

Evaluation of Tyre Pyrolysis Oil Fuel Properties and Their Impact on Diesel Engine Performance: A Comprehensive Review

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Abstract

The study reviews the properties of tyre pyrolysis oil (TPO) as a potential alternative diesel fuel, highlighting its physicochemical characteristics essential for compression ignition engines. Key parameters such as density, viscosity, calorific value, cetane rating, and chemical composition are discussed, revealing that TPO deviates significantly from traditional diesel. While TPO has higher density and variability in viscosity, it also exhibits lower calorific value and cetane rating, alongside poorer cold-flow characteristics. The literature on TPO is fragmented, lacking comprehensive models linking pyrolysis conditions with fuel performance. The review underscores the need for integrated experimental frameworks to enhance TPO's viability as a sustainable diesel substitute, identifying critical research gaps for future exploration.

Keywords: Tyre pyrolysis oil (TPO); waste tyres; alternative diesel fuel; pyrolysis; fuel characterization; physicochemical properties; GC–MS analysis; FT-IR spectroscopy; structure–property relationship; diesel engine applications.

Introduction

The environmental degradation and energy crisis are some of the problems mankind is currently experiencing. These issues are due to population growth, rapid industrialization and large amounts of waste material generated on a daily basis as a result of different activities. There is instability of world fuel markets and depletion of oil reserves hence different attempts have been made to find alternatives to fossil fuels [1]. This situation has culminated in the use of suitable technology from non-conventional sources for the future recovery of oil. One of the non-conventional sources includes the recycling of waste material to get energy [2]. Used tyres are some of the waste material around us.

Natural rubber trees are a source of latex which is the base material for tyres [3]. Latex is extracted by slicing a thin strip of bark and allowing it to seep into a collecting jar for several hours [4]. The rubber tree is mainly cultivated to produce latex, which is the base material for various rubber products e.g. tyres [5,6].

Rubbers are elastic materials with the ability to greatly alter their dimensions dramatically when

stress is applied and removed [7]. Rubber is also an isoprene polymer, which has double bonds between the monomers. Carbon black is another primary component of tyre rubber. In the manufacture of tyres, sulfur and other chemicals are used. Tyres contain approximately 20 different metals elements that cannot be destroyed by fire. Zinc is one of the metals present in tyres in large quantity, since zinc oxide is being used in the process of vulcanization [3,6].

Tyres are made up of complex chemically cross-linked polymers. This makes their recycling by remolding them into various shapes without a serious degradation after getting worn out difficult [8,9]. Disposed tyres present difficulties in land filling and do not degrade easily because their disposal and reprocessing are also difficult due to the same property that makes them attractive as tyres. Using of waste materials as a renewable energy sources has become one of the possible ways of waste tyre management [10]. Worn out tyres can be retreaded and reused, but the resulting tyres are of low quality [11,12], and at the end they will be disposed as waste material.

Another feature of tyres is their tolerance to biological degradation [9,13,14] which makes them resist harsh environmental conditions such as bacteria, friction, ozone exposure and light [13]. Therefore a threat to safety and environmental degradation is the indiscriminate discarding and stockpiling of worn out tyres. Tyres are of low density and an empty space is around 75 percent of their total volume, therefore occupying a greater amount of productive land filling space when piled up [15]. As a result, given the issues associated with disposing of used tyres, recycling them is the most viable option remaining. Pyrolysis is one of the processes for decomposing used tyres into valuable materials and energy that is environmentally friendly [11,16].

Worn out car tyres can be used to make foot wears but they are limited to sections that don't contain wires. Handles for some hand tools (e.g. panga machete, slasher and knives) can be made up of pieces of tyres, but there are always pieces of tyres which will remain after their usage. They will need to be disposed when they have no any other use and some individuals will burn them in order to reduce their quantity. Disposable tyres can as well be used in landscaping in some areas but the quantity of disposable tyres is high compared to what can be used [6]. Tyres will always continue to be produced as long as there are vehicles running on the roads.

Despite extensive research on tyre pyrolysis oil (TPO) as an alternative diesel fuel, the literature is fragmented and focuses mainly on individual properties such as density and viscosity. While analyses confirm TPO is a complex mixture, there is little quantitative linkage to fuel properties or engine performance, resulting in a weak structure–property–process understanding. Pyrolysis conditions have not been systematically integrated with molecular evolution, limiting predictive capability. Additionally, studies often overlook interdependencies among fuel properties and do not employ integrated optimization tools. There is a clear need for unified frameworks that connect pyrolysis conditions, molecular composition, and fuel performance for more efficient and sustainable diesel engine applications.

2.0 Fuel characterization

A compression ignition (CI) fuel produce power when it is atomized mixed with air in the cylinder and ignited at a high pressure. The fuel should ignite at the appropriate time and release the required energy per unit volume during combustion. The fuel should also be able to flow easily and burn readily at the required temperature and pressure [17].

There should be no excessive pollution when the fuel is used. It is also desirable for the fuel to be safe in terms of toxicity and flammability [18]. Some of the important characteristic parameters of tyre pyrolysis oil that need to be determined before the fuel is used in running the engine are described in this section.

2.1 Density

A fuel's density is given as the proportion of its mass to the volume occupied at a specific temperature. Usually, fuel density is measured using a density meter at a normal temperature of 15 °C. The knowledge of density can be applied to quantity estimates and the evaluation of ignition quality [17,19]. The density of TPO is generally higher compared to diesel fuel [8,20,29–32,21–28] and use of a catalyst e.g. sodium carbonate can increase the density of TPO [3,19]. The density is directly amount of double bonds and inversely proportional to chain length [33–36]. Density is a very significant characteristic property of the fuel, as it is used to calculate the quantity of fuel supplied by injection pumps into the engine cylinders using their density [12,17].

