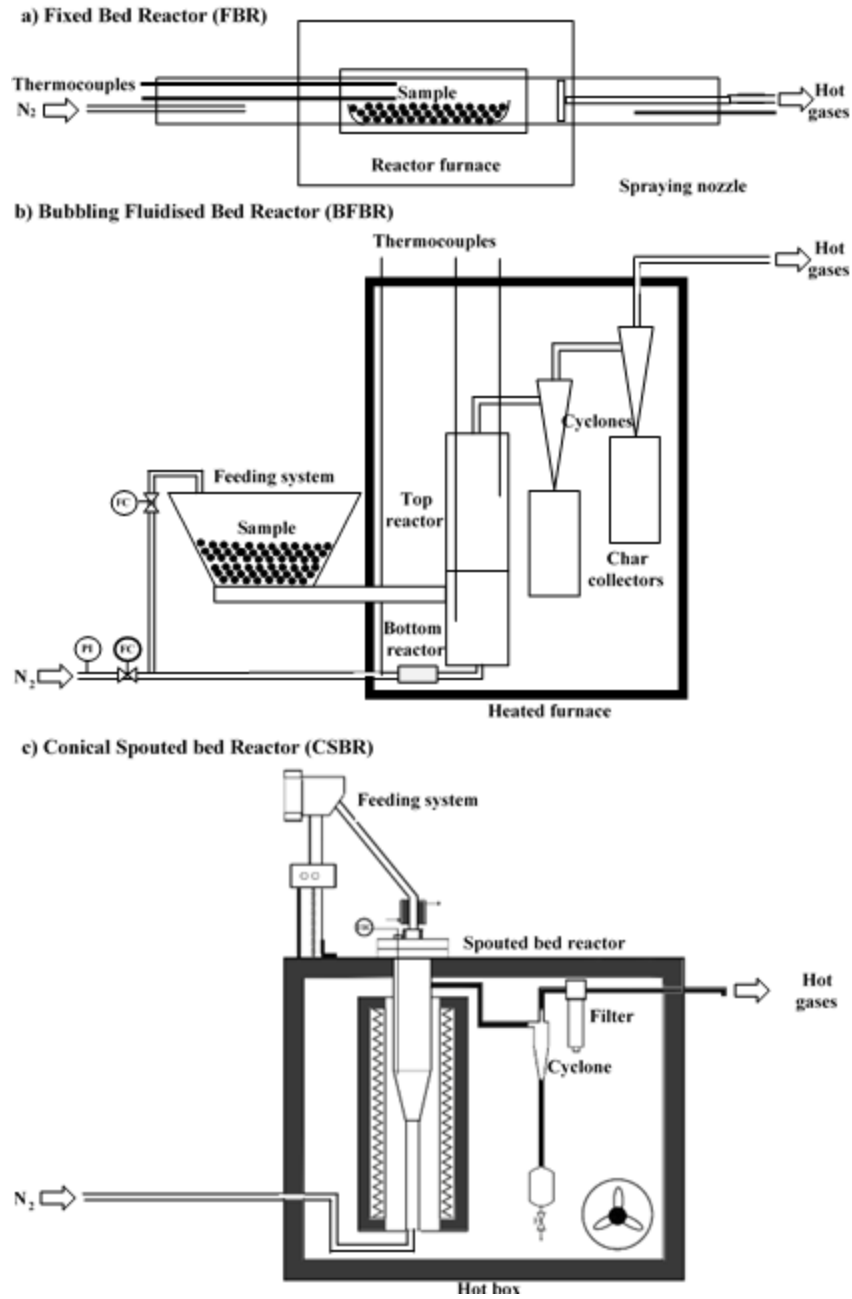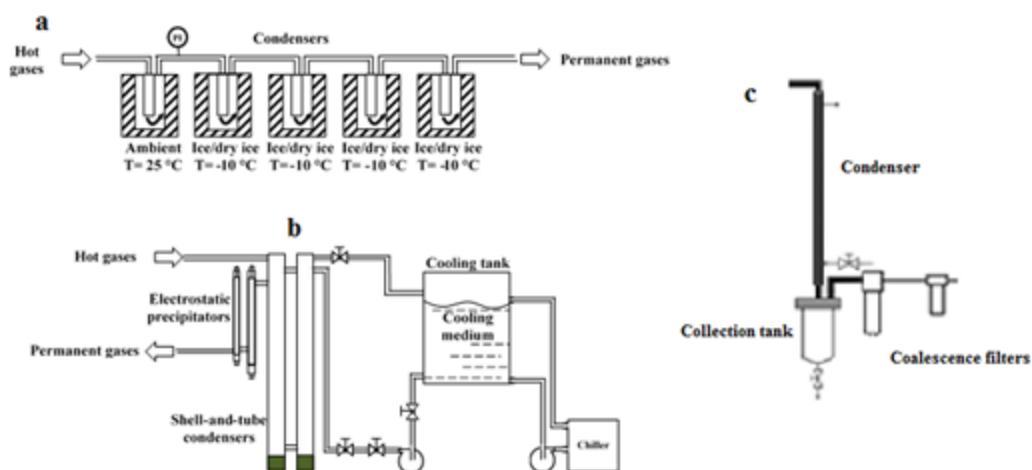
Figure 1. Schematic diagram of the a) FBR, b) BFBR, and c) CSBR pyrolysis units.
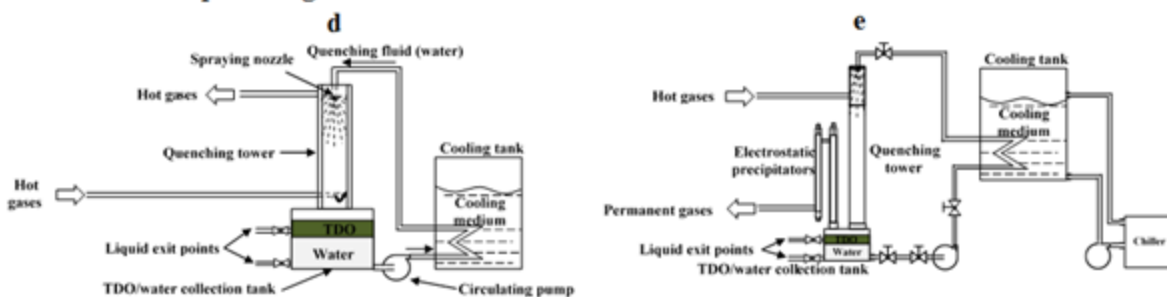
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Figure 2. Schematic diagram of the indirect contact tube-and-shell condeser for the FBR (a), BFBR (b) and CSBR (c) and that of the direct contact quenching condenser for the FBR (d) and BFBR (e).

