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Combustion engine applications of waste tyre pyrolytic oil – a comprehensive review

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Abstract

There is a huge amount of worldwide research into combustion engine applications for tyre pyrolysis oil. Differing pyrolysis methods provide different process efficiencies and fuel qualities. There also are various fuel post-treatment methods and blending strategies. Testing has been carried out on a variety of engine platforms. Consequently, this wide range of variables means that the results of all the research into the use of tyre pyrolysis oil in combustion engines can be difficult to comprehend. So, despite substantial availability potential, the role of fuel derived from waste tyres is far from certain in the transport sphere. There is an urgent need to cover this knowledge gap if global greenhouse gas reduction targets are to be met. That is the fundamental premise of this review work. It gathers the results of over 180 original research papers, directly relevant to the topic of the discussion, aiming to answer the governing research questions related to tyre pyrolytic oil production and quality, post-processing and quality improvement methods and its final end-use engine validation. The critical discussion on the key issues, including the most relevant drivers and boundaries, points towards tyre pyrolytic oil's use as a fuel component in marine, off-road and heavy-duty road applications. The results indicate that state-of-the-art production methods yield a fuel that could be used directly in bunkering chains for marine transport as low-sulphur fuel oil. Automotive applications are limited to blends not exceeding 10% tyre pyrolytic oil, where sulphur content, cetane number, viscosity and particulate mass emissions are the main constraints. The availability and flexibility of feedstock, combined with high process efficiency, make waste-derived pyrolytic oils a supplementary solution to biofuels, so blends of both fuel categories can take advantage of their complementary properties.

Key words: tyres, pyrolysis, pyrolytic oil, fuel quality, fuel characterisation, combustion engines, compression ignition, emissions.

Nomenclature and abbreviations:

Al_2O_3	aluminium oxide
BF	blast furnace
BMEP	brake mean effective pressure
BR	butadiene rubber
bTDC	before top dead centre
C	carbon
CA	crank angle
$CaCO_3$	calcium carbonate

CaO	calcium oxide
$Ca(OH)_2$	calcium hydroxide
CH_3COOH	acetic acid
CI	compression ignition
CN	cetane number
CO	carbon monoxide
CO_2	carbon dioxide
CR	common rail
DF	diesel fuel
DTPO	distilled tyre pyrolytic oil
DMC	dimethyl carbonate
DTG	derivative thermogravimetry
EGR	exhaust gas recirculation
ECA	Emission Control Area
EEDI	energy efficiency design index
ELT	end-of-life tyre
EPR	extended produced responsibility
ETRMA	European Tyre and Manufacturers Association
EU	European Union
FAME	fatty acid methyl esters
Fe_2O_3	iron oxide
H	hydrogen
H_2	molecular hydrogen
H_2O_2	hydrogen peroxide
H_2S	hydrogen sulphide
H_2SO_4	sulphuric acid
HFO	heavy fuel oil
HHV	higher heating value
HRR	heat release rate
HVO	hydrotreated vegetable oil
IMO	International Maritime Organisation
JME	jatropha methyl esters
K_2O	potassium oxide
LHV	lower heating value
MgO	magnesium oxide
MJ/kg	megajoules per kilogram
MJ/Nm^3	megajoules per normal cubic metre
N	nitrogen
$NaOH$	sodium hydroxide
NCV	net calorific value
NEDC	new European drive cycle
$NiMO\text{-}Al_2O_3$	nickel-molybdenum on alumina
NO	nitric oxide
NO_X	oxides of nitrogen
NBR	natural polybutadiene rubbers
P_2O_5	phosphorus pentoxide
PAH	polycyclic aromatic hydrocarbons
PM	particulate matter
PRR	pressure rise rate
RPM	revolutions per minute
SBR	styrene-butadiene rubber
SiO_2	silica

SOC	start of combustion
SOI	start of injection
SO_3	sulphur trioxide
SOX	oxides of sulphur
TGA	thermogravimetric analysis
TiO_2	titanium dioxide
TPO	tyre pyrolysis oil
UHC	unburnt hydrocarbons
ZnO	zinc oxide
ZSM-5	zeolite Socony Mobil-5

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1 Introduction

Global demand for crude oil continues to increase, propelled by economic and population growth. Meeting the Paris Agreement's CO_2 (carbon dioxide) reduction goals requires radical changes around the world. A significant reduction in fossil fuels is needed across all fronts, from power generation to manufacturing and transport. Although renewables' share is increasing at a rate of 4 % per year, it is foreseen that in 2030 they can still only cover half of the global increase in energy demand [1].

Looking at fuel production, growth of gasoline consumption is being retarded mainly by fast progress of electrification in the light-duty transport sector. Heavy-duty goods transport continues to rely on diesel fuel (DF) due to its high energy density and the high efficiency of compression-ignition (CI) engines [2]. Here, the fast track towards sustainability is mainly via scaling up new generation drop-in fuels that can be readily used in existing fleets. Currently, there are two feasible renewable fuel production technologies that have reached industrial-scale production volumes: transesterification and hydrotreatment of carboxylic acids. Transestrification, producing mainly fatty acid methyl esters (FAME), is more widespread due to simplicity of the process. Hydrotreatment, yielding hydrotreated vegetable oil (HVO) is less common but offers greater potential because the end product has higher quality than esters or even diesel [3]. Moreover, HVO can be produced using existing refinery infrastructure providing high process efficiency. Both processes have one significant downside: limited flexibility on feedstock, which heavily relies on first-generation bio-components, competing with food production [4].

Pyrolysis is another promising concept for renewable diesel and other types of fuels. The main advantage here is that a variety of bio and synthetic waste materials (plastics, rubber, etc…) can be used in the same reactor. More importantly, recent works indicate a synergistic effect when co-pyrolysis of bio and synthetic material is applied, reporting potential for process efficiency enhancement and increasing the fuel mass yield [5].

Another part of the sustainability challenge is efficient recycling of waste materials. Management of automotive shredder residue and management of end-of-life tyres (ELTs) is in the spotlight [6,7]. Waste tyres cannot be used in landfill due to poor biodegradability and environmental hazards like fire and water stagnation (supporting the proliferation of insects and bacteria) [8]. The complex material structure which makes ELTs difficult to process also creates a variety of residual streams. Steel fibres, shreds, oils and carbon filler can be recovered from used tires. Waste tyres' high calorific value make them suitable as fuel substitute in waste-to-energy plants or as a feedstock to alternative thermochemical conversion plants for both energy and carbon material production [4].

In the above context, pyrolysis of waste tyres is currently a widely explored topic, with many works focusing on improving the process efficiency and tyre pyrolysis oil (TPO) fraction yield [9,10]. At the same time, crude tyre pyrolytic oils and also their different distilled fractions have been studied by many researchers as standalone fuel [11,12]. Others have studied the large-scale blending of TPO with other fossil fuels [13] and biofuels [12], or, in case of light distillates, as a renewable fuel additive (improver) [14]. This research involves both laboratory analysis of fuel properties and evaluation of performance by engine tests. Grasping the current status of engine research is particularly difficult due to a diversity of engine platforms used in tests. Qualitatively, all researchers agree that TPO retards combustion, but quantitatively the results differ substantially [15,16]. Contradictory results are quite often reported when exhaust emission effects are considered [17,18]. These ambiguities result from differences in engine sizes, technological levels of the test platforms, or combustion modes realized.

The objective of this work is a comprehensive assessment of the current state of the art in waste tyre conversion to mechanical power through internal combustion engine applications. The introduction section provides a background for the present work. It describes the overall scale of the problem and its legislation boundaries, placing pyrolysis in the context of other re-processing technologies. The introduction is summarised by discussing the premise of the present research in terms of its significance and the particular knowledge gaps it aims to fill. The main body of the work reviews the current state of the art in tyre pyrolytic fuels, following the process chain from production (section 2), through analytics and upgrading (section 3) and finishing with end-use engine performance (Section 4). The work is summarised with a discussion and outlook section (section 5) and wrapped-up with conclusions.

1.1 Waste tyres - the scale of the problem, recycling routes and legislation framework

The number of used tyre in the European Union (EU) is trending upwards, mainly because of the developing road transport and light-duty automotive sectors in Eastern Europe. A report from the European Tyre and Rubber Manufacturers' Association (ETRMA) indicates there were 2.88 million tonnes of used tyres (EU, Norway, Switzerland, and Turkey) in 2013 with an average growth rate of 4 % per annum [19]. A similar trend is observed on a world-wide basis, with a global tyre output estimated at 1.5 billion units per annum [20,21].

Currently, the management of used tyres in most countries is regulated by legislation. A comprehensive review of specific EU regulations affecting tyre deposition and treatment can be found in [4]. Of over 15 sets of legislative regarding the matter, certainly the most important one is the Directive on the Landfill of Waste 1000/31/EC issued in 1999. This initiative basically prohibited stockpiling of whole tyres in landfills starting from July 2003 and scrapped tyres from July 2006. As a result, in 2010, 96 % of the EU's used tyres were recovered for residual management [19]. The EU Circular Economy Package of December 2015 also helped close the loop in used tyres management. It put particular emphasis on product reuse and supporting sustainability by extending the product's lifetime. Reuse, export and retreading (all falling under reuse) cumulatively account for around 20 % of all recycled tyres. In terms of ELTs (tyres that cannot be re-used), ERTMA identifies material recycling and energy recovery as primary handling routes. Fig. 1. depicts how utilisation of waste tires evolved due to legislation over the years. It is based on merged data from two sources [22,23].

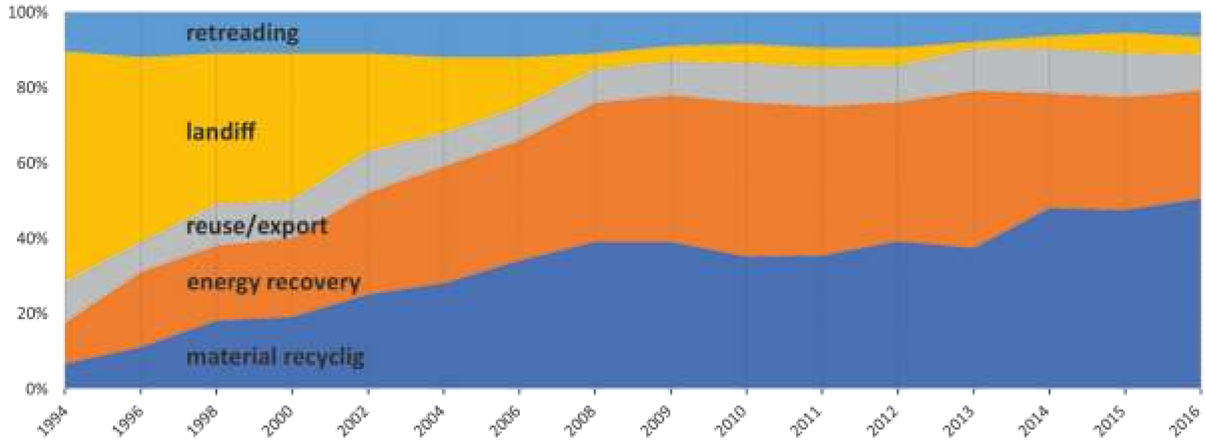


Fig. 1. Used tyres management routes and their percentage contribution in handling available material in EU. Based on data merged data from [22] - until 2009; [23] – until 2015; [24] – year 2016.

Generally, the ELT market is currently stable in Europe with the country to country variation being more significant than the change in global trend. Material recycling is now the main handling route (50 %), followed by energy recovery (29 %). The ELT management system in EU countries consists of three different models: Extended Producer Responsibility (EPR), the liberal system (free market) and the tax system. Under the first system, introduced in the majority of EU member countries, manufacturers and importers of tyres are obliged to ensure that tyre wastes are disposed of in an appropriate manner that does not harm the environment [19]. The free market system assumes that the ELTs are important sources of valuable raw material and that their recovery and recycling are profitable, so the onus rests on commercial companies to harness the ELTs. That system operates in Austria, Switzerland and Germany. In the case of the tax system, applied in Denmark and Croatia, recovery/recycling organisations are responsible for used tyres management, which is financed by the state via a tax levied on tyre manufacturers [19].

Depending on the country/system, different stakeholders take primary responsibility for management of ELTs and, ultimately, for phasing-in new processing technologies. One of the main barriers to application of tyres pyrolysis is unclear legal process definition. According to the EU, depolymerisation of tyres by gasification or pyrolysis is classified as a destructive process, equivalent to incineration (thermal waste treatment with or without heat recovery). In fact, pyrolysis of ELTs should be considered as an energy and material co-recovery process. Pyrolysis oil (e.g. TPO) and remaining gas both can be used as energy sources or inputs for new materials synthesis [25]. Thus, pyrolysis shows considerable environmental benefits over combustion/incineration which releases significant amounts of CO_2 and extremely toxic substances. The former contributes to climate change; the latter are dangerous for the environment and human health [26,27]. Still, the emission legislation is quite liberal for waste incineration processes, effectively inhibiting the more energy-efficient and environmentally friendly processes.

In summary, current EU legislation suppresses the opportunity for tyre pyrolysis to take a major share in ELTs management. To address this, closer collaboration between the joint alternative management system of each country and the research community should be promoted. Even more beneficial is the heavily lobbied transition [28,29] from Extended Producer Responsibility to the free market system, creating a value-based drive towards more efficient and socially acceptable solutions.

1.2 Waste tyre pyrolytic oil as a fuel for combustion engines: drivers and boundaries

For simplicity, this discussion concerning the drivers and boundaries for TPO as engine fuel focuses purely on compression ignition (CI) engines. These have the biggest demand for alternative fuels, as indicated in Section 1. Fossil DF, and on the alternative side, FAME and HVO, currently the most feasible alternative for CI engines, are mentioned in these discussions as references.

In terms of drivers, TPO fuels face the same economics as other alternative fuels. Global fuel demand is rising by around 10% per year and at the same time crude oil exploration is becoming more expensive, increasing the economic feasibility for alternatives [1]. This momentum is reinforced by numerous CO_2 reduction initiatives, with the 2015 Paris agreement being the most relevant globally.

Tyre pyrolytic oils are produced from waste material and so are classified as second-generation fuels. They have a more favourable CO_2 factor on a well-to-wheel basis than popular biofuels FAME and HVO, assuming these are still majorly produced from first-generation components (competing with food production) like palm or rapeseed oil. In this respect, the biggest challenge for FAME and HVO is limited flexibility of feedstock. Data in the previous section (1.1) suggests waste tyres potentially available for TPO production in 2016 could be estimated at around 2 million tonnes per year in Europe alone, and growing at 4% per annum. This is assuming the current ELTs stream split for applications other than energy. For comparison, European availability of oilseeds and vegetable oils (which currently underpin over 86% of biofuel production) accounts for 50 million tonnes, but only around 13 % of that (ie about 6.5 million tonnes) is available for fuel purposes due to strong competition with food production [30]. However, when measured in energy terms, both feedstocks are of the same order of availability, since tyre energy density is estimated at around 3.2 MJ/kg –roughly double that of mixed biomass [31,32]. Waste tyre availability for energy generation would increase if more sustainable and economically feasible solutions are developed, making this use of ELTs more attractive than direct material recovery. Pyrolysis (and gasification) also provides feedstock flexibility, meaning the same reactor, in principle, can be used to convert biomass, plastics and rubbers from waste tyres. This co-pyrolysis of different feedstocks provides further pathways to improve TPO composition and yield [33].

Aside from the general push to cut CO_2 emissions, light and heavy-duty road transport sector has its own country-specific (or EU-wide) fleet-level CO_2 targets. The off-road sector is currently discussing the adoption of similar limits, while the marine sector has its EEDI (Energy Efficiency Design Index). Without going into detail, it is sufficient to say that, because all initiatives refer to tank-to-wheel CO_2 emissions, none of them actually supports development of diesel-like alternative fuel. This applies equally to TPO, FAME and HVO since all have a similar carbon to hydrogen ratio, dependent more on the feedstock and refining processes rather than on the fuel category itself.

The constraints for TPO as a fuel are mostly dependent on the domain where the fuel is intended for use. In the road transport sector, EN 590 defines the fuel properties for compression ignition engines. Crude TPO does not comply with EN 590 as a stand-alone, drop-in fuel because of its high viscosity and large amounts of impurities [12]. Thus, most authors typically consider blending TPO with DF and/or other alternatives. The other commonly considered option is further refining to produce TPO more compliant with EN 590, with distillation as one of the more straightforward methods [14]. Poor miscibility with diesel is another constraint if TPO is considered as an additive [31]. In terms of further upgrading TPO, standard refinery infrastructure can be used to treat crude TPO with similar processes as those for fossil crude oil or vegetable oils, including hydrotreating, to arrive at ultra-clean distillates. These are covered in detail in sections 3 and 4, considering both energy demand/quality and end use in engines.

The properties of crude TPO do not disqualify its use in CI engines as such. The marine domain is still quite inclusive in terms of fuel quality. At the moment, the ISO 8217 standard governs bunker fuel quality, and crude TPO, depending on the process and feedstock quality, can be directly considered in one of heavy fuel oil (HFO) categories. Also, heavy fractions from distilled tyre pyrolysis oil (DTPO) can be used to valorise the off-stream from lighter distillates production. High viscosity and high contamination do not pose a challenge, because HFO marine engines use on-board fuel pretreatment (centrifugal separators and preheaters). However, sulphur legislation might be challenging for TPO. The 2020 International Maritime Organization (IMO) sulphur cap limits a fuel's total sulphur content to 0.5 % on all international waters [14,34]. In the IMO's Emission Control Areas (ECAs) the fuel's sulphur limit is only 0.1 % [14]. Although crude TPO's actual sulphur content depends on the quality of feedstock, it poses a challenge even for marine fuels.

Aside from the fuel standards outlined above, emissions legislation has an indirect impact on fuel phase-in. Currently, all domains where combustion engines operate are subject to strict emission limits. In Europe, Euro 6 is in force for light- and heavy-duty vehicles, limiting emissions of nitrogen oxides (NO_X), unburnt hydrocarbons (UHC), carbon monoxide (CO) and particulate matter (PM). Stage V regulations cover the off-road sector (including inland waterways), but impose slightly less stringent NO_X, UHC and CO limits, dependent on engine power output. In the marine sector, the IMO imposes NO_X limits: Tier III regulations apply in ECAs and Tier II regulations apply in waters outside the ECAs. For a complete overview of current emission norms, the reader is referred to DieselNet: Engine & Emission Technology Online [35].

The case of how emission legislation either supports or suppresses individual fuel alternatives has three dimensions. One is the engine-out emissions (i), where different fuels have a different internal predisposition to creating certain hazardous species. The second factor (ii) relates to how the fuel affects engine performance, since all emission limits are given in values specific to generated power. Finally, (iii) all of the discussed emission legislation currently in force, except IMO Tier II, require some sort of exhaust gas aftertreatment for CI engines to meet the imposed limits. However, TPO can have a profound effect on performance of catalysts used in aftertreatment. Section 4 of this review (Engine tests) looks in more detail at the TPO studies that evaluated legislated and unlegislated emissions.