When working in a cold environment, it is desirable to fast warm-up the fuel and it is required to have the adequate amount of volatile and low density components in order to enable the starting of the vehicle easily. The fuels should also have denser elements that will provide power once the engine reaches its operating temperature. The needed fuel density is determined by the engine size, load variations, speed characteristics, starting, design, and atmospheric conditions. Engines that operate at a high rate of change in speed and load, such as trucks and buses, may require more volatile and less dense fuels to obtain better performance, particularly in terms of smoke emissions. However,

because denser fuels, such as diesel, have a higher energy content than less dense fuels, they provide superior fuel economy [17,19]. Increasing density results to an increase in particulate emission [36,37].

Although previous studies have established that tyre pyrolysis oil (TPO) generally exhibits higher density than conventional diesel fuel and that catalysts such as sodium carbonate can further increase its density, the current body of literature remains fragmented and largely descriptive. Most available studies focus on comparing density values between TPO and diesel or reporting catalyst effects in isolation, with limited systematic quantification of how pyrolysis conditions, feedstock composition, and molecular structure jointly govern density variation. In particular, the relationships between density and underlying structural characteristics such as chain length distribution and degree of unsaturation are still not sufficiently modeled within an integrated predictive framework.

Furthermore, despite the recognized influence of fuel density on injection characteristics, ignition quality, and particulate emissions, most studies treat density as a standalone property rather than embedding it within multi-objective engine performance and emissions optimization. The trade-off between improved energy content associated with higher-density fuels and the simultaneous increase in particulate emissions has not been rigorously optimized for TPO-based fuels under varying engine loads and operating conditions. Consequently, there remains a critical need for integrated experimental and modeling approaches that link catalytic pyrolysis parameters, molecular fuel structure, and density-driven combustion behavior to determine an optimal density range that balances engine performance, fuel economy, and emission control.

2.2 Kinematic viscosity

The kinematic viscosity of a fluid is a measure of its internal friction, which opposes dynamic changes in fluid motion at a given temperature. The kinematic viscosity of TPO is closely comparable to that of jet fuel and is significantly lower in most cases than that of diesel fuel [3,20–22,25–27,29,31,38] but

Rofiquel *et. al.*, [39] found it to be more and use of a catalyst in pyrolysis e.g. MgO and CaCO₃ can lower it [40]. In general, different fluids have different temperature-viscosity relationships, and because viscosity is temperature-dependent, all viscosity values should be presented alongside the corresponding temperature values [17].

A viscometer is used to determine the viscosity of a fluid, and the Stokes or Centistokes unit is the most commonly used unit. The amount of previous heating necessary for storage, handling, and adequate atomization is determined by the kinematic viscosity of the fuel. Highly viscous fuels are difficult to pump, atomize poorly, and burn slowly [1,41,42]. Insufficient atomization can result to carbon deposition on cylinder walls or burner tips, it is normally improved by pre-heating [41].

By increasing the gear train and causing the system to wear out due to the increased injection force required, a high fuel viscosity can damage either the engine or the fuel pump. Starting of the engine will be difficult due to poor atomization [1,12,17]. The kinematic viscosity is generally directly proportional to the organic liquids' chain length [34–36,43–47]. Viscosity is inversely proportional to the degree of unsaturation and is controlled by the configuration of the double bond, with the trans-configuration having a higher viscosity than the cis-configuration [34,35,44,47,48]. Branching also influences liquid viscosity because it reduces carbon chain interaction by preventing neighboring molecules from approaching each other [49].

Fuel viscosities greater than 5.5 centistokes at 40°C are usually used in slow-moving engines and may require preheating before injection. Each engine has a minimum required viscosity to avoid power loss owing to the injection pump and its leakage. The highest fuel's viscosity is determined by factors such as fuel temperature, injection structural features, engine size and design [17]. Low viscosity will result in more leaks past the injection pump's piston [1].

Although extensive studies have reported that the kinematic viscosity of tyre pyrolysis oil (TPO) is generally comparable to jet fuel and often lower than diesel, the available literature remains inconsistent and fragmented, with some reports

indicating higher values depending on feedstock type and catalytic conditions. While catalysts such as MgO and CaCO₃ have been shown to reduce viscosity, most studies provide empirical observations without establishing a unified understanding of how pyrolysis parameters, molecular structure, and catalytic mechanisms collectively govern viscosity behavior. In particular, the relationships between viscosity and structural features such as chain length distribution, degree of unsaturation, and molecular branching remain insufficiently quantified for TPO systems.

Furthermore, although kinematic viscosity is a critical determinant of fuel atomization, injection performance, and engine wear, most research treats it as an isolated fuel property rather than integrating it into engine performance and emissions optimization frameworks. The strong temperature dependence of viscosity and its interaction with injection system design, preheating requirements, and operating conditions are often reported separately, limiting predictive capability for real engine applications. Consequently, there is a clear need for integrated experimental–modeling approaches that link catalytic pyrolysis conditions, molecular composition, and temperature-dependent viscosity behavior to determine optimal viscosity ranges that ensure efficient atomization, stable combustion, and reduced engine deposits in TPO-fueled engines.

2.3 Calorific value

The fuel's calorific value is the amount of thermal energy emitted when fully burned per unit mass of fuel. It indicates the energy contained in a given fuel. The suitability of a material or substance to be used as fuel is also determined [50]. It is measured in joules per unit mass of a material (kilograms).