2.2.2. Bubbling fluidised bed reactor

A total sample size of 200 g waste tyre crumb was fed into the BFBR pyrolysis reactor at a rate of 6 g min^{-1}. The optimal pyrolysis temperature (475 °C) was fixed based on our previous studies [10,11,38], and those by other authors in the literature [16,43]. The BFBR consists of, i) the feeding system, ii) the reactor; and iii) the char separation system, see Figure 1b. In the feeding system, the tyre crumb is initially loaded in the hopper and then fed into the reactor using a screw feeder. The hopper is slightly over pressurised with nitrogen gas (99.5% purity, Afrox, South Africa) to prevent hot volatiles pushing back from the reactor. The reactor (cylindrical) is divided into two compartments, bottom (100 OD x 180 mm) and top section (100 OD x 516 mm), with the maximum throughput being 1 kg h^{-1}. The entire reactor is heated by a hot cylindrical chamber consisting of eight 6.6 kW heating elements. To ensure rapid pyrolysis (high heating rates higher

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than 10000 ℃ min^{-1}) of the tyre crumb, the reactor and fluidising nitrogen gas entering the reactor were preheated at 475 °C. A residence time of approximately 2 s was achieved by setting N$_2$ flow rate at 42 NL min^{-1}, i.e., an operating velocity 1.5 times the minimum for fluidization. This flow rate was the optimum for maintaining the fluidizing material bubbling and suspended in the reactor (without material removal), and, at the same time, purging out the char and hot volatiles formed during pyrolysis. ~~This flow rate was also required to keep the fluidising material bubbling and suspended without being purged out from the reactor, as well to purge out char and hot volatiles from the reactor.~~ It should be noted that the fluidizing agent (nitrogen) may be replaced by the non-condensable gases formed during the pyrolysis, when operation is conducted at large scale in steady-state, thus lowering operating costs [44]. The fluidising material was silica sand (0.4 – 0.6 mm sieved AFS 45 fused silica sand, supplied by CONSOL (Pty) Ltd, South Africa), with the initial amount in the bed being 450 g in each run. ~~at an amount of 450 g per experiment~~. The char separation system is also maintained at 475 °C in the hot chamber to prevent condensation of the hot volatiles before they are introduced into the condenser. The hot volatiles from the reactor are separated from the char by means of the two cyclones and char collectors in the char separation system.

Finally, the hot volatiles are introduced into the condensation system. The indirect contact condenser consists of two water-cooled tube-and-shell condensers (i.e., arranged in series) made of stainless steel (Figure 2b). Cooling water temperature is maintained below 5 °C by circulation through a tank and using a chiller. The TDO obtained is collected for further analysis.

In the direct contact condensation system for the BFBR (Figure 2e), the hot volatiles from the pyrolysis reactor are introduced at the top half of the quenching tower through an inlet pipe connected to the pyrolysis reactor. To prevent condensation of the hot volatiles before they are introduced into the quenching tower, the inlet pipe is maintained at a temperature of 350 °C. Using a spraying nozzle, the quenching liquid (demineralised water) was introduced at the top of the quenching tower. The nozzle is a spiral type, supplied by Spraying Systems Company, South Africa, standard type, 0.9525 cm NPT removable cap male, and made of stainless steel (316SS). Maximum contact between quenching water spray and the hot volatiles that are flowing upward in the quenching tower was achieved by the nozzle spray pattern designed to form a spiral cone-

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spray profile covering the whole cross-sectional area of the quenching tower. The TDO/quenching water tank was initially fed with a volume of 14 L demineralised water. Quenching water was continuously circulated from the bottom of the tank (while TDO floats on the water) to the top of the quenching tower. Quenching water circulated in a close loop, whereas the polar compound continually accumulated until all the crumb in the hopper was fed. Water withdrawal flow rate from the bottom was maintained at a flow rate of 4 L min^{-1}, using a pump. The temperature of the quenching water at the quenching tower inlet was maintained below 5 °C by driving it through a copper coil submerged into a cooling tank. The hot volatiles are introduced, contacted with the quenching water spray, and the TDO recovered similarly as in the FBR.

2.2.3. Conical spouted bed reactor

The main components of the CSBR are illustrated in Figure 1c and are as follows: i) solid and gas feeding devices, ii) a pyrolysis reactor, and iii) a fine particle retention system.

To feed the solids, the vessel is equipped with a vertical shaft connected to a piston placed below the solids. The piston is raised at the same time as the vessel is vibrated by an electric engine, which introduces the tyre particles into the reactor. The waste tyre crumb feed rate can be varied by adjusting the piston raising velocity between 0.5 and 8 g min^{-1}. The gas feeding device consisted of a Brooks SLA5800 mass flow meter in order to control de nitrogen flow rate. Prior to entering the reactor, the fluidizing gas is heated to the reaction temperature by means of a preheater.