1.3 Motivation, knowledge gaps and detailed scope of the present work

The above introduction clearly shows that ELTs are an attractive feedstock for energy generation. Pyrolysis as fuel production technology has potential to combine clean utilisation of tyres with an efficient way of material recycling and energy recovery, while avoiding the food-fuel dilemma. Furthermore, the flexibility of the reactor permits greater feedstock availability through co-pyrolysis of other synthetic waste (plastics) and biomass. In the face of the global CO_2 reduction targets, this seems to be increasingly recognized. The main hurdles for TPO to overcome relate to legislation, production technology development and the technical aspects of its use as an engine fuel. In all of those fields, there is currently rapid development regarding TPO and many research works are bringing new insights, greater knowledge and more efficient solutions. This is communicated in original research papers but there are also broader review works that summarise progress. Reviews by Torretta [8] and Antoniou and Zabaniotou [4] provide good insight into legislation, feedstock availability and detail forecasts for ELTs management stream. The latter review by Antoniou and

Zabaniotou [4] is by far the most comprehensive study covering the topics of tyre waste handling through pyrolysis. It has an extensive review of the production process, pyrolysis kinetics and its products, including TPO. This study gives an excellent overview of the topic yet it does not cover the fuel applications in great depth and does not reflect the current state of the art in end-user validation of TPO fuels through engine tests. Furthermore, it is now seven years since the study was published, a period that has seen significant development in tyre pyrolysis technology.

In terms of the fuelling applications, the knowledge gap is partially filled by a more recent review by Czajczyńska et al. [36]. This work is very detailed but focuses solely on the gaseous fraction. Furthermore, the combustion applications are limited solely to furnace combustion, providing heat to the pyrolysis process itself. Due to higher energy density (by volume) and easier logistics, it is the liquid fraction of pyrolysis (TPO), not the gaseous fraction, that holds potential as a transport fuel.

The last decade has seen a surge in research into TPO's use as combustion engine fuel. Grasping the current status is very difficult due to the wide discrepancy in TPO quality, different blending strategies and the variety of engine platforms used hitherto. It was this combination of rapid progress, coupled with the difficulty of building a complete and accurate picture from so many disparate studies of TPO's use for combustion engine applications, that motivated us to bridge this substantial knowledge gap. The research questions addressed here are as follows:

i. What is the progress in pyrolysis technology with respect to maximizing the TPO yield and resulting fuel quality?
ii. What are the available TPO-upgrading technologies and what is their effect on the end fuel quality?
iii. How do different fuel compositions of TPO and TPO-derived fuels perform in the engine in terms of combustion characteristics, efficiency and emissions?

As well as finding knowledge gaps, we recognize that there is not widespread familiarity with TPO as an alternative fuel for combustion engines. So, aiming to provide a complete picture, this review also provides an updated description of the state-of-the-art process for tyre pyrolysis. The level of detail is sufficient to understand the dependencies and to valorise the of-streams. This is covered in section 2 along with providing the input necessary for the research question (i). Consequently, the remaining input for research questions (i) and (ii) is gathered in section 3. Section 4 provides a critical review of all aspects of the research question (iii). The introduction section provides the necessary legislative framework to conduct the review in all sections. Finally the discussion and summary in section 5 combine the individual inputs into a concise roadmap of TPO fueling applications.

The work is directed to scientists and engineers working in the fuel industry and engine technology. The automotive and aviation sectors are already claiming over 90% of available biofuel supplies, living limited alternatives on the liquid fuel side for the marine (and off-road) sector. Thus these sectors might be particularly interested in the work. Hence the discussion is led with both automotive and bunkering fuel legislation in mind. All sectors are considered when assessing engine emissions.

2 The state of the art in tyre pyrolysis

2.1 The role of pyrolysis when processing ELT into TPO

Pyrolysis is described as an incomplete process of thermal degradation taking place in the absence of air, generating char, liquids, tars and gaseous products [37]. Fig. 2. shows the typical tyre decomposition route through pyrolysis. The tyres' steel components are removed before thermal processing and rubber parts are chopped, cleaned and dried. Tyre pyrolysis generally consists of two stages: primary pyrolysis and secondary cracking. During the initial phase the vapour or volatile products are generated, consisting of a variety of hydrocarbons. The liquid product is TPO, while the gaseous fraction can be re-used to power the pyrolytic reactor and make the process self-sustainable in energy terms. Crude TPO can be further processed. That usually involves sulphur removal, distillation and cracking. In practice, the end fuels for engines are produced from TPO via fractionation (fraction blending to obtain desired fuel properties) and thus are referred to as DTPO [38].

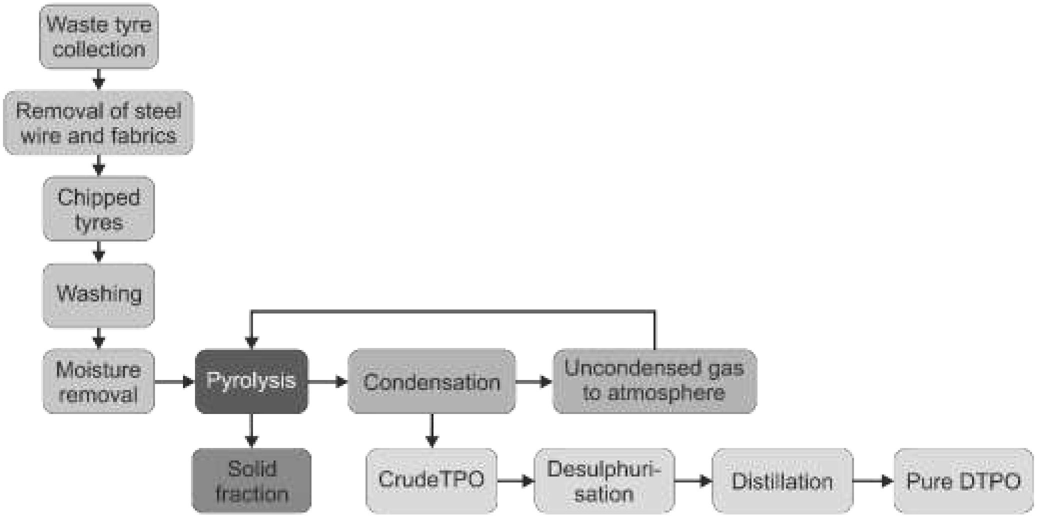


Fig. 2. Tyre decomposition through the pyrolysis route.

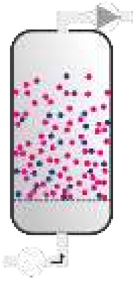
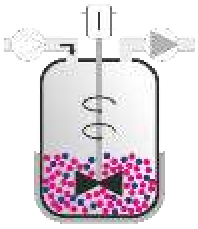
2.2 Mechanisms of tyre pyrolysis

Commonly used types of pyrolysis process reflect the residence time: slow, fast and ultra-fast. Looking at the type of reactor used, these can be: fixed, moving, fluidised, spouted and vacuum types (refer Table 1 for detail). There are also some novel technologies, such as microwave [39,40] and ultrasonic [41–43]. Moreover, various catalysts can be used to increase the yield in a process called catalytic pyrolysis [44–52]. Typical catalysts are copper nitrate, ZSM-5 zeolite, magnesium oxide (MgO), calcium carbonate ($CaCO_3$), sodium hydroxide (NaOH), sodium carbonate ($NaCO_3$), zeolite and activated alumina. Finally, it should be noted that there is a processing technology that allows pyrolysis of whole tyres [53]. It was achieved via a special reactor shape, designed to accommodate a pile of 10 tyres.

Comparing slow and fast pyrolysis [54] summarized that the slower process is related to a lower decomposition rate and temperature, coupled with a longer heating rate and residence time. Fixed bed reactors are normally used for slow pyrolysis whereas rotary kiln and fluidized bed reactors are the main types for fast processes. Furthermore, the main product of slow pyrolysis is a solid fraction, while fast pyrolysis gives liquid fraction.

The atmosphere (the injection of gases or vapour) is an important variable during pyrolysis because it can affect the process. Gases that are used to replace atmospheric oxygen during pyrolysis are steam, nitrogen and helium (see Table 1). The gasses hinder the generation of oxides and limit the partial pressures of substrats. The second phenomena reduces of the condensation rate of aromatics, and supports carbon-black binidng. Ramirez-Canon et al. [55] and Kan et al. [56], independently presented that an enhancement of TPO can be obtained by the use of hydrogen as an inert gas, stabilising the hydrocarbons chains. It works through gas fractions formation and the reduction of the re-polymerisation process during pyrolysis,

Table 1. Type of reactors used during pyrolysis process

Type of reactor	Inert gas used	References	
fluidised bed 	nitrogen	Lee et al. (1995)	[57]
	helium	Williams and Besler (1995)	[58]
	nitrogen	Rodrígez et al. (2001)	[59]
	nitrogen/steam	Kaminsky and Mennerich (2001)	[60]
	steam	Dai et al. (2001)	[61]
	nitrogen	Williams and Brindle (2002)	[44]
	helium	Díez et al. (2004)	[29]
	nitrogen/pyrogas/steam	Kaminsky et al. (2009)	[62]
	nitrogen	Raj et al. (2013)	[63]
	n.a.	Choi et al. (2014)	[64]
	ultra helium	Zhang et al. (2014)	[65]
	nitrogen	Wang and Jan (2018)	[66]
fixed bed 	n.a.	Mastral et al. (2000)	[67]
		Mastral et al. (2002)	[68]
	nitrogen	Ucar et al. (2005)	[69]
	nitrogen	Berrueco et al. (2005)	[70]
	n.a.	Murillo et al. (2006)	[71]
		Islam et al. (2008)	[72]
		Acevedo et al. (2013)	[73]
		Choi et al. (2013)	[74]
	nitrogen	Khan et al. (2016)	[75]
	n.a.	Hopa et al. (2017)	[76]
		Aziz et al. (2018)	[77]
moving bed	n.a.	Aylón et al. (2008)	[78]
	nitrogen	Aylón et al. (2010)	[79]
vacuum 	n.a.	Roy et al. (1990)	[80]
		Benallal et al. (1995)	[81]
		Chaala and Roy (1996)	[82]
		Roy et al. (1997)	[83]
		Roy et al. (1999)	[84]
		Rombaldoa et al. (2008)	[85]
		Zhang et al. (2008)	[48]
		Vihar et al. (2015)	[86]
		Tudu et al. (2016)	[87]
not specified	nitrogen	González et al. (2001)	[20]
	helium	Seidelt et al. (2006)	[88]
	nitrogen	Dũng et al. (2009)	[89]
	nitrogen	Kar (2011)	[49]
Other reactor types			
spouted bed reactor  López et al. (2010), Alvarez et al. (2017)	stirred tank reactor  Ayanoğlu and Yumrutaş (2016) Ramirez-Canon et al. (2018)	rotary (auger) reactor  Martínez et al. (2014) Choi et al. (2016)	respectively [38,90] [50,55] [11,91]

The process of thermal decomposition is most often characterised by curves of the mass loss versus temperature. Thermogravimetry, often called thermogravimetric analysis (TGA), is an analytical technique that measures the mass over a period of time as the temperature changes [58]. So-called derivative thermogravimetry (DTG) functions, using the same method but with different presentation data, are used to show the rate of decomposition.

The tyre rubber pyrolysis process TGA curve in Fig. 3 exhibits two main stages. The first is the slow stage, related to the decomposition of oils, plasticisers and additives present in rubber. The second is the active pyrolysis stage which involves cracking and rapid decomposition of the other rubber components. The intermolecular associations and weaker chemical bonds are destroyed during this second stage, resulting in gas and liquid fraction separation. Beyond a certain temperature, active pyrolysis is essentially completed, with only minor weight loss thereafter. This interpretation of pyrolysis mechanisms was introduced by Williams and Besler [58] and commonly adopted by others, e.g. Juma et.al [92].

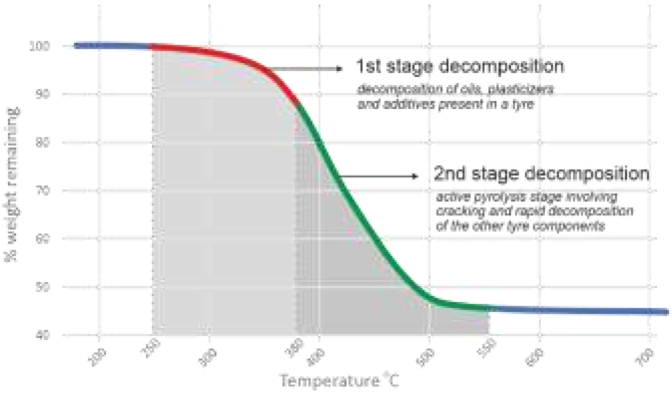


Fig. 3. Typical TGA curve for pyrolysis process, based on [93].

Leung et al. [37] stated that the first stage's temperature range was between 150 °C and 350 °C. This where oil, moisture, plasticisers and other additives decomposed. During the second stage, above these temperatures but below 550 °C, natural polybutadiene and polybutadiene-styrene rubbers (NBR and SBR respectively) were decomposed. Using DTG function, the maximum decomposition rates were observed at approximately 380 °C and 450 °C. Pradhan and Singh [93] conducted a TGA analysis of waste bicycle tyres in a laboratory-scale batch reactor. They observed that the first stage of decomposition occurred at between 250 °C and 380 °C, followed by the second stage at between 380 °C and 550 °C. This is depicted in Fig. 3. Above 550 °C, the decomposition process was practically finished. TGA analysis conducted by Berrueco et al. [70] presented the thermal decomposition of a used car tyre (Michelin radial X type) sliced into 20 mm × 20 mm pieces. Decomposition started at 200 °C and complete conversion of the sample had occurred when the temperature reached 500 °C. However, the cited authors isolated three stages. The first was between 200 °C and 325 °C, the second between 325 °C and 400 °C and the third stage was between 400 °C and 500 °C. A DTG analysis of tyre pyrolysis by Seidelt et al. [88] proven that curves of a rubber DTG were characterised by three temperature peaks, such as at 378 °C, 458 °C and 468 °C. The cited authors attributed the first step to depolymerisation of the BR, while at 468 °C the decomposition of the cyclised and cross-linked polymer residue was observed. Han et al. however, conducting a thermogravimetric mass spectrum analysis of waste tyres, identified four stages of this product's thermal decomposition [94]. The first stage started below 320 °C and contributed a minor reduction of mass due to vaporisation of water and decomposition of plasticiser. The next stage occurred at 320-400 °C and related to the decomposition of natural rubber. The third stage, at 400-520 °C, involved the decomposition of synthetic rubber. Very little weight loss was observed during the fourth and final stage, above 520 °C.

2.3 Process efficiency and oil fraction yield

Maximising the yield of TPO is essential from the perspective of CO_2 efficiency in many applications, particularly those without valorisation of the off-streams. Much research has focused on process efficiency, with temperature being one of the most important parameters in this endeavour. The literature, however, presents three partially contradictory trends with regard to the impact of pyrolysis temperature on oil yield.

The first trend (i) implies a more or less monotonic increase of TPO mass with process temperature. That tendency was reported by amongst others: Murillo et al. [71], Rombaldo et al. [85], Dũng et al. [89], Pradhan and Singh [93] and Luo and Feng [95]. Examining the effect of operating conditions in a vacuum pyrolysis reactor at 400 and 600 °C, Rombaldo et al. compared it with a steam-activated process at 700, 800, and 900 °C [85]. Shredded tyres from the same batch were used as feedstock in both cases. The authors observed a similar increase in mass fraction yield in both processes. Dũng et al. [89] conducted catalytic pyrolysis at 500, 600 and 700 °C and reported respective TPO yield efficiencies of 40 %wt., 41.7 %wt. and approximately 44 %wt. The cited authors also found that higher amounts of polar-aromatics were identified in the produced TPO as the temperature increased. Murillo et al. [71] carried out tyre pyrolysis in a fixed-bed reactor, in a nitrogen atmosphere and raising the temperature in 100 °C increments from 100 °C to 700 °C. They noted corresponding yield efficiencies from 37 %wt. to 45 %wt. The conversion yield increase was the most intensive at 300-400 °C. At 400 °C the yield was 43.7 %wt. but beyond that temperature the conversion rate increased very slowly towards 45 %wt.

Luo and Feng [95] conducted catalytic co-pyrolysis of waste tyres and blast-furnace (BF) slag. The experimental conditions included variable process temperature (600, 800 and 1000 °C), while sweeping the ratio of BF slag to tyre powder from 0.2:1 to 1.0:1 The TPO yield increased clearly with temperature and, less evidently, with BF slag to tyre powder ratio. The maximum conversion efficiency was observed at the highest temperature and a ratio of around 0.8. Díez et al. [29] carried out pyrolysis in a helium atmosphere at three temperatures: 350, 450 and 550 °C. They observed a gradual increase in TPO yield: respectively 30, 33, and 38 %wt. The limited temperature range makes it difficult to unambiguously determine whether saturation or change in monotony occurred in this type of pyrolysis process. Interestingly, the authors revealed that at the elevated reaction temperature, the TPO was characterised by higher carbon and sulphur content, while the oxygen content decreased. What is more, the higher and lower heating values (HHV and LHV respectively) increased with pyrolysis temperature. In contrast, Rodríguez et al. [59] and Aylón et al. [79] did not observe any significant changes in the elementary composition of TPO obtained by pyrolysis conducted while the temperature increased from 300 °C to 700 °C in 100 °C increments and at 600-800 °C.

Another group of reviewed works reported similar trends as described above in medium temperature ranges, yet claimed the existence of a distinct extremum (maximum) in TPO yield with temperature. This is more often reported as saturation at certain temperature levels, the second (ii) of the three trends. Berrueco et al. [70] carried out pyrolysis of waste tyres in an atmospheric-bed batch reactor at temperatures between 300 °C and 700 °C. There was a lack of sensitivity in TPO yield below 400 °C but yield was observed to gradually increase as the temperature rose from 400 °C to 500 °C and reached a maximum at this measurement point. Further temperature increase did not affect pyrolysates yields. Similar results were presented by Rodríguez et al. [59], conducting pyrolysis at a wide range of temperatures (300, 400, 500, 600 and 700 °C) in a nitrogen atmosphere. The cited authors observed that a significant yield increase occurred at 300-500 °C and peaked at 500 °C (38.0 %). The yield remained at a similar level at temperatures above 500 °C. The same tendency was noticed for the gaseous fraction. Laresgoiti et al. [96] carried out pyrolysis in identical conditions to Rodrígez et al. [59] and presented the same results. Laresgoiti et al. [97] observed the same tendency in earlier work too. Aydın and İlkılıç [98] also noticed that the maximum TPO yield (40%) was achieved at 500 °C and that it remained at a similar level as the temperature was increased to 750 °C. However, the cited authors observed no correlation between gases and oil fractions formation, contrary to the results of previous scientific works.

