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Review

Exploring the Potential of Lignocellulosic Biomass-Derived Polyoxymethylene Dimethyl Ether as a Sustainable Fuel for Internal Combustion Engines

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Abstract: The most effective way to reduce internal combustion engine emissions is to use a sustainable alternative fuel that contains oxygen molecules. Alternative fuels may be used to address a future global energy crisis. Different oxygenated alternative fuels have been investigated in internal combustion engines. Polyoxymethylene di-methylene ether (PODE), which contains 3–5 CH_2O groups, is currently superior in the field of oxygenated fuels due to its physical and chemical properties. Furthermore, using PODE as a fuel does not necessitate any significant engine modifications. When compared to standard diesel fuel, the use of PODE results in near stoichiometric combustion with less hazardous exhaust gas. It also significantly reduces NO_x emissions due to the lack of C-to-C bonds. Several articles in the literature were found on the manufacturing and application processes for the production of PODE. However, the current review focuses primarily on simplifying the various production technologies, the physical and chemical properties of PODEn and its advantages and disadvantages in ICEs, PODEn application in internal combustion engines and its characteristics, PODE spray analysis, and measurements of the fuel's physical and chemical characteristics. This review emphasizes the fact that PODE can be used as a sole fuel or in conjunction with fossil fuels and advanced combustion technologies. Because C-C bonds and higher oxygen molecules are not available, the trade-off relationship between nitrogen oxides and soot production is avoided when PODEn is used as a fuel, and combustion efficiency is significantly improved.

Keywords: soot-free fuel; oxygenated fuel; degree of polymerization; high cetane number; polyoxymethylene dimethyl ether; diesel engine

Citation: Kowthaman, C.N.; Rahman, S.M.A.; Fattah, I.M.R. Exploring the Potential of Lignocellulosic Biomass-Derived Polyoxymethylene Dimethyl Ether as a Sustainable Fuel for Internal Combustion Engines. *Energies* **2023**, *16*, 4679. https://doi.org/10.3390/en16124679

Academic Editors: Hubert Kuszewski and Paweł Woś

Received: 23 April 2023
Revised: 9 May 2023
Accepted: 15 May 2023
Published: 13 June 2023

1. Introduction

Presently, the reduction in internal combustion engine emissions is necessitating the automotive industries to eliminate the environmental degradation caused by internal combustion engines [1,2]. This situation is further exacerbated by COVID-19 pandemic [3]. The most effective way to reduce engine emissions and carbon dioxide emissions is to switch to a renewable alternative fuel with a lower carbon-to-hydrogen ratio, a higher cetane number, and inherent oxygen [4–6]. Furthermore, the fuel must maintain a molecular structure that is similar to the range of petroleum diesel fuel so that it can be used in existing engine structures without modification [7]. A notable reduction in regulated and non-regulated emissions with biodegradability and enhanced safety characteristics have been provided. So far, various alternative fuels, including biodiesel, alcohol fuels, and ether fuels, are used in diesel engines in a pure form, a blended mode, and a dual-fuel mode. Commonly, alcohol fuels are used in gasoline engines that have a high octane number and volatile characteristics. However, they have a lower cetane number and are insoluble in fossil fuels [8,9], and these are the challenging factors for diesel engines. Ester fuels are usually used in diesel engines that have a high cetane number and a high oxygen content. However, properties such as a poor low-temperature flow and a high cloud point present several difficulties in fuel supply systems [10]. Further, esters have only one carboxyl (COOH) group, which means that they only provide a lesser impact on PM reduction [11].

Ether fuel is generally in the form of R-O-R, where R and R′ are the hydrocarbyl groups [12] and O is an oxygen atom, and it has a shorter molecular structure and a higher cetane number, which is preferred for enhanced combustion [13]. Further, ether fuel has inherent oxygen molecules, which assist in improving combustion, which leads to a reduced emission of unburned fuel [14]. Among the different ether fuels, dimethyl ether (DME) and polyoxymethylene dimethyl ether (PODE) exhibit better fuel characteristics and provide better performance and lower emissions [15–17]. However, DME is in a gaseous form under atmospheric conditions, hence handling the fuel is very difficult [18]. In addition, DME fuel easily degrades rubber materials [19]. Hence, the utilization of DME is difficult even though it has more benefits. PODE is in a liquid form under atmospheric conditions, and it also has similar characteristics to DME. Hence, more investigations are presently being carried out using PODE instead of DME fuel [20].

Polyoxymethylene dimethyl ether is also called oxy-methylene ether, and it can be abbreviated as PODEn, DMMn, OMEn, POMDMEn, and OMDMEn. PODEn can be synthesized and derived from methanol produced from various renewable and non-renewable resources. Presently, PODEn is also used as a sustainable alternative for internal combustion engines. Hence, for the past 10 years, in-depth investigations have been carried out using PODE as a fuel. However, understanding the properties of PODE and its influence on engine performance and emission is imperative. Further, knowing the production technologies and their impact on the environment and the challenges presented while using ICE is imperative for the complete replacement of diesel fuel. Hence, the objective of this review article was to summarize the various production technologies, properties of PODEn and its advantages and disadvantages in ICEs, the application of PODEn in internal combustion engines, and its combustion, performance, and emission characteristics.

2. International Research Status of PODE

In the middle of the 19th century, Staudinger and Lüthy [21] started the production of polyoxymethylene dimethyl ether from methanol fuel. The research on polyoxymethylene dimethyl ether was conducted intensively due to its physical and chemical properties, which are favourable for diesel engines. Figure 1 shows the number of research articles published year by year; these data were derived from Scopus. The number of publications may be slightly different due to non-Scopus-indexed publications. So far, as per the Scopus information, more than 120 research articles on PODEn have been published from all around the world. From Figure 1, it can be observed that the amount of research on PODEn increased from 2015 due to an increased demand for energy sources and stringent emission norms for diesel engines. Further, it can also be observed that most of the research articles were published in China due to the abundant availability of polyoxymethylene dimethyl ether [22]. The country-wise research status of polyoxymethylene dimethyl ether is as follows: China was the country with the highest number of publications on PODE, which was followed by the US, the United Kingdom, and Brazil, who published eight, five, and three articles, respectively. India and Singapore produced two publications, and a few other European countries, such as Germany, Portugal, Spain, and Switzerland, published one article.

