



Review

A review of dipentene (DL-limonene) production from waste tire pyrolysis



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ARTICLE INFO

Article history:

Received 12 August 2014

Accepted 27 December 2014

Available online 7 January 2015

Keywords:

Dipentene
DL-Limonene
Waste tire
Pyrolysis

ABSTRACT

The present review concerns the production of dipentene (DL-limonene) from the pyrolysis of waste tires and is divided into three parts, which discuss (1) the mechanism of dipentene formation from polyisoprene, (2) the reported dipentene yields from experimental studies and (3) the separation and purification of dipentene from a tire-derived oil. Dipentene is formed via an intramolecular cyclization reaction of the allylic radicals formed by random scission of the β bonds with respect to the double bonds in the polyisoprene chains. Dimerization of two isoprene molecules to form dipentene seems unlikely under pyrolytic conditions. Especially at higher temperatures, the formed dipentene transforms further into either isoprene or aromatic compounds, the latter possibly via a diallyl diradical. Both the pyrolysis operating conditions and the tire type and brand have significant influence on the dipentene yield. Among these, the pyrolysis temperature is the most important variable, with temperatures between 400 and 500 °C resulting in maximum dipentene yields. Vacuum pyrolysis and basic additives have been propounded as a means of further improving this yield, but additional results are required to confirm this conclusively. Based on the presently available information in the literature, at least 2.5 wt% of a steel-free tire can be converted to dipentene. Finally, the literature has shown that it is not a trivial exercise to obtain a highly concentrated dipentene fraction of sufficient quality from the tire-derived oil. In particular, the removal of sulfur-containing compounds and the separation of dipentene from 1,2,3-trimethylbenzene, *m*- and *p*-cymene and indane are challenges that need to be addressed in the future.

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1. Introduction

The continually growing global automobile industry unavoidably results in also steadily increasing amounts of end-of-life or waste tires. It is estimated that about 1.5 billion waste tires are produced annually worldwide (see Table 1). Until recently, the majority of these scrap tires were landfilled; it is reported that

about 4 billion waste tires are currently in landfills and stockpiles world-wide [1]. However, this type of disposal can result in significant environmental disturbances, such as, uncontrolled fires (with accompanying pollution of the atmosphere, soil and groundwater) or by supplying breeding grounds for, e.g., rats or mosquitoes [2]. Also, the voluminosity of a tire, in combination with its resistance to down-sizing, makes that landfilling requires very large spaces.

Due to legislation becoming more stringent over the last years, in combination with the above-mentioned issues, valorization of waste tires is gaining both academic and industrial attention. For example, two European Commission Directives (the Waste Landfill

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Table 1
Number of annually generated waste tires in some countries.

Country	Waste tires (millions year ⁻¹)	Year
World-wide [1,7]	1500	2011
USA [15]	500	2007
European Union [15]	289	2011
Australia [15]	53	2008
South Korea [46]	28	2011
South Africa [85]	11	2012

Directive, which bans landfilling of tires, and the End Life Vehicle Directive, which stipulates the separate collection of tires from vehicle dismantling and encourages the recycling of tires) have led to a decrease from 62% of the generated waste tires being landfilled in the European Union in 1994 to 4% in 2010 [3]. Thus, as large parts of generated waste tires are currently revalorized, the waste tire problem has become both an environmental and an economic challenge.

From a technical viewpoint, several approaches have been employed for the revalorization of waste tires, such as, tire retreading, mechanical grinding, rubber reclaim, direct combustion or incineration, amongst others [4]. At present, the majority of waste tires are reused as ground rubber, e.g., as a binder in asphalt or in artificial sporting grounds [5]. Furthermore, large quantities of waste tires serve as a direct energy source (so-called tire-derived-fuel or TDF), due to their relatively high calorific value (around 32 MJ kg⁻¹) compared to other fuels, such as coal or wood [3]. Applications of energy utilization include cement kilns, power plants and co-incineration with other wastes. However, drawbacks of using waste tires directly for incineration are its relatively high SO₂ and polynuclear aromatic hydrocarbon (PAH) emissions [6]. One way to overcome these difficulties is to pyrolyze the tire before energy recovery.

Pyrolysis is a thermal degradation process of volatile matter in the absence of oxygen which generates a three phases product; a gas, a liquid and a solid. The volatile matter of a tire mainly consists of rubbers, the most important being natural rubber (NR), synthetic polyisoprene (PI), butadiene rubber (BR) and styrene-butadiene rubber (SBR). Apart from these rubbers, a tire additionally includes a plethora of processing oils, additives, fillers, vulcanization accelerators/inhibitors, which are all added during either the rubber or tire processing. Generally, a waste tire pyrolysis process results in 5–20 wt% gas, 40–60 wt% liquid and 30–40 wt% solid, depending on operating conditions [1,7]. The solid-phase product or pyrolytic char consists mostly of carbon black and other additives or fillers (zinc, sulfur, clays and silica) [8,9]. The char can be used as a fuel directly, or, after upgrading, as an activated carbon or carbon black [8,10,11]. The gas-phase products are typically C1–C4 hydrocarbons and hydrogen [12] and can be used on-site as a fuel to provide the energy requirements for the pyrolysis process [13]. The liquid-phase products or tire-derived-oil (TDO) are typically a mixture of paraffins, olefins and aromatic compounds [14] and have a very high calorific value between 40–45 MJ kg⁻¹ [7,15]. As part of the sulfur and most of the ash remains in the char, both the gas and liquid can be used more readily for energy recovery. Several excellent reviews have been published recently regarding waste tire pyrolysis focusing on energy recovery from the pyrolytic products [1,7,15].

The drawbacks of tire pyrolysis for the recovery of fuels are twofold. Firstly, the pyrolysis process is endothermic, thus less energy can be recovered compared to direct incineration of the tire. Secondly, there is the lack of industrial acceptance of the TDO, and to a lesser extent also the char. Companies that are currently involved in waste tire pyrolysis face significant challenges finding a market for their liquid and solid pyrolytic products.

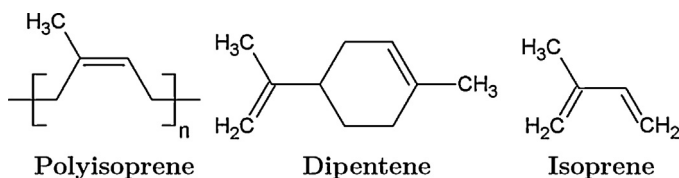


Fig. 1. Chemical structure of *cis*-1,4-polyisoprene, dipentene (*DL*-limonene, 1-methyl-4-(1-methylethenyl)-cyclohexene) and isoprene (2-methyl-1,3-butadiene).

One possible approach to make the pyrolytic processing of waste tires more attractive (from an economical point of view) is the recovery of valuable chemicals. It is known that the TDO contains many valuable chemicals, such as, dipentene, benzene, toluene, xylenes, ethyl benzene, amongst others. Also in the gaseous product there are compounds such as isoprene and butadiene, which are monomers of the rubbers that are found in tires, that have high market values. As most studies report that the dipentene concentration in the TDO (from pyrolysis processes operated at relatively low temperatures) is predominant, this compound has attracted the most attention. The present review will therefore focus on the production of dipentene from waste tire pyrolysis.

Dipentene comprises of the racemic mixture of the two enantiomers *D*- and *L*-limonene [14,16]. Its systematic name is 1-methyl-4-(1-methylethenyl)-cyclohexene, an unsaturated hydrocarbon classified as a monoterpene. It is the dimer of two isoprene units, which originate from the (either natural or synthetic) polyisoprene content of the tire. In Fig. 1 the chemical structures of polyisoprene, dipentene and isoprene are presented. At room temperature dipentene is a colorless oily liquid. Its molecular formula is C₁₀H₁₆, molar mass is 136.24 g mol⁻¹, boiling point is 176 °C and melting point is -74 °C. The price of dipentene currently ranges between 1500 and 2500 US\$ per metric tonne, depending mostly on its purity. It is mainly used as an industrial solvent, as a cleaning agent for, e.g., electrical circuit boards, as a dispersing agent for pigments, or as an active ingredient in different pesticide products [7,15–17]. Furthermore, carvone can be synthesized from dipentene, which can be used as a mosquito repellent. Finally, while *D*-limonene smells like oranges, *L*-limonene has the smell of pine. Due to these typical smells, it can also be employed for fragrances and flavorants, that is, if the two enantiomers can be sufficiently separated. It has to be noted here that most of the current dipentene demand is satisfied by citrus-derived pure *D*-limonene. Since a tire-derived dipentene is the racemic mixture of the two enantiomers and probably has a lower consumer appeal, it is also less suitable as a fragrance or flavorant. Therefore, the price for a tire-derived dipentene will be slightly lower than that of citrus-derived limonene.