The mentioned work by Pradhan and Singh [93] reported high TPO yield in a laboratory-scale batch reactor fed with scrapped bicycle tyres in 10 mm chunks. The peak TPO conversion (49.6 %) was reported at 600 °C, a considerably higher temperature than in the other referred works by Berrueco et al. [70], Rodrígez et al. [59], Laresgoiti et al. [96,97] and Aydın and İlkılıç [98]. The temperature dependency of TPO yield was explained, following Islam et al. [72] (originally referring to Cunliffe and Williams [99]), by strong cracking of tyre rubber during second-stage reactions in the mid-temperature range (Fig. 4.). The insensitivity of TPO yield to temperature, after reaching the maximum yield point, following Rodrígez et al. [20] and Nisar et al. [100], can be explained with the observation that the liquid fraction was subsequently cracked to a gaseous fraction. This was further attributed to the rapid extraction of generated products from the autoclave.

Results presented by González et al. [20], and Dai et al. [61] also indicated that peak TPO yields were reached at a certain temperature (respectively, 55.6 % at 550 °C and approximately 50 % at 450 °C). However, further increases in temperature (explored range up to 700 and 800 °C respectively) led to a reduction in oil fraction. This was correlated with the increase of the gaseous fraction yield. Mkhize et al. [101] analysed the effects of the temperature and heating rate on TPO yields, using a fixed-bed, slow pyrolysis reactor with a nitrogen atmosphere. They established for individual temperatures (309, 350, 450, 550, 591 °C) that the maximum oil fraction yield varied greatly depending on the heating rate (0.86, 5, 15, 25, 29.14 °C/min). Generally, the best results (around 45 % oil mass fraction yield) were achieved in medium ranges of temperatures and heating rates.

The third general trend (iii) implies that TPO yield decreases with increasing temperature. This was reported by Williams and Brindle [44], Galvagno et al. [102], Mastral et al. [68] and Aylón et al. [79]. Aylón et al. [79] conducted nitrogen atmosphere pyrolysis at 600, 700 and 800 °C. They observed that as the temperature rose there was a significant decrease in TPO yield fraction, an increase of gas fraction and a relatively constant solid fraction yield. The decrease of the oil fraction and an increase of gases were explained by the cracking of liquids. The same tendency was found by Galvagno et al. [102], who examined three pyrolysis temperatures: 550, 600 and 680 °C. The highest TPO yield (38.12 %) occurred at 550 °C while the lowest (31.82 %) was at 680 °C. The gas fraction yield increased from 2.39 % at the lowest pyrolysis temperature to 10.75 % at the highest.

Williams and Brindle [44] conducted pyrolysis using Y-zeolite (CBV-400) and ZSM-5 catalysts. While examining the effect of different catalyst bed temperatures (400-600 °C, at 50 °C increments) they found the highest TPO yield (40 % and 45 % for each catalyst respectively) in the temperature range of 425-475 °C. Further increases in temperature increased gaseous fraction production but reduced the oil fraction: it was approximately 33% at 600 °C for both catalysts. It is worth noting that in the cited work, pyrolysis was also conducted without the catalyst, which actually resulted in higher TPO yield (55.8 % at 500 °C). A gradual decrease of TPO yield with increasing temperature was clearly observed in the work of Mastral et al. [68], where the maximum yield was found at an initial temperature of 450 °C.

In summary, the current state of the art in tyre pyrolysis is capable of achieving a crude oil mass fraction yield of around 55%. But with a large spread of yields reported by different authors, depending on reactor setup and test conditions, even this value shows further optimisation potential, especially if co-pyrolysis of tyre and biomaterial is considered [5]. The studies in this direction are just beginning. Most studies aimed at optimising the yield of tyre pyrolysis focus on process temperature, with other parameters, such as heating rate and mixing, as secondary measures. Despite identifying different trends, most authors underline that pyrolysis temperatures between 450 °C and 600 °C are most efficient in terms of TPO production versus energy consumed by the process itself. This was assessed by the individual authors, mostly on a high level (i.e. without quantification), as a trade-off between process energy requirement (increasing with temperature), complete reaction time (decreasing with temperature) and maximum TPO yield achieved. This efficiency-optimised temperature range should be taken into account when assessing TPO in terms of composition (reviewed in detail in subsection 2.4.3) and resulting physicochemical parameters (covered in subsection 3.1). Both parameter groups are dependent on process temperature and are relevant to the end-use engine performance (discussed in section 4).

In terms of energy efficiency it is sufficient to say that when optimised for oil production, pyrolysis can be self-sustainable, with only around 9.5 % of total tyre energy used to power the process and with only around 2 % of total energy released to the ambient surroundings [103]. The rest of the products can be properly valorised. The process Sankey diagram (Fig. 4.) showing the energy flow uses averaged heating values and yields of the individual fractions, garnered from the detailed review in section 2.3 and 2.4. Figure 4 is considered self-explanatory and left without detailed comments.

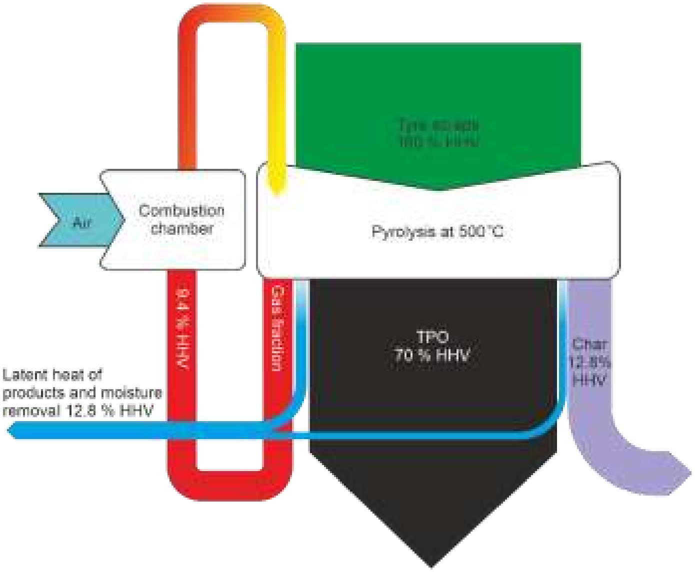


Fig. 4. Sankey diagram for tyre pyrolysis at 500 °C. Averaged values for HHV and yields based on data gathered in section 2.

2.4 General characterisation of pyrolysates

2.4.1 Solid fraction

The solid fraction is made up of hydrocarbons with more than 10 carbon atoms and consists of aromatics, non-aromatics and ingredients containing sulphur, nitrogen and oxygen [104]. Analysing the elemental composition of solid fraction, De Marco Rodriguez et al. [59] found that it was predominantly carbon, accounting for approximately 83 % by weight. The share of other compounds was significantly lower. Hydrogen was 2.4 %wt. at 400 °C and approx. 0.6 %wt. at 500, 600, 700 °C. Nitrogen was approx. 0.3 %wt., sulphur was approx. 2.4 %wt. Oxygen and others accounted for approximately 1 %wt. The cited authors also found that the obtained pyrolytic residues were characterised by the concentration of ash (from 9.0 to 13.2 %wt.), far higher than for commercial carbon black, which has an admissible concentration of no more than 0.5 %wt. The ash in the pyrolytic residues comes from the original tyre inorganic fillers. Lopez et al. [90] presented that tyre rubber ashes consisted of ZnO (48.01 %wt., SiO_2 (35.17 %wt.), SO_3 (4.59 %wt.), Al_2O_3 (3.91 %wt.), CaO (1.84 %wt.), K_2O (1.12 %wt.), Fe_2O_3 (0.89 %wt.), P_2O_5 (0.85%wt.), MgO (0.68 %wt.), TiO_2 (0.17 %wt.).

The solid fraction obtained by tyre pyrolysis can be used as a solid fuel [105], a carbon black for rubber manufacturing [59], a filler in road bitumen [106–108] or an adsorbent material. For the latter application, however, the carbon residue requires activation, which may be accomplished by either physical or chemical methods [4,109–111]. Physical activation is conducted by partial gasification using steam or CO_2 as activating agents [109,110,112]. Chemical activation entails treating the char with nitric acid, hydrogen peroxide, ammonium persulfate or impregnated by potassium hydroxide and phosphoric acid: these act as a dehydrated activating agent [4,111].

2.4.2 Gaseous fraction

The gaseous compounds include H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and slight amounts of higher hydrocarbons [20,44,61,70,102,113–117]. Note, however, that Rodríguez et al. [59] and Lopez et al. [110] amongst others did not identify the presence of H_2 in the generated gases. Table 2 provides a comprehensive review of gas fraction composition for different pyrolysis processes.

Table 2. Basic characterisation of pyrolytic gases fraction

Temp.	Basic gases fraction composition (%vol.)												Calorific value	References	
	H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	$C_{2+}H_n$	$C_{3+}H_n$	C_3H_8	C_4H_8	H_2S	others			
350	0.02	0	0.08	0.04	0	0	n.a.	n.a.	n.a.	n.a.		n.a.	12.40 MJ/Nm^3	González et al. (2001)	[20]
400	0.29	0.1	0.33	0.13	0	0							11.97 MJ/Nm^3		
450	0.48	0.27	0.57	0.4	0.07	0.1							19.86 MJ/Nm^3		
500	0.52	0.4	0.52	0.56	0.17	0.39							28.37 MJ/Nm3		
550	0.47	0.33	0.41	0.63	0.24	0.81							36.74 MJ/Nm^3		
575	0.51	0.28	0.52	0.9	0.28	0.94							37.33 MJ/Nm^3		
600	0.81	0.5	0.46	1.4	0.34	1.42							38.59 MJ/Nm^3		
700	2.64	0.43	0.59	4.93	1.05	4.57							42.87 MJ/Nm^3		
400	n.a.	4.2	10.7	4.4	4.5	4.3					2.6		84.0 MJ/Nm^3	Rodríguez et al. (2001)	[59]
500		4.8	9.4	19.8	9.1	9.4					5.1		75.5 MJ/Nm^3		
600		6.5	8.8	20	9	9.7					3.6		75.3 MJ/Nm^3		
700		10.4	11.4	20.6	8.1	8.9					3.9		68.5 MJ/Nm^3		
550	0.49	0.1	0.21	0.22	0.17	0.16					0.08		5268 kcal/Nm^3	Galvagno et al. (2002)	[102]
600	1.4	0.31	0.7	1.11	0.67	0.67					0.21		5732 kcal/Nm^3		
680	1.13	0.52	0.69	2.45	1.02	1.32					0.22		6938 kcal/Nm^3		
500	0.16	0.09	0.32	0.81	0.3	1.16					n.a.		n.a.	Williams and Brindle (2002)	[44]
500	0.39	0.11	0.15	2.45	1.28	1.19									
500	0.37	0.09	0.13	0.79	0.65	2.53									
800	20.7	2.6	1.8	44.5	4.4	17.3							38.10 MJ/Nm^3	Leung et al. (2002)	[113]
500	21.5	5.1	26.2	17.3	8.2	8.7							30.30 MJ/Nm^3	Kyari and Williams (2005)	[114]
400	2.61	1.08	1.41	1.02	0.43	0.25							n.a.	Berrueco et al. (2005)	[70]
500	14.17	0.25	1.01	4.29	1.54	0.66									
550	17.86	0.26	0.78	5.64	1.75	0.83									
700	10.1	0.38	1.18	5.43	1.56	1.15									
500	0	n.a	2	0.19	0.16	0.49								Lopez et al. 2009	[110]
600	19.39	18.63	17.03	18.25	n.a.		7.36	13.8			1.79			Luo et al. (2010)	[115]
700	22.07	17.78	13.76	14.73			11.8	14.51			1.86				
800	28.18	16.02	10.26	12.69			13.54	12.76			1.41				
900	32.24	10.57	8.84	17.01			12.81	11.43			1.8				
1000	39.06	8.11	9.5	9.32			17.03	9.81			1				
550	22.27	1.98	2.54	21.32	4.19	2.32	n.a.	n.a.			n.a.		68.70 MJ/Nm^3	López et al. (2011)	[116]
550	7.9	9		9.9	5.9						2.9		65.60 MJ/Nm^3	Fernández et al. (2012)	[117]
497	n.a.	0.5	1.1	0.7	0.4	0.5			0.5	2.6	n.a.	1.2	n.a.	Choi et al. (2016)	[91]
614		1	1.1	5.7	1.9	1.9			1.9	3.4		2.1			
516		0.4	2.2	0.6	0.3	0.5			0.6	4.9		1.7			
617		0.8	3.6	2.1	0.7	1.7			1.9	6.2		3.4			
506		0.4	0.6	1.7	0.5	0.6			0.5	1.4		1.1			
511		0.8	1.1	2	0.6	0.9			0.7	1.8		1.5			
616		0.3	0.4	1.1	0.4	0.4			0.4	1		0.8			

Laresgoiti et al. [97] suggested that light hydrocarbons are formed as a result of SBR rupture but Berrueco et al. [70] explained that those compounds can be generated from secondary cracking reactions. González et al. [20] found that the presence of CO and CO_2 in the gaseous fraction resulted from the decarboxylation and decarbonylation reactions, or from the carbon's secondary oxidation reaction. On the other hand, hydrogen and methane are generated as a result of secondary aromatisation reactions. Furthermore, Martínez et al. [118] explained compounds consisting of C_4 are formed as a consequence of BR and SBR thermal degradation.

The composition of the gaseous fraction generated during pyrolysis is determined by the process condition (Table 2). Dai et al. found that with increased temperature (from 350 to 800 °C) the amounts of CH_4, H_2, CO also increased, while CO_2 and higher hydrocarbons decreased [61]. Furthermore, the cited authors observed that the yield of unsaturated C_2H_4 and C_3H_6 exceeded the yield of saturated

C_2H_6 and C_3H_8, as a consequence of the decomposition of saturated compounds to unsaturated ones. Furthermore, Dai et al. [61] explained that the observed changes in gases profile are attributed to the reactions of char reduction, cracking of the char and shift reactions. On the other hand, González et al. [20] noticed that concentration of almost all identified gases gradually increased with the increase of temperature from 350 to 700 °C. The exceptions were CO and CO_2, in which case the concentration was not differentiated by temperature. The cited authors also found that while increasing the pyrolysis temperature, the higher heating value (HHV) of the produced gas also increased, from 12.40 MJ/Nm3 at 350 °C to 42.87 MJ/Nm3 at 700 °C.

On the other hand, an inverse tendency was presented by Rodrígez et al. [59]. The observed trend in calorific value resulted from rather complex temperature dependencies in the individual species creation. The concentrations of CO and CH_4 gases gradually increased with temperature. In the case of C_2H_4 and C_2H_6, their concentrations reached the maximum at 600 °C; further elevating the temperature resulted in their faster decomposition. Furthermore, the CO_2 and N_2 balance in nitrogen atmosphere pyrolysis accounted for an overall reduction in heating value. Interestingly, the produced gas contained hardly any H_2, but rather high amounts of hydrogen sulphide (H_2S) were recorded.

Small concentrations of hydrogen sulphide were also recorded by Galvagno et al. [102], Fernández et al. [117] and Luo et al. [115]. The latter also reported an exceptionally high concentration of hydrogen in the pyrolytic gas, ranging from roughly 20 % to almost 40 % for the lowest and the highest process temperatures respectively. The authors attributed this to the catalyst effect. Relatively high concentrations of hydrogen (17-22 %) were also noted by Leung et al. [113], Kyari and Williams [114], López et al. [116] and Berrueco et al. [70]. In all these cases the pyrolysis process was supported by catalyst addification.

Galvagno et al. [102] investigated the changes in gas fraction composition during a temperature increase from 500 °C to 680 °C. They found that concentrations of almost all identified gases, such as CO, CO_2, CH_4, C_2H_6, C_2H_4 and H_2S were increased. The exception was H_2 concentration, which peaked at 600 °C. On the other hand, Berrueco et al. [70] found that temperature had a different influence on the formation of the gases fraction profile. Concentrations of CH_4 and C_2H_4 increased with temperature, while CO decreased. In the case of H_2 and C_2H_6, it was observed that concentrations of these gases increased up to 550 °C but decreased at 700 °C. The inverse trend was noted for CO_2 concentration. Luo et al. [115] observed the effects of incremental 100 °C temperature increases across a wide range of 600 – 1000 °C. Concentrations of H_2 and C_2+H_n gases increased, while CO, CO_2 CH_4, and C_3+H_n were reduced. Looking at the effect of catalysts on pyrolysis, it was observed that the presence of the catalyst contributed to the significant increase in the concentration of identified gases. The exception was observed for CO_2 [44] .

The obtained gaseous fraction is characterised by good heating value, mostly from 30MJ/Nm3 [114] to approximately 80MJ/Nm3 [59]. Theoretically, after desulphurisation, it could be used for combustion engine applications, especially as a complement to natural gas or liquefied petroleum in a gas network, providing large scale availability and infrastructure compatibility. It is customary for the gaseous fraction to provide internal heat for the pyrolysis process itself. The pyrolytic off-gas may cover the full energy needs of a pyrolysis plant optimised for liquid yield [4]. Bearing that in mind, combustion engine applications of pyrolytic gases will not be considered further in this work.

As a side note, one shortcoming of the available literature is that neither of the studies focused on analysing the gas fraction yield revealed data regarding the liquid fraction. It would be interesting to assess how heating value and mass fraction yield of one fraction impacts the other. It seems likely that there is a trade-off between fractions here, so this has to be taken into account when critically assessing the results discussed above.

2.4.3 Liquid fraction (tyre pyrolysis oil – TPO)

Oil fraction obtained as a result of tyre pyrolysis (TPO) is composed of hydrocarbons between C_5 and C_{20} and is generally a mixture of alkanes, alkenes and aromatic compounds

[20,62,71,84,89,95,104]. The exact composition depends on the type of feedstock and parameters of the process[20,62,71,84,89,95,104].

Debek and Walendziewski [53,119] performed pyrolysis at the relatively low temperature of 400 °C. The TPO produced in this process, on a mass basis, consisted of approximately 11.9 % alkanes, 7.7 % dienes, 4.5 % cycloalkanes, 3.7 % cycloalkenes and 47.4 % aromatic hydrocarbons. Arabiourrutia et al. [104] found that increasing the pyrolysis temperature from 425 °C to 610 °C increased the share of aromatics almost three-fold. The aromatics content (unfavourable for engine applications due to their contribution to in-cylinder soot production) reached 16.44 % of the total TPO mass at the highest pyrolysis temperature. But even that was three times less than aromatics content obtained by Dębek and Walendziewski [119]. Simultaneously, the non-aromatic compounds ($C_5 – C_{10}$) decreased from 30.48 %wt. at 425 °C to 23.70 %wt. at 610 °C. This increase in aromatics was associated with a reduction in liquid fraction yield, which was mainly due to the reduction in C_{10} lump. Furthermore, the cited authors noted that the predominant aromatic compounds presented in the TPO fraction obtained at 425 °C were 1-methyl-4-(1-methylethnyl)-benzene, 1-methyl-4-(1-methylethyl)-benzene, 1,2,3-trimethyl-benzene, 1-methylethenyl-benzene and styrene. These all had concentrations above 0.5 %wt.