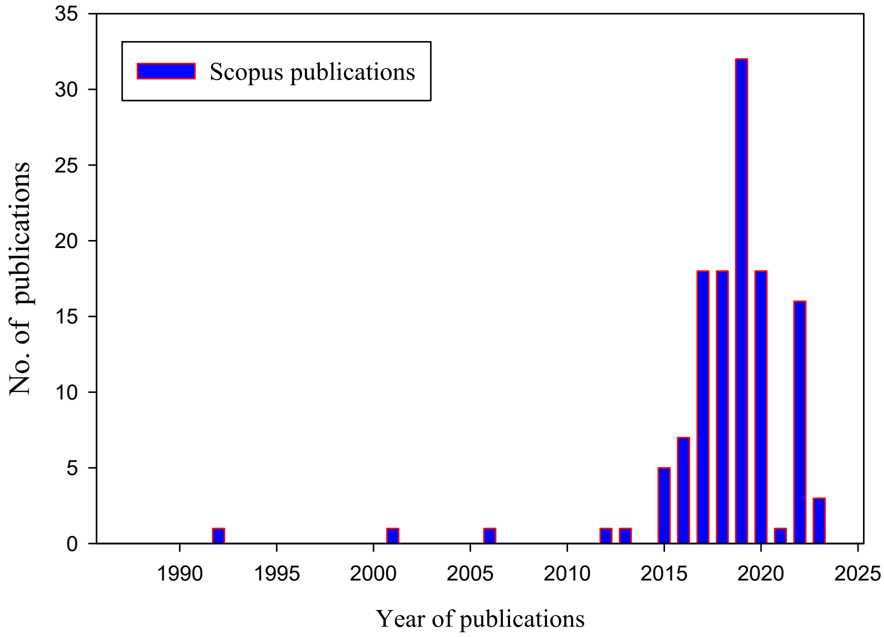

Figure 1. Year-wise publications on polyoxymethylene dimethyl ether.

3. Production Technologies of Polyoxymethylene Dimethyl Ether

So far, various production methods have been proposed by researchers for producing polyoxymethylene dimethyl ether fuel. Staudinger and Lüthy [21] initially prepared polyoxymethylene dimethyl ether in the 1920s and determined the various physical and chemical properties of PODE fuel. Based on their determination, various chemical industries started the production of PODE in the middle of the twentieth century. Particularly between 1999 to 2002, the BP plc. multinational oil and gas company produced a variety of PODE products based on the chain length, which includes PODE1, PODE2, PODE3, PODE4, and PODE5. Then, the BASF chemical company started the production of PODE through the synthesis process. Presently, Chinese and German companies have started the production of PODE with the use of coal as a primary feedstock [23]. Several feedstocks, including -CH_2O- chain-group providers and CH_3O- end-group providers, are used in the synthesis process. Examples of chain-group (-CH_2O-) providers include trioxane, formaldehyde, and paraformaldehyde, and examples of end-group providers include methanol and dimethyl ether. Based on the existing literature [24], it was found that the synthesis process is divided into three methods, including (i) anhydrous synthesis [25], (ii) aqueous synthesis [26], and (iii) the oxidation of methanol [27] by a selective catalyst. In the anhydrous synthesis process, trioxane and OME1 are used as reactants. OME1 is produced from methanol by continuous two-step processes such as (i) the production of a mixture of methanol, formaldehyde, and water by the oxi-degradation of methanol with Ag as a catalyst (gas phase), and (ii) the acid-catalyzed condensation of methanol and formaldehyde under a liquid phase. Trioxane provides methanol by a reversible process, which then reacts with OME1 and provides PODE. The reaction mechanism of the anhydrous synthesis process is given in Equations (1)–(3) [25]. In the aqueous synthesis process, methanol is used as the main source and reacts with formaldehyde under acidic conditions, which is obtained from aqueous sources. The reaction mechanism of the aqueous synthesis process is given in Equation (3) [26]. The third method is a direct synthesis process carried out by the oxidation of dimethyl ether or methanol with a catalyst.

$$C_3H_6O_3 \rightarrow 3CH_2O \quad (1)$$

$$CH_2O + OME_{1(n)} \rightarrow OME_{2(n+1)} \quad (2)$$

$$2CH_3OH + n\,CH_2O \rightarrow OME_n + H_2O, (n > 1) \quad (3)$$

4. Properties of Polyoxymethylene Dimethyl Ether

Polyoxymethylene dimethyl ether is produced from various feedstocks through a synthesis process. Due to the synthesis process, there are no petrogenic PAHs in the fuel, which is helpful for reducing the formation of soot emissions [28,29]. Furthermore, the different physical and chemical properties of PODE provide it with many advantages compared to conventional diesel fuel. Table 1 shows the important physical and chemical properties of PODE, as listed by the researchers. The following section explains the advantages and disadvantages of the key properties of PODE using a conventional diesel engine compared with a replacement diesel engine.

Table 1. Properties of Poly oxy dimethyl ether ($PODE_{3–4}$).

Properties	Unit	Haoye Liu et al. [30,31]	Junheng Liu et al. [32]	Bowen Li et al. [33]	Ganesh et al. [34]	Barro et al. [35]	Jialin Liu et al. [36]	Haifeng Liu et al. [37]
Chemical structure	No unit	$CH_3O-[CH_2O]_n-CH_3$		_	_	_	_	$CH_3O-[CH_2O]_n-CH_3$
Carbon content	%	43.97	44.03	43.97	_	_	43.5	43.53
Hydrogen content	%	8.78	8.78	8.78	_	_	8.5	8.52
Oxygen content	%	46.98	47.2	46.98	_	_	48	47.95
Cetane number	No unit	78.6	76	78.4	78	47	60.7	87.7
Research octane number	No unit	_	_	_	_	_	13.3	_
Density	g/cc	1.019	1.050 at 20 °C	1.0190	1.047 at 25 °C	1.046 at 25 °C	1.047 at 20 °C	1.047 at 20 °C
Viscosity	mm^2/s	1.05 at 25 °C	_	_	1.1 at 20 °C	0.97 at 25 °C	_	1.11 at 20 °C
Lower heating value	MJ/kg	19.05	17.8	19.05	20.9	19.4	21.8	21.77
Enthalpy of vaporisation	kJ/kg	_	359	_	_	_	_	300
Boiling range/point	°C	156–202	180	156–242	_	_	_	156
Surface tension	N/m	28.8–30.7	_	_	_	_	_	_

4.1. Advantages

Chemical structure: The general chemical structure of the polyoxymethylene dimethyl ether is $CH_3O-[CH_2O]_n-CH_3$, where n denotes the number of $-O-CH_2-$ groups (polymerization degree) present in the molecule [29]. From the generalized chemical structure, it can be observed that there is no C-C bond, which is beneficial for reducing the formation of soot emissions [38]. Furthermore, PODE fuel has an inherent oxygen molecule, which constitutes nearly 48% of the compound on a weight basis. The inherent oxygen in the fuel provides it with a positive effect in the form of a wider load limit and increases its combustion efficiency [39].