The calorific value is commonly determined by use of a bomb calorimeter [51]. The gross calorific value for TPO has been found to be slightly less compared to diesel fuel [8,11,38–40,52–58,20,59–67,21,24–27,30,32]. Diez *et al.* [68] concluded that TPO calorific value varies proportionally to pyrolysis temperatures between 350 °C–500 °C.

When comparing saturated and unsaturated hydrocarbon fuels, un-saturated hydrocarbon fuels have a reduced calorific value, and this condition

could be due to the following factors: First, functional groups in the molecular structure such as $\text{C}=\text{C}$ - and $\text{C}-\text{OH}$ limit both vapour emission and energy release from the combustion reaction [69–72]. Second, the oxidation of light hydrocarbon molecules into end products, such as CO₂, necessitates the addition of oxygen-containing moieties as well as the breaking of C-C bonds [69,73]. The increase in chain length increases the calorific value and it decreases with increase in unsaturation [34,36,46,48].

Although extensive literature consistently reports that tyre pyrolysis oil (TPO) exhibits a lower gross calorific value than conventional diesel fuel, the findings remain largely descriptive and lack a unified mechanistic understanding of how pyrolysis conditions and molecular composition collectively determine energy content. While some studies indicate that calorific value increases with pyrolysis temperature (typically 350–500 °C), most available work does not systematically quantify the competing effects of chain length distribution, unsaturation level, and oxygenated functional groups on the final heating value. As a result, predictive relationships linking process parameters, structural evolution of TPO, and its energy density remain insufficiently developed.

Furthermore, although the influence of molecular structure on calorific value is qualitatively acknowledged—where increased chain length enhances energy content while unsaturation and oxygenated groups reduce it—these relationships are rarely integrated into optimization or engine performance frameworks. Most studies evaluate calorific value as an isolated property using bomb calorimetry without connecting it to catalytic effects, fuel upgrading strategies, or combustion efficiency under real engine conditions. Consequently, there is a clear need for integrated experimental and modeling approaches that correlate pyrolysis operating conditions, fuel molecular structure, and calorific value to establish optimized production pathways that maximize energy yield and improve the practical suitability of TPO as an alternative fuel.

2.4 Cetane rating

The ability of fuel to ignite at the requisite pressure and temperature in the cylinder following fuel injection is the most important quality for a diesel engine [74]. The igniting qualities of a fuel are determined by its cetane rating [51]. This is made up of the cetane number and the cetane index. The cetane number may be measured directly when fuel is burned in a Cooperative Fuel Research (CFR) engine under normal test settings [75], whereas the cetane index is calculated from the fuel parameters, such as its distillation temperature or chemical structure [8,21,22,75].

Cetane number: The cetane number is a measurement of the ignition quality of a fuel. It describes the engine's rough or smooth operation as a function of the fuel's ignition delay and the rate at which pressure rises. Ignition quality is defined as the amount of time that passes between the commencement of fuel injection into the cylinder and the start of combustion; the shorter the period, the better the ignition quality. If the ignition delay is excessively long, a considerable volume of fuel may be injected before combustion begins, causing the combustion to proceed with an accelerated intensity and a rapid rise in pressure. When it comes to starting and running in a cold environment and at a low speed, a high cetane number implies smoothness [76,77]. Presence of highly unsaturated hydrocarbons and branching result to low cetane number and poor combustion [46,48,78]. It is also proportional to the chain length [34,46,48] and inversely proportional to unsaturation [34,48,77]. Decreasing the cetane number results to an increase in particulate emission [37].

Cetane index: The cetane index is used when no direct determination the traditional cetane number is possible. It is possible to achieve a good estimate of cetane rating of the fuel by calculating the cetane index (CI). The cetane index can be approximated using equation 2.1 [8,21,22,74,75].

$$CI = 454.74 - 1641.416D + 774.74D^2 - 0.544T_{50} + 97.803[\log_{10}(T_{50})]^2 \quad \text{Eq. 2.1}$$

Where CI = Cetane Index

$$D =$$

Fuel Density at 15 degrees centigrade

$$T_{50} =$$

50 % Recovery Temperature (degrees centigrade)

Although extensive studies have investigated the ignition quality of tyre pyrolysis oil (TPO) through cetane number and cetane index, the current literature remains largely empirical and lacks a unified mechanistic and predictive understanding of how fuel composition and production conditions influence ignition behavior. Most available studies report that TPO generally exhibits lower cetane ratings than conventional diesel due to its higher unsaturation and branching; however, these findings are often based on isolated measurements without systematically linking molecular structure (chain length distribution, degree of unsaturation, and oxygenated species) to ignition delay and combustion stability. In addition, the dependence of cetane index on density and distillation characteristics is frequently applied without validating its accuracy for chemically complex TPO systems.

Furthermore, while it is well established that lower cetane number leads to longer ignition delay, higher pressure rise rates, and increased particulate emissions, most research treats cetane quality as a fixed fuel property rather than an optimizable output of pyrolysis and upgrading processes. Limited attention has been given to integrating direct cetane measurements with predictive correlations and engine performance outcomes under varying operating conditions, particularly for catalytic TPO production routes. Consequently, there is a clear need for integrated experimental and modeling approaches that connect pyrolysis parameters, molecular composition, and ignition quality indices to establish optimized fuel design strategies that enhance combustion stability and reduce emissions in diesel engine applications.

2.5 Pour point

The pour point (PP) is the temperature at which gasoline freezes and ceases to flow freely, resulting in the formation of a semi-solid. The pour point is a measurement of the lowest temperature at which fuel can be safely transferred until it turns into a gel in the liquid state. In low-temperature conditions, fuels with a high pouring point are difficult to use.

It is important to heat these fuels before the engine starts [17].