Ucar et al. [69] compared the composition of TPO derived from passenger car and truck tyres, processed under identical conditions. They found that the TPO profile from cars is shaped in the following order: paraffins < aromatics < olefins. The TPO profile from heavy-duty truck tyres showed: paraffins < olefins < aromatics. Interestingly, increasing the pyrolysis temperature did not affect the share of the individual types of compounds. The same conclusion was drawn by Murillo et al. [71], who carried out pyrolysis at 400 °C, 500 °C and 600 °C. They found that the share of aromatic compounds was approximately 73 %, amongst them the saturated ones being approximately 6-7 % and polar aromatics contributing 20 % at all temperature conditions.

Research by Rodríguez et al. [59], on the other hand, proved a strong thermal dependency for TPO composition. Similar findings were later mentioned by Arabiourrutia et al. [104] and Choi et al. [91]. The original study by rodrigez Rodríguez et al. [59] observed that the share of aromatic compounds gradually increased from 34.7 % at 300 °C to 75.6 % at 600 °C. Further elevating the pyrolysis temperature to 700 °C reduced aromatic content to 57.4 %. The inverse trend was noticed for aliphatic compounds [91]. The authors, conducting single-stage pyrolysis with an atmosphere of product gas at 497 °C and 614 °C; and with nitrogen gas at 516 °C and 617 °C also noted an inverse correlation between aromatics and aliphatic compounds. Conversion of aliphatic compounds to aromatics resulted from the secondary atomisation reaction, with the Dies-Alder mechanism and condensation occurring at higher temperatures [83,99,120].

Rodríguez et al. [59] stated that the correlation between aromatics and aliphatics is related to the recombination reaction among free radicals of these compounds. Choi et al. [91] also observed that the dominant compounds of aromatic fraction, independent from the pyrolysis parameters, were xylenes, while $_{DL}$-limonene was the main aliphatic fraction. The same compounds also dominated in the aromatics and aliphatic fractions during other work by Choi et al. [121], irrespective of the process conditions. That work was conducted with an auger reactor and a fluidised bed reactor, using different fluidised bed material (natural dolomite and natural olivine).

Table 3 summarises the elemental composition of different TPO samples reported by individual authors and compares it the composition of typical fuels, including those for engine and furnace applications. The pyrolysis process temperature is also given.

Table 3. Elementary analysis of TPO

References	Temp. (^{o}C)	Experimental conditions	TPO elemental composition (%)				
			C	H	N	S	O + others
[95]	600		78.65	16.97	0.39	1.71	2.37

Luo and Feng (2017)		700	pyrolysing using BF (blast-furance) slag (B/T ratio 1.0)	80.55	15.45	0.58	1.28	3.14
		800		84.23	9.28	0.66	1.76	4.07
		900		87.36	8.10	0.81	1.36	2.37
		1000		88.47	8.03	0.97	1.23	1.30
Rada et al. (2012)	[122]	400	reactor – a quartz tube batch	84.60	14.2	0.20	n.a.	n.a.
Aylón et al. (2010)	[79]	600	reactor – a moving-bed reactor, atmosphere N_2	88.58	10.40	1.43	1.05	
		700		91.00	8.17	1.39	1.12	
		800		90.56	7.66	1.28	0.93	
Ucar et al. (2005)	[69]	650	passenger car tyre	87.57	10.35	<1	1.35	
		650	truck tyre	86.47	11.73	<1	0.83	
Mastral et al. (2002)	[68]	450	reactor – fixed-bed reactor, atmosphere N_2	85.62	11.11	0.20	0.90	
		500		85.59	11.12	0.21	0.91	
		550		85.67	11.08	0.19	0.89	
Galvagno et al. (2002)	[102]	550	reactor – a rotary kiln, atmosphere N_2	85.62	11.55	0.44	2.49	
		600		87.82	9.42	0.55	2.21	
		680		87.35	10.01	0.65	1.99	
Rodrígez et al. (2001)	[59]	300	reactor – an autoclave, atmosphere N_2	86.50	10.70	0.30	1.00	1.40
		400		85.90	10.60	0.30	1.10	2.00
		500		85.60	10.10	0.40	1.40	2.50
		600		86.20	10.20	0.40	1.20	2.10
		700		86.00	10.20	0.40	1.20	2.20
Roy et al. (1999)	[84]	520	vacuum pyrolysis, passenger car tyres	86.5	10.8	0.50	2.20	0.67
		500	vacuum pyrolysis, passenger car tyres with silica filler	87.6	10.50	0.40	1.50	0.69
		485	vacuum pyrolysis, truck tires	87.9	11.2	0.70	0.20	0.65
				Diesel elemental composition (%wt.)				
Ucar et al. (2005)	[69]	diesel fuel		86.50	13.20	<1	<0.70	nd
Nabi et al. (2006)	[123]	diesel fuel		86.80	13.10	-	0.042	0.00
Lotero et al. (2006)	[124]	diesel fuel		87.00	13.00	nd.	0.05	0.00
Buyukkaya (2010)	[125]	diesel fuel		85.40	15.00	nd.	nd.	0.00
				Biodiesel elemental composition (%wt.)				
Lotero et al. (2006)	[124]	rapeseed biodiesel		77.00	12.00	nd.	0.05	11.00
Nautiyal et al. (2014)	[126]	pond water algae biodiesel		71.49	11.00	0.31	0.19	17.01
		Spirulina biodiesel		78.44	12.04	0.20	0.08	9.23
		Karanja biodiesel		78.10	11.39	0.07	0.06	10.39
				Coal elemental composition (%wt.)				
Pietrzak (2009)	[54]	high volatility, bituminous coal		78.10	5.10	1.20	0.70	14.90
		demineralised, ashless coal		78.70	4.80	1.30	0.50	14.70
		demineralised, ashless coal subjected to carbonisation		94.00	1.90	1.10	0.30	2.70
		demineralised, ashless coal subjected to ammoxidation		69.10	2.20	17.3	0.30	11.10
				Wood elemental composition (%wt.)				
Telmo et al. (2010)	[127]	*Pinus pinaster*		48.40	6.00	0.10	0.00	45.30
		Bowdichia nitida		52.30	6.10	0.20	0.03	41.30
		Eucalyptus globulus		46.20	5.80	0.20	0.02	47.20

Analysis of Table 3’s summary of the TPO compositions shows two tendencies are emerging. Luo and Feng [95] found that pyrolysis temperature significantly affected the profile of individual elements: increasing temperature significantly increased the shares of C and N, while the H share gradually decreased. In contrast, Rodrígez et al. [59], Galvagno et al. [102] and Aylón et al. [79] did not observe significant changes in the elemental composition of TPO with temperature.

Crude pyrolytic oil obtained from waste tyres has quality that made it generally suitable for use as fuel in a CI engine. TPO’s heating value of approximately 43 MJ/kg is close those of other engine fuels, such as diesel (43.3 MJ/kg), methane (50 MJ/kg), gasoline (44.4 MJ/kg) and biodiesel (36.8 MJ/kg) [128,129]. It also has similar molecular composition [54,59,84,95,122–127]. The mass-based hydrogen to carbon ratio (affecting tank-to-wheel CO_2 emissions) for crude TPO averages 0.128, similar to that of refined diesel oil.

TPO's properties relevant to its use in a combustion engine are discussed in detail in the following section. One should bear in mind that the TPO's composition, and hence its related combustion parameters, depend on reactor type, inert gas used, process temperature, quality of feedstock and their pre-treatment. Post-treatment (level of refining) will also have a bearing.

3 Pyrolytic oil as engine fuel

Already in the early 1980s, it was found that pyrolytic oil samples and condensates produced by petroleum residues coking (by thermal and steam cracking of gasoil fraction and gasoline) are similar to olefins [84]. For this reason, these products can be blended and thermally treated under the same conditions. Furthermore, Miandad et al. [52] suggested that TPO generated by catalytic and non-catalytic pyrolysis consisted mainly of aromatics with some aliphatic compounds, which have similar physical properties as conventional diesel fuel.

As discussed in the introduction, this review focuses on CI engine applications because these are the most feasible from the future demand perspective. TPO samples should be evaluated against legal and functional requirements in order to verify if TPO is suitable as fuel for CI engines. Important properties, among others, are kinematic viscosity, density, acidity, water content, sulphur content, flash point and cetane number. The following chapters review TPO's engine-relevant properties and possible quality improvement measures. Table 3 summarises the results of the assessment of TPO as a CI-engine fuel. Automotive diesel EN 590 standard is used as a reference in this table and in the discussion.

3.1 Properties of crude TPO

Heating value (or calorific value) is one of the most important indicators for fuel since it translates to the vehicle/vessel range and the well-to-wheel CO_2 economy (fuel cost of transport). It should be noted here that mass-based heating value of hydrocarbon fuels is straightforwardly shaped by the ratio of hydrogen to carbon and the presence of oxygen and nitrogen. In the case of biofuels and also TPO, water content can significantly harm calorific value. Heating values for the TPO samples in Table 3, are depicted in one of three forms, depending on the measurement principle used by the individual authors: higher and lower heating value (HHV and LHV respectively) or as gross calorific value (GCV). The difference between the three approaches relates to how water and ash content is handled in the calculation. For further elaboration of this, refer, for instance, to Heywood [130].

The energy density of crude TPO can be optimised to give diesel-like values, with HHV ranging from 38.9 to 42.5 MJ/kg [50,52,95]; LHV can range from 38.1 to 44.1 MJ/kg [11,12,16,86,95,131]. GCV can range from 41.6 to 44.8 MJ/kg [69,72,84,132–135]. Some studies, with calorific values ranging from 39.2 to 48.7 MJ/kg, fail to specify the method used for its determination [51,55,87,136–138]. This spread of values stems from differences in feedstock quality and different pyrolysis process parameters. Looking at Table 3, there is no straightforward correlation between heating value and process temperature. Luo and Feng [95] for instance observed that both parameters increase simultaneously, while Ramirez-Canon et al. [55] observed a significant drop in HHV after elevating the process temperature above 600 °C. More detailed analysis, however, reveales the direct correlation of heating value with TPO yield. Importantly, there is no trade-off here: maximising yield also results in a higher energy density of the end fuel. As with the case of mass fraction yield, catalytic pyrolysis tends to produce more energetic fuel [51]. Note that, according to Ramirez-Canon et al. [55], the increase of mass fraction yield translates to higher heating value by virtue of increased density of the TPO sample.

The increased density was observed and ranged from 830 to 987 kg/m^3 at 15 °C, the latter value significantly beyond that of EN 590 diesel.

Most of the kinematic viscosity values for TPO (measured at 40 °C) were in accordance with the permissible range for diesel fuels, varying between 2.0-4.5 mm^2/ [11,12,136,137,139,140,15,16,50,51,69,87,95,131]. However, Ramirez-Canon et al. [55] and Miandad et al. [52] both reported low viscosities - below 1.90 mm^2/s. On the other hand, Islam et al. [133], Sebola et al. [134], Islam and Nahian [135], Bhatt and Prajapati [141], Hürdoğan et al. [138] and Ambrosewicz-Walacik et al. [142] obtained highly viscous TPO, well above the level for proper operation of most injection systems. Roy et al. [84] for instance, recorded kinematic viscosity (at 50 °C) of 23.5 mm^2/s for his TPO obtained from passenger car tyres filled with silica (fixed-bed reactor). It should be noted that viscosity depends heavily on temperature, with hyperbolic characteristics differing from fuel to fuel. For the discussed sample the viscosity at 100 °C was 5.2 mm^2/s. Its potential direct engine application, for marine use, for instance, would require preheating to around 120 °C.

Water and sulphur concentrations in crude TPO are usually above the levels specified as maxima for EN 590 diesel (water, 200 mg/kg; sulphur, 10 mg/kg). According to the available data, water contents varied between 330 mg/kg and 46 g/kg [11,16,55,84,95,131]. The exception was the study of Vihar et al., where the TPO's water content was as low as 120 mg/kg [86]. Turning to sulphur content, all the samples presented in Table 3 significantly exceeded the sulphur limit for EN 590 diesel. Values ranged from 88 mg/kg to 15 g/kg [11,12,131,132,134,140–142,15,16,50–52,55,75,84]. Note that desulphurisation measures are covered in more detail in subsection 3.3.1.

The flash point is the lowest temperature at which a liquid can form an ignitable mixture with air, when the surface of the liquid is exposed to an ignition source. The EN 590 standard regulates the flash point of diesel to be at least 55 °C, enabling safe storage and handling. However, most research determines TPO's flash point to be less than 30 °C [11,50,52,69,84,131,133,139]. Some put it higher, from 31 °C to 54 °C [12,15,51,55,132,135,137,141–143]. Only a few studies assessed TPO's flash point to be in accordance with the requirements of the EN 590 standard, reporting values from 58 °C to 94 °C [16,84,87,134,136].

Diesel's EN 590 standard specifies a minimum cetane number (CN) of 51, measuring the fuel's ability to auto-ignite in engine conditions. Cetane number values for crude TPO are rather lower, ranging from 25 to 48 [12,51,84,87,137,140,141]. Such values indicate that compression ignition in typical engine conditions is still possible, but with significant ignition delay. One should note that the cetane number is shaped by chemical composition of hydrocarbons. Generally, normal paraffinic hydrocarbons exhibit the best auto-ignition properties, whereas branched paraffins, olefins and aromatics reduce the cetane number. Additionally, a greater number of C atoms leads to better auto-ignition properties, but carries the penalty of higher viscosity [130,144].

3.2 Properties of TPO distillates (DTPO)

Distillation is one of the main methods to improve TPO fuel quality, with different fractions being more suitable for different applications, either as fuel or as a fuel additive. Literature specifying the properties of different TPO fractions is, however, limited. Where available, properties of TPO distillates are included in Table 3, providing comparison with the properties of the crude TPO obtained via the same pyrolysis process.

The recent work by Ambrosewicz-Walacik et al. [143] outlines the systematic fractionation of TPO, along with an assessment of the physicochemical properties of the fractions obtained. Three levels of distillation were considered: A) Light Fraction: consisting of components with boiling temperature > 160 °C. This fraction was distilled in order to separate components with high volatility, significantly influencing the low flash point of the pyrolytic oil. B) Medium Fraction: boiling temperature from 160 °C to 204 °C. This fraction was considered as a diesel fuel component and subjected to further engine tests in [14] and [142]. C) Heavy Fraction: components with boiling temperature from 205 °C to 350 °C. Note that at over 350 °C, only a tar-like substance remained in the distillation flask. As well as the physicochemical comparison given in Table 4, the differences in the appearance of crude TPO and its distillates is seen in Fig. 5. It clearly shows that the added value of the distillation is the reduction of ash and tar content in the fuel [142].

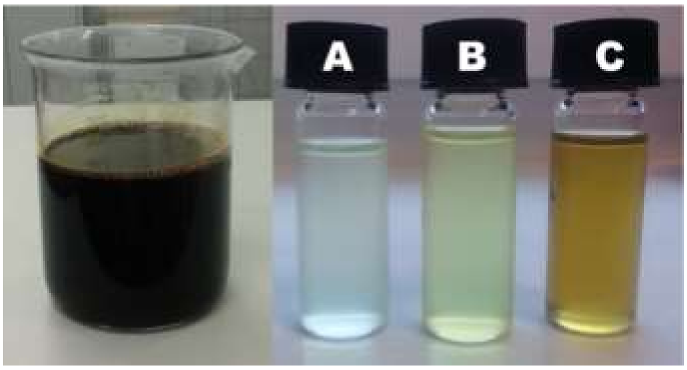


Fig. 5. Crude TPO sample (left) and products of its distillation analysed in Ambrosewicz-Walacik et al. [142]; A – light naphtha fraction, B – medium fraction, C – heavy fraction; Author's archive.

It was shown that the distillation process dramatically reduced kinematic viscosity (to below 0.9 mm^2/s for all samples) while also contributing to the unfavourable decrease of the flash point (Table 4). The flash point for the light fraction was below 3.5 °C: it was 12 °C and 25 °C for the medium and heavy fractions respectively. The crude TPO's flash point was 53 °C, almost meeting EN 590's threshold value of 55 °C for diesel.

Other authors had studied only selected distillates, usually medium and light fractions, but the above trends were confirmed by Al Mamun et al. [75], Islam and Nahian [135] and Murugan et al. [132]. Describing what they called a light TPO fraction, Tudu et al. [139] reported viscosities within EN 590's permitted range (3.06 mm^2/s) and a moderate flash point of 30 °C.

Murugan et al. [132], Sebola et al. [134] and Islam and Nahian [135] recorded that the distillation process contributed to the increase in calorific value of analysed samples. Theyer medium fractions had respectively 2.8 MJ/kg, 0.7 MJ/kg and 1.6MJ/k higher energy density than their individual crude TPO samples. At the same time, it is difficult to assess how distillation affects CN. Actually, only Tudu et al. [139] reported that their fractionated light DTPO product had a CN of 25-30 (depending on the pyrolysis temperature) while having a more or less constant calorific value of 39.2 MJ/kg. However, that work lacks any comparison with the crude TPO. Its authors also reported the light fraction's very high sensitivity to sulphur penetration, depending upon pyrolysis process temperature. Its sulphur content varied from 1.2 % to above 3 %wt. From Ambrosewicz-Walacik et al. [143] we can deduce that the sulphur content of fractions follows the same trend as density. The light fractions accumulated less sulphur than the baseline TPO (0.40 %wt. vs 0.49 %wt.), while having significantly lower density than crude TPO (770 kg/m^3 vs 955 kg/m^3). Note that the medium fraction already had both indicators slightly above baseline TPO. The heaviest fraction had a density of 1360 kg/m^3 and sulphur concentration of 0.85 %wt.