This review aims at supplying an exhaustive overview of the currently available literature on the production of dipentene from waste tires and is subdivided threefold. Firstly, in the subsequent section, the mechanism of polyisoprene degradation under pyrolytic conditions is reviewed. Secondly, reported dipentene yields, assembled from literature sources of experimental studies on waste tire pyrolysis, are overviewed and discussed. The extensive analysis of the dipentene yields based on initial tire sample weight (in contrast to dipentene concentrations in the tire-derived oil) allows for indications for future research and technical assessment of dipentene production from waste tires. Finally, the (scarcely) available information on dipentene separation and purification from a pyrolytic oil is summarized.

2. Reaction mechanism

The degradation or depolymerization of natural rubber (NR) or (synthetic) *cis*-1,4-polyisoprene is a radical reaction, initiated by

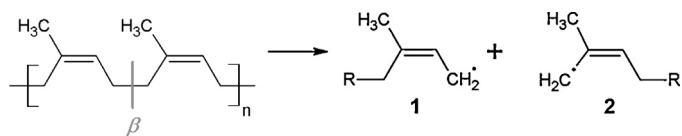


Fig. 2. Radical generating depolymerization initiation by scission of the β bond with respect to the double bonds in *cis*-1,4-polyisoprene.

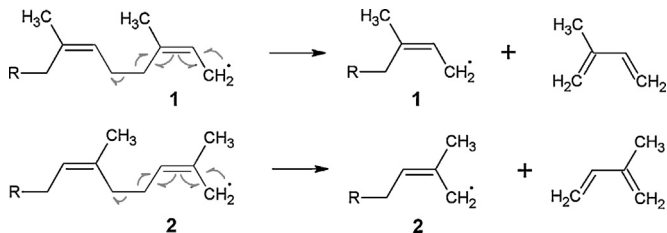


Fig. 3. Depropagation (unzip) of allylic radicals **1** and **2** to isoprene monomer.

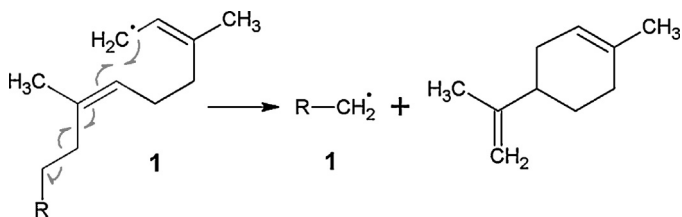


Fig. 4. Intramolecular cyclization and scission of allylic radical **1** to dipentene.

scission of the β bond with respect to the double bonds of the main polymer chain [18–23]. Whereas Bhowmick et al. also considered radical formation by scission of the α bond and methyl scission, Chien argues, due to differences in bond strengths, that scission of the β bond is energetically the most favorable among these [18,19].

Fig. 2 shows that scission of the β bond in *cis*-1,4-polyisoprene results in two different allylic radicals, with the radical either two carbons (radical **1**) or one carbon (radical **2**) separated from the methylated carbon. Cataldo shows that these allylic radicals can be terminated by adventitious agents (such as oxygen) under milder conditions than pyrolytic conditions (temperatures not exceeding 380 °C), resulting in a liquid polyisoprene with a lower average molecular weight [24]. However, under pyrolytic conditions, both radicals can depropagate or unzip towards the monomer isoprene [18,19,22]. In Fig. 3 this depropagation reaction is shown for the two radicals.

Simultaneously, both radicals **1** and **2** can also undergo an intramolecular cyclization followed by scission [22]. Such a reaction of radical **1** will yield dipentene, while radical **2** will yield 1,5-dimethyl-5-ethenyl-cyclohexene [18,19,22]. Remarkably, the yield of dipentene is much higher than that of 1,5-dimethyl-5-ethenyl-cyclohexene, which has been attributed to steric hindrance of the methyl group in the cyclization reaction of radical **2** and to higher stability of radical **1** due to hyper-conjugation [18,19]. In Fig. 4 the intramolecular cyclization of radical **1** yielding dipentene is presented [18,19,22,25].

Accordingly, the presence of structural units other than 1,4 units (such as 3,4 units) in the polyisoprene polymer can be identified by the presence of appreciable amounts of various other C10 compounds among the degradation products, such as 1-methyl-5-(1-methylethenyl)-cyclohexene (diprene) or 3,4-dimethyl-4-ethenyl-cyclohexene [18,19]. It is noted by Golub that 2,3-polyisoprene also results in dipentene, next to the dimer diprene [22].

While in most studies concerning the composition of a TDO dipentene is mentioned as the most prevalent product, Bhowmick

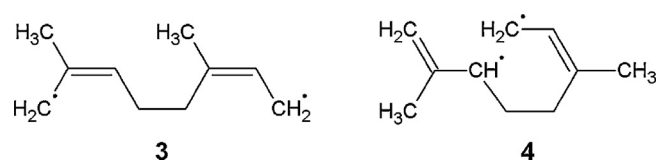


Fig. 5. C10-diradical from scission of two β bonds in polyisoprene (**3**) [29,30], and diallyl diradical of dipentene (**4**) [33,34].

et al. surprisingly recorded isoprene as the most abundant product [19]. This was explained by the fact that they used Guayule rubber, which consisted of 100% 1,4 units, allowing for higher unzipping to isoprene. Kwon et al. explained the abundance of dipentene compared to isoprene to a radical termination reaction between two radical **2** molecules [23].

Some researchers have propounded that dipentene can also be formed via dimerization of two isoprene monomers [16,19,20,25]. Groves et al. based this assumption on the fact that the monomer/dimer ratio increases for higher temperatures and decreases for larger particle sizes [25]. These observations made the authors conclude that the dimers are formed by a Diels–Alder type recombination reaction within the melt. Chen and Qian explicitly did not exclude the possibility of isoprene recombination via Diels–Alder addition based on similarities with butadiene recombinations (from polybutadiene rubbers) [20].

However, as already postulated by Chien and Kiang, this mechanism seems unlikely, since it should lead to significant yields of other isoprene dimers [18]. Indeed, Kar et al. has modeled the dimerization of isoprene using predictive force-field calculations [26]. It was calculated that between 25 and 1000 °C the conformer diprene was the energetically more favorable product of the dimerization, not dipentene. Moreover, Sauer states that the steric hindrance for 1,3-disubstituted Diels–Alder products from this type of reaction is of little significance [27]. Finally, experimental results of the Diels–Alder addition of methyl acrylate (dienophile) to isoprene (diene) show that, at temperatures between 20 and 400 °C, at least significant amounts of the 1,3-disubstituted isomer should be formed [27,28]. Thus, it is concluded that, although isoprene dimerization cannot be conclusively excluded, the lack of diprene as a pyrolysis product indicates that this reaction seems unlikely.

An alternative mechanism for the direct formation of dipentene from polyisoprene has been proposed [29,30]. After scission of two β bonds with respect to the double bonds in the main chain, a C10-diradical is formed (see radical **3** in Fig. 5), which subsequently isomerizes to its cyclic form (dipentene), analogously to the isomerization of propene towards cyclopropane. However, no experimental data are supplied to substantiate the proposed mechanism. Moreover, it is also not specified how (simultaneously or subsequently) or why the main chain is scinded specifically to form this C10-diradical. Actually, the scission of the β bonds in the main polyisoprene chain is mostly considered to be random. The fact that Groves et al. and Hall et al. observed isoprene oligomers (up to hexamers) as the product of the thermal degradation of natural rubber and latex gloves, respectively, also stipulates that the scission is random [25,31].

Finally, it is considered that although isoprene and dipentene were the two predominant products of polyisoprene pyrolysis below a temperature of around 410–430 °C [20,32], at higher pyrolysis temperatures their yield decreases. This can be due to further fragmentation or aromatization of the formed monomers and dimers [14,19], and/or due to fragmentation of the polymer (competitively with unzipping and internal cyclization reactions) [20]. It has been shown that the pyrolysis of dipentene around 450 °C yields isoprene, other terpenes and aromatics [33,34]. The formation of these products were explained by reactions of dipentene

via a diallyl diradical, see radical **4** in Fig. 5. Furthermore, the production of isoprene from the pyrolysis of dipentene has also been demonstrated by Davis et al. [35]. The fact that maximum isoprene concentrations have been reported at slightly higher pyrolysis temperatures than those for maximum dipentene yields, could be a result of this latter reaction [36–39]. Thus, as the fragmentation and aromatization of dipentene under pyrolytic conditions seems proven, the decrease of the dipentene yields at higher temperatures is either solely due to these reactions, or due to the combination of them with competitive fragmentation of the main polyisoprene polymer.

