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Araştırma Makalesi / Research Article

Production of Wood Pyrolysis Oil for Use as an Alternative Fuel in the Automotive Sector and Improvement of Its Physicochemical Properties

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ABSTRACT: Biomass resources have the potential to replace petroleum-based fuels. Biomass can be converted into pyrolysis oil by pyrolysis method and this oil is of interest as an alternative to fossil fuels used in many areas such as automotive sector. However, pyrolysis oil is difficult to use directly in diesel engines due to its low energy density, high viscosity and water content. The easiest solution is to create mixtures with high cetane content. In this study, polyethylene glycol 400 (PEG), Wood Pyrolysis oil (WPO), n-butanol (B) and 2-ethylhexyl nitrate (2-EHN) (PEG0/PY10/B85/2-EHN5) were obtained by blending them as wt%. Then, by increasing PEG400 by 10% and decreasing n-butanol by 10% (PEG10/PY10/N-B75/2-EHN5, PEG20/PY10/B65/2-EHN5, PEG30/PY10/B55/2-EHN5, PEG40/P10/B45/2-EHN5), other blend fuels were obtained. Thus, the poor properties of pyrolysis oil were improved by blending with n-butanol and two cetane improvers PEG400 and 2-EHN as additives. The viscosity of pyrolysis oil was effectively reduced to a suitable level for use in conventional diesel engines by blending with n-butanol. In addition, the autoignition of PY blend fuels was improved by adding PEG400, 2-EHN and n-butanol. As a result, the blended fuels showed increased calorific value and cetane number and decreased kinematic viscosity, density and water content compared to pyrolysis oil in terms of physicochemical properties. Thus, the cetane numbers of the blended fuels were improved by 2,5%, 8,3%, 27,1% and 34,3%, respectively, with a 10% increase in PEG400 by weight. Thus, it was determined that the blended fuel containing 40% PEG400 by weight (PEG40/P10/B45/2-EHN5) in terms of physicochemical properties could be used as an alternative fuel in the automotive sector.

Keywords: Wood pyrolysis oil, PEG 400, N-butanol, 2-EHN, Alternative fuel

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1. INTRODUCTION

Sustainability and environmental impacts of energy sources are of great importance in the modern world. The search for renewable energy alternatives is necessary due to the finite resources and environmental harm caused by fossil fuels. Given their potential to be both carbon neutral and renewable, biomass-based fuels stand out as a significant choice in this regard. One of the well-known types of biomass-based fuels is wood pyrolysis oil (WPO), however it has certain performance issues. In recent years, problems such as air pollution, global warming and the depletion of fossil fuels have made the use of alternative fuels important. Biooil or pyrolysis oil (PO) obtained from biomass is a clean, sustainable and renewable energy source (Bridgwater et al., 1999; Zhang et al., 2007). The use of pyrolysis oil in internal combustion engine applications has been emphasized in research (Kleinert and Barth, 2008; Jones et al., 2009; Yalçın et al., 2024). The potential of this fuel to reduce exhaust gas emissions and its sustainability have led to increased interest in recent years (Kim and Lee, 2015; Kim et al., 2015; Lee et al., 2019; Midhun Prasad and Murugavelh, 2020). Particularly in nations with a wealth of WPO resources, it has drawn interest as an alternative to conventional petroleum-based fuels (Ivanova et al., 2018). In this regard, creating and using alternative biofuels is essential to resolving environmental issues.

The content and characteristics of pyrolysis oil, a thick liquid produced by pyrolyzing biomass at high temperatures without oxygen (Bridgwater, 2013), differ according on the kind of biomass utilized and the pyrolysis circumstances (Yuan et al., 2018; Lee et al., 2019). However, its low cetane number, poor calorific value, high kinematic viscosity, high acidity, and high water content prohibit its direct application in diesel engines (Kim and Lee, 2015; Kim et al., 2015; Lee et al., 2019, Lee et al., 2020). Various methods have been tested to improve these properties (Chiaramonti et al., 2003; Ikura et al., 2003; Xiaoxiang and Ellis, 2009; Huang et al., 2012; Lu et al., 2012; Alcala and Bridgwater, 2013; Lee et al., 2013, Lee et al., 2019, Lee et al., 2020; Kim et al., 2015; Lin et al., 2016), the most effective approach is to physically enhance the fuel properties by blending pyrolysis oil with hydrocarbon fuels (Ikura et al., 2003; Honnery et al., 2008; Murugan et al., 2009; Doğan et al., 2012; Huang et al., 2012; Lu et al., 2012; Lee et al., 2013, Lee et al., 2020; Martínez et al., 2014; Karagoz, 2020).