Table 4. Physicochemical characteristics of TPO and DTPO (part 1)

Reference		Additional information	temperature of pyrolysis (°C)	crude or distilled	calorific value (MJ/kg)	density 15 °C (kg/m^3)	kinematic viscosity 40 °C (mm^2/s)	water content (%)	sulphur content (%wt.)	flash point (°C)	cetane number
EN 590	[145]	-	-	-	42-44[a)]	820-845	2-4.5	0.02	0.001	≥ 55	≥ 51
TPO, DTPO or fraction of TPO (light, medium and heavy)											
Roy et al. (1999)	[84]	passenger car tyres	520	Crude	43.6 (GCV)	950 (20 °C)	9.7 (50 °C), 3.2 (100 C)	0.3	0.8	28	44
		passenger car tyres filled with silica	500	Crude	43.8 (GCV)	976 (20 °C)	23.5 (50 °C), 5.2 (100 °C)	1.6	1.5	59	n.a.
		fixed-bed reactor, truck tyres	485	Crude	44.8 (GCV)	939 (20 °C)	17.8 (50 °C), 6.0 (100 °C)	1.5	1.0	22	
Ucar et al. (2005)	[69]	fixed-bed reactor, passenger car tyre	650	Crude	41.6 (GCV)	943	4.62	n.a.	n.a.	<30	
		truck tyre	650	Crude	42.4 (GCV)	913	3.85			<30	
Murugan et al. (2008)	[15]	steel pyrolysis reactor, atmosphere vacuum	450-650	Crude	38.0 (net calorific value)	934	3.77		0.72	43	
Murugan et al. (2008)	[132]	steel pyrolysis reactor,	450-650	Crude	42.8 (GCV)	935	3.20		0.95	43	
				Distilled	45.6 (GCV)	871	1.70		0.03	36	
Islam et al. (2008)	[72]	fixed-bed reactor	575	Crude	42.0 (GCV)	957	4.75 (30 °C)		n.a.	≤ 32	
Islam et al. (2010)	[133]	fixed-bed reactor	475	Crude	41.6 (GCV)	943	4.62			≤ 30	
İlkılıç and Aydın (2011)	[140]	pyrolysis reactor was electrically heated	700	Crude	n.a.	945 (20 °C)	3.85		0.90	50	44
Sebola et al. (2013)	[134]	n.a.	n.o.	Crude	43.0 (GCV)	926 (20 °C)	9.0	3.54	0.91	94	n.a.
				Distilled	43.7 (GCV)	807 (20 °C)	1.50	0.065	0.41	44	
Wongkhorsub et al. (2013)	[136]	batch pyrolysis reactor	350-400	Distilled	43.2	n.a.	2.69	n.a.	n.a.	68	
Frigo et al. (2014)	[16]	thermo-mechanic cracking reactor	500	Crude	41.96 (LHV)	903	2.90	0.033	0.97	58	
Martínez et al. 2014	[11]	continuous auger reactor	550	Crude	40.5 (LHV)	917	2.39	0.068	0.83	23	
Tudu et al. (2014)	[139]	rotary type reactor	375-440	light fraction	39.2	910	3.06	n.a.	1.17-3.00	30	25-30
Al-Lal et al. (2015)	[131]	n.a.	no data	Crude	40.5 (LHV)	917	2.40	0.069	0.83	23	n.a.
Vihar et al. (2015)	[86]	vacuum pyrolysis	600-700	Crude	40.6 (LHV)	n.a.	3.22 (20 °C)	0.012	n.a.	n.a.	
Ayanoğlu and Yumrutaş (2016)	[50]	n.a.	450	Crude	41.0 (HHV)	830	3.21	n.a.	0.013	28.1	
Al Mamum et al. (2016)	[75]	fixed-bed reactor	320-390	Distilled	-	840	0.668	nil	0.629	8	
Islam and Nahian (2016)	[135]	cylindrical chamber as a reactor	450-600	Crude	42.0 (GCV)	956	16.39	n.a.	n.a.	50	
			450-600	Distilled	43.6 (GCV)	835	0.89			< 10	

a) Wang et al. (2016), Verma et al. (2018), Sharma and Murugan (2017) [12,137,146]

Table 4. Physicochemical characteristics of TPO and DTPO (part 2)

Reference		Additional information	temperature of pyrolysis (°C)	crude or distilled	calorific value (MJ/kg)	density at 15 °C (kg/m^3)	kinematic viscosity at 40 °C (mm^2/s)	water content (%vol.)	sulphur content (%wt.)	flash point (°C)	cetane number
Wang et al. (2016)	[137]	lab-scale fixed-bed reactor, N_2 atmosphere	350	Crude	42.1	887.2	2.71	n.a.	n.a.	39	44
			400		42.1	889.1	2.74			40	43
			450		42.2	890.4	2.81			43	45
Ambrosewicz-Walacik et al. (2017)	[143]	n.o.	450-500	Crude	n.a.	955	5.68		0.49	53	n.a.
Bhatt and Prajapati (2017)	[141]	rotary reactor	430	Crude		910	8.65	nil	0.0088	32	42
Hürdoğan et al. (2017)	[138]	axis rotary type reactor	500-550	Crude	40.1	907	4.98	n.a.	n.a.	> 100	n.a.
Luo and Feng (2017)	[95]	sole pyrolysis	1000	Crude	38.5 (LHV)	982.7	3.91	1.56		n.a.	
		pyrolysis with ceramin balls	1000	Crude	40.2 (LHV)	944.8	3.62	2.07			
		catalytic pyrolysis with BF slags	1000	Crude	44.1 (LHV)	935.2	2.10	4.57			
		pyrolysis using BF slag	600	Crude	38.9 (HHV)	941.2	3.69	1.56			
			700	Crude	40.6 (HHV)	961.9	3.06	2.68			
			800	Crude	41.0 (HHV)	986.9	3.29	3.97			
			900	Crude	41.6 (HHV)	955.0	2.35	4.11			
			1000	Crude	42.1 (HHV)	982.7	2.10	4.57			
Sharma and Murugan (2017)	[12]	n.a.	n.a.	Crude	38.1 (LHV)	n.a.	3.35	n.a.	0.95	49	28
Ambrosewicz-Walacik et al. (2018)	[142]		450-500	Crude	n.a.	955.0	5.68		0.49	53	n.a.
		pyrolytic oil distilled at three different temperatures		Light		770.0	0.823		0.40	< 3.5	
				Medium		1003.0	0.842		0.60	12.0	
				Heavy		1360.0	0.891		0.85	25.0	
Banihani and Bani Hani (2018)	[51]	pyrolysis without catalyst	550	Crude	43.5	911.7 (20 °C)	4.60		1.13	50	45
		pyrolysis with alumina catalyst	551	Crude	45.5	862.8 (20 °C)	3.90		0.37	55	45
		pyrolysis with zeolite catalyst	552	Crude	48.3	858.6 (20 °C)	3.60		0.34	56	48
Miandad et al. (2018)	[52]	pyrolysis with activated alumina	600	Crude	42.5 (HHV)	900	1.90		n.a.	27	n.a.
Ramirez-Canon et al. (2018)	[55]	pyrolysis with hydrogen steam	450	Crude	48.7	0.83 (g/mL)	1.59	0.90	1.09	32.0	
			500		47.2	0.85 (g/mL)	1.88	0.75	1.06	32.5	
			550		47.4	0.88 (g/mL)	2.77	0.75	0.89	30.5	
			600		46.9	0.86 (g/mL)	2.65	0.35	1.07	35.5	
			450 with H_2		45.9	0.86 (g/mL)	2.35	0.55	0.87	34.5	
			500 with H_2		48.1	0.85 (g/mL)	2.41	0.40	0.78	30.5	
			550 with H_2		47.3	0.87 (g/mL)	2.48	0.25	0.67	31.0	
			600 with H_2		47.9	0.88 (g/mL)	3.07	0.30	0.80	31.0	

3.3 Quality improvement measures for TPO/DTPO

Subsection 3.1's and 3.2's review of TPO/DTPO parameters related to use as fuel in a CI engine reveal a large spread in the results obtained in different reactors. Nevertheless, it is clear that most of TPO's physicochemical parameters did not meet the EN 590 standard. In the case of a few determinants, depending on pyrolysis methods, nor did TPO comply with other standards. For example, it did not meet ISO 8217 for bunker fuel quality: sulphur content and moisture levels of the TPO fuel represent the biggest issues. Moisture removal does not pose a challenge, and can be achieved by distilling-out the water fraction [132,139,147]. That helps increase the heating value and improve the CN, amongst others [87]. The next step should be desulphurisation, described in the following subsection, 3.3.1. Blending or addification can be considered as inexpensive measures to improve the other fuel parameters that are challenging for TPO, such as its high viscosity or low values of flash-point and CN number. Progress is this sphere is discussed in subsection 3.3.2. At this point, it is necessary to mention that, in principle, TPO can be used as feedstock to standard refinery processes to produce automotive-grade diesel and other fuels. However, this route has not been demonstrated openly and consequently will not be covered in this review.

3.3.1 Desulphurisation

Sulphur content of liquid engine fuels has been drastically reduced in the past few decades, cutting the sulphur compounds in exhaust emissions. These are environmentally harmful, mainly because of their potential to cause acid rain. Furthermore, fuel sulphur increases particulate matter and soot emissions in internal combustion engines [148]. There are also technical reasons for cutting fuel sulphur: sulphur causes corrosion and has a deleterious effect on advanced catalytic systems used for CO, HC, NOx and particulate reduction [149,150]. This underlines the importance of desulphurisation for TPO, especially bearing in mind the possible direct use of TPO in shipping, where IMO has introduced 0.5/0.1 %wt. fuel sulphur limits. The automotive EN 590 standard is already very stringent, limiting fuel sulphur content to just 10 mg/kg (0.001 %wt.).

The sulphur in pyrolytic oil is related to the fact that this compound is used as a cross-linking agent during tyre manufacturing. Sulphur-containing compounds undergo different reactions (recombination and/or disproportionation) during pyrolysis. As discussed in subsections 3.1 and 3.2, TPO/DTPO may contain different amounts of sulphur, depending on the process conditions and distillation temperature.

A conventional hydrodesulphurisation (HDS) process can be used to reduce sulphur content in fuel, yet its application is primarily limited to distillates (light to medium fractions) [151]. Due to the fact that the process is difficult to achieve without dedicated refinery infrastructure, HDS has hardly been demonstrated in the case of TPO, to the best of our knowledge. Debek and Walendziewski [53] applied hydrotreatment with a NiMo–Al_2O_3 catalyst, cutting sulphur content from 1.1 % to 0.2 %. Additionally, double carbon bonds were effectively destroyed. This required quite strict hydrorefining conditions, using 360 °C and 5 MPa H_2 pressure. It should be noted that high consumption of both hydrogen and expensive molybdenum catalysts are additional disadvantages of this method [151]. Refining processes that remove sulphur from the fuel also simultaneously reduce the fuel's lubricity.

Another popular desulphurisation method uses oxidation of the sulphur compounds, either by methanol extraction or silica gel column adsorption of the more polar, oxidized sulphur compounds from methanol. Al-Lal et al. [131] used both methods on TPO provided by a third-party, yet failed to lower the sulphur content to a significant degree.

There were a couple of successful attempts to reduce TPO's sulphur by optimising the pyrolysis process itself, either by dedicated reactor conditioning or adding catalysts. Analysis of Table 4 shows that the application of catalysts during pyrolysis could be effective in lowering TPO's sulphur content. Banihani and Bani Hani [51] cut sulphur in pyrolytic oil by around 70 % by using catalysts. The sulphur content of 1.13% in their TPO with baseline tyre pyrolysis without catalyst was cut to 0.37 % and 0.34 %

when alumina and zeolite catalysts respectively were added to the process. Importantly, in both catalytic cases, the reduction in sulphur was accompanied by improvement of all the other properties of the TPO (refer to Table 4 for details).

Note that already in 2000 Murena [152] considered using hydrogen during pyrolysis to reduce TPO's sulphur content. Coupled with optimising the feedstock pre-treatment (tyre scrap vs tyre powder), the author observed that the use of hydrogen cut sulphur by 30 %. However, the large amount of hydrogen required for the sulphur reduction achieved means this method is not economically feasible.

Choi et al. [91,121] tackled sulphur reduction by use of different reactor conditions and reactor addification. They concluded that, independent of the pyrolysis process (single-stage or two-stage) and type of inert gas (product gases or N_2), increasing pyrolysis temperature generally increases the sulphur content, with different sensitivities for individual pyrolysis types [91]. Using N_2 as the fluidising medium with two-stage pyrolysis generally facilitated the lowest sulphur in crude TPO. Sulphur accumulation decreased from 0.92 %wt. at baseline conditions (single-stage; product gases; temperature optimised for liquid yield), to 0.55 % at optimised operation (sulphur content co-optimised with temperature for maximum TPO yield and heating value). In the follow-up work, Choi et al. started from the previously optimised pyrolytic reactor and experimented with different process additives (dolomite and olivine, both natural and calcined) in search of a further reduction in the TPO's sulphur [121]. The TPO sample produced with natural and calcined olivine contained low amounts sulphur (0.46 and 0.45 %wt. respectively). Interestingly, the addition of natural dolomite increased sulphur to 0.70 %wt., while calcine dolomite had no significant effect.

Aydın and İlkılıç [98] investigated the effect of adding CaO and $Ca(OH)_2$ as sulphur-mitigating agents to a pyrolytic reactor fed with tyre scraps. After optimising the amount and ratio of both compounds the authors demonstrated a reduction in sulphur content from 1.4 %wt. to 0.9 %wt., without significantly impacting other TPO parameters. Additional post-pyrolysis desulphurisation with sulphuric acid (10 % aqueous solution) cut the sulphur content to 0.2 % wt.

This latter post-treatment method is commonly referred to as desulphurisation through ionic solutions or liquid-liquid extraction. Ahmad et al. [153] analysed the impact of various desulphurising ionic agents on TPO, using sulphuric acid; a combination of hydrogen peroxide and acetic acid; Fuller's earth; and calcium oxide. A 15 %wt. solution of sulphuric acid as the extracting medium gave the maximum sulphur reduction, cutting the TPO's sulphur content from the baseline approximately 1 %wt. to 0.63 %wt. Interestingly, calcium oxide showed only a marginal desulfurization ability although the cited authors did refer to the already mentioned successful result by Aydın and İlkılıç [98]. Ahmad et al. supposed that using calcium oxide at higher temperatures would give a bigger sulphur reduction [153]. They also found that the viscosity of tyre pyrolysis oil significantly decreased with increasing addition of sulphuric acid and the hydrogen peroxide/acetic acid combination. Viscosity was not similarly affected by the addition of calcium oxide, however. Also evaluating ionic solutions, Koc and Abdullah [154] started desulphurisation by preparing a binary solution of tetraoctylammonium bromide and hydrogen peroxide (30% purity), to which a phosphotungstic acid catalyst was added. The presented solution cut the sulphur content in the TPO sample from 0.768 %wt. to 0.321 %wt.

In summary, recent years have brought significant progress in new desulphurisation techniques for TPO. Despite this progress, none of the reviewed works actually managed to demonstrate compliance with EN 590's stringent sulphur limit of just 10 mg/kg (0.001 %wt.) for automotive diesel. However, the IMO ECA sulphur limit of 0.1 %wt. is apparently already within range for TPO and further sulphur reduction can be achieved by combining the individual measures discussed in this section [141].

3.3.2 Blending with other fuels and TPO addification

One way of improving crude TPO's physicochemical properties such as density, viscosity, sulphur content, flash point and cetane number is blending TPO/DTPO with diesel fuel, biodiesel and crude rapeseed oil or with other chemical compounds. The review is summarized in Table 5.

Currently, there appears to be little attention paid to research into use of crude TPO in binary mixtures with mineral diesel. Hürdogan et al. [138] analysed blends consisting of 50, 80 and 90 %vol. of crude TPO and corresponding amounts of diesel fuel (DF). The authors observed a gradual reduction of the mixture's density and kinematic viscosity as the proportion of DF was increased. Values of density and kinematic viscosity for TPO50 (50 % TPO) were significantly lower than for neat TPO and in accordance with the requirements of EN 590. Note that the flash point of their baseline TPO was surprisingly high (>100 °C), so the authors did not consider this as a constraint. CN, however, was not reported.

Martínez et al. [11] investigated a blend of 5 %vol. crude TPO and 95 %vol. of DF. They achieved a fuel compatible with the automotive diesel standard in all aspects except water and sulphur content: their values exceeded EN 590 limits by 100 %. This was due to a rather high content of both species in the crude TPO.

Sharma and Murugan [155] used biodiesel produced from jatropha oil to prepare blends using the addition of 10, 20, 30, 40 and 50 % crude pyrolytic oil. The cited authors found that increasing the share of Jatropha methyl esters reduced the blend's density, while kinematic viscosity and flash point increased. A similar tendency was observed in the later work of the same authors [12]. The authors claimed that biodiesel and TPO are complementary in terms of viscosity (too high for biodiesel), flashpoint (too high for TPO) and CN (too low for biodiesel). The TPO20 sample was considered the nearest to meeting EN 590: only its sulphur content and viscosity were slightly too high. This could have been corrected by more efficient desulphurisation of the baseline TPO and by use of a viscosity improver. Flash point values of all samples complied with EN 590. However, it is worth noting that the claimed flash point values reported for corresponding blends in Sharma and Murugan [12] and their earlier work [155] are significantly different (see Table 5). Thus, the absolute values should be treated with caution but the general statement regarding compliance of all the tested mixtures with EN 590's flash point limit still holds.

Other authors considered the use of distilled TPO to produce binary mixtures with diesel or biodiesel. Murugan et al. [132,147] examined DTPO blends with DF, using 80 and 90 %vol. DTPO and 20 and 10 %vol. DF. They observed little changes in analysed properties such as density, kinematic viscosity, sulphur content and flash point compared with neat DTPO. Addition of DF obviously improved all these properties but such high proportions of DTPO (80 % or more) with DF should be rather considered as an academic idea because the resultant blend still falls well short of EN 590. Al Mamum al. [75] investigated the parameters of a 50/50 blend of TPO and DF: their results led them to conclude even a 50/50 blend cannot satisfy EN 590. The authors, however, pointed out that DTPO's very low viscosity of 0.668 mm^2/s makes it suitable as a viscosity improver. Tudu et al. [87] added 40 % DF to their baseline DTPO and noticed the significant reduction in kinematic viscosity and density. The calorific value and cetane number were close to the weighted (by volumetric shares) average of the values of individual components. As a cautionary note, the 40 % addition of DF reduced the flash point from the neat DTPO sample's 75 °C to just 32 °C, implying that the fuel used as DF representative did not meet the EN 590 flash point requirement.

Tudu et al. also prepared a ternary blend, with 40 %vol. of DTPO, 50 %vol. of DF and 10 %vol. of dimethyl carbonate (DMC) [87]. This had significantly lower density and slightly lower kinematic viscosity than the binary blend, but suffered from reduced calorific value and cetane number index. Hariharan et al. [156] also suggested that diethyl ether could be used as a cetane number improver for TPO. The second part of Table 5 and the following discussion review ternary mixtures using TPO/DTPO as a component.