The plant's main component is the CSBR, which has a lower conical section joined to an upper cylindrical one. The detailed design and dimensions of the CSBR have been described elsewhere [11]. This reactor configuration allows a vigorous cyclic movement, which leads to high heat and mass transfer rates (> 10000 ºC min^{-1}) and low residence times of the volatiles (between 30 and 500 ms in the hot zone) in order to minimize secondary reactions of the volatiles, and therefore attain the maximum TDO production in the fast pyrolysis process. The CSBR and BFBR used in this work have different solid and flow patterns, and therefore the fluidizing agent flow rates required to operate under stable conditions, and the corresponding residence times, greatly differ. In the case of the BFBR, higher fluid flow rates than in the CSBR are required to suspend the solid material. Furthermore, the CSBR reactor volume is much lower than that of the fluidized bed for the same operating capacity, which allows for a much compact piece of equipment [45]. Based on

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these features, the residence time of the volatiles is much shorter in the CSBR than in the BFBR for similar hydrodynamic conditions under stable fluidizing/spouting regime. It is noteworthy that this Furthermore, CSBR technology allows using draft tubes of different designs and dimensions in order to optimize the spouting regime, improve its stability and, at the same time, reduce fluidizing agent requirements [46]. The design and main dimensions of the draft tubes are also shown elsewhere [38].

The volatile products leave the reactor together with the inert gas and pass through a fine particle retention system, which consists of a high efficiency cyclone and a 5 μm sintered steel filter in order to retain the solid particles entrained from the reactor. The tubing, cyclone and filter are located within a forced convection oven maintained at 300 ºC to prevent the condensation of heavy compounds before the condensation system.

The gases leaving this filter circulate through a double water-cooled tube-and-shell condenser cooled by tap water, and the condensed stream circulates then through a 60 μm stainless steel filter (also cooled with tap water), which promotes the retention of fine TDO droplets from the gas (Figure 2c). This element increases the collection efficiency of typical tube-and-shell condensers, given that it plays the role of an impingement device, and therefore promotes contact surface during the condensation. In fact, the volatile stream collides with the cool surface of the filter, which promotes the retention of fine droplets and aerosols in the gaseous stream. Moreover, the steel filter is located inside a 1 L vessel, where the condensed TDO is collected. The liquid falls then by gravity to a glass vessel throughout the run length and is finally weighed and stored for its characterization. In order to ensure retention of all the TDO, a coalescence filter has been placed subsequent to the tube-and-shell condensers and steel filter. In fact, coalescence is the process of causing agglomeration of liquid aerosols to form larger droplets, which are large enough to drain away gravitationally. This device is essential to avoid problems in the microGC used for analyzing the composition of the gas stream.

The runs have been carried out in continuous mode by feeding 1.3 g min^{-1} of waste tyre crumb. The bed was initially made up of 150 g of sand (particle size 0.3–0.8 mm). Sand is used as thermal carrier to rapidly transfer heat from hot nitrogen to the waste tyre in the reactor and ensure bed isothermicity. The fluidizing gas (nitrogen) flow rate was 8 NL min^{-1}, corresponding to 1.5 times

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the minimum spouting one. In order to ensure operation under steady state conditions and reproducibility, the duration of each run was of around 30 min and repeated at least 3 times. The total amount of tyre fed in each experiment with the CSBR technology was of around 40 g.

2.3. TDO analysis

All the experiments were conducted in triplicate and a representative TDO sample was taken for further analysis. Gravimetrical methods were used to determine the char and TDO yields, while chromatographical methods were used for DL-limonene yield and benzothiazole concentration in the TDO. The gas fraction was estimated from the mass balance. When the quenching condenser was used, two liquid phases were obtained in the storage tank and separated using a separation funnel (12 h), which are the TDO itself (non-polar lighter fraction containing most of the DL-limonene) and the quenching water (polar heavier fraction containing most of the benzothiazole). The TDO was qualitatively and quantitatively analysed. A Hewlett Packard 5890 Series II model gas chromatography (GC) coupled with a Hewlett Packard 5973 mass spectrometry (MS) was used to analyse the TDO. A volume of 1 μl containing a mixture of TDO, internal standards, and dichloromethane solvent (99.9% purity, Sigma Aldrich, South Africa) was injected into a 60 m x 0.18 mm ID x 0.10 μm film thickness, non-polar Rxi-5% Sil-MS capillary column. Helium gas (99.999 % purity, Air Products, South Africa) was used as a carrier gas at a constant flow rate of 1.20 ml min^{-1} (linear velocity of 27.9 cm s^{-1}) at 348 kPa. The carbon, nitrogen and sulphur content of TDO samples was measured with a Carlo Erba 1108 elemental analyser. Unfortunately, given that the samples have a low sulphur content, analyses have been performed using a filter for eliminating the water from combustion products in order to obtain a better resolution of the sulphur signal, and therefore H and O could not be measured. Additionally, water content and higher heating values (HHV) of TDO samples were determined using titration methods and a Parr 1356 isoperibolic bomb calorimeter, respectively.

3. Results and discussion

3.1. Effect of the reactor type

Table 2 shows the results obtained operating in the FBR and BFBR, both equipped with either a tube-and-shell condenser or a quenching condenser, as well as the CSBR equipped with a tube-and-shell condenser. Thus, this table displays the product distribution (gas, liquid and char yield),

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as well as DL-limonene and benzothiazole concentration in the TDO for each technology. As observed, the total TDO yield in the BFBR is 3.4 wt.% higher than that in the FBR, i.e., it increased from 46.6 to 50.0 wt.% when the tube-and-shell condenser was used. A further increase in the TDO yield by 8.2 wt.% (58.2 wt.%) was observed when the CSBR technology was used. The gas yield decreased by 3.1 and 11.8 wt.%, when the BFBR and CSBR were used, respectively, instead of the FBR. Given that the char yields are similar with three technologies (35.7, 35.4 and 35.9 wt. % for the FBR, BFBR and CSBR, respectively), it can be concluded that the TDO yield increase is at the expense of the gas. These results highlight the effect of reactor design on the product distribution. The BFBR and CSBR designs are characterised by bubbling and cyclic vigorous circulation, respectively, leading to higher mass and heat transfer rates between phases, which leads to higher TDO yields and lower gases yields. Besides, the lower residence times of the CSBR and BFBR technologies hinder secondary reactions of the volatiles, thus avoiding the formation of gases at the expense of the TDO. On the contrary, the FBR bed is static and the volatile residence time is of around 41 s. Longer hot volatile residence times in the hot reaction zone in the FBR promote cracking of the longer chain molecules to form non-condensable gases. Therefore, the gas yield from the FBR is higher than from both the BFBR and CSBR, with that from the BFBR being higher than that from the CSBR. Comparatively, higher TDO yields are obtained with the CSBR (58.2 wt. %) than with the fluidized bed technology (50 and 55.9 wt. %, depending on the condenser efficiency). These results are related to the excellent features of the CSBR: (i) uniform and low residence time of the volatiles (milliseconds), which minimizes secondary cracking reactions in the reaction zone [22]; (ii) intense gas-solid contact, which favours devolatilization reactions, thus resulting in higher TDO yields [21].