Tamura et al. have investigated the thermal degradation of *cis*-1,4-polyisoprene and its vulcanizates, containing either carbon or sulfur cross linkages [21]. Generally, scission of the main polymer chain starts at 300 °C, but the devolatilization of the polyisoprene with sulfur cross linkages started at lower temperatures (around 200 °C). This was attributed to the breaking of the polysulfide cross linkages, which occurs at lower temperatures, due to their lower bond dissociation energies [40]. The formed polythiyl radicals abstract allylic hydrogen from the polyisoprene, which is followed by scission of the main chain and subsequent mono- and dimer production.

Finally, it has been reported (erroneously) by some authors that dipentene can also be formed from polybutadiene [14,30]. This claim was based on a misinterpretation of the papers by Brazier et al. and Madorsky [41,42]. The pyrograms presented by Miguel et al. confirm that no dipentene is formed from polybutadiene [43].

Thus, it can be concluded that both isoprene and dipentene are mainly formed via direct depolymerization of polyisoprene, initiated by random scission of the β bonds with respect to the double bonds in the main polymer chain. The monomers and dimers are formed by unzipping and intramolecular cyclization reactions, respectively. The lack of dipentene conformers among the pyrolytic products indicates that dimerization of isoprene is unlikely. However, dipentene itself (especially at higher temperatures) can transform further into either isoprene or aromatic compounds, the latter possibly via a diallyl diradical.

3. Dipentene production from waste tire pyrolysis

In this section an exhaustive overview is presented of reported experimental yields of dipentene from waste tire pyrolysis. At present such an overview is lacking in the literature. While Pakdel and Zhang made an effort on presenting selections of reported yields (either in text or tabulated, respectively), both authors report dipentene concentrations in the pyrolytic oil [17,40]. Since it is known that the oil yield can vary significantly between different pyrolysis operating conditions, this seems unsatisfactory. Therefore, in this work the dipentene yields are based on the initial tire or crumb sample weight fed to the reactor.

It is, however, noted that the current approach is still accompanied by some difficulties, which induce some caution for direct comparison of the presented results. Firstly, some authors report that they used tires including the fibers, whereas others explicitly separated them from the sample. Secondly, while in some studies the steel content of the tires was present in the pyrolysis reactor, all reported yields were compensated for the steel content. Thirdly, and more importantly, the separation, identification, and accordingly the quantification, of specific compounds is notoriously difficult in TDO's. Due to the plethora of compounds present, the oil cannot be completely separated using highly optimized 1-dimensional GC methods. This is clearly confirmed by comprehensive 2-dimensional GC (GC \times GC) separation of TDO's, see for example the GC \times GC chromatograms of Rathsack et al. [44]. To overcome this difficulty some authors use a pre-fractionation

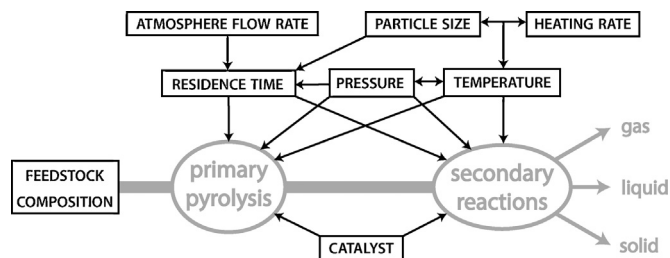


Fig. 6. Graphical overview of governing variables in pyrolysis.

step before analysis. This inevitably introduces other inaccuracies, such as variable recoveries, combined with the fact that many different fractionation methods are used, which further complicates direct comparison of the results. Finally, the various ways of detecting and quantifying compounds also show major variations. Only a few studies explicitly mention that analytical standards were used [14,45–52]. The paper of Kyari et al. supplies very insightful results in this respect, as they report for one experiment both the %-area (13.79%) using a GC/MS instrument and the calibrated wt% (3.11%) of dipentene [52]. Although the peak area of a Flame Ionization Detector (FID) can be used to estimate the weight percentage for hydrocarbons, the definition of the total peak area will have a large influence on the calculated percentage area. In a typical GC-FID chromatogram of a TDO, a large ‘hump’ of unresolved material is often encountered (especially for relatively fast separations) [52,53]. The inclusion and integration of this hump has a significant effect on the final wt% of the individual compounds. In order to assist the reader with the correct interpretation of the presented data, it was therefore decided to include in the overviews which analysis method was used and whether calibration with analytical standards was performed for determining the dipentene yield.

Taking into account these difficulties, the trends in the dipentene yields will be mostly discussed per study. Merely those values that were (explicitly) calibrated will be compared among each other.

In the remainder of this section, the results are presented and discussed based on the main pyrolysis variables that have been studied in the literature. In Fig. 6 the most important governing variables in pyrolysis are schematically overviewed, these being the pyrolysis temperature, heating rate, pressure, sample particle size, feedstock composition, inert atmosphere flow rate, the residence time in the reactor and finally the use of catalysts. A distinction has been made between primary and secondary pyrolytic reactions. The primary reactions include radical initiation reactions and subsequent depolymerization (and possible fragmentation) of the polymer chain. Cross linking or condensation reactions of the polymer chains, which are due to reactions of the radicals with the main chain, are also considered as primary reactions. The secondary reactions then comprise of the thermal fragmentation of the remaining condensed product, as well as any further reactions of the volatile products of the primary reactions (e.g., cracking, aromatization and recombination reactions). Thus, it is noted that the primary and secondary reactions both include not only devolatilization but also solid formation reactions.

In the following, results will be subsequently presented for studies focusing on varying the temperature, pressure, type of tire and catalytic pyrolysis, respectively. It is noted here that the residence time is also a very important variable, mainly due to secondary reactions in the gaseous phase of the formed monomers and dimers. However, since measured or estimated values of the residence time are scarcely reported, a thorough discussion of this variable would be highly speculative and was therefore not included in this review. Finally, the influence of the type of reactor is discussed.

Table 2
Dipentene yields from studies that have varied the pyrolysis temperature. ACR, autoclave reactor; CSBR, conical spouted bed reactor; FBR, fluidized bed reactor; FID, flame ionization detection; FR, feeding rate; HR, heating rate; GC, gas chromatography; KR, Kiln reactor; MR, microreactor; n.m., not mentioned; *p*, pressure; PCT, passenger car tire; (Q)MS, (quadrupole) mass spectrometry; RKR, rotary kiln reactor; SS, sample size; *T*, temperature; TDO, tire-derived oil; TT, truck tire; XBR, fixed bed reactor with fire tubes; XBR-FT, fixed bed reactor with microwave.