The pour point (PP) is an essential fuel property which needs to be determined in places that experience very low temperatures. Fuels must be combined with appropriate additives in this location in order to supply the requisite energy and performance, hence eliminating difficulties associated with low temperatures [17]. Pour point for TPO is higher compared to diesel fuel hence TPO will have more problems at lower temperature places compared to diesel fuel [8,24,25,27,28,39].

Although previous studies consistently report that tyre pyrolysis oil (TPO) exhibits a higher pour point than conventional diesel fuel, the existing literature remains largely descriptive and lacks a mechanistic understanding of the factors governing low-temperature flow behavior. Most available studies simply compare pour point values between TPO and diesel, without systematically linking cold-flow properties to molecular composition, such as wax content, chain length distribution, and degree of unsaturation. In addition, the influence of pyrolysis conditions and catalytic upgrading on wax formation and crystallization behavior has not been adequately quantified, resulting in limited predictive capability for improving cold-flow performance.

Furthermore, while the pour point is recognized as a critical limitation for TPO use in cold climates due to fuel gelling, poor flow ability, and the need for preheating or additives, most studies treat it as an isolated fuel specification rather than integrating it into broader fuel optimization and engine operability frameworks. The interaction between pour point, fuel handling systems, and real engine starting performance under low-temperature conditions remains insufficiently explored. Consequently, there is a clear need for integrated experimental and modeling studies that relate production pathways, molecular structure, and cold-flow behavior to establish optimized strategies for improving low-temperature operability of TPO as a viable diesel substitute.

2.6 Flash point

The flash point is defined as the temperature at which a liquid fuel releases enough flammable

vapor from its surface to ignite in the presence of a flame [44,74,79]. It differs from fire point where by at flash point once the source of ignition is eliminated the flame goes off but at fire point the flame continues when the source of ignition has been withdrawn [80]. It has no effect on the combustion performance of the engine, but it is a critical quality for its safety and storage. When compared to fuels with a low flash point, fuels with a high flash point are safer to store and handle [74,81]. The chain length of the fuel's hydrocarbons is directly proportional to the fuel's flash point [44,77]. The flash point is used to determine the flammability of liquid fuels [79].

Flash point of tyre pyrolysis oil has been found to be lower than diesel fuel, this indicates that it can ignite at a lower temperature compared to diesel fuel [8,9,82,20,21,25–28,31,39]. Use of a catalyst has an effect on flash point that is when Na_2CO_3 and CaCO_3 are used, the flash point increases [3,40]. When MgO_2 is utilized as a catalyst in the synthesis of TPO, the resultant TPO has a higher flash point than diesel fuel [40]. Hydrocarbons with branched molecules of the same carbon number have a lower boiling point and flash point than linear molecules [83].

Although previous studies consistently report that tyre pyrolysis oil (TPO) exhibits a lower flash point than conventional diesel fuel, the existing literature remains largely empirical and safety-oriented, with limited mechanistic understanding of how molecular composition and pyrolysis conditions govern flammability behavior. Most available studies focus on direct comparisons between TPO and diesel or on the effect of selected catalysts (e.g., Na_2CO_3 , CaCO_3 , and MgO) in increasing flash point, but they do not systematically quantify how hydrocarbon chain length, branching, and unsaturation collectively influence vapor formation and ignition characteristics. As a result, predictive relationships linking fuel molecular structure and flash point behavior in TPO systems remain insufficiently developed.

Furthermore, although flash point is widely recognized as a critical safety and storage parameter rather than a direct combustion performance indicator, it is often treated in isolation from other fuel quality and upgrading

considerations. The interplay between flash point, fuel volatility, and catalytic pyrolysis pathways has not been adequately integrated into optimization frameworks aimed at improving both safety and fuel usability. Consequently, there is a clear need for integrated experimental and modeling studies that connect production conditions, molecular structural evolution, and flash point behavior to establish optimized processing strategies that enhance the safe handling and practical deployment of TPO as an alternative diesel fuel.

2.7 Water

One of the key characteristics used to determine a fuel's efficiency is its ability to complete combustion. Water vapor is produced during the burning of the most regularly used organic fuels, and its energy content can be recovered by condensing it. Moisture, on the other hand, has a detrimental impact on combustion efficiency, thus it should be kept to a minimum in the fuel [84].

Tyre pyrolysis oil contains more water content compared to the maximum that is recommended for diesel fuel [8,21,22,26]. Demirbasa *et al.* [3] found TPO to contain water that was within the allowable limit when using sodium carbonate as a catalyst. The water content in the TPO can also be reduced when the feed material to the reactor is dry.

Although previous studies consistently report that tyre pyrolysis oil (TPO) contains higher moisture content than conventional diesel fuel, the existing literature remains largely descriptive and lacks a comprehensive understanding of the mechanisms governing water incorporation during pyrolysis and subsequent fuel separation processes. Most studies simply compare measured water content against diesel standards or report reductions achieved through specific catalysts (e.g., sodium carbonate) or dry feedstock conditions, without systematically quantifying how operating parameters, condensation behavior, and phase separation dynamics influence final moisture levels in TPO. As a result, predictive control of water content during TPO production remains insufficiently developed.

Furthermore, while it is well established that excess moisture negatively affects combustion efficiency, ignition stability, and overall engine performance,

most research treats water content as an isolated quality parameter rather than integrating it into broader fuel upgrading and engine optimization frameworks. The interaction between moisture content, fuel stability, and combustion behavior under real engine operating conditions has not been adequately explored, particularly in relation to catalytic pyrolysis strategies and feedstock pretreatment. Consequently, there is a clear need for integrated experimental and modeling studies that link production conditions, phase behavior, and water removal mechanisms to optimize moisture control and improve the combustion efficiency of TPO as a viable alternative fuel.