The results obtained by different authors in the tyre fast pyrolysis are in most cases difficult to compare, as product distribution and composition not only depends on the reactor characteristics, but also on the feedstock composition (tyre type) and particle size, as well as reaction temperature. The most common pyrolysis reactors in the literature include fixed-beds, rotary/screw kilns, and fluidized-beds [6]. The highest TDO yields in FBRs at the optimum operating conditions are in the 35-55 wt. % range [5,12,14,43,47], whereas those reported for rotatory/screw kilns are of around 40 wt. % [48,49]. Regarding the fluidized bed technology, the TDO yields reported usually are higher than 50 wt. %, similar to those obtained in this work [25,41]. It is noteworthy that the

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highest TDO yields reported in the literature are obtained with the CSBR configuration, which are generally of around 60 wt. % [40,50-53].

With respect to DL-limonene, which is the chemical of highest value, its yield increased from that corresponding to the FBR to those for the BFBR and CSBR (Table 2), i.e., from 7.62 to 8.04 and 8.39 wt.%, respectively, when the tube-and-shell condenser is used, and from 7.90 wt.% (FBR) to 8.13 wt.% (BFBR) when the quenching condenser is used. The formation of DL-limonene depends on the pyrolysis pressure and temperature, sample size and composition, as well as the heating rate and the vapors residence time inside the reactor [16,54]. Given that all parameters mentioned were the same in the three technologies, except the heating rate and the volatile residence time, the increase in DL-limonene yield can be attributed to the rapid heating of the waste tyre crumb and the lower residence time of the volatiles in the BFBR and CSBR compared to the FBR. Secondary reactions transform DL-limonene into aromatic compounds, such as BTX, trimethylbenzene and indane, amongst others [16]. Hence, the excellent features of the CSBR mentioned above (especially the lower residence time of the hot volatiles) lead to the highest DL-limonene content.

The maximum yields of DL-limonene have been attained between 400 and 500 ºC. However, its content in the TDO varies significantly depending on the operating conditions [10]. It should also be taken into account that there are various ways of detecting and quantifying it, which may also lead to certain uncertainty in the results. Based on CG/MS and GC-FID analytical methods, the highest limonene yield in the literature has been obtained with the CSBR technology, in the 7-24 wt. % range [47,53,55], and with the fixed bed reactor containing fire tubes, in the 10-26 wt. % [56]. With the fluidized bed technology, Choi et al. [41] obtained a maximum DL-limonene yield of 10.3 wt. %.

Regarding benzothiazole, which is the main heteroaromatic compound in the TDO, its concentration is quite different depending on the technology used for pyrolysis. The concentration of benzothiazole in the TDO increased from 5382 to 6287 and 6354 ppm when the FBR, BFBR and CSBR were used, respectively (Table 2). Benzothiazole is mainly formed from the thermal degradation of thiazoles (mainly 2-mercapto-benzothiazol) and sulfonamides (e.g., N-cyclohexyl-2-benzothiazolsulfenamide), which are vulcanization accelerators used in tyre manufacturing, and to a lower extent from the recombination or disproportionation reactions caused by free radicals from sulfur containing heteroatom compounds and polythil radicals from polysulfide

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(vulcanization agent) cross-linkages [4]. Accordingly, the reaction pathways would change with pyrolysis conditions (temperature, residence time and heat and mass transfer rate), and therefore with the technology selected, thus leading to different amounts of benzothiazole or other sulphur containing compounds in the pyrolytic oil. Indeed, high residence times promote cracking reactions, which obviously reduce the benzothiazole concentration, as observed with the FBR compared to BFBR and CSBR. Note that other heteroatom compounds, i.e., tiophene isomers (2-methyl-thiophene or 2,7-dimethyl-1-benzothiophene), phenols (4-ethyl-phenol and 4-tert-butylphenol), quinolone isomers (2,8-dimethylquinoline), amines (diphenylamine) or carboxylic acids (tetradecanoic acid) were also detected in the TDO, as proven in a previous study [11]. With respect to heteroaromatic species, Choi et al. [41] observed that, when a two-step pyrolysis (first in an auger reactor and then in a fluidized bed reactor) was compared with the one in a single-step in an auger reactor, their concentrations in the TDO were reduced.

Table 2. Yields of products for the waste tyre pyrolysis in FBR, BFBR and CSBR with the tube-and-shell and quenching condensers.

		Condensation system				
	Parameters	Tube-and-shell condenser			Quenching condenser	
		FBR	BFBR	CSBR	FBR	BFBR
Reactor operating conditions	Heating rate (°C min^{-1})	20	$> 10^4$	$> 10^4$	20	$> 10^4$
	Gas residence time(s)	~ 41	~ 5	~ 0.5	~ 41	~ 5
Quenching condensation	Cooling water (L)	–	–	–	2.10	14
	Water spray flow rate (L min^{-1})	–	–	–	0.96	4
Main product yield	Tyre derived oil TDO (wt.%)	46.6	50.0	58.2	49.2	55.9
	Solid residue or char (wt.%)	35.7	35.4	35.9	35.7	35.4
	Non-condensable gases (wt.%)	17.7	14.6	5.9	15.1	8.7
Organic	DL-limonene yield (wt.%)	7.62	8.04	8.39	7.90	8.13

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phase (TDO)	Benzothiazole concentration (ppm)	5382	6287	6354	2168	1862
	Water content (wt.%)	0.7	0.1	0.1	0.3	0.3