The use of WPO in diesel engines is limited by technical difficulties such as low cetane number and high viscosity. Low cetane number delays the ignition process of the fuel and negatively affects engine performance, while high viscosity reduces atomization and combustion efficiency. These problems prevent the efficient use of WPO in engines. In this context, the potential of various cetane improvers and additives to improve performance is gaining importance. Additionally, some researchers are studying the possibility of wood-based biofuels becoming the primary fuel for diesel engines (Solantausta et al., 1993; Beld et al., 2013; Beld et al., 2018; Chiaramonti et al., 2003).

Due to polarity and density differences, pyrolysis oil creates miscibility problems with conventional hydrocarbon fuels and phase separation occurs in a short time (Kim and Lee, 2015; Lin et al., 2016; Lee et al., 2019, Lee et al., 2020). To overcome this situation, additives are needed for the pyrolysis oil to be successfully mixed with conventional fuels and burned in engines. According to Alcala and Bridgwater, using organic solvents such as alcohol increases miscibility and allows the formation of stable mixtures; in this context, the type and amount of alcohol used are critical. When n-butanol and PEG400 are mixed with pyrolysis oil, it provides the widest homogeneous stable mixture (Alcala and Bridgwater, 2013) and has a better autoignition property (Nguyen and Honnery, 2008). Therefore, n-butanol was selected as the blend component to blend WPO with PEG 400.

PEG400 and 2-EHN, used as cetane improvers, aim to improve engine performance by increasing the cetane number of WPO. PEG400 stands out as an economical and chemically stable option, while 2-EHN is known as a more costly but effective cetane improver. Both components can optimize the combustion properties of WPO.

N-butanol is another significant additive. By raising the cetane number, N-butanol increases combustion efficiency and lowers the high viscosity of WPO. Furthermore, n-butanol's ability to suppress polymerization improves the fuel's chemical stability, reducing wear and engine clogging issues. These characteristics facilitate the more effective use of fuels derived from biomass in diesel engines. N-butanol can lower the viscosity of the blended fuel since its viscosity of 2.2 mm^2/s is comparable to the kinematic viscosity of 2.7 mm^2/s for diesel fuel (Lee et al., 2020). Furthermore, by dissolving the solid particles in the pyrolysis oil, it can prevent the sticky polymers created by the polymerization of tar, enhancing the pyrolysis oil's engine performance and fuel qualities (Jin et al., 2011; Alcala and Bridgwater, 2013; Kim and Lee, 2015). In this context, our study aimed to improve the performance properties of the fuel mixture by using n-butanol as an additive.

Our study assessed the impact of PEG 400, 2-EHN, and n-butanol on the physicochemical characteristics of WPO-based fuel performance. It was examined how the engine's ideal fuel properties could be raised and how the combinations of the components made by varying their ratios enhanced the fuel's qualities. Kinematic viscosity, density, water content, cetane number, lower heating value (LHV), and major components were used to characterize the chosen samples (Alcala and Bridgwater, 2013; Chong and Bridgwater, 2017; Lee et al., 2020). In order to compensate for the unfavorable physicochemical characteristics of the pyrolysis oil, stable homogenous mixtures between WPO were formed with the addition of n-butanol, PEG400, and 2-EHN. In addition, the cetane number and calorific values of the blended fuels were improved by the addition of PEG400 and 2-EHN. The results offered strategies to enable wider applications of biomass-based fuels and reduce their environmental impact.

2. MATERIALS AND METHODS

The biomass waste wood sawdust to be used in the studies was supplied from a private company operating in Afyonkarahisar province, as shown in Figure 1. In the study, wood sawdust weighed as 100 gr on a precision scale was subjected to the pyrolysis process in order to subject the raw material to the pyrolysis process homogeneously.