Ref.	Tire type	Particle size	FR (kg/h) SS (kg)	Reactor type	<i>T</i> (°C)	HR (°C min ⁻¹)	<i>p</i> (kPa)	Carrier gas	Flow (L/min)	TDO (wt%)	Dipentene (wt%)	Analysis method	Calib?
[54]	n.m.	13–15 mm	12–15	RKR	450	Fast	85	N ₂	n.m.	43.0	2.34	GC/MS	No
	n.m.	13–15 mm	12–15	RKR	500	Fast	85	N ₂	n.m.	45.1	0.85	GC/MS	No
	n.m.	13–15 mm	12–15	RKR	550	Fast	85	N ₂	n.m.	44.6	0.19	GC/MS	No
	n.m.	13–15 mm	12–15	RKR	600	Fast	85	N ₂	n.m.	42.7	0.05	GC/MS	No
	n.m.	13–15 mm	12–15	RKR	650	Fast	85	N ₂	n.m.	42.9	0.03	GC/MS	No
[86]	n.m.	4 mm	0.03	ACR	450	Fast	101	N ₂	1.5	37.8	0.69	GC/MS	No
	n.m.	4 mm	0.03	ACR	750	Fast	101	N ₂	1.5	10.9	0.02	GC/MS	No
[46]	n.m.	1–2 mm	0.05	XBR, 2.2 L	500	10	101	N ₂	2	38.3	2.55	GC-FID/MS	Yes
	n.m.	1–2 mm	0.05	XBR, 2.2 L	600	10	101	N ₂	2	30.9	1.16	GC-FID/MS	Yes
	n.m.	1–2 mm	0.05	XBR, 2.2 L	700	10	101	N ₂	2	30.5	1.27	GC-FID/MS	Yes
	n.m.	1–2 mm	0.05	XBR, 2.2 L	800	10	101	N ₂	2	29.8	1.24	GC-FID/MS	Yes
[47]	n.m.	1–0.5 tires	310	KR, 4300 L	700	n.m.	101	N ₂	n.m.	27.3	0.63	GC	Yes
	n.m.	1–0.5 tires	771	KR, 4300 L	850	n.m.	101	N ₂	n.m.	32.5	0.42	GC	Yes
	n.m.	1–0.5 tires	770	KR, 4300 L	800	n.m.	101	N ₂	n.m.	23.9	0.26	GC	Yes
	n.m.	1–0.5 tires	1015	KR, 4300 L	950	n.m.	101	N ₂	n.m.	24.0	0.24	GC	Yes
[14]	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	450	5	101	N ₂	n.m.	58.1	1.82	GC-FID	Yes
	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	475	5	101	N ₂	n.m.	58.2	1.77	GC-FID	Yes
	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	500	5	101	N ₂	n.m.	56.2	1.63	GC-FID	Yes
	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	525	5	101	N ₂	n.m.	56.9	1.65	GC-FID	Yes
	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	560	5	101	N ₂	n.m.	55.4	1.36	GC-FID	Yes
	PCT	3 × 1.5 × 50–150 cm	3	XBR, 16.3 L	600	5	101	N ₂	n.m.	53.1	1.33	GC-FID	Yes
[48]	PCT	1–1.4 mm	0.15	FBR, 1.2 L	570	5	101	N ₂	1.5	57.1	2.06	GC-FID	Yes
[53]	PCT	20–30 mm	0.175	ACR, 3.5 L	300	15	101	N ₂	1	4.8	1.01	GC/MS	No
	PCT	20–30 mm	0.175	ACR, 3.5 L	400	15	101	N ₂	1	24.8	2.04	GC/MS	No
	PCT	20–30 mm	0.175	ACR, 3.5 L	500	15	101	N ₂	1	38.0	1.95	GC/MS	No
	PCT	20–30 mm	0.175	ACR, 3.5 L	600	15	101	N ₂	1	38.2	1.22	GC/MS	No
	PCT	20–30 mm	0.175	ACR, 3.5 L	700	15	101	N ₂	1	38.5	1.27	GC/MS	No
[37]	PCT	n.m.	1.20E–05	MR	450	Fast	101	He	0.1	43.2	14.00	GC-FID	No
	PCT	n.m.	1.20E–05	MR	500	Fast	101	He	0.1	52.3	9.42	GC-FID	No
[36]	PCT	< 1 mm	0.002	CSBR	425	Fast	101	N ₂	6.5	65.4	23.93	GC/MS	No
	PCT	< 1 mm	0.002	CSBR	500	Fast	101	N ₂	6.5	62.0	16.94	GC/MS	No
	PCT	< 1 mm	0.002	CSBR	550	Fast	101	N ₂	6.5	63.0	13.59	GC/MS	No
	PCT	< 1 mm	0.002	CSBR	610	Fast	101	N ₂	6.5	62.7	6.34	GC/MS	No
[39]	PCT	< 1 mm	0.18	CSBR	425	Fast	101	N ₂	9.5	64.3	20.40	GC-FID	No
	PCT	< 1 mm	0.18	CSBR	500	Fast	101	N ₂	9.5	62.3	10.29	GC-FID	No
	PCT	< 1 mm	0.18	CSBR	600	Fast	101	N ₂	9.5	54.4	0.94	GC-FID	No
[30]	TT	4000 mm ³	0.75	XBR-FT, 2.1 L	425	15	101	N ₂	8	52.0	26.42	GC/MS	No
	TT	4000 mm ³	0.75	XBR-FT, 2.1 L	475	15	101	N ₂	8	55.0	27.97	GC/MS	No
	TT	4000 mm ³	0.75	XBR-FT, 2.1 L	525	15	101	N ₂	8	51.0	12.67	GC/MS	No
	TT	4000 mm ³	0.75	XBR-FT, 2.1 L	575	15	101	N ₂	8	48.0	10.20	GC/MS	No
[45]	n.m.	1–4 mm	0.01	XBR, 0.24 L	400	5	101	N ₂	–	38.8	0.66	GC/MS	Yes
	n.m.	1–4 mm	0.01	XBR, 0.24 L	400	35	101	N ₂	–	31.1	0.01	GC/MS	Yes
[56]	PCT-1	20 × 20 mm	0.21	XBR-MW, 1 L	599	6 kW	101	N ₂	–	31.5	1.17	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.23	XBR-MW, 1 L	491	3 kW	101	N ₂	–	42.6	1.46	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.25	XBR-MW, 1 L	493	1.5 kW	101	N ₂	–	20.7	0.52	GC/(Q)MS	No
	PCT-1	20 × 20 mm	1.5	XBR-MW, 5 L	514	3 kW	101	N ₂	–	39.3	1.86	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.5	XBR-MW, 1 L	471	3 kW	101	N ₂	–	44.0	2.06	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.06	XBR-MW, 1 L	344	3 kW	101	N ₂	–	30.1	2.89	GC/(Q)MS	No

Many studies have investigated the influence of the pyrolysis temperature on the dipentene yield, see Table 2. The investigated temperatures range from 300 °C up to 950 °C. All these studies report lower dipentene yields at higher temperatures. This trend is in accordance with the reported temperature range at which dipentene is formed (between 410 and 430 °C) and its propounded degradation and/or aromatization at higher temperatures (see previous section). At relatively low temperatures (below around 450 °C) the final dipentene yields are reduced due to low liquid yields (and thus incomplete pyrolysis). For example, the high dipentene concentration in the oil from an experiment at 300 °C, as reported by Laresgoiti et al., is much lower when considered on weight basis of the sample. Actually, about double amounts of dipentene are obtained at 400 and 500 °C [53]. There seems to be a maximum in the dipentene yield within the temperature range 400–500 °C. This maximum is reported at 400 [53], 425 [36,39], 450 [14,37,54], 475 [30], or 500 °C [46] for the different studies. The variation in this temperature for maximum dipentene yield is mainly due to the influences of the other governing variables. The highest calibrated dipentene yields are 2.06 and 2.55 wt% at 500 and 570 °C, respectively [46,48], while above 600 °C these yields do not exceed about 1.5 wt% [14,46,47]. Moreover, it has to be noted that if the heating rate is low and the (final) pyrolysis temperature exceeds the temperature at which the tire is completely pyrolyzed (i.e. around 550 °C), this final pyrolysis temperature will have no effect on the product distribution [14,46,47,53].

There is only one study that specifically investigated the influence of heating rate on the final dipentene yield [45]. Two different heating rates were compared (5 and 35 °C min⁻¹), with a final pyrolysis temperature of 400 °C, and the highest dipentene yield was obtained with the lower heating rate. Thus, the supposedly lower thermal degradation rates allowed for more production of dipentene. Unfortunately, this study did not report dipentene yields at higher pyrolysis temperatures for the different heating rates. As can be observed in Fig. 6, the heating rate also has an influence on the temperature within the tire particle, mainly in concordance with the sample particle size, see also [55]. So the trend observed by Banar et al. could be different for different particle sizes [45]. Unfortunately, no results are available for the influence of the particle size on the dipentene yield.

Undri et al. have studied the pyrolysis of waste tires using microwave heating [56]. As it turned out to be very complicated to measure (or even estimate) the actual pyrolysis temperature, they mainly use the microwave power over the sample mass squared (Pm^{-2}) instead. However, the values of the Pm^{-2} do not show a straightforward relation with the temperatures they did measure. From the results it can be concluded that highest dipentene yields are obtained at a power of 3 kW and with the smallest investigated sample size.

Next, studies that either use reduced pressure or vary the operating pressure are discussed, see Table 3. The group of Laval University in Canada has investigated waste tire pyrolysis on different scales for dipentene production at vacuum conditions [16,17,57–59]. From all their papers, Roy reported the highest dipentene yield of 5.0 wt% for a fixed bed reactor at 500 °C [59]. The experimental results of vacuum pyrolysis by Zhang et al. confirm this value (they show a dipentene yield of 4.9 wt% at 500 °C) using similar analytical apparatus [40]. Generally, the use of vacuum pyrolysis is considered as promising for dipentene production since the residence times of the evolved volatiles are shorter compared to atmospheric pyrolysis (avoiding secondary reactions of the dipentene). However, since all the presented values were obtained from non-calibrated analyses, it is not yet possible to conclusively state that vacuum pyrolysis actually results in higher dipentene yields. Actually, Lopez et al. investigated the decrease of pressure systematically from atmospheric pressure to 25 kPa in a spouted

bed reactor [60]. They show that the dipentene yield decreases with decreasing pressure. Simultaneous to this decrease in dipentene, an increase in the isoprene concentration is observed. The authors explain these trends by assuming that the dimerization of isoprene in vacuum is inhibited. However, it needs to be noted here that these experiments are performed at reduced pressure, rather than in vacuum. An alternative explanation (if dimerization is assumed to be unlikely, see previous section) is that unzipping reactions (which yield one isoprene molecule per isoprene unit) are favored over internal cyclization reactions (which form one dipentene molecule for every two isoprene units) at reduced pressures, analogously to Le Chatelier's principle for chemical equilibria.