Table 3 shows the carbon, nitrogen and sulphur content, as well as the HHV of the TDOs obtained with different technologies and condensers. As observed, all TDOs have similar carbon content (in the 84.6-86.3 wt. % range in all cases), thus leading to almost the same HHV. Comparing the sulphur content values obtained with the different technologies, it can be observed that they follow the same trend as the one for benzothiazole concentration. Thus, sulphur content increases from 0.72 wt. % to 0.94 wt. % and to 1.17 wt. % when the FBR, BFBR and CSBR are used, respectively. These suggests that the higher residence time of the volatiles in the FBR reactor promotes C-S bond decomposition in the sulphur species in the TDO, leading to the formation of non-condensable gases, such as SO_2 or H_2S, by reacting with the H_2 or oxygen functionalities in the reaction medium [57]. On the contrary, as the residence time of the volatiles is reduced, the secondary cracking reactions are hindered, which leads to higher concentrations of sulphurous compounds in the TDO collected from the CSBR. Nevertheless, although the concentration of sulphur is slightly higher in the TDO from the CSBR compared to that from the FBR, the increase in TDO yield is much more significant in the former.

Table 3.   Ultimate analysis of the TDOs obtained with different technologies equipped with tube-and-shell or quenching condensers.

	Type of condensation					
	Tube-and-shell condenser			Quenching condenser		
	FBR	**BFBR**	**CSBR**	**FBR**	**BFBR**	
Ultimate analysis (wt. %)						
Carbon	86.32	85.97	86.10	84.60	86.03	
Sulphur	0.72	0.94	1.17	0.59	0.82	
Nitrogen	0.47	0.32	0.32	0.32	0.35	
HHV (MJ kg^{-1})	42.3	41.9	42.7	42.1	42.7	

3.2. Effect of the condensation system design

As observed in Table 2, substituting the tube-and-shell condenser by a quenching condenser in the FBR improved the TDO collection efficiency, increasing the liquid collected from 46.6 wt.% to 48.9 wt.%. In addition, the gas yield was lower (14.6 wt. %) when the quenching condenser was

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used. A similar trend was observed when the BFBR reactor was equipped with a tube-and-shell or a quenching condenser. As observed, the TDO collection efficiency was higher for the direct contact heat exchanger, with the TDO yield being 55.9 wt. %, whereas the gas yield decreased from 14.6 wt.% to 10.0 wt.%. In the case of both the FBR and BFBR, the decrease in the gas yield is of the same order as the increase in the yield of the TDO. Therefore, the quenching condenser improves the condensation of the volatiles that may have not been retained when the tube-and-shell condenser was used. This rapid and efficient cooling and condensation achieved by the direct contact heat exchanger is attributed to the increase in the contact area for heat transfer between the quenching liquid and the pyrolysis volatiles [35]. In fact, the hot volatiles exchange their heat with the quenching water droplets sprayed by the atomizer nozzles located at the top of the condensation chamber, thereby increasing the condensation efficiency. The works reported in the literature about the efficiency of quenching and tube-and shell-condensers are limited, but most of the authors agree that quenching using either the liquid product (TDO) or immiscible solvents promotes oil collection efficiency due to the faster cooling rate [24,26-28,30].

The efficiency of the condensation systems for collecting high value chemicals was also analysed, such as DL-limonene or selectively reducing undesired heteroaromatic compounds, such as benzothiazole. In this study, all the pyrolysis parameters have been kept constant, except the type of condensation system. The results show that DL-limonene yields obtained using the quenching condenser connected to the BFBR (8.13 wt. %) and FBR (7.9 wt. %) were higher than those with the tube-and-shell condenser (8.04 wt. % and 7.6 wt. %, respectively). Furthemore, a decrease in the benzothiazole concentration was observed in the TDOs obtained in both the BFBR and FBR when a quenching condenser was used instead of a tube-and-shell condenser (from 6287 to 1862 ppm in the BFBR and from 5382 to 2168 ppm in the FBR, respectively). Thus, the direct contact condenser improved the features of the TDO obtained in both reactors. It should be noted that, although some polar heteroaromatic compounds are partially removed with the quenching condenser, the TDO yield hardly changes because the contribution of these heteroaromatic species to the total TDO yield is negligible.

The higher DL-limonene yield with the direct contact condenser can be attributed to the higher cooling rate of the hot volatiles when contacted with the quenching water (due to the higher vapour/liquid contact area). Moreover, the decrease in benzothiazole concentration is attributed to

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its solubility in water. Several authors in the literature have confirmed that benzothiazole is soluble [58,59] or partially soluble [60] in water. Hence, the benzothiazole contained in the hot volatiles and TDO is partially dissolved in the quenching water during the direct contact between hot volatiles and the cooling agent. Then, the benzothiazole rich water phase and the non-polar TDO phase, which mainly contains non-polar aliphatic and aromatic compounds, are separated at the end of the pyrolysis process [28]. It must be highlighted that several studies [11,15-17,38,61] have identified benzothiazole as one of the main heteroatomic compounds in the TDO, and therefore it has been selected as the most representative compound in this family. According to Dung et al. [37], polar-heteroaromatic compounds are aromatic substances containing sulphur, oxygen, or nitrogen atoms in their aromatic rings and, particularly in the case of TDO, most of the polar-aromatic compounds are sulphur-containing species derived from the vulcanization agents used in the tyre manufacturing.

Therefore, if benzothiazole content is reduced, other heteroaromatic components with polar nature in the TDO may also have partially dissolved in the quenching water. This hypothesis is confirmed in Table 3, which shows that sulphur and nitrogen content in the TDO are reduced from 0.72 to 0.59 wt. % and from 0.94 to 0.82 wt. %, respectively, when tube-and-shell condenser is replaced with the quenching condenser. Therefore, the direct contact heat exchanger improves the quality of the TDO for use as fuel because its desulphuratio/denitrogenation requirements will be considerably lowered.