Table 5. Basic characteristics of monocomponent, binary and ternary mixtures of TPO/DTPO (part 1)

Reference		Composition of mixtures (%v/v)						calorific value (MJ/kg)	density at 15 °C (kg/m3)	kinematic viscosity 40 °C (mm^2/s)	water content (%)	sulphur content (%wt.)	flash point °C	cetane number
		TPO	DTPO	DF	biodiesel	rapeseed oil	others							
Monocomponent mixtures (TPO/DTPO)														
Murugan et al. (2008b)	[132]	100	-	-	-	-	-	42.80 (GCV)	935	3.2	n.a.	0.95	43.0	n.a.
		-	100	-	-	-	-	45.60 (GCV)	871	1.7		0.03	36.0	
Murugan et al. (2008c)	[147]	-	100	-	-	-	-	43.7 (GCV)	807 (20 °C)	1.5	0.065	0.41	44.0	
Sharma and Murugan (2013)	[155]	100	-	-	-	-	-	39.2	920 (20 °C)	5.4	n.a.	n.a.	43.0	
Martínz et al. (2014)	[11]	100	-	-	-	-	-	42.70 (HHV), 40.49 (LHV)	917	2.39	0.069	0.83	23.0	
Al Mamun et al. (2016)	[75]	-	100	-	-	-	-	-	840	0.668	nil	0.629	8.0	
Tudu et al. (2016)	[87]	-	100	-	-	-	-	39.20	910	3.06	n.a.	n.a.	75.0	25-30
		-	-	-	-	-	100 DMC	15.78	1.079	0.625			18.0	35-36
Ambrosewicz-Walacik et al. (2017)	[143]	-	100	-	-	-	-	n.a.	870	1.05		1.22	12	n.a.
Hürdogan et al. (2017)	[138]	100	-		-	-	-	40.13	907	4.98		n.a.	>100	
Sharma and Murugan (2017)	[12]	100	-	-	-	-	-	38.10	913	3.35		0.95	49.0	28
Ambrosewicz-Walacik et al. (2018)	[142]	-	100		-	-	-	n.a.	955	5.68		0.49	53	n.a.
Binary mixtures (part I)														
Murugan et al. (2008b)	[132]	-	80	20	-	-	-	46.40 (GCV)	832	1.94	n.a.	0.23	47.0	n.a.
		-	90	10	-	-	-	45.80 (GCV)	865	1.73		0.23	37.0	
Murugan et al. (2008c)	[147]	-	80	20	-	-	-	45.90 (GCV)	860	1.76		0.21	39.0	
		-	90	10	-	-	-	45.90 (GCV)	865	1.73		0.23	37.0	
		-	5	95	-	-	-	44.8 (GCV)	837 (20 °C)	2.9	0.021	0.067	50.0	
		-	10	90	-	-	-	44.8 (GCV)	837 (20 °C)	2.8	0.021	0.085	48.0	
		-	15	85	-	-	-	44.7 (GCV)	837 (20 °C)	2.5	0.014	0.106	42.0	
		-	20	80	-	-	-	43.7 (GCV)	837 (20 °C)	2.4	0.017	0.206	44.0	
		-	25	75	-	-	-	43.7 (GCV)	836 (20 °C)	2.2	0.011	0.226	38.0	
		-	30	70	-	-	-	43.7 (GCV)	836 (20 °C)	2.0	0.007	0.233	34.0	
Sharma and Murugan (2013)	[155]	10	-	-	90 (Jatropha)	-	-	39.24	883.5 (20 °C)	5.73	n.a.	n.a.	64.0	
		20	-	-	80 (Jatropha)	-	-	37.74	887.0 (20 °C)	5.60			60.0	
		30	-	-	70 (Jatropha)	-	-	36.40	892.3 (20 °C)	5.41			55.0	
		40	-	-	60 (Jatropha)	-	-	35.12	894.0 (20 °C)	5.29			49.0	
		50	-	-	50 (Jatropha)	-	-	33.89	897.5 (20 °C)	5.15			44.0	

*DMC - dimethyl carbonate, **NCV- net calorific value

Table 5. Basic characteristics of monocomponent, binary and ternary mixtures of TPO/DTPO (part 2)

Reference		Composition of mixtures (%v/v)						calorific value (MJ/kg)	density at 15 °C (kg/m³)	kinematic viscosity 40 °C (mm²/s)	water content (%)	sulphur content (%wt.)	flash point °C	cetane number
		TPO	DTPO	DF	biodiesel	rapeseed oil	others							
Binary mixtures (part II)														
Martínz et al. (2014)	[11]	5	-	95	-	-	-	45.02 (HHV), 42.23 (LHV)	848	2.73	0.008	0.04	n.a.	n.a.
Al Mamun et al. (2016)	[75]	-	50	50	-	-	-	-	833	1.44	nil	0.621	8.0	
Tudu et al. (2016)	[87]	-	40	60	-	-	-	41.96	862	2.87	n.a.	n.a.	32.0	41.17
Hürdogan et al. (2017)	[138]	90	-	10	-	-	-	41.91	872	4.15			75.7	n.a.
		80	-	20	-	-	-	42.80	843	3.13			73.5	
		50	-	50	-	-	-	44.05	839	2.91			72.5	
Sharma and Murugan (2017)	[12]	20	-	-	80 (jatropha)	-	-	38.82	887	5.20		0.18	132	52
		40	-	-	60 (jatropha)	-	-	38.60	894	4.90		0.39	119	48
		60	-	-	40 (jatropha)	-	-	38.00	901	4.79		0.56	108	45
Jeyakumar et al. (2018)	[13]	20	-	80	-	-	-	43.17 (NCV)**	831	2.93		n.a.	65	54
Ternary mixtures														
Tudu et al. (2016)	[87]	-	40	50	-	-	10 DMC*	39.15	779	2.78	n.a.	n.a.	38.8	40.60
Ambrosewicz-Walacik et al. (2017)	[143]	-	1.00	49.50	49.50 (frying oil)	-	-	n.a.	853	3.30		0.0061	37	n.a.
		-	0.91	35.78	63.31 (frying oil)	-	-		848	3.38		0.0063	36	
		-	2.00	49.00	49.00 (frying oil)	-	-		849	2.93		0.0123	31	
		-	1.98	38.62	59.40 (frying oil)	-	-		852	3.21		0.0122	29	
Ambrosewicz-Walacik et al. (2018)	[142]	-	5	40	-	55	-		865	11.42		0.027	55	
Jeyakumar et al. (2018)	[13]	20	-	80	-	-	$CaCO_3$	43.10 (NCV)**	830	2.89		-	68	55
		20	-	80	-	-	TiO_2	43.08	829	2.87		-	67	55
Mikulski et al. (2019)	[14]		5	40	-	55	-	39.5 (LHV)	868	11.56		0.0271	54.5	n.a.
			5	45	-	50	-	39.6 (LHV)	861	8.94		0.0277	55.0	
			5	50	-	45	-	40.1 (LHV)	860	8.43		0.0275	56.0	
			5	55	-	40	-	40.7 (LHV)	852	7.97		0.0276	56.5	
			5	65	-	30	-	41.1 (LHV)	851	6.63		0.0140	57.0	

The distilled medium fraction of TPO obtained by Ambrosewicz-Walacik et al. [143] had extremely low viscosity. Hence, it was considered that only minor addition of this DTPO (0.91, 1.0, 1.98 and 2.0 %vol.) would allow it to serve as a viscosity improver. This was tested by adding it to a variety of blends comprising diesel and methyl esters produced from frying oil, all of which suffered from viscosity issues. The thesis was verified negatively since the density and kinematic viscosity of the blends did not improve significantly after the addition of DTPO. However, even this small addition of pyrolytic oil contributed to a significant increase in sulphur content and a reduction of flash point. The amount of sulphur was mostly determined by how much DTPO was added.

Follow-up works by Ambrosewicz-Walacik et al. [142], and Mikulski et al. [14] disregarded the sulphur constraint (assuming desulphurisation is possible) and increased the DTPO share to 5 %vol. It was added to methyl esters/diesel blends and to crude (cold pressed and filtered) rapeseed oil blends with diesel, mixed at different ratios. The aim was to find an economically feasible fuel needing only limited processing and with major shares of renewables. A detailed characterisation of the different blends can be found in Table 5. The flash point of all the blends was close to that of EN 590 diesel. The addition of 5% DTPO greatly improved viscosity (by 20-50 %, depending on the amount of biocomponent) although it was still well above EN 590's requirement. The parameters, however, were still considered suitable to operate modern diesel engines and so the samples were subjected to engine tests focused on analysis of combustion and on their full emission and efficiency profiles [14,142].

One of the newest methods used to improve fuel characteristics involves nano-additives. Nanoparticles of titanium dioxide (TiO_2) can reduce pollutants such as NO_x and SO_x [157]. The effects of those additives were already confirmed by Fangsuwannarak and Triratanasirchai, who tested blends of palm biodiesel with fossil diesel and 0.1 % or 0.2 % addition of TiO_2. [158]. The TiO_2 addition contributed to the reduction of kinematic viscosity of different fuels blends. Results of tests using an automotive engine showed that nano-particles improved combustion completeness. Jeyakumar et al. [13] analysed the effect of calcium carbonate and titanium dioxide nano-additives on a mixture of 20 % TPO with 80 % of DF. They noted slight decreases of viscosity and density, but greater reductions of cloud and pour points. The flash point and cetane number both increased.

The overall fuel properties obtained by TPO/DTPO blending differ significantly, depending on the share and quality of the individual components (bio and synthetic). However, from the above discussion it is possible to make the general observation that pyrolytic oils and biofuels seem complementary in terms of their properties. This relates mostly to viscosity (too high for biofuels) and flash point (too high for TPO) This complementary relationship also holds true, albeit to a lesser extent, to heating value (lower energy density of biofuels can be compensated by TPO) and density. Note that almost none of the authors considering a high bio component share or a high TPO share in diesel (above 50%) was able to demonstrate full compliance with EN 590. Nevertheless, the synergy of pyrolytic oils and biofuels, along with favourable results achieved through addification of TPO with active particles, suggests that future renewable liquid fuel research should focus on multicomponent mixtures. Using multiple components adds complexity but addresses the feedstock availability issue.

4 Engine tests

There is a handful of engine research results involving TPO but it is difficult to draw firm conclusions about how TPO impacts combustion, performance and emissions. This ambiguity stems from the variation in the tested engine platforms, operation conditions and control strategies used by different authors. Additionally, differences in feedstock quality, pyrolysis conditions and post-processing also muddy the waters because they influence TPO's combustion properties and its propensity to produce toxic exhaust compounds. Finally, TPOs can be admixed to different base fuels, along with other additives, creating binary, ternary or even more complex blends. We have attempted to use a systematic approach to this complex issue, presenting a summary of the most important findings which, in our opinion, form the best thinking in this field. It starts with the effects of mixture formation on combustion and then deals with emissions. Additionally, the results obtained for different engine platforms and for raw TPO, DTPO and more complex blends are separated to provide a reliable benchmark in each major sub-category of influential factors.

4.1 Mixture formation and combustion

Tests with crude TPO on basic engine platforms

Basic engine platforms include those that are naturally aspirated, without exhaust gas recirculation (EGR) and with low-pressure mechanical injection systems providing single injection. Such engines seem obsolete when compared with modern automotive designs, but their simplicity facilitates combustion study at a fundamental level. The limited number of control parameters enables reliable comparison of different research works. All the research platforms included in this review section have a cylinder bore ranging from 80 mm to 110 mm (light- to mid-duty, high-speed engines) and share a similar combustion system design, using direct fuel injection with multi-hole injectors and in-piston toroidal combustion chamber.

Murugan et al. [15] performed a series of experiments using a single-cylinder, naturally-aspirated, air-cooled engine with 17.5:1 compression ratio. Fuel was delivered in a single dose, using a low-pressure mechanical injection system. Experiments were performed at a fixed speed of 1500 rpm and under variable loads, with fixed start of injection (SOI) timing. Raw TPO was mixed with DF in fractions of 10 %, 30 % and 50 % vol. It was observed that increasing the TPO fraction led to a longer auto-ignition delay, which was attributed to the TPO's higher viscosity, poorer atomisation and slower vaporisation. More importantly, it was noted that because of the longer ignition delay of TPO blends, these binary fuels were characterised by higher pressure rise rates (PRR), which was associated with the combustion mode moving from diffusion-controlled to premixed.

Frigo et al. [16] used a similar experimental platform, but with a high compression ratio of 20.3:1. The single-pulse, low-pressure injection was commenced at 12° of crank angle (CA) bTDC. The engine tests were performed at full load and at speeds from 2000 rpm to 3500 rpm. When the content of TPO in DF did not exceed 20%, the combustion process was very similar to that of pure DF. However, higher fractions of TPO provided substantial delay of auto-ignition, and additionally rapid increase of cyclic variability, especially at low engine-speeds. A 40% TPO mixture at 3000 rpm provided approximately 5°CA delay of SOC when compared to DF. As with previous studies, a low CN and high viscosity were indicated as reasons to limit TPO content in DF.

Uyumaz et al. [159] used a single-cylinder, air-cooled, naturally-aspirated engine with 18:1 compression ratio running at 2200 rpm with fixed SOI timing at 24°CA bTDC and with variable loads, i.e. amounts of injected fuel. Comparison of DF and its mixture with 10% of TPO showed that auto-ignition delay was longer for the TPO blend. Addition of TPO delayed auto-ignition at low loads by approximately 0.1 ms, which, at the given rotational speed, translated to 1.3°CA. Differences in SOC diminished as the load increased.

Chwist et al. [160] also used a basic engine platform, with 16.8:1 compression ratio. The fuel was injected with SOI set to 28°CA bTDC. Rotational speed was 1500 rpm under fixed, medium load. As with the above-mentioned studies, the results showed SOC delay with increasing TPO content. Using pure TPO, SOC was delayed by approximately 8°CA in comparison with DF. The in-cylinder pressure curves from this study are shown in Fig. 5. This study also showed that the average SOC demonstrated higher variability, where ignition timing was highly affected by dropping in-cylinder temperature [160].

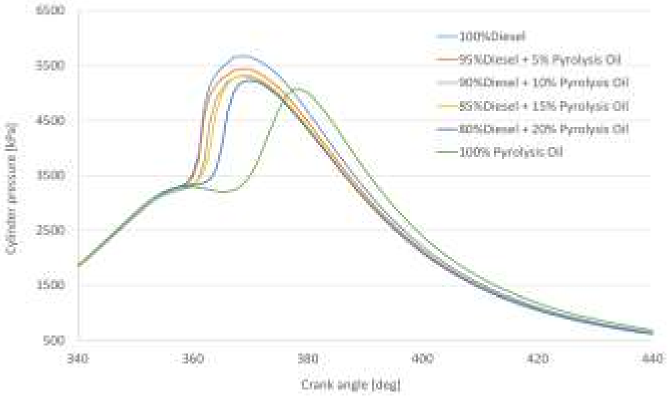


Fig. 5. In-cylinder pressure for variable admixture of TPO to DF. Data acquired at 1500 rpm, medium load, single low-pressure injection, SOI = 28 °CA bTDC [159]. Courtesy of Prof. Stanislaw Szwaja, Czestochowa University of Technology.

The picture that appears after analysis of the above studies shows that low admixtures - up to 20 % - of raw TPO in DF can be combusted in diesel engines without any modifications. SOC is distinctly delayed at higher TPO concentrations, so most authors advise advancing injection timing to compensate for increased ignition delay. However, this technique also increases mixing time, thus moving combustion towards the more premixed mode.

Using a single-cylinder diesel engine with mechanical injection, Van de Beld et al. [161] found that it would be possible to burnt almost pure TPO provided that inlet-air temperature was increased to 100-120 °C with an engine compression ratio of 17.6:1. Furthermore, if the compression ratio is increased to 22.4:1, the inlet-air temperature could be reduced by approximately 40 °C. The cited authors also underlined that TPO's high acidity makes it necessary to substantially modify the fuel injection system to achieve appropriate material compatibility.

Tests of DTPO and DF on basic engine platforms

It should be noted that addition of TPO in DF must be limited to ensure that the final properties of the blended fuel remain within the specifications set by the relevant standards, especially for automotive applications. Thus, the studies applied a variety of treatment methods, including distillation and hydrotreatment, to upgrade the TPO's properties to enable its blending with DF at higher ratios. Many authors did not mention the distillation process in their works, but the viscosity values indicated that purified, light fractions of TPO were used. Thus, we apply the term DTPO to all fuels with viscosity within or below the range specified in EN 590 [145].

Murugan et al. [132,147] performed engine tests with fuels containing large amounts of DTPO, up to 90%. Their experiments were performed on the basic engine platform and under the same conditions as described in the previous subsection, for crude TPO [15]. The results showed that despite DTPO's viscosity, which is half of that of TPO, increasing the DTPO content still lengthened auto-ignition delay proportionally. SOC delay of approximately 2.5°CA was evident when using 90 % DTPO admixture instead of DF. Importantly, this delay remained constant across the whole spectrum of engine loads.

Kumar and Prabu [162] performed their tests using a single-cylinder, water-cooled engine with mechanical injection, where SOI was fixed at 21°CA bTDC. Engine load was varied from idling to 0.435 MPa of brake mean effective pressure (BMEP) at 1500 rpm. In line with other studies, raising DTPO content in DF delayed combustion and increased the peak heat release rate (HRR) when compared with pure DF. However the higher HRR applied only until DTPO's admixture rate reached 75 %. The peak HRR was reduced with higher admixtures due to a substantial combustion delay of ca. 12°CA. The peculiar effect observed was that auto-ignition was back advanced at 85% DTPO: the peak HRR location was between the one for DF and the one for 75% DTPO. Importantly, end of combustion appeared at nearly the same location for all tested fuels, from pure DF to the blend with 85% DTPO.

Tests of TPO derived fuels and DF on automotive-grade engine platforms

The studies presented in the previous subsection were intended primarily to understand TPO's combustion, whereas the experiments using automotive engine platforms, reviewed in this section, are rather aimed at verification of TPO as a drop-in fuel.

Martínez et al. [11] performed their research on a modern, light-duty, automotive engine equipped with turbocharging and EGR. It also had common-rail (CR) fuel-injection, enabling the authors to apply split fuel-injection. The engine was operated in the steady states used in the new European drive cycle (NEDC), reproducing loads typical of city driving. The engine was fuelled with DF and its mixture containing 5% TPO. The combustion analysis showed only negligible increase of combustion duration when using the TPO admixture.

Vihar et al. [86] used a medium-duty, turbocharged and intercooled engine but with a mechanical fuel-injection system. It was run at 1500 rpm and 2400 rpm at various loads. The engine was fuelled with 100 % DTPO, distilled to achieve diesel-like fractions. DF served as a benchmark. To compensate for TPO's lower CN, the authors experimented with by-passing the intercooler when fuelling with DTPO. The objective of this technique was to raise the temperature of the intake air to help auto-ignition. The results are depicted in Fig. 6., showing how intake temperature compensated for DTPO's lower CN. By-passing the intercooler increased the intake air temperature from ca. 70 °C to ca. 170 °C at full load and rated speed, making DTPO's combustion rate the same as that of DF. However, at lower speeds, although the increase of intake temperature provided the same auto-ignition timing, the TPOs combustion was shifted towards a more premixed, kinetic mode.

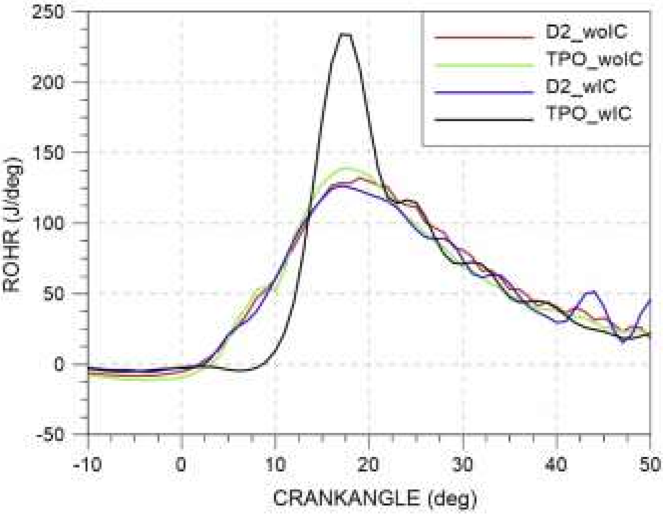


Fig. 6. Heat release rates for DTPO and DF. Data acquired at 2400 rpm, full load (turbocharged), single injection at ~650 MPa, SOI = 1.1 °CA bTDC for DF, SOI = 1.5 °CA bTDC for TPO, intake temperature ≈ 170 °C woIC (without intercooler) and ≈ 70 °CA wIC (with intercooler). Reproduced from [86] with premision from Fuel, Elsevier.