In Table 4 the experimental yields of studies varying the type of tire used are overviewed. There are two studies that compare dipentene yields from both truck tires (TT) and passenger car tires (PCT) [38,61]. Lopez et al. report higher dipentene yields (almost double) for a PCT (with 30 wt% NR) compared to a TT (with 60 wt% NR) at 425 °C in a spouted bed reactor [38]. At higher temperatures (500 and 600 °C) the dipentene yields are comparable for the two tires. Admittedly, the isoprene concentrations are lower for the PCT, however, the sum of these mono- and dimers are still higher for PCT than for TT. Actually, at 425 °C the reported isoprene and dipentene concentrations sum to 25 wt%, with an initial NR content in the sample of 30 wt%. Ucar et al. show that dipentene covers almost 30 % area in the GC chromatogram for a pyrolytic oil from TT (with 51 wt% NR) using a fixed bed reactor at 650 °C [61]. When PCT is used (with 35 wt% NR) at the same conditions, no peak for dipentene is observed. The comparative study of Roy et al. of pyrolysis of a TT and poly-isoprene also shows that higher dipentene yields are to be expected from a tire with a higher NR content [59].

Islam has reported dipentene yields from the pyrolysis of truck tires (TT), motorcycle tires (MT) and bicycle tires (BT) [62,63]. The amount of dipentene formed decreases for these tires in the order TT > MT > BT. Although no exact rubber contents are presented for the three tires types, it can be estimated from the presented DTG curves of MT that it has more BR and SBR than natural rubber or synthetic polyisoprene [62]. Hall shows dipentene yields for the pyrolysis of latex gloves [31].

Kyari et al. and Undri et al. have both reported the dipentene yields for different brands of PCT [52,64]. Both use a fixed bed reactor, but Undri uses a microwave for heating, which makes direct comparison more complicated (see above). The main conclusion that can be drawn from these two studies is that also different brands of PCT (can) result in significant differences in the dipentene yield. For example, Undri observes consistently higher dipentene yields from PCT-2 (BFGoodrich) compared to PCT-1 (Michelin). Kyari shows that Michelin tires produce average amounts of dipentene, compared to the other tire brands. These differences can most probably be explained by the specific rubber compositions of the different PCT's.

There are many studies that have used different types of catalysts in order to increase the concentrations of targeted valuable chemicals in the TDO. Most of these studies use acidic catalysts (various types of zeolites), see Table 5 [31,37,49–51,65–70]. Generally, the objective (and the result) of the usage of this type of catalyst is an increase in the yield of single-ring aromatics. This improvement in the benzene–toluene–xylenes content is however at the expense of the dipentene yield. For all the experiments reported using zeolites a distinct decrease in the dipentene yield is observed, see also the pyrograms of Miguel et al. [43]. The governing variables for the catalysis are catalyst pore size, silica/alumina ratio and catalyst to sample ratio. Generally, it is assumed that the volatile hydrocarbons from pyrolysis (including dipentene) are cracked (secondary reactions) by the acidic zeolites, followed by reforming reactions [50,65]. Olazar et al. substantiated this hypothesis by their observation of an increase in the lighter hydrocarbon fraction in the

Table 3
Dipentene yields from studies that have varied the pyrolysis pressure. ACR, autoclave reactor; CSBR, conical spouted bed reactor; FID, flame ionization detection; FR, feeding rate; GC, gas chromatography; HR, heating rate; (IT)MS, (ion trap) mass spectrometry; MBR, moving bed reactor; n.m., not mentioned; *p*, pressure; PCT, passenger car tire; (Q)MS, (quadrupole) mass spectrometry; SBR, sliding blade reactor; SHF, six-hearth furnace; SS, sample size; *T*, temperature; TDO, tire-derived oil; TT, truck tire; XBR, fixed bed reactor.

Ref.	Tire type	Particle size	FR (kg/h) SS (kg)	Reactor type	<i>T</i> (°C)	HR (°C min ⁻¹)	<i>p</i> (kPa)	Carrier gas	Flow (L/min)	TDO (wt%)	Dipentene (wt%)	Analysis method	Calib?
[57]	n.m.	n.m.	<100	SBR	525	Fast	1.3	–	–	n.m.	2.26	n.m.	No
[16]	PCT	6–13 mm	3.5	SHF, 770 L	510	Fast	1	–	–	55.0	2.20	GC-FID	No
[58]	PCT	6 × 12 mm	19	MBR, 850 L	500	Fast	13	–	–	50.0	0.69	GC/(Q)MS	No
[59]	TT	2000 mm ³	1	XBR, 15 L	500	15	1	–	–	62.2	5.00	GC/(Q)MS	No
	TT	2000 mm ³	1	XBR, 15 L	500	15	6	–	–	61.7	4.20	GC/(Q)MS	No
[17]	PCT	2700 mm ³	21	SHF, 770 L	500	Fast	12	–	–	57.5	2.60	GC/(Q)MS	No
	TT	< 3800 mm ³	42	MBR, 850 L	500	Fast	13	–	–	56.5	1.60	GC/(Q)MS	No
	TT	< 3800 mm ³	25	MBR, 850 L	540	Fast	10	–	–	40.9	0.80	GC/(Q)MS	No
	TT	< 3800 mm ³	33	MBR, 850 L	451	Fast	12	–	–	53.7	3.60	GC/(Q)MS	No
	TT	< 3800 mm ³	0.2	XBR, 1L	480	n.m.	1	–	–	60.0	3.30	GC/(Q)MS	No
	TT	< 3800 mm ³	0.2	XBR, 1L	440	n.m.	1	–	–	43.4	3.30	GC/(Q)MS	No
	TT	< 3800 mm ³	0.2	XBR, 1L	480	n.m.	1	–	–	n.m.	2.80	GC/(Q)MS	No
[40]	n.m.	20–60 mesh	0.1	ACR, 0.1 L	450	20	4	–	–	32.9	3.94	GC/(IT)MS	No
	n.m.	20–60 mesh	0.1	ACR, 0.1 L	500	20	4	–	–	42.1	4.94	GC/(IT)MS	No
	n.m.	20–60 mesh	0.1	ACR, 0.1 L	550	20	4	–	–	47.1	2.22	GC/(IT)MS	No
[60]	PCT	< 10 mm	0.18	CSBR	425	Fast	101	N ₂	9.5	64.3	20.40	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	425	Fast	50	N ₂	5.3	62.3	10.88	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	425	Fast	25	N ₂	3	61.4	9.80	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	500	Fast	101	N ₂	9.5	61.7	10.29	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	500	Fast	50	N ₂	5.3	61.6	9.40	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	500	Fast	25	N ₂	3	60.2	5.07	GC-FID/MS	No

Table 4
Dipentene yields from studies that have varied the type of tire. BT, bicycle tire; CSBR, conical spouted bed reactor; FID, flame ionization detection; FR, feeding rate; GC, gas chromatography; HR, heating rate; (IT)MS, (ion trap) mass spectrometry; LG, latex gloves; MT, motorcycle tires; n.d., not detected; n.m., not mentioned; *p*, pressure; PCT, passenger car tire; (Q)MS, (quadrupole) mass spectrometry; SS, sample size; *T*, temperature; TDO, tire-derived oil; TT, truck tire; XBR, fixed bed reactor; XBR-FT, fixed bed reactor with fire tubes; XBR-MW, fixed bed reactor with microwave.