3.3. Adequate combination of reactor and condenser

Based on the results of the TDOs obtained in this work, certain conclusions about the influence of both the condensation system and the reactor configuration can be drawn. It is clear that the TDO collection efficiency changes depending on the type of heat exchanger used (direct or indirect), whereas the product distribution and composition depend on the features of the reactor, as clearly observed in Figure 3. Therefore, a suitable combination of reactor and condensation system should be used for optimizing the TDO production with a high DL-limonene content and a low benzothiazole concentration. As proven, short residence times of the hot volatiles and high heating rates increased the TDO yield, especially when using the CSBR technology, whereas the quenching condenser improved the contact area between the vapours and the cooling liquid, which enhanced TDO collectection.

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Concerning the DL-limonene concentration in the TDO (Table 2), a slight increase was observed as the FBR was replaced with the BFBR or with the CSBR. The same applies when the tube-and-shell condenser is replaced with the quenching one. This study proves that the waste tyre pyrolysis conducted at high heating rates and short residence times of the hot volatiles in the reaction zone, and using a quenching condenser, benzothiazole concentration in the TDO decreased from 5382 ppm to 1862 ppm, which accounts for a 70% reduction (Table 2). Besides, DL-limonene concentration in the TDO also increased using the CSBR and the direct contact condenser. Therefore, both the pyrolysis reactor and the condensation type have significant effect on the quality of the TDO, i.e., their suitable combination contributes to decreasing benzothiazole concentration and increasing DL-limonene one. Therefore, high heating rates, short residence times of the hot volatiles in the reaction zone and a quenching condenser improve TDO properties.

The fact that heteroatom compound concentration in the TDO is lower is a favourable point for the recovery of valuable chemicals, i.e., as the concentration of these compounds in the TDO is lower, the starting raw material is more suitable for DL-Limonene and fuel production [12]. Furthermore, use of a quenching condenser instead of a tube-and-shell condenser allows reducing the concentration of most heteroatom compounds, or even fully removing certain ones. In fact, the reduction in benzothiazole (a major nitrogen-sulphur containing compound) in the TDO is of the same order as in a conventional post-treatment process through desulphurisation techniques, with the latter being much more complex and costly. Moreover, a lower concentration of benzothiazole, as well as of other sulphur and nitrogen compounds in the TDO eases further upgrading of the TDO for fuel production, since refining processes will be less intensive and expensive once the sulphur and nitrogen contents are reduced. Therefore, a quenching condenser is the preferred technique for cooling and condensing the hot volatiles, particularly those obtained under high heating rates and short residence times of the volatiles in the hot pyrolysis reaction zone, which is specifically the case in the CSTR technology. Moreover, the benzothiazole recovered in the quenching water may be used again in the tyre manufacturing.

Although the content of sulphur/nitrogen compounds in the TDO should be reduced in order to be used directly as a liquid fuel, its high HHV, boiling point and storage stability (the properties remained unaltered with time as proven in a previous study [11]) make it an interesting alternative

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to commercial fuels. Accordingly, partial separation of heteroaromatic species (and reduction in S and N) will result in a higher quality TDO for fuel applications or at least for reducing desulphuration requirements.
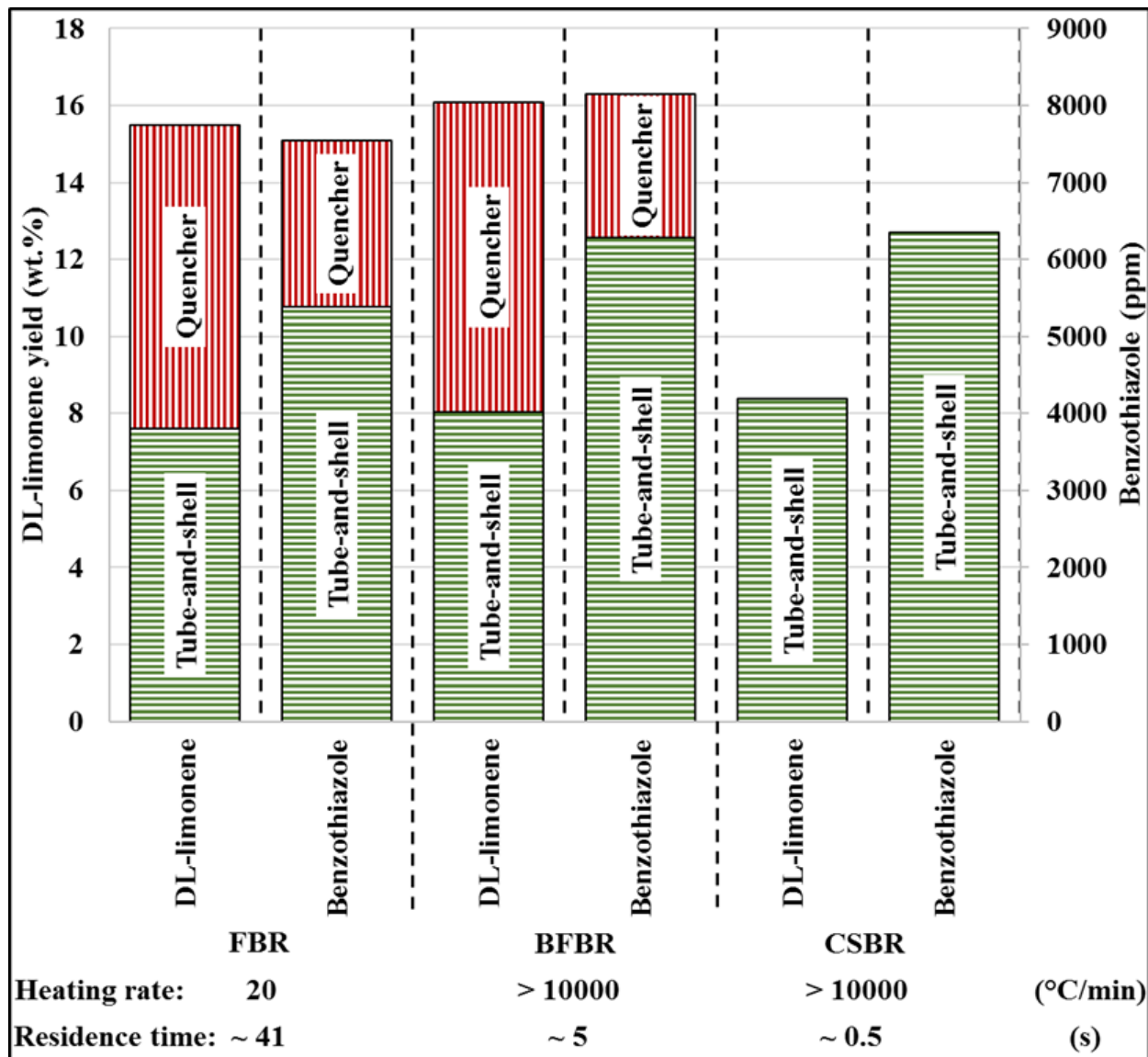

Figure 3. Effect of the condensation device, heating rate and residence time of the hot volatiles on DL-limonene yield and benzothiazole concentration in the TDO from the FBR, BFBR and CSBR.