Figure 1. Wood dust

WPO was converted to vapor by thermal decomposition in an oxygen-free environment and cooled to liquid form. The resulting pyrolysis oil is a dark brown liquid. In addition, gases containing flammable components, called pyrolytic gases, are separated from the reactor, while solid coal residues are formed at the end of the process. The pyrolysis process is shown schematically in Figure 2.

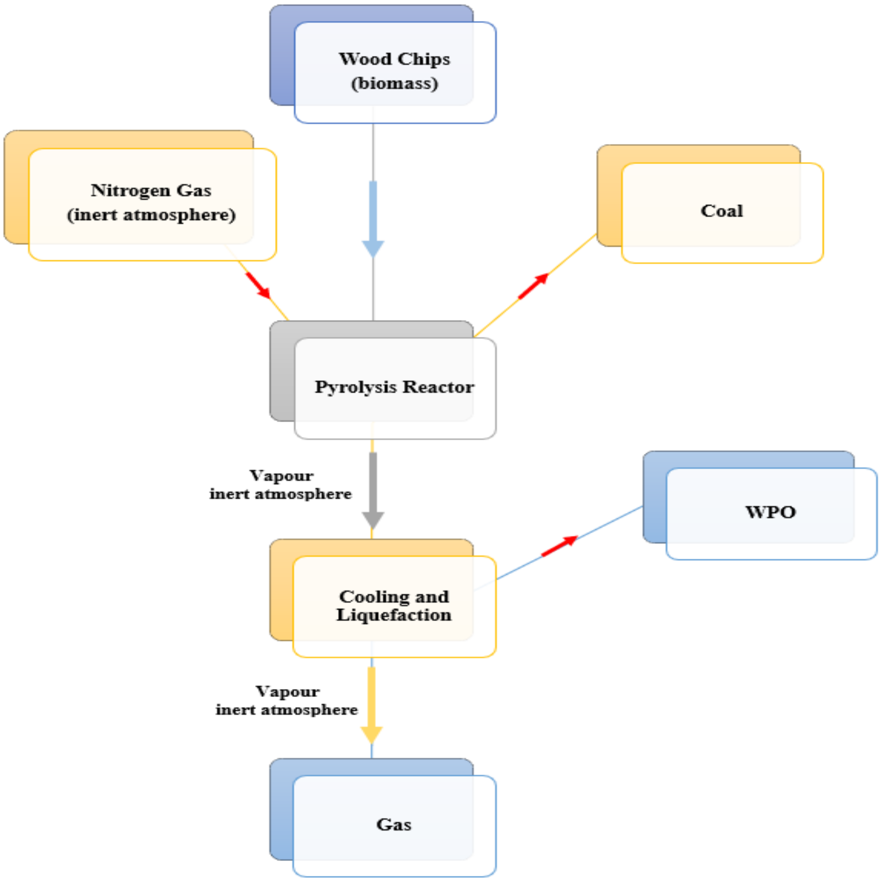

Figure 2. WPO production scheme

Optimization studies to obtain the optimum level of wood sawdust oil obtained by subjecting it to the pyrolysis process were carried out in the existing pyrolysis reactor in the Automotive Engineering Biofuel Laboratory of Afyon Kocatepe University, Faculty of Technology (Figure 3).

The pyrolysis reactor used in this study has a laboratory type, vertically placed, 0.5 liter stainless steel tank. The reactor system is equipped with a temperature sensor containing a K-type thermocouple that can operate stably at high temperatures, a PID-controlled digital panel that provides automatic temperature control (0–800°C operating range), a heating system with programmable ramp function, and leak-proof gaskets and connection devices to create a vacuum/nitrogen environment. High purity (≥99.99%) nitrogen gas was used to provide an inert atmosphere, and the gas flow rate was adjusted to 0.5 L/min with the help of a regulator and a gas flow meter. The glass condenser in the condensation system ensures the separation of liquid products, and the cooling circuit operates according to the principle of continuous circulation with tap water. The phase separation funnel used in the separation process of the obtained pyrolytic liquid allows the separation of liquid phases according to their density differences. Filtration was carried out with Whatman No.1 filter paper to remove solid particles. A rotary evaporator was used for solvent (dichloromethane) removal. The evaporator device operates at a rotation speed of 200 rpm, with the support of a 50°C hot water bath and a vacuum pump, and purifies the pyrolytic oil by evaporating the dichloromethane. The presence of water in the fuel is an undesirable situation as it negatively affects combustion. Therefore, the pyrolytic liquid product was first subjected to phase separation in the separating funnel to separate the water phase and the pyrolytic oil + dichloromethane phase. Afterwards, during the evaporation process carried out with the rotary evaporator operating in a 50°C hot water bath under vacuum in order to remove dichloromethane, a small amount of volatile water was also removed from the system.