Ref.	Tire type	Particle size	FR (kg/h) SS (kg)	Reactor type	<i>T</i> (°C)	HR (°C min ⁻¹)	<i>p</i> (kPa)	Carrier gas	Flow (L/min)	TDO (wt%)	Dipentene (wt%)	Analysis method	Calib?
[61]	PCT	1.5–2 mm	0.13	XBR, 0.6 L	650	7	101	N ₂	0.025	48.4	n.d.	GC/MS	No
	TT	1.5–2 mm	0.13	XBR, 0.6 L	650	7	101	N ₂	0.025	56.0	16.12	GC/MS	No
[38]	TT	< 10 mm	0.18	CSBR	425	Fast	101	N ₂	9.5	62.8	12.75	GC-FID/MS	No
	TT	< 10 mm	0.18	CSBR	500	Fast	101	N ₂	9.5	60.9	11.00	GC-FID/MS	No
	TT	< 10 mm	0.18	CSBR	600	Fast	101	N ₂	9.5	54.9	0.93	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	425	Fast	101	N ₂	9.5	64.3	20.40	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	500	Fast	101	N ₂	9.5	61.7	10.29	GC-FID/MS	No
	PCT	< 10 mm	0.18	CSBR	600	Fast	101	N ₂	9.5	55.9	0.94	GC-FID/MS	No
[62]	MT	4000 mm ³	0.75	XBR-FT, 2.1 L	475	Fast	101	N ₂	8	49.0	14.47	GC/MS	No
[63]	BT	4000 mm ³	0.75	XBR-FT, 2.1 L	475	Fast	101	N ₂	8	46.0	5.04	GC/MS	No
	TT	4000 mm ³	0.75	XBR-FT, 2.1 L	475	Fast	101	N ₂	8	55.0	27.97	GC/MS	No
[52]	PCT-1	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	59.8	1.69	GC/(IT)MS	Yes
	PCT-2	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	59.7	1.79	GC/(IT)MS	Yes
	PCT-3	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	56.6	2.22	GC/(IT)MS	Yes
	PCT-4	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	60.1	2.86	GC/(IT)MS	Yes
	PCT-5	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	59.7	2.61	GC/(IT)MS	Yes
	PCT-6	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	57.1	1.84	GC/(IT)MS	Yes
	PCT-7	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	58.7	1.91	GC/(IT)MS	Yes
	PCT's	25 × 30 mm ²	0.045	XBR, 0.2 L	500	10	101	N ₂	0.2	60.1	1.87	GC/(IT)MS	Yes
[56]	PCT-1	20 × 20 mm	0.21	XBR-MW, 1 L	599	6 kW	101	N ₂	0	31.5	1.17	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.23	XBR-MW, 1 L	491	3 kW	101	N ₂	0	42.6	1.46	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.5	XBR-MW, 1 L	471	3 kW	101	N ₂	0	44.0	2.06	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.06	XBR-MW, 1 L	344	3 kW	101	N ₂	0	30.1	2.89	GC/(Q)MS	No
[64]	PCT-2	20 × 20 mm	0.25	XBR-MW, 1 L	n.m.	6 kW	101	N ₂	0	42.8	2.04	GC/(Q)MS	No
	PCT-2	20 × 20 mm	0.25	XBR-MW, 1 L	n.m.	3 kW	101	N ₂	0	38.8	1.25	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.24	XBR-MW, 1 L	n.m.	6 kW	101	N ₂	0	27.8	1.04	GC/(Q)MS	No
	PCT-2	20 × 20 mm	0.25	XBR-MW, 1 L	n.m.	6 kW	101	N ₂	0	35.7	3.58	GC/(Q)MS	No
	PCT-1	20 × 20 mm	0.24	XBR-MW, 1 L	n.m.	3 kW	101	N ₂	0	27.6	1.34	GC/(Q)MS	No
	PCT-2	20 × 20 mm	0.25	XBR-MW, 1 L	n.m.	3 kW	101	N ₂	0	26.9	0.94	GC/(Q)MS	No
	PCT-2	20 × 20 mm	0.5	XBR-MW, 1 L	n.m.	6 kW	101	N ₂	0	37.0	2.10	GC/(Q)MS	No
	PCT-2	20 × 20 mm	0.5	XBR-MW, 1 L	n.m.	3 kW	101	N ₂	0	31.9	3.41	GC/(Q)MS	No
[31]	LG	100 mm ²	0.01	XBR, 0.4 L	380	10	101	N ₂	0.2	57.9	0.11	GC-FID/MS	Yes
	LG	100 mm ²	0.01	XBR, 0.4 L	480	10	101	N ₂	0.2	79.8	0.12	GC-FID/MS	Yes

Table 5
Dipentene yields from studies that used catalytic pyrolysis with acidic catalysts. CSBR, conical spouted bed reactor; GC, gas chromatography; HR, heating rate; FBR, fluidized bed reactor; FID, flame ionization detection; FR, feeding rate; MR, microreactor; MS, mass spectrometry; n.m., not mentioned; *p*, pressure; PCT, passenger car tire; S/C, sample-to-catalyst ratio; SS, sample size; *T*, temperature; TDO, tire-derived oil; XBR, fixed bed reactor; XBR-MW, fixed bed reactor with microwave; ZB, zeolite beta type; ZSM, zeolite ZSM-5 type; ZY, zeolite Y type.

Ref.	Tire type	Particle size	FR (kg/h) SS (kg)	Reactor type	<i>T</i> (°C)	HR (°C min ⁻¹)	<i>p</i> (kPa)	Carrier gas	Flow (L/min)	Catalyst	S/C (–)	<i>T</i> .catalyst (°C)	TDO (wt%)	Dipentene (wt%)	Analysis method	Calib?
[49]	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	–	–	500	53.8	2.31	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	0.25	500	50.0	1.85	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	0.5	500	48.0	1.49	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1	500	46.0	1.29	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1.5	500	45.6	0.96	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	0.5	500	49.0	1.72	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1	500	48.0	1.25	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1.5	500	46.0	1.06	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	2	500	43.0	0.82	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1	450	48.0	1.92	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1	550	45.0	0.68	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1	600	42.0	0.17	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1	450	49.0	2.25	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1	550	47.5	0.67	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1	600	40.0	0.12	GC-FID/MS	Yes
[50]	PCT	1–1.4 mm	0.22–0.23	FBR	450	Fast	101	N ₂	n.m.	–	–	500	55.0	2.75	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	–	–	500	53.5	2.09	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	525	Fast	101	N ₂	n.m.	–	–	500	52.0	1.30	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	550	Fast	101	N ₂	n.m.	–	–	500	51.0	0.41	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	600	Fast	101	N ₂	n.m.	–	–	500	43.5	0.04	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	450	Fast	101	N ₂	n.m.	ZY	1	500	48.5	1.75	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZY	1	500	46.5	1.40	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	525	Fast	101	N ₂	n.m.	ZY	1	500	44.0	1.06	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	550	Fast	101	N ₂	n.m.	ZY	1	500	42.5	0.51	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	600	Fast	101	N ₂	n.m.	ZY	1	500	39.0	0.08	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	450	Fast	101	N ₂	n.m.	ZSM	1	500	49.5	1.88	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	500	Fast	101	N ₂	n.m.	ZSM	1	500	45.5	1.18	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	550	Fast	101	N ₂	n.m.	ZSM	1	500	43.5	0.65	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.22–0.23	FBR	600	Fast	101	N ₂	n.m.	ZSM	1	500	41.0	0.12	GC-FID/MS	Yes
[51]	PCT	1–1.4 mm	0.2	XBR, 1.2 L	500	10	101	N ₂	n.m.	–	–	500	55.8	2.01	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.2	XBR, 1.2 L	500	10	101	N ₂	n.m.	ZY-1	4	500	48.0	0.24	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.2	XBR, 1.2 L	500	10	101	N ₂	n.m.	ZY-2	4	500	48.0	0.12	GC-FID/MS	Yes
	PCT	1–1.4 mm	0.2	XBR, 1.2 L	500	10	101	N ₂	n.m.	ZSM	2	500	47.0	0.14	GC-FID/MS	Yes
[65]	PCT	8–10 mm	0.02	XBR, 0.1 L	500	200–250	101	–	0	ZY	2	400	32.7	0.55	GC/MS	No
[66]	PCT	8–10 mm	0.02	XBR, 0.1 L	500	10	101	–	0	–	–	400	52.0	5.33	GC/MS	No
	PCT	8–10 mm	0.02	XBR, 0.1 L	500	10	101	–	0	ZSM	2	400	32.6	2.81	GC/MS	No
	PCT	8–10 mm	0.02	XBR, 0.1 L	500	10	101	–	0	ZY	1/2	400	40.4	0.36	GC/MS	No
[67]	PCT	8–10 mm	0.01	XBR, 0.1 L	500	10	101	–	0	–	–	400	45.9	3.89	GC/MS	No
	PCT	8–10 mm	0.01	XBR, 0.1 L	500	10	101	–	0	ZY	4	400	31.0	1.02	GC/MS	No
	PCT	8–10 mm	0.01	XBR, 0.1 L	500	10	101	–	0	ZY	2	400	24.0	0.22	GC/MS	No
	PCT	8–10 mm	0.01	XBR, 0.1 L	500	10	101	–	0	ZY	1.3	400	20.0	0.07	GC/MS	No
	PCT	8–10 mm	0.01	XBR, 0.1 L	500	10	101	–	0	ZY	1	400	13.8	0.04	GC/MS	No
[37]	PCT	n.m.	1.20E–05	MR	450	Fast	101	He	0.1	–	–	–	43.2	14.00	GC-FID	No
	PCT	n.m.	1.20E–05	MR	500	Fast	101	He	0.1	–	–	–	52.3	9.42	GC-FID	No
	PCT	n.m.	3.50E–06	MR	450	Fast	101	He	0.1	ZSM	0.2	In-situ	44.1	0.12	GC-FID	No
	PCT	n.m.	3.50E–06	MR	450	Fast	101	He	0.1	ZY	0.2	In-situ	51.1	0.93	GC-FID	No
	PCT	n.m.	3.50E–06	MR	450	Fast	101	He	0.1	ZB	0.2	In-situ	42.2	0.01	GC-FID	No
	PCT	n.m.	8.00E–06	MR	450	Fast	101	He	0.1	ZSM	5.3E–05	450	24.5	0.26	GC-FID	No
	PCT	n.m.	8.00E–06	MR	450	Fast	101	He	0.1	ZSM	1.9E–08	450	25.5	0.21	GC-FID	No
[68]	PCT	n.m.	0.002	CSBR	425	Fast	101	N ₂	n.m.	–	–	–	64.7	23.93	GC/MS	No
	PCT	n.m.	0.002	CSBR	425	Fast	101	N ₂	n.m.	ZSM	0.13	In-situ	58.3	5.51	GC/MS	No
	PCT	n.m.	0.002	CSBR	425	Fast	101	N ₂	n.m.	ZY	0.13	In-situ	62.2	1.99	GC/MS	No
	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	–	–	–	63.2	16.94	GC/MS	No
	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	ZSM	0.13	In-situ	45.5	3.78	GC/MS	No
	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	ZY	0.13	In-situ	61.8	2.37	GC/MS	No
[69]	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	–	–	–	63.2	16.94	GC-FID	No
	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	ZSM	0.13	In-situ	45.5	3.79	GC-FID	No
	PCT	n.m.	0.002	CSBR	500	Fast	101	N ₂	n.m.	ZY	0.13	In-situ	61.8	2.39	GC-FID	No