4. Conclusions

The yields of tyre derived oil (TDO) and DL-limonene increased when a bubbling fluidized bed reactor (BFBR) was used instead of a fixed bed reactor (FBR), either when the condensation was carried out with a tube-and-shell condenser or a quenching condenser. Benzothiazole

concentration increased when the BFBR was used, but a quenching condenser used instead of the tube-and-shell one managed to decrease it. A further increase in the TDO and DL-limonene yield was observed when a CSBR was used in combination with a tube-and-shell condenser. However, the low residence time of the volatiles led to a higher benzothiazole concentration. Use of a quenching condenser instead of a tube-and-shell condenser in both the FBR and the BFBR improved the TDO yield and quality (high DL-limonene concentration and low benzothiazole concentration). High DL-limonene concentration in the TDO is evidence of its potential for use as a source of DL-limonene production and recovery when it is further processed. Moreover, low S and N concentrations are also encouraging for TDO upgrading for fuel production, since TDO refining processes will be less intensive and expensive. The quenching condenser is the preferred technique for cooling and condensing the hot volatile stream, particularly that obtained under high heating rates and short residence times of the hot volatiles in the reaction zone. Furthermore, a high benzothiazole concentration in the quenching water may lead to benzothiazole recovery in order to use it again for the tyre manufacturing.