2.8 Sulphur Content

In a diesel engine, Sulphur has no effect on combustion. Burning Sulphur, on the other hand, produces Sulphur oxides, which dissolve in condensed water formed by the combustion of hydrogen to produce Sulphuric acid. As a result of the increased Sulphur content, corrosion effects in turbo blowers, silencers, and exhaust pipes are likely to occur [74]. The presence of Sulphur in fuel causes environmental pollution whenever the fuel is used.

TPO has been found to contain Sulphur that is above the required set standards [3,22,23,38,39,53,68,85]. However, the use of catalyst can reduce the Sulphur content in the resulting TPO [3,19,40]. The Sulphur content is also directly proportional to pyrolysis temperature [56,68].

Although previous studies consistently report that tyre pyrolysis oil (TPO) contains higher sulphur content than conventional diesel fuel, the existing literature remains largely descriptive and regulatory-focused, with limited mechanistic understanding of sulphur formation, retention, and transformation during the pyrolysis process. Most studies simply report sulphur levels in final TPO products or demonstrate that catalysts such as those used in upgrading processes can reduce sulphur content, without systematically quantifying how operating parameters (e.g., pyrolysis temperature, residence time, and feedstock composition) influence sulphur partitioning between gas, liquid, and solid phases. As a result,

predictive control of sulphur content during TPO production remains insufficiently developed.

Furthermore, while the environmental and operational impacts of sulphur—such as SO_x emissions, acid formation, and corrosion in engine and exhaust systems—are well recognized, most research treats sulphur as an isolated impurity rather than integrating its behavior into a broader fuel upgrading and engine compatibility framework. The relationship between sulphur content, catalytic treatment pathways, and emission formation mechanisms has not been adequately established for TPO systems. Consequently, there is a clear need for integrated experimental and modeling studies that link pyrolysis conditions, sulphur transformation mechanisms, and upgrading strategies to optimize sulphur reduction and improve the environmental and operational safety of TPO as an alternative diesel fuel.

2.9 pH

The pH of a substance is a measure of alkalinity or acidity of a substance. The degree of alkalinity or acidity is expressed in a pH scale. This scale extends from 0 to 14, with 7 a neutral point [19,66]. TPO has been found to be acidic [25,27] but Martínez *et. al.* [62] found it to be slightly neutral. Acidity may be reduced by the use of a catalyst e.g. sodium carbonate [3,77].

Although previous studies consistently report that tyre pyrolysis oil (TPO) is generally acidic in nature, with only a few exceptions indicating near-neutral pH under specific processing conditions, the existing literature remains largely empirical and lacks a clear mechanistic explanation of acidity formation and variability. Most studies simply report bulk pH values of final TPO products or demonstrate that catalysts such as sodium carbonate can reduce acidity, without systematically linking acidity to the underlying chemical composition, particularly the concentration of oxygenated compounds (e.g., carboxylic acids, phenols) formed during pyrolysis. As a result, the chemical pathways governing acid formation and their dependence on process parameters remain insufficiently understood and poorly predictive.

Furthermore, although fuel acidity is known to influence storage stability, corrosion potential, and material compatibility in fuel systems, most research treats pH as an isolated quality indicator rather than integrating it into broader fuel upgrading and engine applicability frameworks. The relationship between pyrolysis operating conditions, catalytic upgrading mechanisms, and acid neutralization pathways has not been adequately quantified for TPO systems. Consequently, there is a clear need for integrated experimental and modeling studies that correlate production conditions, molecular composition, and acid formation mechanisms to optimize pH control and enhance the stability and usability of TPO as an alternative diesel fuel.

2.10 Lubricity

Fuels used in engines should attain the required lubricity to enable lubrication of the injection systems to prevent extreme system wearing. Some methods employed in reducing Sulphur from fuel (desulphurization) can also result to decrease in its natural lubricating qualities. Certain additives that are used to increase fuel lubricity cause certain negative effects when applied in appropriate quantities or when blended with other additives on basis of lubricity improvement [17].

The high lubricity level ensures that the engines' injection systems are adequately lubricated under most operating situations [17]. Lubricity of TPO is usually less when it is compared to diesel fuel [22,26,39]. Therefore, In order to achieve the necessary lubricity, TPO needs to be blended with diesel or additives.

Although previous studies consistently indicate that tyre pyrolysis oil (TPO) exhibits lower lubricity than conventional diesel fuel, the current literature remains largely empirical and lacks a mechanistic understanding of the factors governing lubricity loss and improvement in TPO systems. Most available studies simply compare lubricity values between TPO and diesel or suggest blending with diesel or lubricity additives to meet engine requirements, without systematically linking lubricity behavior to molecular composition, particularly the presence of polar compounds, sulfur species, and oxygenated functional groups.

As a result, the fundamental chemical and interfacial mechanisms responsible for boundary lubrication performance in TPO remain insufficiently characterized and poorly predictive.

Furthermore, although fuel lubricity is critical for protecting fuel injection systems and preventing excessive wear, most research treats it as an isolated fuel specification rather than integrating it into broader fuel upgrading, blending optimization, and engine durability frameworks. The trade-offs associated with desulfurization, additive incorporation, and blending strategies are often reported qualitatively without establishing optimal formulations that balance lubricity improvement with combustion performance and emissions behavior. Consequently, there is a clear need for integrated experimental and modeling approaches that correlate fuel composition, additive interactions, and tribological performance to develop optimized lubricity enhancement strategies for TPO as a viable alternative diesel fuel.