TDO of catalytic pyrolysis [69]. Furthermore, this catalytic behavior holds both for studies where a separate catalytic bed was used [37,49–51,65–67], and for studies where the catalyst was present in the pyrolysis reactor itself (in-situ) [37,68–70].

Apart from these acidic catalysts, only a few other catalysts have been investigated, see Table 6. Most promising from a dipentene point of view is the use of basic additives [40]. Zhang et al. showed that the dipentene yield can be improved significantly when using NaOH as the catalyst at vacuum conditions. Although the dipentene concentration in the TDO is comparable with that of their uncatalyzed experiment, the fact that more oil is obtained when using NaOH indicates that more dipentene is formed. Analogously, Kar showed an increase in the oil yield using expanded perlite as the catalyst [71]. However, the dipentene concentration in this oil was slightly lower, resulting in comparable final dipentene yields.

Finally, the influence of the type of reactor is assessed. For this purpose, the calibrated dipentene yields of experiments at 500 °C in different reactors of comparable size, i.e., fixed-bed (XBR) and fluidized-bed reactors (FBR), are compared. These values are 2.55 wt% [46], 2.01 wt% [51] and 1.69–2.86 wt% [52] for XBR's and 2.31 wt% [49] and 2.09 wt% [50] for FBR's. These values do not indicate any significant differences for these two reactor types. It has to be noted that the dipentene yields obtained in a conical spouted bed reactor (CSBR), where residence times are assumed to be even shorter than in a FBR, are significantly higher than above-mentioned values [36,39]. However, these latter values have not been calibrated, so they should be considered with care.

Few other studies need to be mentioned in this section. Three studies have presented dipentene yields of the co-pyrolysis of waste tires with (waste) lubricant oil [70,72] and with lignite [73]. Unfortunately, all these studies did not calibrate their analytical apparatus. Since the composition of the obtained co-pyrolytic oils can differ significantly from that of pyrolysis of waste tires alone, in these cases, it seems difficult to compare the results even among themselves. For general informative purposes, the results are included in Table 6 nevertheless.

Furthermore, it is just noted here that several papers have reported dipentene yields for experiments with relatively low oxygen levels in the reactor [74–76]. From a comparison between fully inert and slightly oxidative pyrolysis of latex gloves it is concluded that lower dipentene yields are obtained when oxygen is present [31,76]. Because this review focuses on pyrolysis proper, the results are not included in the overviews. It is noted that Boxiong et al. also did not use an inert carrier gas or vacuum, but as their reactor is closed air-tight, only the initially present oxygen is available in the reactor [65–67]. Because this is a relatively small amount and it is readily removed from the reactor, their reaction conditions are still considered to be pyrolytic.

Finally, both Dai et al. (waste tires in a fluidized bed reactor) and Pradhan et al. (bicycle tires in a fixed bed reactor) reported dipentene yields in their TDO, however, in both cases the operating conditions, under which these TDO's were produced, were not specified [77,78].

It can be concluded, based on presently available information in the literature, that at least 2.5 wt% of the steel-free tire can be converted to dipentene. The main operating conditions during pyrolysis influence this yield significantly, of which temperature seems to be the most important (and also the most investigated) one. Also, the importance of tire type and tire brand is stressed here, while most probably these two variables are both linked to the polyisoprene content of the tire. Additionally, some studies have indicated that the above mentioned yields can be further improved. The use of vacuum pyrolysis has been propounded as such a possible improvement. Also, the use of basic additives, e.g., NaOH, seems to improve the final dipentene yields. However, more conclusive

Table 6
Dipentene yields from studies that used catalytic pyrolysis using non-acidic catalysts and co-pyrolysis. ACR, autoclave reactor; FID, flame ionization detection; FR, feeding rate; GC, gas chromatography; HR, heating rate; (IT)MS, (ion trap) mass spectrometry; n.m., not mentioned; p, pressure; PCT, passenger car tire; S/C, sample-to-catalyst or sample-to-cocatalyst ratio; SS, sample size; T, temperature; TT, truck tire; TDO, tire-derived oil; XBR, fixed bed reactor.

Ref.	Tire type	Particle size	FR (kg/h) SS (kg)	Reactor type	T (°C)	HR (°C min ⁻¹)	p (kPa)	Carrier gas	Flow (L/min)	Catalyst	Co-pyrolysis	S/C (-)	T _{catalyst} (°C)	TDO (wt%)	Dipentene (wt%)	Analysis method	Calib?
[40]	n.m.	20–60 mesh	0.1	ACR, 0.1 L	500	20	4	-	-	-	-	-	-	42.1	4.94	GC/(IT)MS	No
	n.m.	20–60 mesh	0.1	ACR, 0.1 L	500	20	4	-	-	NaOH	-	33	In-situ	48.1	5.75	GC/(IT)MS	No
	n.m.	20–60 mesh	0.1	ACR, 0.1 L	500	20	4	-	-	Na ₂ CO ₃	-	33	In-situ	42.0	5.20	GC/(IT)MS	No
[71]	PCT	2 mm	0.01	XBR, 0.3 L	425	10	101	N ₂	0.1	-	-	-	-	60.0	0.87	GC/MS	No
	PCT	2 mm	0.01	XBR, 0.3 L	425	10	101	N ₂	0.1	-	EP	10	In-situ	65.1	0.92	GC/MS	No
[72]	PCT	1.5–2 mm	0.065	XBR, 0.6 L	550	7	101	N ₂	0.025	-	WLO	1	In-situ	66.5	1.50	GC-FID/MS	No
	TT	1.5–2 mm	0.065	XBR, 0.6 L	550	7	101	N ₂	0.025	-	WLO	1	In-situ	72.3	21.25	GC-FID/MS	No
[70]	PCT	10 × 30 mm	0.01	XBR, 0.06 L	430	10	101	N ₂	-	-	-	-	-	33.3	2.69	GC/MS	No
	PCT	10 × 30 mm	0.01	XBR, 0.06 L	430	10	101	N ₂	-	-	LBO	2000	In-situ	33.5	2.14	GC/MS	No
	PCT	10 × 30 mm	0.01	XBR, 0.06 L	430	10	101	N ₂	-	ZSM-5	-	2000	In-situ	33.6	2.53	GC/MS	No
	PCT	10 × 30 mm	0.01	XBR, 0.06 L	430	10	101	N ₂	-	ZSM-5	LBO	1000	In-situ	48.0	6.52	GC/MS	No
[73]	PCT	n.m.	0.05	XBR	700	10	101	N ₂	0.03	-	-	-	-	20.0	1.31	GC/MS	No
	PCT	n.m.	0.05	XBR	700	10	101	N ₂	0.03	-	Lignite	1	In-situ	18.0	4.61	GC/MS	No

data (such as calibrated dipentene yields for systematic studies of vacuum or NaOH catalyzed pyrolysis) are required.