Acknowledgements

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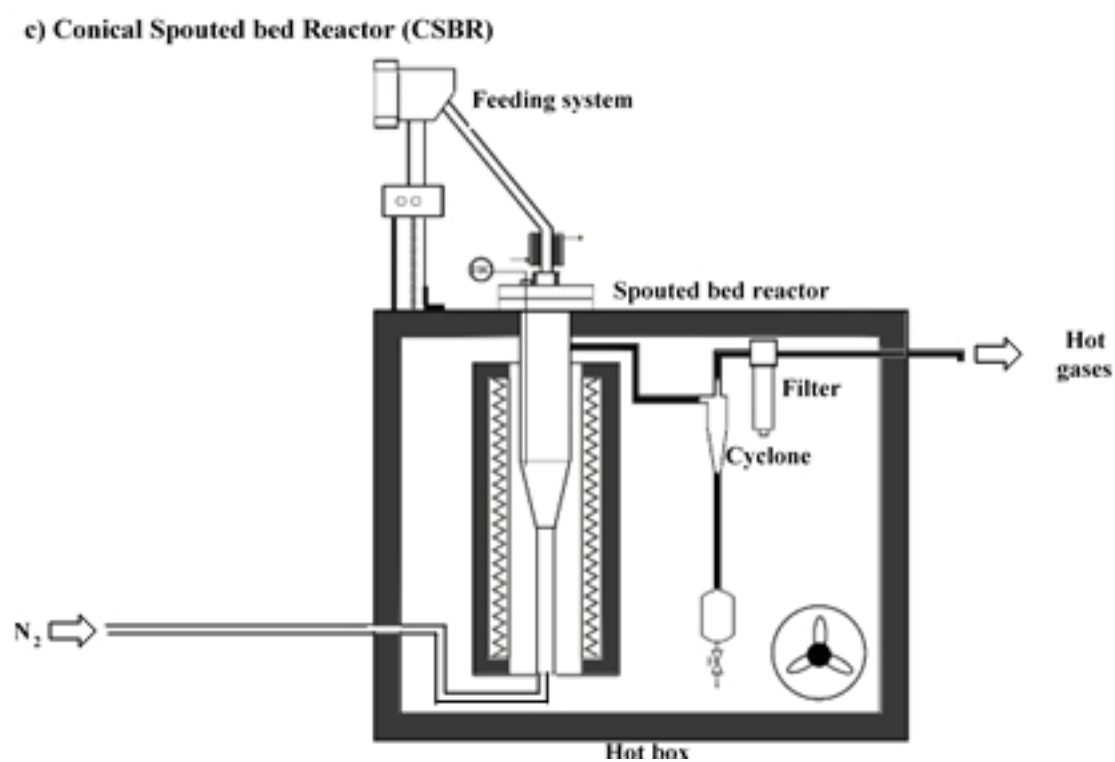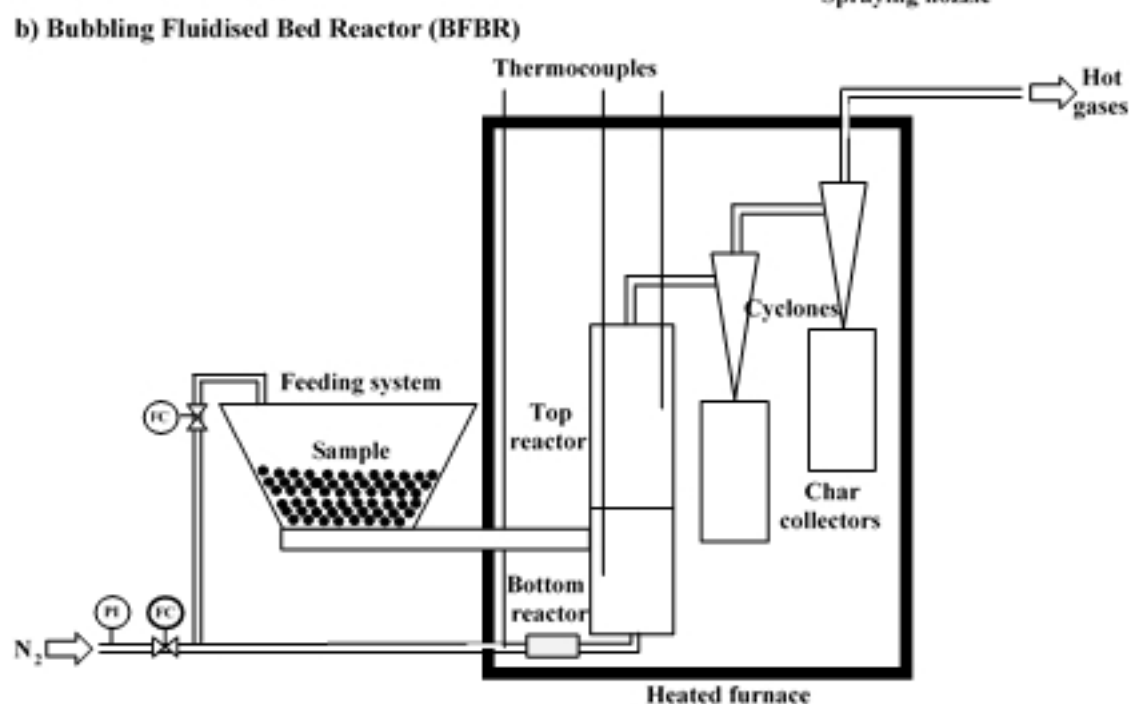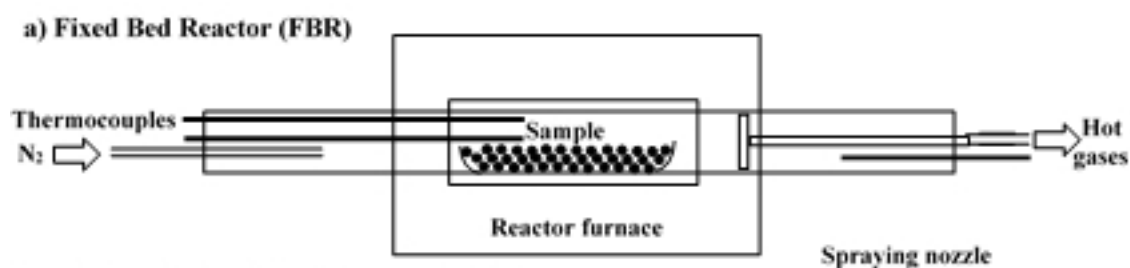
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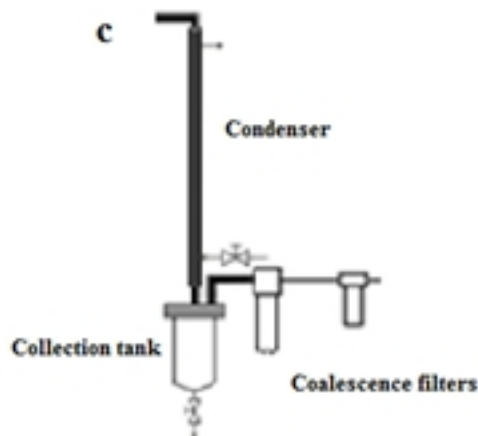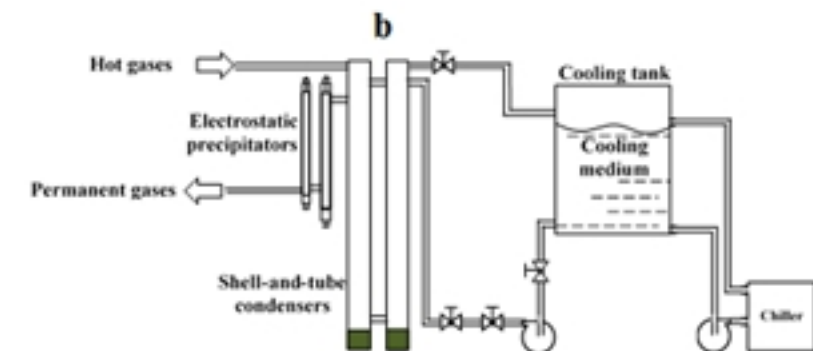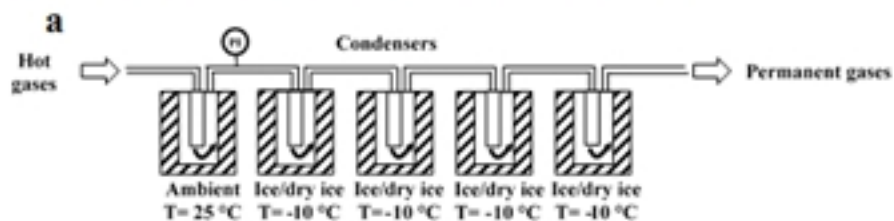
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a) Fixed Bed Reactor (FBR)

b) Bubbling Fluidised Bed Reactor (BFBR)

c) Conical Spouted bed Reactor (CSBR)

Indirect contanct shell-and-tube condenser

a

Hot gases → | Condensers | → Permanent gases

Ambient T= 25 °C | Ice/dry ice T=-10 °C | Ice/dry ice T=-10 °C | Ice/dry ice T= -10 °C | Ice/dry ice T= -40 °C

b

Hot gases →

Electrostatic precipitators

Permanent gases →

Cooling tank

Cooling medium

Shell-and-tube condensers

Chiller

c

Condenser

Collection tank

Coalescence filters

Direct contact quenching condenser

d

Spraying nozzle

Quenching fluid (water)

Hot gases →

Quenching tower →

Hot gases →

Cooling tank

Cooling medium

Liquid exit points

TDO

Water

TDO/water collection tank

Circulating pump

e

Hot gases →

Electrostatic precipitators

Permanent gases →

Quenching tower

Cooling tank

Cooling medium

Liquid exit points

Water

TDO/water collection tank

Chiller