Cetane Number: The cetane number is the main property that decides whether the fuel is suitable for compression ignition engines [40]. PODE has an average cetane number of more than 75, which is higher than fossil-based diesel fuel [30,31,41]. Due to its higher cetane number, the auto-ignition of the fuel is faster, and complete combustion inside the cylinder can be achieved.

Volatility: PODE has higher volatility, which helps in improving the mixing of the fuel–air mixture when compared to diesel fuel, which results in enhanced engine performance.

Solubility: The molecular structure of PODE provides it with a better solubility in fossil fuels, which means it can be used as an additive fuel without any further impact on fuel supply systems.

4.2. Disadvantages

Flashpoint: Lower degrees of polymerized PODE (i.e., PODE1 and PODE2) have a low flash point and do not fulfill any fuel security criteria. However, if the n value is from 3 to 5, the value of the flashpoint is reasonable, and thus it may be used as a fuel [41].

Surface tension: The surface tension of PODE gradually increases while decreasing the temperature of the fuel blend and results in the worst solubility in fossil fuels [31].

Heating Value: The heating value of PODE is lower (approximately 18 to 21 MJ/kg) when compared with that of diesel, which is 44 MJ/kg, meaning that it requires a larger tank to meet the same power output of an engine.

5. Application of Polyoxymethylene Dimethyl Ether in Internal Combustion Engines

Due to the superior physical and chemical properties of PODE, a lot of studies have been conducted in recent years using PODE as a fuel. So far, researchers have utilized and investigated the advantages of PODE in internal combustion through using it as a 100% sole fuel [19,34,35,42,43], blending it with fossil fuel [32,40,44–47], and by using advanced combustion technologies such as homogeneous-charge compression ignition (HCCI) [36,45,47], premixed-charge compression ignition (PCCI) [48,49], and reactivity-controlled compression ignition (RCCI) [50,51]. The following section details and summarizes the outcomes of these investigations.

5.1. Application of PODE in ICEs through 100% Sole Fuel

Some investigators have utilized PODEn as a 100% sole fuel in diesel engines without any major modifications to the test engine. A detailed summary of the results obtained while using PODEn as a 100% sole fuel is listed in Table 2.

Härtl et al. [42] investigated the effect of PODEn on the soot and particulate number of a heavy-duty diesel engine. Experiments were performed at 13 bar BMEP and at a constant speed of 1200 rpm. It was observed that the combustion started earlier and released a higher amount of total heat energy in the case of PODEn operation compared to diesel operation. Further, it was observed that indicated specific soot emission was drastically reduced by nearly 92%, and the total particulate number was also reduced drastically with marginally increased NO_x emissions.

Pellegrini et al. [37] carried out experiments aimed at investigating the emissions and performance attributes of an aging light-duty diesel vehicle. The study involved substituting fossil-based diesel with pure PODE and a blended diesel fuel consisting of 10% PODE. An increase in emissions such as HC (15%), CO (60%), CO_2 (11%), and NO_x (39%) was observed for the neat-PODE-fueled engines. However, the amount of particulate matter decreased by nearly 77%. In the case of the 10%-PODE+diesel blended fuel, it exhibited nearly 5%, 3%, and 18% reduced HC, CO, and PM emissions, respectively, when compared to neat diesel operation. Further, a nearly 6% increase in NO_x emissions was observed with the 10%-PODE-blended operation compared to the neat diesel operation. They also studied the effect of neat-PODE and 10%-blended-PODE fuel on non-regulated emissions. It was observed that compared to diesel operation, nearly 161%, 138%, and 72% higher formaldehyde, acetone, and total aldehyde with ketone emissions, respectively, were observed when using the engine with neat-PODE-fuel operation.

Table 2. Application of 100% sole PODEn fuel in diesel engines. (All results are compared to diesel combustion).

Investigators	Engine Specifications	Operating Conditions	Combustion Characteristics	Performance Characteristics	Emissions Results
Härtl et al. [42]	Single-cylinder MAN D20 Series CI engine Displacement: 1.75 L Bore: 120 mm Compression ratio: 17	IMEP: 13.0 bar P_{Boost}: 1.91 bar Speed: 1200 rpm T_{intake}: 40 °C $P_{inj.pressure}$: 1800 bar CA50 8° CA aTDC	• 3 ms shorter ignition delay • 2° CA shorter combustion duration • 2 bar/deg lower rate of pressure rise	0.9% improved thermal efficiency	• Soot–NO_x trade-off completely vanished • 20 to 30% reduced HC and CO emission • Lower formaldehyde (CH_2O) and ammonia (NH_3) concentrations
Pellegrini et al. [43]	Four-inline-cylinder CI engine Displacement: 1.91 L Bore × stroke: 82 × 90.4 mm Compression ratio: 18.45	New European driving cycle	Not specified	73% increased specific fuel consumption	• 16% increased HC amount • 60% increased CO amount • 39% increased NO_x amount • 77% reduced particulate matter amount
Barro et al. [35]	Single-cylinder diesel engine Displacement: 3.96 L Bore × stroke: 165 × 185 mm	BMEP: 5.6 bar $P_{inj.pressure}$: 703 bar SOI: 10° CA bTDC	Higher heat-release rateShorter combustion duration	Not specified	• HC and CO concentration is higher • Significant reduction in particulate emissions (below 20 nm)
Duraisamy et al. [34]	Three-cylinder turbocharged automotive diesel engine Displacement: 1.478 L Bore × stroke: 80 × 98 mm Compression ratio: 17.2	BMEP: 3.4 bar Speed: 1500 rpm CA50: 10° CA aTDC $P_{inj.pressure}$: 480 bar	• 2° CA shorter ignition delay • 5° CA shorter combustion duration • 2 bar lower in-cylinder pressure	• A 2% improved IMEP • A 3% reduced cyclic variation	• 12% decreased CO emission • 17% reduced HC emission • 30% decreased soot emission • 12% increased NO emission