Baškovič et al. [163] performed tests on a light-duty automotive diesel engine with EGR and CR injection system, enabling the use of split fuel-injection. The engine was fuelled with pure TPO, but with a viscosity in accordance with EN 590. The authors manipulated the pilot injection timings to compensate for delayed auto-ignition and the resulting severe HRR of TPO. Diesel-like combustion of pure TPO was achieved by retarding pilot injection few degrees in comparison with the engine's original control map. Moreover, the higher the engine load, the larger pilot injection retardation was required .

Tests with TPO and DTPO blended with other fuels

Sharma and Murugan [155] tested different blends of TPO and jatropha methyl esters (JME) and DF on a basic engine platform with a single-cylinder, non-EGR, mechanical injection with a three-hole injector and a compression ratio of 17.5:1. The engine was run at 1500 rpm and at various loads. SOI timing was set constant at 23°CA bTDC. Pure JME exhibited shorter auto-ignition delay under these conditions than the reference DF, due to JME's higher CN. An admixture of TPO, with cetane number lower than DF's, compensated for this combustion advance. Adding 20 % of TPO in JME gave auto-ignition 1°CA earlier than with DF; adding 30 % of TPO in JME gave auto-ignition 1°CA later than with DF. These results suggest that it could be assumed that JME with 25% admixture of TPO would provide auto-ignition properties the same as DF's. However, differences in viscosity mean that burn durations and HRR profiles differ, despite the same auto-ignition timings. So although JME ignited earlier than DF, slower vaporisation extended JME's combustion more towards diffusion mode. Addition of TPO, which also acted as a combustion retarder, resulted in a substantial extension of combustion duration. These effects are clearly visible in Fig. 7., comparing HRR curves for different fuels and their blends. Continuation of the above work by Sharma and Murugan was aimed at improving oxidation stability of 20 % TPO admixture in JME, and at verification of the effects of antioxidants on combustion [12]. The engine's compression ratio was raised from 17.5:1 to 18.5:1, aiming to tailor the engine parameters to the new fuel. Some delay of combustion was noted when antioxidants were added, but not to a significant degree.

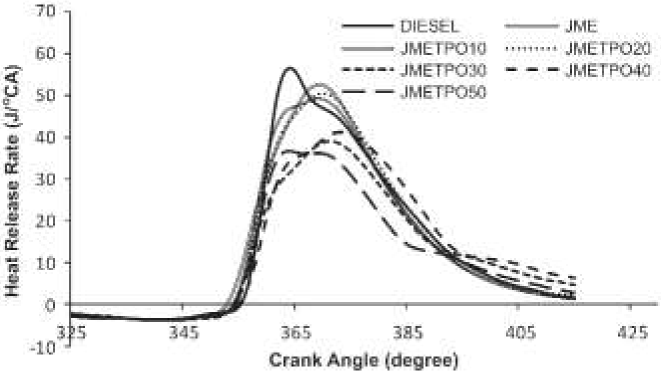


Fig. 7. Heat release rates for variable admixture of TPO to JME, with DF and pure JME as references. Data acquired at 1500 rpm, full load (naturally aspirated), single low-pressure injection, SOI = 23 °CA bTDC. Reproduced from [12] with premision from Fuel, Elsevier.

Ambrosewicz-Walacik et al. [142] distilled light TPO fraction to produce a low-viscosity fuel component. This DTPO was mixed with DF and raw rapeseed oil in proportions 5 %, 40 % and 55 % respectively. The tests were performed using an automotive diesel-engine with CR fuel-injection. The tests covered the whole operational range and included split fuel-injection at low speeds and single injection at high speeds. Although the engine was operated using standard calibration, the detailed HRR analyses showed some specific combustion behaviour of the ternary mixture. Namely, although at split fuel injection the HRR traces for the mixture were similar to DF's, clear low-temperature combustion of pilot fuel was observed in the case of the ternary mixture. The research was continued by Mikulski et al. [164] using different blends of the above-mentioned fuels. All the tested blends included 5 % DTPO but had differing quantities of rapeseed oil, ranging from 20 % to 55 %: DF made up the remainder of each blend. The HRR curves for split fuel injection did not show any significant differences between all tested blends and pure DF. However, the low-temperature combustion fraction was increasing as the biofuel share rose.

4.2 Emissions

This section considers the validations of TPO-based fuels in end-use engine performance from the perspective of emissions. It aims to shed light on the potential and limitations of using TPO as an alternative to conventional diesel. As a preliminary remark, it should be noted that fuel-related exhaust emission trends depend strongly upon (i) a fuel's physical properties, which determine injection, atomisation, mixture formation etc., and (ii) a fuel's chemical properties, which determine auto-ignition timing and combustion chemistry itself. Therefore, both physical and chemical parameters should be considered when discussing emissions.

The most problematic species in diesel exhaust are particulate matter (PM) and NO_X. A temperature/fuel-air ratio map (Fig. 8.) helps us to understand fully the paths of their creation. It shows the soot/NO_X trade-off typical of diesel-engine combustion. Generally, if combustion is more premixed, it tends to produce NO_X. Alternatively, less premixed fuel and oxidiser generates more soot, because combustion operates with a local oxygen deficiency. Soot is a carrier for other compounds that form PM. Finally, it should be noted that although combustion process always runs along the reaction line presented in Fig. 8, the amount of fuel that undergoes combustion along the indivual mechanism, determines the emissions.

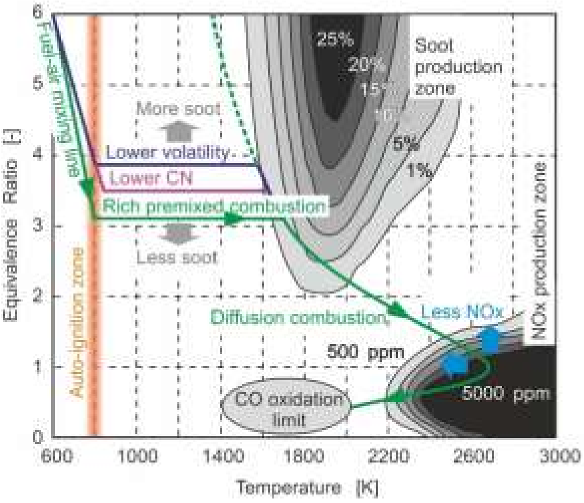


Fig. 8. Regimes of soot and NO_X formation on the flame fuel-air ratio and flame temperature. Redrawn basing on the data in [165].

4.2.1 Nitrogen oxides

There are recognized paths of NO_X formation during combustion. The three predominant mechanisms are: Zeldovich (thermal), Fenimore (prompt) and N_2O (fuel). The first and the last of these are the prevailing mechanisms in diesel engines [130,166]. Most NO_X in raw diesel exhaust gas is NO, produced mainly in the boundary layer of the diffusion flame, where the excess air ratio is nearly stoichiometric, providing favourable temperature (above 1800 K) and access to oxygen. Fuel's effects on NO_X emissions from diesel engines were extensively investigated also when researching various biofuels and waste fuels. Generally, in the case of the first generation biofuels (fatty acid esters), much engine research indicated that they led to increased NO_X emissions when compared to DF [167]. In the case of paraffinic fuels, NO_X emissions were reported to be lower [3,167]. The review by Bergthorson and Thomson [167] revealed that NO_X emissions from pyrolytic fuels are roughly half of that from DF. However, this conclusion was based mostly on research of liquids obtained from biomass, mainly wood.

Tests with crude TPO on basic engine platforms

Murugan et al. [15] performed engine tests without EGR and with single injection. They found that increasing the TPO content in DF from 10% to 50% reduced NO_X concentration, but only at low loads: NO_X concentration increased at higher loads. This non-monotonic trend was explained by the fuel's effect on a combination of local stoichiometry and temperature. Additionally, it was pointed out that a higher aromatics content in TPO can increase propensity to form NO_X. Observed trends in NO_X concentrations were correlated with trends in exhaust temperature, which suggests predominating effects of fuel on global stoichiometry. The trends at low loads were confirmed by Chwist et al. [160]. They achieved ca. 20% reduction of NO_X emissions when the fuel was changed from neat DF to 20%

TPO/DF mixture. Interestingly, NOx emissions from 100% TPO were double that of neat DF. Combustion of pure TPO was heavily delayed (refer to Fig. 5), thus giving a higher premixed fraction.

Tests with refined TPO on basic engine platforms

Rising trends in NOx emissions were not consistent with increasing engine loads when using mixtures containing 20 %, 80 % and 90 % of DTPO. NO_X emissions reduced for higher shares of DTPO at high loads, whereas there was no significant fuel effect observed at low loads [132,147]. The discrepancy between these results indicated that emissions were affected by the reduction in viscosity (reduced by about 50% via distillation) and the removal of heavy hydrocarbons. Similar results were achieved by Frigo et al. [16] on a similar engine platform and using TPO with similar viscosity. Both 20 % and 40 % TPO samples provided reduction of NO_X emissions at full load, whereas results were inconclusive at the medium and low loads.

Doğan et al. [17] used a basic engine platform with mechanical injection system and a fuel dose fixed to the maximum torque. They found that increasing DTPO fraction in DF reduces excess air. NO_X concentration increased with DTPO admixture for all investigated engine speeds (Fig. 8.). Additionally, the trend was not linear at low speed (1400 rpm), with rapid increase of NO_X concentration at the highest (90 %) admixture of DTPO. Zółtowski [18] compared DF with pure DTPO and found that emissions from both fuels were comparable at moderate load, but DTPO reduced emissions by ca. 25% at nearly idling regime.

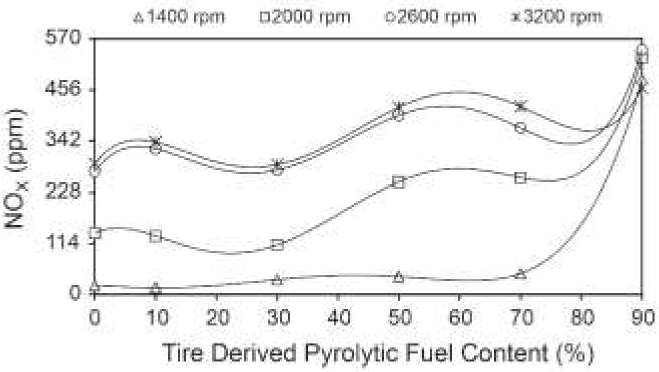


Fig. 8. Trends in NO_X concentrations in exhaust gas for DF and its variable mixtures with TPO. Research on a basic, naturally aspirated engine with single low-pressure injection, without EGR, full load at variable engine speeds. Reproduced from [17] with premision from Fuel, Elsevier.

Comparison of emission performance of distilled and crude TPO from the same feedstock was performed by Murugan et al. [168]. They tested DF and its blends containing 30% of TPO or DTPO. They showed that admixture of TPO did not change emission levels over the whole load range whereas admixture of DTPO reduced NO_X emissions. Moreover, the difference increased in line with engine load, with the NO_X reduction growing from ca. 10 % at close to idle conditions to ca. 20 % at full load.

Recently, Uslu [169] has attempted to optimise a blend consisting of low viscosity TPO and DF, using legacy engine experiments.The optimised parameters were TPO fraction and injection pressure. It was found that increasing TPO admixture content above 30 % lead to a rapid increase in NO_X emissions, whereas TPO's effect on NO_X was negligible when admixture was below 30 %. As could be forecasted, NO_X emissions dropped with reduced injection pressure, although other emission factors deteriorated.

Tests with TPO-derived fuels on automotive engines

Martinez et al. [11] conducted testing using a multi-cylinder Euro V–certified (EGR) engine, exploring different operating points. He found that 5 % admixture of TPO slightly increased engine-out NO_X emissions for all operating conditions, except low loads. This result contradicted others using similar platforms. Bodisco et al. [170] used 10 % admixture of TPO in DF to fuel a Euro 5 passenger car with a modern common-rail fuel-injection system, but without NO_X trap. The tests were realised in real driving conditions that included equal urban and rural driving. The authors showed no significant changes to NO_X emissions from fuel to fuel across the whole cycle, but underlined more significant differences at particular load/speed combinations.

Baškovič et al. [163] used pure DTPO to fuel an automotive common-rail direct injection engine, advancing the pilot injection to achieve nearly the same combustion course as when using DF. Comparison of NO_X concentrations at similar HRR profiles showed that DTPO increases emissions by ca. 20 %, both at low-load and high-load conditions. After eliminating the combustion rate effect, it was concluded that DTPO produces more NO_X due to its fuel-bound nitrogen.

Tests of TPO blends with other fuels

Using mixtures of TPO and JME Sharma and Murugan [155] achieved clear NO_X emissions trends, importantly the same for various engine loads (Fig. 9.). Combustion of pure JME produced ca. 20 % more NO than DF. However, increasing TPO admixture from 10 % to 50 % served to reduce NO_X emissions, compensating for JME's effect. These trends could be attributed to the opposite physical and auto-ignition properties of biofuel and TPO. Biofuels ignite earlier but have a higher boiling temperature, which contributes to mixing-controlled combustion. TPO has a lower CN, and thus ignites later, but it contains light fractions which evaporate earlier. Overall, and under most conditions, emissions from combustion of 50 % TPO and 50 % JME blend were a few percentage points higher than DF's emissions.

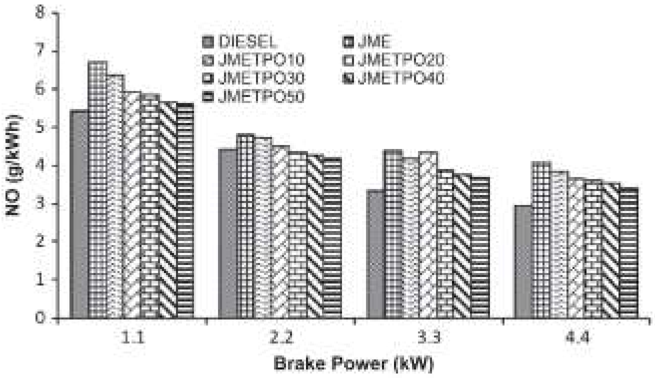


Fig. 9. Trends in NO emissions for DF and variable admixtures of TPO in JME. Research on basic, naturally aspirated engine with single low-pressure injection, without EGR. The brake power from 1.1 to 4.4 kW at 1500 rpm corresponds to BMEP from 1.3 bar to 5.3 bar. Reproduced from [155] with premision from Fuel, Elsevier.

Mikulski et al. [164] used a light fraction of DTPO to reduce viscosity of raw vegetable oil. The test fuels were composed of 5 % DTPO and from 30 % to 55 % of rapeseed oil, with DF making up the remainder. Tests were performed using a common-rail automotive engine with standard calibration. There were no differences in NO_X emissions between different fuels and the reference DF at low loads, but a clear trend was evident at higher loads. The higher the rapseed oil content, the higher emissions were observed here. At the 80% load the addition of DTPO to the crude oil – diesel mixture was responsible for higher NO_X emissions than a comparable mixture of FAME and diesel.

4.2.2 Particulate matter and smoke opacity

PM consist of insoluble and soluble fractions. Soot and ash are components of the insoluble fraction; whereas the soluble one consists of organic carbon, sulphate and nitrate [171]. Soot, which is a precursor of PM, is intensively created in the first stage of combustion, typically at the tip of the fuel spray, where a rich mixture is burnt volumetrically and then turns into mixing- controlled combustion. The production of PM is chemically increased by the presence of alkynes and polycyclic aromatic hydrocarbons (PAH), so TPO's poorer atomization and high PAH content should lead to the production of more PM than is the case with DF. Additionally, it is worth noting that NO_X and PM emissions usually are subjected to a trade-off when combustion shifts between premixed and diffusion-controlled. More premixed combustion produces more NO_X, whereas diffusion- controlled combustion produces more PM. Finally, sulphur's effect on PM creation cannot be neglected when considering TPO. The sulphur content increases the mass of sulphates bound in PM, although this effect is not substantial, because most of the sulphur is converted to SO_2 [172].

Note, that in the majority of available research, exhaust opacity was measured as an indicator of PM concentration. These two parameters are always correlated in CI engines and enable comparative analyses, although opacity does not provide quantitative information about PM emissions.

Tests with TPO/DTPO on basic engine platforms

The trends in PM and smoke emissions on engines with single-pulse injection and in non-EGR conditions are summarised below. Murugan et al. [15] used blends of DF with TPO admixtures ranging from 10 % to 50 %. They did not report any significant changes in exhaust opacity across the whole load range, except at maximum power, where 50 % addition of TPO increased opacity by 7 %. However, the 40% TPO addition slightly reduced opacity compared with DF. In other works [132,147], the same research group found that DTPO produces more smoke than DF and they recorded that increasing the proportion DTPO admixture increases exhaust opacity. Moreover, comparison of emissions from TPO and DTPO 30% admixtures showed that TPO did not affect smoke emissions across the whole range of engine loads. At the same time, admixture of DTPO increased smoke emission by ca. 20%, but only at higher engine loads. Fuel effects on PM and smoke emissions were negligible or at least inconclusive at low loads.

Tests with TPO-derived fuels on automotive engines

Martínez et al. [11] performed detailed analysis of smoke and PM emissions from an automotive engine fuelled with a 5 % TPO blend in DF. At different points of the engine operating map both opacity and PM emissions were higher than with only DF. This was attributed to TPO's higher aromatics content and also to its poorer vaporisation, due to higher final boiling point. The measurements of PM emissions were supported by analysis of particle size distribution. It was found that the size distributions of both tested fuels were the same at low loads, whereas under higher loads the distributions for fuel containing TPO shifted towards smaller particles. This was ascribed to TPO's sulphur and metals contents. Analysis of PM composition showed that PM generated by TPO contains a higher volatile organic fraction.

Tests of TPO blends with other fuels

Measurements of exhaust opacity by Sharma and Murugan [155] when using blends of TPO with JME show a clear trade-off with NO_X emissions. See Fig. 10 for details. Combustion of pure JME reduced opacity in comparison with DF: the reduction was substantial - approximately 30 % - at higher loads. Increasing TPO content in JME from 10 % to 50 % gradually increased exhaust opacity to a level slightly above that of DF. Opacity with 20 %-30 % admixtures of TPO in JME was comparable to that with DF.