2.11 Chemical Analysis

Gas Chromatography Mass Spectrometry (GC-MS): The objective GC-MS test is to have an idea of types and nature of the present compounds (hydrocarbons) [6,86,87]. TPO has been found to be a very complex mixture that is made up of C_5 – C_{16} organic compounds with a high concentration of the unsaturated compounds [22,52,56,62,88] while Laresgoiti *et al.* [54], Banar *et al.* [63] and Kan *et al.* [89] found that carbon content was ranging between (C_7 – C_{32}). It mainly contains aliphatic and aromatic compounds [22,25,52,63,90,91] such as n-undecane, n-pentadecane, n-heptadecane, n-hexadecane, n-tetradecane and some other high molecular weight alkanes, phenanthrenes, alkylated naphthalenes and alkenes especially limonene [63,92].

Although previous studies using GC–MS analysis have confirmed that tyre pyrolysis oil (TPO) is a highly complex mixture of hydrocarbons ranging broadly from light (C_5 – C_{16}) to heavier fractions (up to C_{32}), the existing literature remains largely descriptive and lacks a unified, quantitative understanding of how pyrolysis conditions govern product distribution at the molecular level. Most studies report qualitative identification of

compounds such as aliphatic hydrocarbons, aromatics, n-alkanes, alkylated naphthalenes, and phenanthrenes, but do not systematically correlate operational parameters (e.g., temperature, residence time, heating rate, and catalyst type) with the evolution of specific chemical families. As a result, predictive control over molecular composition and product selectivity in TPO remains insufficiently developed.

Furthermore, while it is well established that the chemical complexity of TPO—particularly its high proportion of unsaturated and aromatic compounds—strongly influences key fuel properties such as viscosity, density, cetane quality, and emissions behavior, most studies treat GC–MS results as standalone characterization outputs rather than integrating them into fuel property prediction or engine performance optimization frameworks. The absence of standardized compositional modeling limits the ability to translate GC–MS data into actionable fuel design and upgrading strategies. Consequently, there is a clear need for integrated experimental and modeling approaches that link pyrolysis conditions, molecular composition derived from GC–MS, and resulting fuel properties to enable predictive control and optimization of TPO as a viable alternative diesel fuel.

Fourier Transformation Infrared (FT-IR): The FT-IR is not the most appropriate analytical tool for determining aromatic, polar and saturated components [27,28,39,52,58,63]. Nevertheless, it enables the identification of functional groups which reveal the chemical characteristics of the liquids [27,52,58,63,85,90,93] and specifies the types of bonds [85]. TPO has been found to contain aromatic, aliphatic and hydroxyl compounds [52,58].

Although previous studies have widely employed Fourier Transform Infrared (FT-IR) spectroscopy for the characterization of tyre pyrolysis oil (TPO), the current literature remains largely qualitative and lacks a rigorous quantitative interpretation of functional group distributions and their relationship to fuel performance. Most studies use FT-IR primarily to confirm the presence of broad chemical classes such as aromatic, aliphatic, and hydroxyl compounds, without systematically de-

convoluting spectra to quantify relative functional group abundance or track compositional changes under varying pyrolysis conditions. As a result, the ability of FT-IR to provide predictive insights into TPO chemical evolution remains underutilized and insufficiently developed.

Furthermore, although FT-IR-derived functional group information is known to influence key fuel properties such as viscosity, density, stability, and combustion behavior, most research treats FT-IR analysis as a standalone qualitative tool rather than integrating it with advanced chemometric modeling or other analytical techniques such as GC–MS. The lack of integrated spectral–property correlations limits the development of predictive models that can link molecular structure to fuel performance. Consequently, there is a clear need for combined experimental and data-driven approaches that quantitatively relate FT-IR functional group distributions to pyrolysis conditions and fuel properties, enabling more accurate characterization and optimization of TPO as an alternative diesel fuel.

3.0 The Overall Integrated Research Gap

Despite extensive characterization of TPO across physicochemical and chemical properties, the existing literature remains largely fragmented, empirical, and descriptive. Most studies evaluate individual properties in isolation without establishing integrated structure–property–process relationships that link pyrolysis conditions, molecular composition, and engine performance behavior. As a result, predictive understanding of how catalytic upgrading and feedstock variations simultaneously influence density, viscosity, ignition quality, stability, emissions, and chemical composition remains insufficiently developed.

Consequently, there is a critical need for integrated experimental–modeling frameworks (including RSM, machine learning, and thermochemical modeling) that unify GC–MS and FT-IR chemical insights with fuel property evolution and engine performance outcomes. Such approaches are essential for optimizing TPO production pathways and establishing it as a reliable, high-performance alternative diesel fuel. Table 1 shows the physicochemical and chemical Properties of tyre pyrolysis oil.

Table 1: Physicochemical and Chemical Properties of Tyre Pyrolysis Oil (TPO)

Property	Observed Trends in TPO (Compared to Diesel)	Key Influencing Factors	Major Limitations in Literature	Research Gap (Summary)
Density	Generally higher than diesel	Chain length (inverse), unsaturation (direct), catalysts (e.g., Na_2CO_3)	Mostly descriptive; weak predictive models	Lack of integrated models linking molecular structure, pyrolysis conditions, and density-driven engine performance
Kinematic Viscosity	Varies; often lower than diesel, sometimes higher	Chain length, unsaturation, branching, temperature, catalysts (MgO , CaCO_3)	Inconsistent results; poor temperature-dependent modeling	Need predictive models linking composition, temperature, and atomization behavior
Calorific Value	Lower than diesel	Chain length ($\uparrow$), unsaturation ($\downarrow$), oxygenated compounds	Mostly empirical; weak structure–energy relationships	Need mechanistic models linking pyrolysis conditions to energy density