Recently, Duraisamy et al. [34] conducted experiments in a light-duty commercial automotive diesel engine fueled with 100% PODE without any modifications to the fuel supply systems. Experiments were conducted at 3.4 bar BMEP and with an engine speed of 1500 rpm with a constant CA50 of about 10 deg CA aTDC. The results showed a shorter ignition delay and combustion duration while using PODE as a fuel compared to using diesel fuel. Further, the peak in-cylinder pressure and peak heat-release rate were higher in the case of PODE-fueled operation compared to diesel-fueled operation. The net indicated mean effective pressure of the engine increased, and its coefficient of variation decreased when using PODE instead of diesel as fuel. The amount of soot produced drastically decreased from 0.044 g/kWh to 0.02 g/kWh while using PODE as a fuel. However, the amount of NO emissions marginally increased due to the inherent oxygen in PODE and the higher in-cylinder pressure. Both HC and CO emissions were reduced by nearly 17% and 12%, respectively, while using PODE as a fuel compared to using diesel.

Overall, these investigations have concluded that the ignition delay is significantly shortened when using PODEn instead of diesel fuel due to the higher volatility and higher cetane number characteristics of PODEn. Although there was a shorter ignition delay, the formation of the premixed air–fuel charge increased inside the cylinder due to the higher volatility and higher oxygen content, resulting in an increase in the heat-release rate and peak in-cylinder pressure compared to diesel combustion. Due to the higher in-cylinder pressure and heat-release rate, the formation of oxides of nitrogen is higher while using PODEn as a fuel. Due to the lower calorific value of PODEn, PODEn-fueled engines require a longer injection duration to achieve the same engine power output. Even though a longer injection duration is required, the diffusion combustion phase is lower in the case of pure PODEn fuel compared to diesel fuel due to the non-availability of carbon-to-carbon bonds and the higher oxygen content. Due to the absence of diffusion combustion, the formation of soot/particulate matter is very lower and almost equal to zero. Further, the published data clearly show that when using PODEn as a fuel, hydrocarbon and carbon monoxide emissions are significantly decreased compared to conventional diesel fuel. This may be due to better fuel spray penetration and distribution. However, some articles have shown that the increased hydrocarbon and carbon monoxide emissions due to wider spray penetration result in a leaner burn outside of the region. In the case of fuel economy, most studies show there is no significant variation.

5.2. Application of PODEn in ICEs through Blending with High-Cetane Fuels (Diesel/Biodiesel)

So far, several investigations have been carried out in diesel engines using different diesel fuels with different percentages of blended PODEn without any major modifications to the test engine. PODEn is highly soluble in diesel fuel, which improves the cetane number of the fuel, meaning that the fuel can achieve a better emissions reduction without any impact on the fuel supply systems. Table 3 shows a summary of the investigations of the effects of using PODEn blends in diesel engines. Figures 2–7 show the effect of the PODEn blend ratio on the combustion, performance, and emission characteristics.

Figure 2 shows the effect of the PODEn blend ratio on the heat-release rate compared to diesel. The results indicate a higher heat-release rate when using diesel fuel with blended PODEn compared when using pure diesel. Adding PODE to diesel fuel increases the amount of air–fuel mixing due to its simple molecular structure, higher volatility, and lack of a C-C bond. Owing to an enhanced air-fuel mixture, a greater amount of pre-mixed fuel is present within the cylinder prior to ignition, leading to a heightened peak in-cylinder value in contrast to diesel fuel. Nevertheless, certain researchers have documented a decreased rate of heat release, attributed to the elevated cetane number of PODEn, which reduces the time interval for ignition, consequently leading to a diminished quantity of pre-mixed fuel and a lower peak heat-release rate.

Table 3. Detailed engine specifications and operating conditions for PODE blend investigations.

Investigators	Engine Specifications	Operating Conditions
Iannuzzi [16]	Single cylinder Bore × stroke: 165 × 185 mm Compression ratio: 13.7	BMEP: 8 bar Intake pressure: 1.5 bar Exhaust pressure: 1 bar Injection pressure: 800 bar SOI: 12° CA bTDC
Popp et al. [40]	Six-cylinder HD diesel engine Displacement: 12.4 L Compression ratio: 16 Bore × stroke: 126 × 166 mm	1500 rpm Full-load conditions SOI: 17 to 6° CA bTDC
Wang et al. [45]	Single-cylinder light-duty diesel engine Displacement: 0.5 L CR: 16.7	BMEP: 8 bar 1600 rpm Double injection, <7% in Pilot
Haoye Liu et al. [46]	Six-cylinder heavy-duty diesel engine Displacement: 7.14 L Compression ratio: 18	BMEP: 8 bar, 1600 rpm Injection pressure: 65 MPa SOI_{pilot}: 16° CA bTDC SOI_{main}: 4° CA aTDC
Lv et al. [47]	Single-cylinder diesel engine Compression ratio: 16.5 Bore × stroke: 88.1 × 85 mm	1600 rpm Intake air temperature: 315 K SOI: 7° CA bTDC
Junheng Liu et al. [32]	Four-cylinder diesel engine Bore × stoke: 105 × 118 mm Displacement: 4.09 L, CR 17.5	1500 rpm 100% load of the engine (i.e., 400 Nm)
Jialin Liu et al. [36]	Sixcylinder heavy-duty diesel engine Displacement: 8.42 L Compression ratio: 17.5	CA50: 10° CA aTDC 1503 rpm BMEP: 19.1 bar
Chen et al. [52]	Four-cylinder heavy-duty diesel engine Displacement: 1.99 L Compression ratio: 16.5 Bore × stroke: 85 × 88.1 mm	1600 rpm BMEP: 4 bar SOI: 4° CA bTDC Pinj: 100 MPa

Figure 2. Effect of PODEn blend ratio on heat-release rate compared to diesel [16,30,32,33,40,45,52].