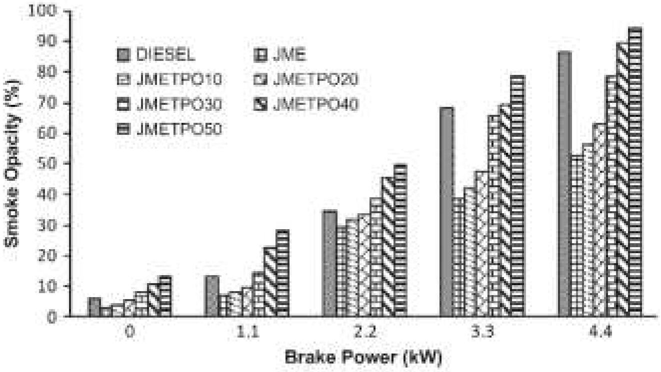


Fig. 10. Trends in exhaust gas opacity for DF and variable admixtures of TPO in JME. Research on basic, naturally aspirated engine with single low-pressure injection, without EGR. The brake power from 1.1 to 4.4 kW at 1500 rpm corresponds to BMEP from 1.3 bar to 5.3 bar. Reproduced from [155] with premision from Fuel, Elsevier.

Recent works by Ambrosewicz-Walacik et al. [142,164] and Mikulski et al. were aimed at making it feasible to use raw bio-oils in diesel engines, employing light fractions of DTPO to reduce viscosity. Addition of 5 % of low viscosity DTPO to mixture containing 40% of DF and 55% of bio-oil produced some reduction of exhaust opacity. However, a dramatic increase in smoke was observed at higher engine loads and with split (pilot and main) injection [142]. This increase was found to be correlated with combustion rates, specifically advance of auto-ignition. Coupled with the poor atomisation of highly viscous fuel, this resulted in rich combustion, producing large amounts of soot. Interestingly, the fuel's effect on smoke was much smaller with a single fuel injection, because the fuel had less of an effect on combustion rates. Finally, it has been found that injection strategy strongly affects the emissions response to fuel type. Further research with the same 5 % DTPO admixture, but with variable amounts of bio-oil and DF, showed that, in general, ternary fuel reduces exhaust opacity using both single and split fuel-injection. However, this effect is most noticeable at moderate load. Moreover, the content of bio-oil did not show any clear trend in opacity.

4.2.3 CO and unburnt hydrocarbons

Emissions of CO and HC from diesel engines are far less problematic than NO_X and PM [173]. The amounts are small and these species can be burnt effectively in oxidation catalytic reactors, provided that the exhaust temperature is high enough [174]. Nevertheless, TPO-derived fuels also affect these emissions. This is mainly due to differences in the physical parameters of fuels. Highly viscous fuels have higher liquid fuel spray penetration, which can result in wall impingement by fuel. This phenomena usually produces high amounts of HC because not all the fuel is burnt during combustion. CO is mainly a residue from incomplete combustion if the mixture is too rich to oxidise CO at the end of combustion. The second dominating mechanism, more likely for diesel engines, is low flame temperature. This can occur when combustion is delayed towards the expansion stroke or if the fuel is highly diluted, by recirculated exhaust, for example. CO and HC emissions trends for TPO-derived fuels and mixtures are summarised here.

Working on a simple engine platform, Murugan et al. observed that both CO and HC concentrations generally increase with increasing TPO admixture to DF, independently of engine load [15,132,147]. The increase in CO with addition of TPO was attributed solely to delayed combustion and thus inhibited CO oxidation. Similarly, Kumar and Prabu [162] reported an increase of concentrations of both components. The trends in both works appear consistent. Shifting fuel from DF to pure TPO almost doubled CO concentration, while the increase in HC content for the same transition would be approximately 50 %. In contrast, Chwist et al. reported a decrease of CO concentration with increasing TPO content [160]. However, it should be noted that the baseline CO concentrations reported in this work were already ultra-high, at 3 %. The trend in HC emissions was not monotonic, but indicated an increase in the exhaust's HC content when 10 % or more TPO was added to DF. Dogan et al. [17], using a naturally aspirated engine at full load, found that the CO and HC trends were dependent on engine speed. At low speed (1400 rpm), using a TPO content of 90 % reduced CO by 50 % and HC by 20 %, when compared to DF. Results were inconclusive at engine speeds beyond this point.

As for TPO mixtures with biofuels, Sharma and Murugan [155] observed that emissions of both CO and HC when using pure JME are about 10 -20 % lower than with DF. Addition of TPO to JME increased both emissions. The CO and HC emissions were similar to those from DF when the TPO admixture to JME reached about 30 %.

Using a more advanced automotive engine platform, Martínez et al. [11] evaluated emissions from a 5 % admixture of TPO to DF. They found the admixture increased emissions of both CO and HC by ca.

10 % compared to DF, but only at nearly idling conditions. Differences between the test fuels were negligible at moderate and high loads. Similar results in terms of HC emissions were achieved by Baškovič et al. [163], although they compared DF with pure TPO. These results revealed sensitivity to EGR of low-CN fuels, like TPO.

5 Discussion and outlook on further research

The last decade has brought an exponential increase of research into use of TPO as a combustion engine fuel. As already mentioned, the wide discrepancy in TPO quality, the different blending strategies and the variety of engine platforms used for testing, all make it difficult to pin down the current status of the research. These factors have been reviewed in sections 3 and 4. This section's aim is to distil the knowledge captured in this review into a concise vision of TPO as a fuel component in combustion engines. We think this is best done by answering the research questions posed in subsection 1.3 of the introduction. Furthermore, an important observation from this review is that most researchers are trying to find the right way to use TPO by picking from an infinite sea of possible blending strategies, often exploring routes that actually are not particularly feasible. The outlook section which follows aims to provide a more focused perspective for future research in this field. This research is most definitely needed if TPO fuels are to become part of a solution capable of solving the sustainability issue and greenhouse gas problem.

What is the progress in pyrolysis technology with respect to maximising the TPO yield and resulting fuel quality?

The review has shown a rapid emergence of pilot tyre-pyrolysis reactors and that the demonstrations are gradually moving towards more advanced reactors, including rotary designs [55]. Catalytic pyrolysis using steam, helium or nitrogen as inert gases has proven to give the best results in terms of simultaneously maximising TPO yield, positively affecting the heating value and reducing sulphur penetration to the liquid fraction [121]. Process temperature is considered the most crucial optimisation parameter here and the best results in terms of yield/HHV/energy input typically are reported to come in the temperature range of 450-650 °C. Further elevation of the temperature demands greater energy input, and the intensified nature of the rubber cracking means more of the high-volatility hydrocarbons are transferred to the gaseous fraction, leading to a slight deterioration of the HHV of the TPO fuel which is produced. Furthermore, the higher temperatures lead to unwelcome increases in the TPO's viscosity, density and sulphur content [55]. However, it must be noted that that some authors did not observe these deteriorations in fuel properties when taking the pyrolysis temperature above 650 °C, suggesting that this limit depends upon the reactor type and feedstock quality.

Turning to TPO yield, the state of the art is currently reported to be around 55 % when coupled with diesel-like or even higher heating values (up to 48 MJ/kg) [55]. Achieving viscosity and density within EN 590 limits is not a problem in itself, yet must overcome the tradeoff with the fuel's flashpoint, also defined by EN 590. The CN of TPO, which is typically around 45, is not far below EN 590's minimum value for DF of 51. The biggest fuel quality challenge for TPO is its sulphur content. Typical sulphur values for crude TPO produced in an optimised reactor are in a range of 0.3 %-1 %, although figures below 0.01 % were also noted. This leaves desulphurisation vital for any automotive application where EN 590's 0.001 % sulphur limit applies, even if blends are considered. TPO's route into marine applications looks easier because it is an inexpensive fuel capable of complying with the IMO global sulphur cap 0.5 %, effective in 2021, and maybe even meeting the IMO ECA sulphur limit of 0.1 %. The moisture content of crude TPO can be high, but it can be effectively and easily fractioned, so this is not considered to be a real issue.

Co-pyrolysis of tyres, with biological material, for instance, is another way of achieving high- quality fuel, increasing the oil yield and at the same time tackling feedstock limitations. This is a relatively new concept, so the number of available works on this topic is limited and scattered over different feedstock configurations. Consequently, this review does not cover tyre co-pyrolysis in detail, but we note that several authors have underlined that the final product of co-pyrolysis is superior in quality to that from pyrolysis of either pure biomass or tyres [175–178].

What are the available TPO-upgrading technologies and what is their effect on the end fuel quality?

Assuming the pyrolysis itself is fairly well optimised, as described above, crude TPO's properties are already close to the diesel EN 590 standard, except in terms of the aforementioned viscosity/flashpoint tradeoff and the sulphur content. Thus, when starting with a relatively high quality of crude oil, it is probably not economically feasible to apply refinery-grade cracking processes, such as hydrocracking, for instance, especially considering the need for distributed TPO production. Indeed, those processes have not been openly demonstrated with TPO. Instead, the three major upgrading processes considered for TPO are desulphurisation, distillation/fractionation and fuel blending.

Application of ionic solutions/liquid - liquid extraction emerges as a feasible and cost-effective alternative to refinery hydrodesulphurisation as a fuel post-processing desulphurisation measure. This was successfully demonstrated on TPO, with different sulphur-binding agents used to halve sulphur content on average. Bearing in mind that the addition of an in-reactor catalyst helps to optimise pyrolysis, and that a TPO sulphur level below 0.01 % has already been achieved, further progress towards EN 590's sulphur limit seems feasible, especially if fuel blending is considered.

Many different strategies of TPO fractionation and blending have been tested while attempting to achieve a fuel composition with properties within EN 590 limits. It has to be said that none is completely successful. TPO distillates (DTPO) generally offer good viscosity and cold properties but their flashpoint is too low to meet EN 590. However both properties do not scale linearly with distillation temperature paving a feasible route for DTPO application as lubricity improver**.** This suggests that a promising route for TPO-derived fuels maybe to take advantage of their complementary properties with biofuels. Biofuels usually suffers from high viscosity (FAME) or poor lubricity (HVO and FAME) yet offer substantial reserves in terms of flashpoint and cetane number: DTPO has the opposite characteristics. Another potential route for non-road applications of DTPO, especially in developing countries, might be to use its light fractions as an effective viscosity improver when raw vegetable oils are admixed to diesel. This was argued by Mikulski et al. [164].

How do different fuel compositions of TPO and TPO-derived fuels perform in the engine in terms of combustion characteristics, efficiency and emissions?

The review of engine test results reveals several trends. Within the constraints of the quality of the TPO samples used, small admixtures of crude TPO (up to 10 %) to diesel can be used without any profound effects on the combustion process and connected efficiency. Using processed (distilled) TPO can further extend this limit somewhat higher than 10 %. At such conditions, NO_X emissions can be slightly elevated (evident only at higher loads) and CO and HC can increase by approximately 10 %, but only at low loads. Note that the above differences in state-of-the-art combustion engines are reported to disappear over the driving cycle when using small-scale TPO additions.

When combustion effects are neglected TPOs tend to emit more NO_X due to higher amounts of fuel-bound nitrogen. Greater CO and HC emissions result from higher viscosity and poorer spray atomisation, limiting oxygen entrainment. TPO increases PM emission because of its high aromatic and soot contents. Both these fractions are found to promote PM formation, which in the case of TPO, usually is composed of small–diameter particulates. These smaller particles are proven to have a more deleterious impact on human health. Note, however, that reports documenting quantitative particulate mass or number for TPO combustion are rather scarce: most authors instead used smoke opacity as the basis for their conclusions on PM. Opacity was more likely to be influenced by local mixture stoichiometry.

The abovementioned fuel-related effects on emission can be scaled with increased TPO fuel content and also can be partially neutralized by optimum fuel composition. Large-scale TPO admixture makes the effect of fuel properties on combustion become more pronounced, in turn influencing emissions to a much greater extent. Delayed auto-ignition is commonly reported for TPO or DTPO additions above 20 %, shifting combustion towards a more premixed mode and elevating NO_X emissions. Long ignition delays also shift combustion from its optimum timing, and thus impact engine efficiency. Fuel viscosity and cetane number are primary drivers for ignition delay. High viscosity is relevant only for non-processed TPO samples and harms combustion at high-load regimes where spray formation is the main limiter for ignition. TPO's lower cetane number is responsible for increased chemical ignition delay manifesting at low loads and at high EGR ratios. Van de Beld et al. proved that this low CN effect can be successfully mitigated by elevating the intake temperature [161]. This technique allowed the combustion of neat TPO samples with diesel-like characteristics and efficiency. Engine control strategies have also been demonstrated to mitigate viscosity effects for TPO, including advancement of injection timing (both main and pilot injection) and elevating injection pressure. Both strategies are, however, limited by the threat of spray wall- wetting. Note that viscosity control by fuel pre-heating is a standard feature in flex-fuel marine diesel engines capable of running on HFO.

As a final discussion note, it is necessary to say that drawing up this summary of emission trends related to TPO fuels was only possible by adding the perspective of fuel properties and combustion analysis. The number of works on engine emissions from TPO that lack this context is in fact far greater than those reviewed in Section 4. Without a combustion perspective, the results from various works seem contradictory, making it impossible to draw accurate conclusions. This reasoning leads to a general concern that incomplete works may put forward biased conclusions that have a possible negative impact on the take-up and commercialisation of alternative fuels. With this rather critical remark, we open the discussion about outlook.

Outlook

An underlying premise of this research is that waste tyres form a considerable feedstock for fuel production, comparable to that of biomass once food production has been prioritised. The evidence considered in this review indicates that TPO has sufficient quality to be used as bunkering fuel. There is a fairly small gap between the quality of fuel from the current state of the art in TPO production technology and the standard set by automotive diesel fuel requirements. Continued research along the suggested lines should be capable of bridging that gap.

Although progress in desulphurisation techniques and developments in pyrolysis process control are improving its quality, TPO's most feasible automotive application role is probably not as a stand-alone fuel. Blends are the favoured route, not only because they facilitate improvement of the end-fuel's properties, but also from the perspective of availability. No single alternative fuel - TPO, biofuels or synthetic electrofuel - will be capable of becoming a full substitute for all fossil diesel. The requirement for sustainablility will shift future fuels towards more complex blends accommodating all renewable resources. Blending strategies should be developed to build on the complementary physicochemical parameters of individual fuels. Blending TPO and FAME has been suggested here as a good example of this complementary approach. According to the present fuel quality and messions review, an exemplary composition of 7 % FAME / 7 % TPO / 86 % diesel could be straightforwardly applied on the market, offering benefits over the current B7 diesel. Other combinations, for instance blending TPO with HVO, should be explored. This fuel blend design challenge should be supported by the development and use of predictive models that can target specific properties or engine performance [179]. Development of these models should be strongly encouraged in order to focus experimental testing and accelerate development of sustainable liquid fuels: climate change does not allow the luxury of time.

Before TPO-derived or any other pyrolytic fuels can be marketed, engine manufacturers must accept them, which in turn, means that more vehicle and engine tests using TPO blends should be picked up by research organisations. The bulk of engine test results with TPO involve legacy (basic) engines: tests with modern (EU Stage V/Euro 6) engines are lacking. Furthermore, the twin threats of PM and PAH are already identified as potential issues, which in our opinion will limit the application of TPO/DTPO to blends not exceeding 10 %. There are many more pending emissions issues for TPO applications that have not been addressed at all so far. Unlegislated emissions need to be considered, especially with respect to aldehydes and aromatics. TPO is expected to generate higher levels of both of these, which may lead to imposition of additional constraints on TPO. Finally, the effect of TPO fuels on modern exhaust aftertreatment systems has been hardly studied at all. Sulphur poisoning of diesel oxidation catalyst is an obvious issue here, and there may be others. Catalyst tests should be conducted in tandem with long-term durability engine tests to check for potential deposit formation (injectors, valves etc.) and performance deterioration over time.

Finally, it is worth remembering that pyrolysis, although nowadays economically feasible, lacks legislative incentive to encourage its large-scale uptake as a clean and efficient way to use waste tyres. Continued lobbying in this respect is required to transition from simple (but destructive) incineration of tyres towards more sustainable pyrolysis. Furthermore, the above pros and cons of pyrolytic oil as a fuel component should be weighed against other possible applications for TPO, such as its use in a closed-loop, tyre-manufacturing process. This comparison should include factors like process economy, well-to-wheel CO_2 footprint and local availability. It should also assess combinations of TPO with other feedstock in fuel- and tyre-producton chains, demanding a complex decision-making equation. Multi-criteria decision-making using artificial intelligence-based approaches would allow complex data from diferent sources to be merged with expert knowledge into reasoned and unbiased decisions [180,181].

6 Conclusions

The objective of this work was to review the current status of tyre pyrolytic oil in combustion engine applications. This fills an important knowledge gap on the sustainability transition roadmap, because the vision of how to best utilise waste tyres is not clear. This feedstock, with its substantial availability and large heating value, can contribute to solving the short-term fuel transition problem for off-road machinery, heavy-duty road vehicles and marine transport. This review's focus was on fuelling diesel engines, as these are the main power units in these sectors.

To this end, this review answers the governing research questions related to TPO production and quality; post-processing and quality improvement methods; and engine validation of the final TPO-derived fuels. These questions are discussed in detail in section 5: these are main conclusions drawn from the discussion:

i. The current state of the art in tyre pyrolysis provides yields of around 55 % of crude oil with diesel-like heating value of approximately 42 MJ/kg. The process energy consumption and ambient losses do not exceed 15 % of the feedstock's total heating value.

ii. The properties of crude TPO enable direct fuelling of compression ignition engines. The fuel can meet the low-sulphur fuel oil standards for bunkering fuel and so can be used in all ships subject to the IMO global sulphur cap (max 0.5% fuel sulphur content) without needing scrubbers. The quality is insufficient for automotive applications governed by the EN 590 diesel fuel standard.

iii. Current technology, such as an economically feasible ionic solution washing process, can reduce sulphur content below 0.01 %.

iv. TPO viscosity can be tailored using distillation, but the tradeoff between viscosity and flash point should be considered.

v. The above limitations narrow down automotive applications of TPO/DTPO to low-level blends (up to 10 %) with mineral diesel and other fuels. Mixtures including DTPO and FAME (or crude bio-oils) are most feasible since these fuels can be compatible in viscosity, flash point and cold properties.

vi. Emissions are an important constraint for TPO fuel applications. Its combustion-related effects can be mitigated either by matching fuel properties or combustion control, but TPO is fundamentally prone to emit more nitrogen oxides, CO and unburnt hydrocarbons than diesel fuel. For typical blends containing up to 10% TPO, the effects are rather small - increases of up to 10%, depending on the operating point, and diminishing over the whole driving cycle.

vii. Major concern is associated with particulate mass emissions when using TPO: these scale up linearly with TPO content in the fuel. The size distribution of the PM and TPO's substantial polyaromatic hydrocarbons (PAH) content are also causes for concern. PAH content is not explicitly legislated yet has profound carcinogenic effect.

viii. Despite the above issues, the major hurdle for TPO remains the issue of how to capture waste tyres. Regulations in this sphere do not introduce the necessary incentive for pyrolysis to compete successfully with incineration.

The above conclusions, complemented by exact numbers in the adjoining discussion, aim to provide an unbiased input to help shape the future fuel roadmap for TPO, so they ultimately do not convey a final decision. That decision-making process should weigh TPO against different feedstocks available for sustainable fuel production, and also against possible competing applications of these feedstocks.

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