4. Dipentene separation and purification

From the previous section it becomes clear that the dipentene yield, and thus also its concentration in the tire-derived oil, varies considerably with pyrolysis conditions as well as tire type and brand. Moreover, the dipentene is also present in the TDO together with a plethora of other components, with studies reporting from an excess of 130 components using one-dimensional GC [53], to several hundreds of compounds using GC×GC [44]. Both the types of components and their concentrations can vary significantly [17,29,52]. Although almost all studies report that dipentene is the most abundant component present in the TDO, should dipentene be produced as a value-added chemical from waste tire pyrolysis, it needs to be separated from the multitude of other components. While a significant number of publications have considered the pyrolysis proper, considerably less work has been performed on the fractionation of TDO or on the separation and purification of possible valuable chemicals from TDO.

Typically, the TDO can be characterized, based on its properties, between a light and medium fuel oil [14]. It consists predominantly of alkylated benzenes, alkylated naphthalenes, alkanes and alkenes [52]. Analysis of the distillation curves of various TDO's show that it has a wide boiling range with up to 50 wt% of the sample distilling before 200 °C [52,61,62]. Approximately 10 wt% of the oil has a normal boiling point between 160 and 200 °C, the fraction in which dipentene would typically be present [53,79].

A number of studies have considered separating the oil into various fractions, by and large for the end use as a fuel or fuel additive [10,48,80]. This can either be achieved with relative ease through distillation [10,80], or, as studied by Williams and Brindle [48], by selective condensation of the reactor outlet. For distillation studies, the majority of the dipentene is present in the so-called light naphtha fraction (normal boiling point below 200 °C) at reported concentrations between 15 and 25 wt% [1,7,16,17]. Further separation of the light naphtha could yield a fraction with a boiling point between 160 and 200 °C, containing the majority of the dipentene. In the selective condensation study of Williams and Brindle the highest concentration of dipentene is present in the lightest fraction, with concentrations up to 7 wt% [48]. This fraction should have a similar composition to the light naphtha fraction and further separation and purification of this fraction may result in a dipentene enriched fraction. It should also be noted that the three condensers used for the selective condensation study of Williams and Brindle were all operated at the same temperature. Operation using a temperature gradient between the different condensers may improve the separation efficiency significantly.

While it is relatively easy to obtain a dipentene enriched light naphtha (or similar) fraction, further purification is not so simple. In a series of publications, Pakdel and co-workers studied the dipentene production from tire-derived oil extensively [16,17,81]. Initially, they fractionated the oil through distillation at atmospheric pressure and the light naphtha fraction, with a normal boiling point below 204 °C contained approximately 15 wt% dipentene. A small sample (1 g) of this fraction was then purified on preparative scale and they succeeded in producing a 95 wt% pure dipentene. However, the methods used are not easily transferable to larger scale, and, as pointed out in their conclusions, further research is required. They suggested that at least two consecutive distillation steps, followed by a purification step, would be required to produce high purity dipentene. In a follow-up study, a much larger scale of operation was considered [17]. The oil was fractionated first in a 300 L batch still, where after

the dipentene in the naphtha fraction was further concentrated in a 5 L batch column. Then, solid liquid chromatography on a dual layer silica and alumina column was used to obtain sub-fractions for analysis. Importantly, fractions containing between 50 and 92 wt% dipentene were obtained. It was also found that separation of dipentene from 1,2,3-trimethylbenzene, 1-methyl-3-(1-methylethyl)benzene (*m*-cymene), and indane is very difficult due to their similar boiling points (all between 175 and 176 °C). Although not specifically mentioned, dipentene is probably also aromatized to *p*-cymene (1-methyl-4-(1-methylethyl)benzene), which also has a boiling point very close to dipentene (177 °C).

Stanciulescu and Ikura also considered the fractionation of a tire-derived oil, with the aim of obtaining relatively pure dipentene for conversion to dipentene esters [82,83]. In their initial study, the TDO was subjected to a double fractionation, but they found that the complexity of the TDO and the low concentration made dipentene collection difficult [82]. In their follow-up study, the TDO was fractionated at 3.33 kPa, using a batch still, with various cuts being obtained [83]. They found that the normal boiling point cuts of 170–180 °C and 180–190 °C both contained approximately 75 wt% dipentene, with these cuts representing 5.4 and 1.2 wt% of the total charge, respectively. They noted that further fractionation was very difficult, again highlighting the challenges in separation.

In addition to obtaining a fraction concentrated in dipentene, it is also important to consider the other components present, in particular the sulfur-containing components. Sulfur-containing components, even in very low concentrations, can result in a foul odor to the oil, thus reducing the quality and economic value thereof. Williams et al. found that the TDO contains approximately 1.4 wt% sulfur, which is rather significant in this respect [84]. Pakdel et al. demonstrated, using pure dipentene, that the odor threshold for thiophene was 15.4 and 20.6 ppm for *D,L*-limonene and *D*-limonene, respectively [17]. While most of the sulfur-containing compounds were removed during the distillation process, Pakdel's concentrated dipentene samples still had an unpleasant smell and contained up to two orders of magnitude higher sulfur component concentrations than the odor threshold they measured [17]. Stanciulescu and Ikura observed a similar foul odor [83].

In conclusion, the literature has shown that it is not a trivial exercise to obtain a highly concentrated dipentene fraction of sufficient quality. Especially, the separation of dipentene from some other compounds present in the TDO (viz. 1,2,3-trimethylbenzene, *m*- and *p*-cymene and indane) and the removal of the sulfur-containing compounds, due to their foul odor, is essential and remain the principle challenges for future research.

5. Conclusions

It is concluded that dipentene is produced by the intramolecular cyclization of the allylic radicals. The allylic radicals are formed by random scission of the β bonds with respect to the double bonds in the polyisoprene chains. Dimerization of isoprene (which is produced by unzipping of these radicals) towards dipentene seems unlikely, due to the lack of other isoprene dimers among the pyrolytic products. Next, dipentene is involved in secondary reactions at pyrolytic conditions, such as aromatization, possibly via a diallyl diradical, or fragmentation towards isoprene, among others. The main operating conditions during pyrolysis influence the dipentene yield significantly. Of these, the pyrolysis temperature seems to be most important, with temperatures between 400 and 500 °C resulting in maximum dipentene yields. Also, the importance of tire type and tire brand is stressed here, while most probably these two variables are both linked to the polyisoprene content of the tire sample. Both the use of vacuum pyrolysis and the use of basic additives, e.g., NaOH, have been propounded as

means to further improve the dipentene yield. However, more conclusive data (such as calibrated dipentene yields for systematic studies of vacuum or NaOH catalyzed pyrolysis) are required. Based on the presently available information in the literature, it can be concluded that at least 2.5 wt% of a steel-free tire can be converted to dipentene. Thus, hypothetically, if a steel-free tire weighs 10 kg, it yields 0.25 kg dipentene, which returns (at a mean dipentene price of 2 US\$ kg⁻¹) about half a US\$ per processed tire. Besides, the remaining hydrocarbons mixtures can still be used as an energy source. Therefore, the production of dipentene from end-of-life tires is a very promising route to add value to the tire pyrolysis process. However, prerequisite for this route to be viable is the recovery of a highly pure dipentene from the TDO. It is evident that there are still some significant challenges in this respect. While a dipentene-enriched fraction can be obtained from the TDO by relatively straightforward distillation, dipentenes with purities between 92 and 95 wt% have been reported using more sophisticated separation principles. To get even purer fractions is very difficult due to other compounds present in the oil (1,2,3-trimethylbenzene, *m*- and *p*-cymene and indane) that have very similar properties as dipentene. Moreover, the removal of the sulfur-containing compounds is essential, due to their foul odor, especially when the dipentene is intended to be used as a fragrant or flavorant.

Acknowledgments

N.M. Mkhize and L. Mulaudzi are kindly acknowledged for their contribution to the compilation of the literature database. Also many thanks go to Dr. A. de Villiers and Prof. C.D. Woolard for sharing their extensive knowledge. Financial assistance of REDISA and the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the funding bodies.

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