Generally, the brake thermal efficiency is used to define the actual output of an engine. Figure 3 shows the effect of the PODE blend ratio on the brake thermal efficiency compared to diesel fuel. A higher brake thermal efficiency was observed when adding PODE to diesel fuel. The addition of PODE to diesel fuel increases the cetane number of the fuel charge, and the inherent oxygen in the fuel helps to complete the combustion inside the cylinder. Due to the increased combustion efficiency, the brake thermal efficiency of the system increases. Further, the higher ignitibility characteristics of PODEn results in a shorter combustion duration and lower heat transfer losses. Popp et al. [40] showed a reduced BTE when using a 20% PODE blend due to a higher exhaust gas energy loss and a higher usage of EGR.

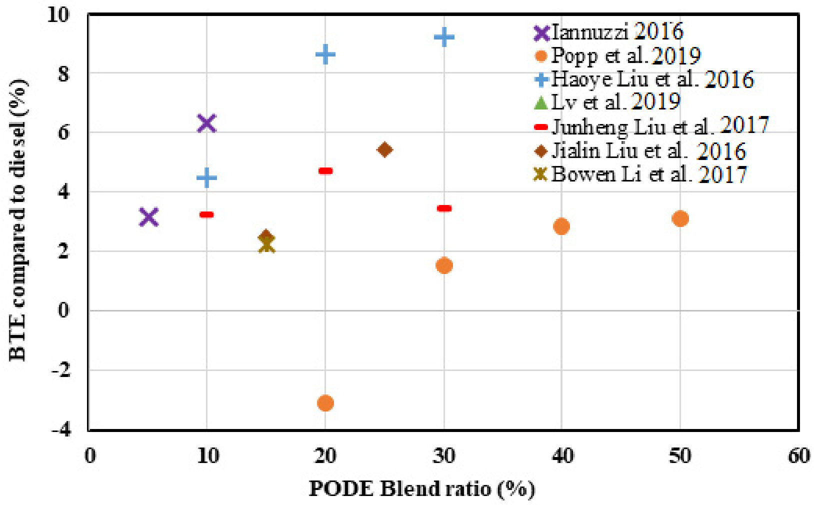

Figure 3. Effect of PODEn blend ratio on brake thermal efficiency compared to diesel [16,30,32,33,36,40,47].

Figure 4 shows the percentage change in oxides of nitrogen with respect to different PODE blend ratios. The amount of oxides of nitrogen was observed to be increased by up to 25% when blending PODEn with diesel fuel. Generally, the formation of oxides of nitrogen depends on the in-cylinder temperature, the availability of oxygen, and the residence time. The inherent oxygen in PODEn fuel and the marginally higher in-cylinder temperature increases the formation of oxides of nitrogen when increasing the PODE blend ratio. When PODE is mixed with neat diesel, the cetane number decreases compared to petroleum-based diesel, and the ignition delay can be increased. Thus, the combustion temperature increases, and the amount of NO_x increases. However, Jialin et al. [36] conducted research that indicated a reduction in the combustion chamber. This reduction was attributed to the greater latent heat of vaporization in comparison to traditional diesel derived from petroleum. Consequently, the increased absorption of heat during evaporation led to a decline in temperature.

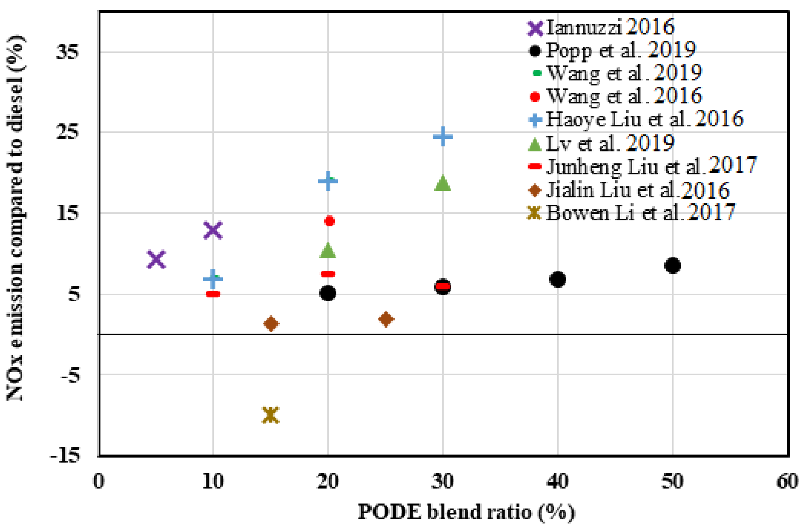

Figure 4. Variation in oxides of nitrogen with different PODEn blend ratios [16,31–33,36,40,41,45,47].

The formation of soot emissions generally occurs due to local rich regions inside the cylinder. Figure 5 shows the variation in soot emissions with different PODEn blend ratios. It was observed that a soot reduction of up to 90% was obtained when using a PODEn blend compared to using diesel fuel. This may be due to the following reasons: (i) the lack of a c-c bond and it being simple molecular fuel, (ii) the higher oxygen content, (iii) the higher volatility, and (iv) the higher cetane number with the high ignitibility characteristics of PODEn fuel. The formation of soot and NO_x are always a tradeoff between each other. As the amount of NO_x increases, the amount of soot decreases, which is due to the fact that the formation of NO_x occurs at a higher temperature, and combustion at a higher temperature is better but results in the production of large amounts of NO_x due to the Zeldovich mechanism [53]. On the other hand, this results in a decrease in soot formation. The larger the amount PODE blended in the fuel, the lower the amount of soot emissions, which may be due to the breakage of C-C bonds and the ease of the molecular bonds and the higher content of oxygen molecules.