Cetane Rating (CN & CI)	Lower than diesel	Unsaturation, branching, chain length, density, distillation temperature	CI often used without validation for TPO complexity	Lack of predictive ignition models integrating composition and engine performance
Pour Point	Higher than diesel (poor cold flow properties)	Wax content, chain length, crystallization behavior	Descriptive studies; limited cold-flow modeling	Need predictive cold-flow behavior models under catalytic modification
Flash Point	Lower than diesel (generally)	Volatility, chain length, branching	Mostly safety-focused; limited mechanistic studies	Lack of models linking molecular structure to flammability behavior
Water Content	Higher than diesel	Condensation, feedstock moisture, phase separation, catalysts	Limited mechanistic understanding of water formation	Need predictive models for moisture formation and separation control
Sulphur Content	Higher than diesel	Feedstock composition, pyrolysis temperature	Mostly regulatory reporting; weak transformation modeling	Need sulfur partitioning and reduction mechanism models
pH (Acidity)	Mostly acidic; sometimes near neutral	Oxygenated compounds (acids, phenols), catalysts	Descriptive; weak chemical linkage	Need mechanistic models linking acidity to oxygenated species formation
Lubricity	Lower than diesel	Polar compounds, sulfur species, oxygenates	Empirical blending strategies only	Need tribological models linking composition and additive interactions
GC–MS Composition	Complex mixture: C5–C32 aliphatic + aromatic compounds	Pyrolysis temperature, residence time, catalysts	Mostly qualitative; weak predictive mapping	Need structure–property–process (SPP) predictive models
FT-IR Functional Groups	Aromatic, aliphatic, hydroxyl groups present	Pyrolysis conditions, oxygen content	Qualitative; lacks quantification	Need chemometric/ML-based spectral–property correlation models

3.1 Proposed Structure–Property–Performance (SPP) Framework for Tyre Pyrolysis Oil

3.1.1 Conceptual Development

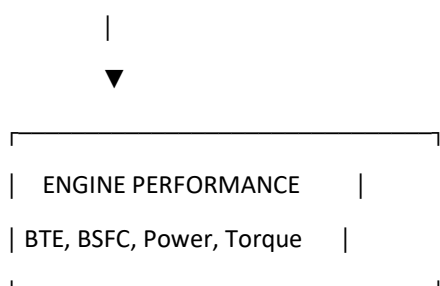
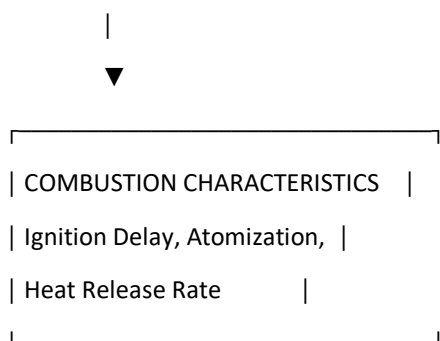
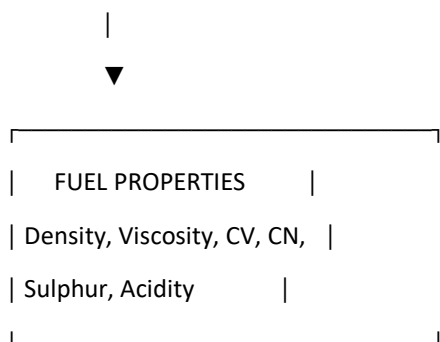
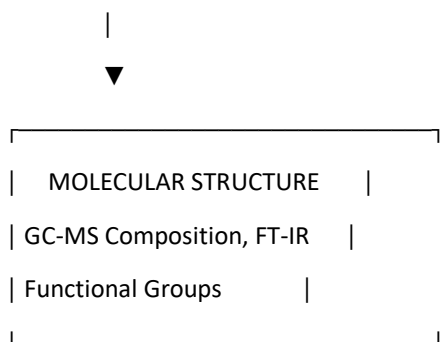
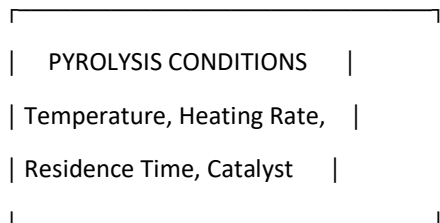
Current studies on tyre pyrolysis oil (TPO) primarily report physicochemical properties such as density, viscosity, calorific value, cetane rating, sulphur content, and chemical composition independently. However, these properties originate from the molecular structure generated during pyrolysis and ultimately determine combustion characteristics

and engine performance. The absence of an integrated framework linking these stages has limited the predictive optimization of TPO production and utilization.

To address this limitation, a Structure–Property–Performance (SPP) framework is proposed. The framework establishes a direct relationship between pyrolysis operating conditions, molecular composition, fuel properties, combustion behaviour, and engine performance outcomes.

To address this limitation, an Integrated Structure–Property–Performance–Emission (SPPE) Framework is proposed. The framework establishes direct relationships among pyrolysis operating

conditions, molecular composition, fuel properties, combustion behaviour, engine performance, emissions, and optimization strategies."