Optimization studies were carried out for each parameter under fixed conditions with three repetitive experiments in accordance with the pyrolysis parameters specified in the Table 1. All parameters except the parameter whose optimum value was desired were kept constant; after determining the optimum value, this value was fixed and the same method was followed for the other parameters. In the first study, the fixed parameter values were determined as: temperature 450°C, gas flow rate 1L/min, pyrolysis time 15 minutes and the heating rate (10 and 20°C/min) was optimized as a variable. The liquid product obtained at the end of the experiments was analyzed by the phase separation method; water and pyrolytic oil amounts were measured, the solid product was determined from the residue remaining in the reactor and the gas product amount was calculated by mass difference. After determining the optimum conditions, pyrolytic oil production was continued under these conditions.

Table 1. Pyrolysis conditions and process parameters

Process parameters	**Pyrolysis conditions**
Flow rate of propellant nitrogen gas	(0, 0.5 and 1) L/min.
Reactor internal temperatures	(300, 350, 400, 450, 500 and 550) °C.
Reactor internal temperature increase rate	(10 and 20) °C/min.
Pyrolysis time	(0, 15, 30, 45 and 60) min.

Figure 3. Pyrolysis reactor

The maximum pyrolysis oil yield was obtained at 500 °C reactor temperature, 0.5 L/min nitrogen gas flow rate and 10 °C/min heating rate. Under these optimum conditions, total product yields were determined as 23.4% pyrolysis oil, 35.3% aqueous phase, 25.9% biochar and 15.4% gas. The yields are shown in Figure 4.

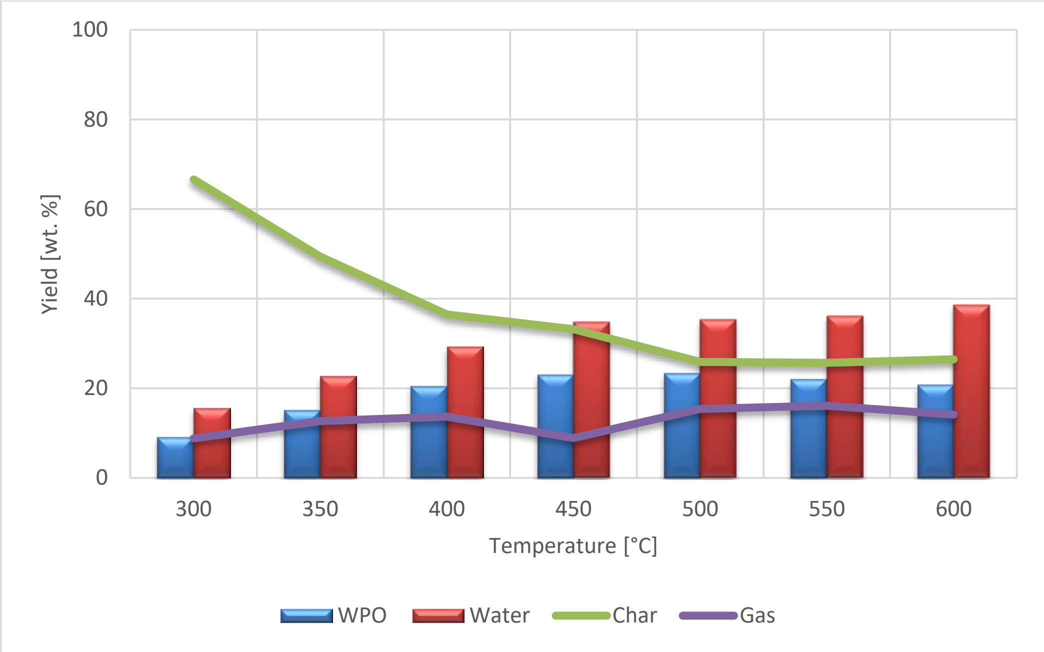

Figure 4. WPO yield change graph depending on temperature

The physicochemical properties of WPO were determined in an external laboratory and the results are presented in Table 2. The kinematic viscosity of PY at 40 °C is 8.9 mm²/s, which is approximately 3.2 times higher than that of conventional diesel; high viscosity may negatively affect engine performance (Alptekin and Canakci, 2008; Maroa and Inambao, 2019). In addition, the density of PO was determined as 1100 kg/m³, which makes miscibility difficult (Lin et al., 2016).