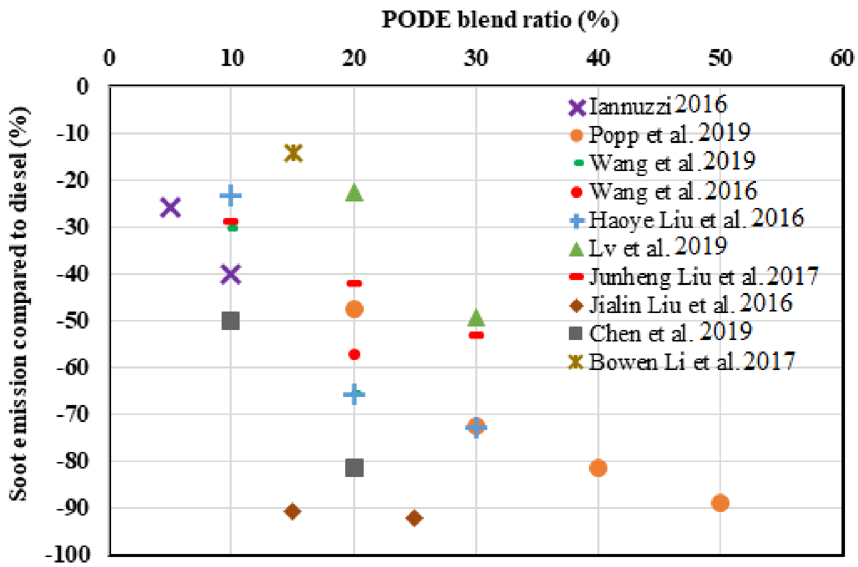

Figure 5. Percentage change in soot emissions with respect to PODE blend ratio [16,31–33,36,40,41,45,47,52].

The formation of HC emissions is generally due to (i) under-mixing regions where oxygen is not sufficient for fuel oxidation, and (ii) over-mixing regions where more oxygen crosses the boundary of the lean-burn limit. Figure 6 shows the effect of the PODEn blend ratio on the amount of hydrocarbon emissions. It was observed that most of the investigations reported reduced hydrocarbon emissions when blending PODEn with diesel fuel. The higher volatility of PODE reduces the under-mixing region inside the cylinder and increases the over-mixing region. The larger over-mixing region inside the cylinder, which is due to the higher cetane number and ignitibility characteristics PODEn fuel, reduces the formation of hydrocarbon emissions inside the cylinder.

The formation of carbon monoxide emissions primarily depends on oxygen availability and the formation of active radicals inside the cylinder. PODEn fuel has higher oxygen content, which helps in the conversion of CO to CO_2 inside the cylinder during the combustion process. Hence, the formation of CO emissions is lower when blending PODE with diesel fuel. This can be clearly observed in Figure 7. It can be observed that a maximum CO reduction of 80 to 90% can be obtained when adding 30% PODE into diesel fuel compared to using only diesel fuel.

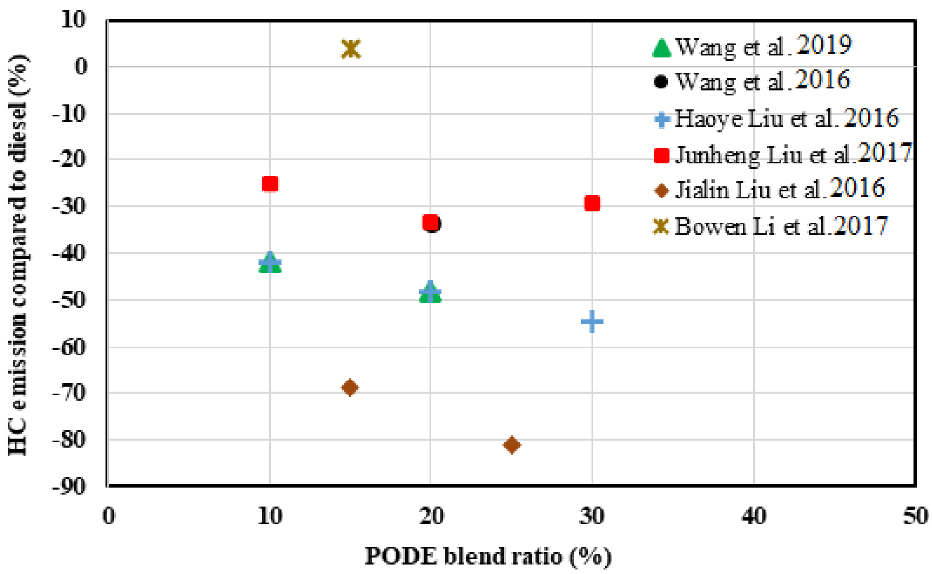

Figure 6. Effect of PODEn blend ratio on hydrocarbon emissions [31–33,36,41,45].

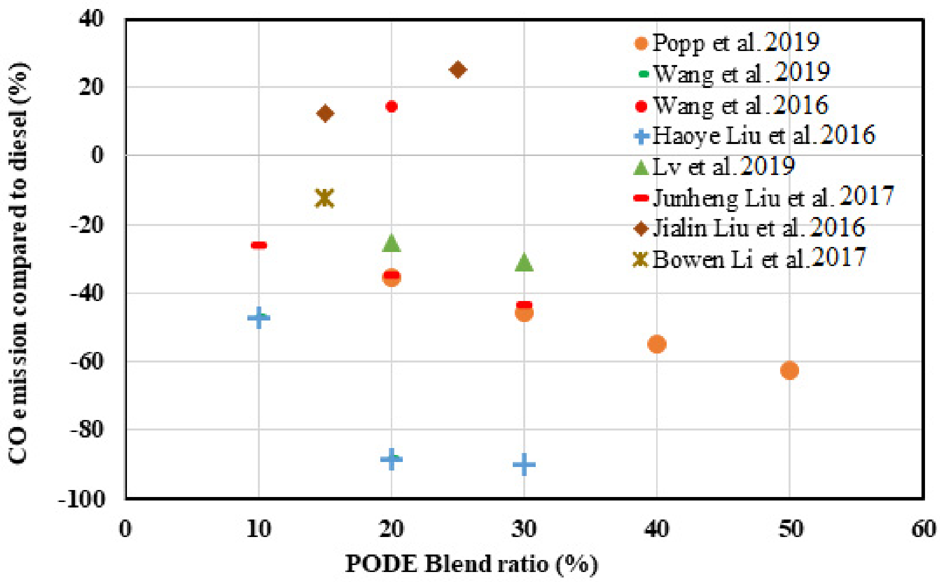

Figure 7. Variation in carbon monoxide emissions with different PODE blend ratios compared to diesel [31–33,36,40,41,45,47].