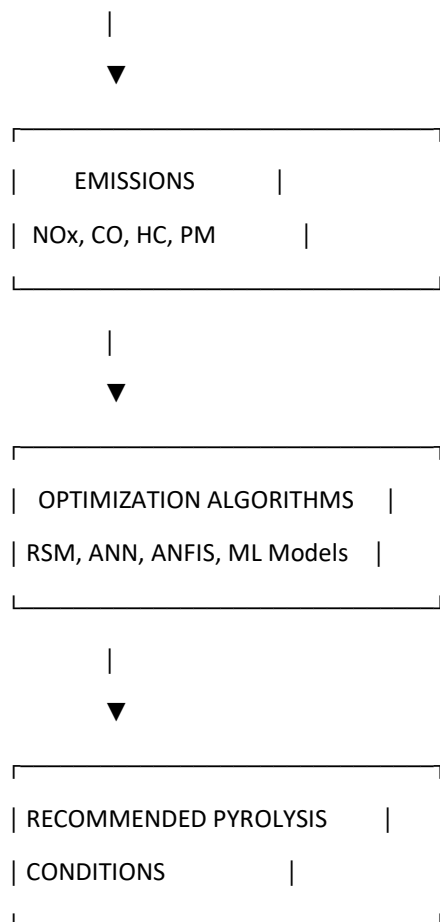


Figure 1. Integrated Structure–Property–Performance–Emission (SPPE) Framework for Tyre Pyrolysis Oil

The framework suggests that fuel properties should not be treated as independent variables but rather as intermediate responses governed by molecular structure and process conditions.

3.1.2 Mechanistic Relationships

The proposed framework further identifies the dominant mechanistic pathways responsible for property evolution.

Density Pathway: Increasing aromaticity and unsaturation generally increase density, while longer paraffinic chains reduce density. Consequently, catalytic pyrolysis conditions that favour aromatic formation tend to produce denser fuels.

Viscosity Pathway: Viscosity is primarily influenced by molecular weight distribution and intermolecular interactions. Longer hydrocarbon chains and polyaromatic compounds increase viscosity, whereas cracking reactions promoted by catalysts reduce viscosity.

Calorific Value Pathway: Calorific value increases with hydrocarbon chain length and decreases with oxygenated compounds and unsaturated structures. Therefore, catalytic upgrading that reduces oxygen-containing species can enhance fuel energy density.

Cetane Quality Pathway: Cetane number is strongly influenced by molecular structure. Straight-chain paraffins promote rapid ignition, whereas aromatic and highly unsaturated compounds increase ignition delay and reduce cetane quality.

Emission Formation Pathway: Fuel molecular composition directly affects pollutant formation. Aromatic compounds and sulphur-containing species contribute to particulate matter and SO_x emissions, while oxygenated compounds may influence NO_x formation through combustion temperature effects.

3.1.3 Predictive Fuel Design Strategy

Based on the SPP framework, the development of high-quality TPO should focus on simultaneously optimizing:

- Hydrocarbon distribution
- Aromatic content
- Sulphur concentration
- Oxygenated functional groups
- Fuel density
- Viscosity
- Cetane quality

Rather than optimizing individual properties independently.

This integrated approach enables predictive fuel design whereby desired engine performance and emissions targets can be translated backwards into required fuel properties, molecular composition, and pyrolysis operating conditions.

3.1.4 Future Integration with Artificial Intelligence

3.1.5 Integrated Structure–Property–Performance–Emission (SPPE) Framework for Tyre Pyrolysis Oil

Molecular Feature	Density	Viscosity	Cetane Number	Emissions
Aromatics ↑	↑	↑	↓	Smoke ↑
Unsaturation ↑	↑	↓	↓	PM ↑
Chain Length ↑	↓	↑	↑	CV ↑
Oxygenates ↑	↓	Variable	↓	CO ↓

3.1.6 Testable Hypotheses of the SPPE Framework

H1: Increasing aromatic content increases density and particulate emissions while reducing cetane quality.

H2: Increasing hydrocarbon chain length increases calorific value and cetane number but may increase viscosity.

H3: Catalytic cracking reduces viscosity by reducing average molecular weight distribution.

H4: Sulphur reduction decreases SO_x emissions and improves engine durability.

The proposed SPP framework provides a foundation for the development of machine learning and artificial intelligence models capable of predicting fuel properties and engine performance directly from pyrolysis operating parameters.

Future studies should integrate:

- Artificial Neural Networks (ANN)
- Adaptive Neuro-Fuzzy Inference Systems (ANFIS)
- Random Forest Models
- Gradient Boosting Algorithms
- Deep Learning Architectures

In order to establish predictive digital twins for tyre pyrolysis systems. Such models could significantly reduce experimental costs while accelerating optimization of TPO production pathways.

H5: Optimization of molecular composition through catalytic pyrolysis can simultaneously improve fuel properties and engine performance.

4.0 Conclusions

The characterization of tyre pyrolysis oil (TPO) reveals that it possesses a complex set of physicochemical and chemical properties that significantly influence its suitability as an alternative diesel fuel. Across density, viscosity, calorific value, cetane quality, cold-flow behavior, flash point, water content, sulphur content, acidity, and lubricity, TPO consistently shows deviations from conventional diesel fuel. In general, it exhibits higher density, variable but often lower viscosity,

reduced calorific value, lower cetane rating, poorer cold-flow properties (higher pour and flash points), higher moisture and sulphur contents, increased acidity, and reduced lubricity. These deviations are primarily attributed to its heterogeneous molecular composition, which is dominated by a mixture of aliphatic, aromatic, and oxygenated hydrocarbons produced under varying pyrolysis conditions.

Overall, the reviewed literature demonstrates that while individual fuel properties of TPO have been extensively studied, the findings remain largely empirical and fragmented. Most investigations focus on isolated property measurements without establishing integrated relationships between pyrolysis operating conditions, molecular structure, and fuel performance behavior. Consequently, predictive understanding and optimization of TPO

as a fuel remain limited. There is therefore a clear need for holistic, integrated experimental and modeling frameworks that unify chemical characterization (GC–MS and FT-IR) with fuel property evolution and engine performance outcomes. Such an approach is essential for optimizing TPO production, improving fuel quality consistency, and enabling its reliable application as a sustainable alternative diesel fuel.

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