5.3. Application of PODEn as an Additive Fuel in Diesel/Alcohol Blends

Presently, several investigations are ongoing on diesel/alcohol fuel blends for reducing the usage of fossil fuels and for the simultaneous reduction in oxides of nitrogen and soot emissions [54]. Alcohol fuel has a higher oxygen content, which is helpful in suppressing the formation of soot emissions [55]. In addition, the higher latent heat of vaporization helps in reducing the amount of oxides of nitrogen [56]. However, the combustion efficiency is significantly affected due to the reduced cetane number of the fuel. To address the above issue, some researchers have used PODEn as an additive fuel for diesel/alcohol blends. PODEn has a higher cetane number, which helps to improve the ignition quality of the fuel–air mixture. In addition, PODEn acts as a stabilizer for the miscibility of diesel/alcohol blends [57].

In another study, it was clearly demonstrated that a PODEn+diesel/biodiesel blend exhibited a better emission reduction except for oxides of nitrogen. The higher oxygen content and higher volatility characteristics of PODE are the main reasons for the higher level of oxides of nitrogen produced in PODEn+diesel/biodiesel-fueled engines. Hence, aggravating this issue, some researchers have conducted experiments with the further addition of alcohol fuel in PODEn+diesel blends, thus forming a tertiary blend [58,59]. Alcohol fuel generally has a higher latent heat of vaporization, which is helpful in suppressing the formation of oxides of nitrogen without further impacts on other emissions.

Huang et al. [60] investigated the effects of PODEn addition on diesel/n-butanol blends. Initially, experiments were performed using diesel/n-butanol blends, and it was found that an 80% diesel + 20% n-butanol (BD20) blend exhibited a better emissions reduction without any impact on the brake thermal efficiency. However, a lower combustion efficiency was observed due to the higher latent heat of vaporization of n-butanol. To enhance the combustion efficiency problem, 5 to 10% $PODE_3$ fuel was added to the BD20 blend. When adding PODEn to the BD20 blend, the ignition delay decreased 2 to 3° CA due to the increased cetane number of the blended fuel. Further, more heat was released within a short period, resulting in a higher peak in-cylinder pressure and a shorter combustion duration. Due to the shorter combustion duration and highly premixed combustion, the brake thermal efficiency was significantly improved. Further, the increased in-cylinder temperature and increased oxygen content inside the cylinder nearly increased the combustion efficiency by 18 to 22%.

Huang et al. [58], conducted further investigations by increasing the fuel injection pressure and splitting the injection. Increasing the injection pressure further increased the combustion efficiency due to the better atomization and improved fuel–air mixture inside the cylinder. However, marginally increased levels of oxides of nitrogen and reduced thermal efficiency were reported due to the higher in-cylinder temperature and higher heat transfer losses. Splitting the injection reduced the amount of hydrocarbon emissions and particulate matter due to the reduced amount of local rich regions. Further, no significant impact on the level of oxides of nitrogen was observed when splitting the injection. Hence, Huang et al. reported that instead of using a higher injection pressure, splitting the fuel injection resulted in better combustion efficiency with less impact on oxides of nitrogen emissions.

In another investigation, Liu et al. [37] studied the effects of adding alcohol to PODE/diesel blends using six-cylinder turbocharged heavy-duty diesel engines with different world-harmonized steady-state cycle points. The blending of ethanol and PODE in the diesel fuel enhanced the combustion rate and reduced the combustion duration, which resulted in a higher brake thermal efficiency compared to diesel combustion alone. The levels of HC, CO, and soot emissions were significantly reduced when adding PODE and ethanol fuel to diesel. The reason may be due to the following: (i) the addition of PODE and ethanol increases the oxygen content of fuel, which is helpful for obtaining a complete combustion, (ii) the lower carbon-to-hydrogen ratio and the smaller molecular structure, (iii) the lower viscosity, higher volatility, and lower boiling point improves the fuel spray atomization and forms a uniform fuel–air mixture inside the cylinder.

5.4. Effect of PODE in Advanced Combustion Technologies

Presently, several investigations on advanced combustion technologies are being conducted due to their better emission-reduction capabilities without increasing the impact on fuel economy and without the aid of high-cost after-treatment devices. However, some limitations still restrict the flexible implementation of advanced combustion technologies in automotive vehicles. Some researchers have attempted to addresses the challenges of advanced combustion technologies by using PODEn as a pilot or as a main fuel due to its superior physical and chemical properties.

Wang et al. [45] investigated PODE-fueled homogeneous-charge compression ignition by varying the equivalence ratio and EGR. Two-stage ignition (i.e., low-temperature heat release (LTHR) and high-temperature heat release (HTHR)) occurred in the PODE-fueled HCCI engine, which resulted in smooth combustion inside the cylinder. The HTHR was further split into two stages when increasing the equivalence ratio due to the rapid oxidation of CO. When increasing the equivalence ratio at a constant EGR, the start of ignition was delayed, and the rate of heat release was increased. When increasing the EGR at a constant equivalence ratio, the charge temperature inside the cylinder decreased at the time at the end of compression, which resulted in a delayed start of LTHR and HTHR. Further, the PODE-fueled HCCI engine exhibited an ultra-low level of NO_x and soot emissions and higher levels of HC and CO emissions due to the lean PODE reducing the formation of reactive intermittent species.

Liu et al. [36] addressed the difficulties (i.e., lower combustion efficiency and combustion stability) faced during gasoline-fueled premixed-charge compression ignition by using PODEn as an additive fuel. While using PODEn as an additive fuel in the gasoline PCCI engine, the coefficient of variation of the indicated mean effective pressure was reduced by 56% and also came within the acceptable level. Further, the combustion efficiency was increased to 99.6% from 85.1% when adding 20% PODE to the gasoline fuel due to the improved ignitibility (i.e., cetane number). In addition, load extension was achieved due to the rate of the pressure rise being reduced by nearly 47% and due to the lower level of NO_x emissions. The addition of PODE further reduced the level of soot emissions due to it being an oxygenated and lower-C/H fuel.

Recently, PODE has been used as a high-reactivity fuel in reactivity-controlled compression ignition combustion modes due to it being capable of enlarging the reactivity gradient, its higher volatility, and its lower C/H ratio [50]. Table 4 shows the combustion emission characteristics results when using PODE as a high-reactivity fuel in RCCI combustion alongside different low-reactivity fuels. In addition, it can be clearly noted that using PODE as a high-reactivity fuel instead of diesel resulted in reduced ignition and combustion durations due to the higher cetane number and better ignition characteristics of PODE fuel.

Overall, PODEn has been found to be a sustainable alternative fuel for diesel engines; however, the following intensive research and developments are required before a final decision can be taken on its potential as a mass-producible fuel for the automotive fuel market: (i) The identification of highly efficient catalysts for a mass-producible synthesis process is required. (ii) The longer chain length can lead to high melting points that can result in the formation of precipitates at low temperatures in the fuel supply system, and this needs to be investigated. (iii) The effects of PODEn on non-regulated emissions needs to be studied. (iv) The corrosion effects on the fuel supply system, including durability testing, is important.

Table 4. Combustion, performance, and emissions characteristics while using PODEn as a high-reactivity fuel in RCCI combustion. (All results compared to diesel as a high-reactivity fuel with same low-reactivity fuel) (↑—max. increase, ↓—max. decrease).

Investigators	Low Reactivity Fuel	Engine Specifications	Operating Conditions	Combustion Characteristics	Performance Characteristics	Emission Characteristics
Tong et al. [50]	Gasoline	Six-cylinder inline diesel engine Displacement: 6.5 L Bore × Stroke: 105 × 125 mm Compression ratio: 16	1500 rpm SOI_{PFI}: −133° CA aTDC P_{DI}: 60 MPa. EGR: 45%	CA50: 0.5 to 1° CA advance. Cylinder pressure: Decreases	η_{BTE}: 2.9%	NO_x: 31% ↑ Soot: 87% ↓
Duraisamy et al. [34]	Methanol	Three-cylinder turbocharged diesel engine Displacement: 1.478 L Bore × stroke: 80 × 98 mm Compression ratio: 17.2	1500 rpm BMEP: 3.4 bar CA50: 10° CA aTDC EGR: 26%	• Ignition delay: 3 to 4° CA ↓ • Combustion duration: 5 to 7° CA ↓ • COV_{IMEP}: 1.2% ↓ • RoPR: 4.5% ↑	$\eta_{combustion}$: 21% η_{BTE}: 1.8%	HC: 51% ↓ NO_x: 26% ↑ CO: 49% ↓ Soot: 72% ↓
Liu et al. [61]	Ethanol	Four-cylinder turbocharged diesel engine Displacement: 4.32 L Bore × stroke: 108 × 118 mm Compression ratio: 17.5	1500 rpm BMEP: 1 MPa SOI_{PODE}: TDC $P_{inj.PFI}$: 4 bar	Compared to CDC, ignition delay increases, CD decreases, and peak cylinder pressure decreases.	Compared to CDC, brake thermal efficiency increases	Compared to CDC, HC: 63% ↑ NO_x: 82% ↓ CO: 72% ↓ Soot: 86% ↓
Song et al. [62]	Natural gas	Single-cylinder CI engine Displacement: 1.85 L Compression ratio: 17.5 Bore × stroke: 123 × 156 mm	Low load IMEP: 4 bar 1000 rpm CNG ratio: 60% P_{intake}: 1.2 bar EGR: Nil	• Ignition delay: 9% ↓ • Combustion duration: No variation at advanced injection 33% ↓ at late injection • CA50: 5° CA advance. • RoPR: 8% ↑	$\eta_{combustion}$: 42% η_{BTE}: 3.8%	HC: 25% ↓ Nox: 21% ↓ CO: 13% ↓

CA50: crank angle of 50% mass fraction burn; COV_{IMEP}: coefficient of variation of IMEP; RoPR: rate of pressure rise.

6. Summary and Future Perspectives

Several investigations into PODE-fueled engines have clearly shown that PODEn can be used as a future sustainable alternative fuel for diesel engines. Polyoxymethylene dimethyl ether is a nontoxic liquid fuel that can be derived from various renewable feedstocks, mainly from methanol fuel. PODEn fuel is produced by various synthesis processes using different feedstocks and catalysts. The physical and chemical properties of PODE fuel clearly show that PODEn can be used as a suitable alternative fuel for diesel engines. PODEn has a higher cetane number, which means that it can act as an efficient alternative fuel for use in compression ignition engines. The higher volatility characteristics of PODEn results in a better evaporation and mixing of the fuel–air mixture. The higher oxygen content and lack of a carbon-to-carbon bond help in generating smokeless combustion. So far, PODEn has been used in internal combustion engines as a 100% sole fuel, and many reviews in the literature have clearly reported that PODEn-fueled engines present a decreased NO_x–PM trade-off relationship alongside lowering the amount of HC and CO emissions without high-cost after-treatment devices.

Author Contributions: Conceptualization, C.N.K. and S.M.A.R.; methodology, C.N.K.; formal analysis, S.M.A.R.; investigation, I.M.R.F.; writing—original draft preparation, C.N.K. and I.M.R.F. writing—review and editing, C.N.K., S.M.A.R. and I.M.R.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the University of Technology Sydney through Strategic Research Support funding with grant number [324100.2200034].

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

amb	Atmospheric pressure
aTDC	After top dead center
BMEP	Brake mean effective pressure
bTDC	Before top dead center
C/H	Carbon-to-hydrogen ratio
CA	Crank angle
CA50	Crank angle at 50% mass fraction burn
C-C	Carbon-to-carbon bond
CH_2O	Formaldehyde
CO	Carbon monoxide
CO_2	Carbon dioxide
COOH	Carboxyl group
DME	Dimethyl ether
D_{nozzle}	Nozzle diameter
EGR	Exhaust gas recirculation
HC	Hydrocarbon
HCCI	Homogeneous-charge compression ignition
HRR	Heat-release rate
HTHR	High-temperature heat release
ICE	Internal combustion engine
IMEP	Indicated mean effective pressure
LRF	Low-reactivity fuel
LTHR	Low-temperature heat release
NH_3	Ammonia
NO	Nitric oxide
NO_x	Oxides of nitrogen
OME	Oxymethylene dimethyl ether

PAH	Polycyclic aromatic hydrocarbon
PCCI	Premixed-charge compression ignition
P_{inj}	Injection pressure
PM	Particulate matter
PODE	Polyoxymethylene dimethyl ether
RCCI	Reactivity-controlled compression ignition
RoPR	Rate of pressure rise
SMD	Sauter mean diameter
SOI	Start of injection
STP	Spray tip penetration

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