Table 2. Compositions and fuel properties of WPO, PEG400, 2-EHN, N-butanol and Diesel

	WPO	**PEG400**	**2-ehn**	**N-butanol**	**Diesel**
Kinematic viscosity (mm²/s) at 40°C (TS 1451 EN ISO 3104)	8.9	4.5	1.8	2.2	2.7
LHV (MJ/kg) (ASTM D 240 / TS 1740)	20.1	23.6	28.5	33.1	42.9
Water content (%) (TS 6147 EN ISO 12937)	1.1	0.3	<0.1	-	-
C (wt %) (ASTM D 5373)	40.2	52.2	54.9	64.8	86.1
H (wt %) (ASTM D 5373)	11.3	9.2	9.7	13.6	13.9
O (wt %) (ASTM D 5373)	49.3	38.6	27.4	21.6	-
Density (kg/m³) (ASTM D 4052)	1100	1126	963	810	822
Cetane number (TS 10317 EN ISO 5165)	-	-	-	15.9	52
Flash point (°C) (ASTM D 93)	98	-	76.1	35	55

The low heating value (LHV) of PO is approximately 20.1 MJ/kg, which is 2.1 times lower than that of conventional diesel, indicating that the energy density of PO is lower than that of diesel. The water content of PO is due to the feedstock and pyrolysis reactions (Alcala and Bridgwater, 2013;

Chong and Bridgwater, 2017). High water content makes PO unstable and separates into oily-aqueous phases (Lee et al., 2020). Water both reduces the heating value and reduces the viscosity (Hossain et al., 2016). In addition, the presence of water can cause ignition delay and corrosion problems in injectors (Oasmaa et al., 2015). The water content in WPO obtained by keeping the evaporation time long is around 1.1%, and at this level, it can provide long-term stability without causing corrosion problems.

In this study, the fuel mixtures required for the improvement of physicochemical fuel properties and the conduction of experimental studies for the usability of pyrolysis oil as an alternative fuel were prepared using a similar methodology to (Kim et al., 2015). Briefly, the mixtures were prepared at room temperature by following a simple procedure at varying weight percentages. Pyrolysis oil, PEG400, n-butanol and 2-EHN were used in the mixture fuel content to obtain blended fuels. The weight percentages given in Table 2 were used while preparing the obtained blended fuels.

Table 3. Weight% contents of blended fuels

Mixed Fuels	PEG400	N-butanol	WPO	2-EHN
Fuel 1 (PEG0/PY10/NB85/2-EHN5)	%0	%85	%10	%5
Fuel 2 (PEG10/PY10/NB75/2-EHN5)	%10	%75	%10	%5
Fuel 3 (PEG20/PY10/NB65/2-EHN5)	%20	%65	%10	%5
Fuel 4 (PEG30/PY10/NB55/2-EHN5)	%30	%55	%10	%5
Fuel 5 (PEG40/PY10/NB45/2-EHN5)	%40	%45	%10	%5

Then, the pyrolysis oil fuel mixtures given in Table 3 were characterized in terms of physicochemical properties. The physicochemical properties of the pyrolysis oil and homogeneous mixtures were analyzed in a nationally accredited laboratory by following standard methods (ASTM / EN ISO), which is an indicator of the suitability of the mixtures for use in CI engines, and measured as shown in Table 4.

Table 4. PEG 400, PH, NB and 2-EHN blend components and fuel properties

Mixed Fuels	Kinematic viscosity (mm^2/s) 40°C	LHV (MJ/kg)	Water content (%)	Intensity (kg/m^3)	Cetane number	C	H	O
Fuel 1	2,9	31,6	2,51	847	27,7	61,8	13,2	24,6
Fuel 2	3,1	30,6	2,54	878	28,4	60,6	12,7	26,3
Fuel 3	3,3	29,7	2,57	910	30	59,3	12,3	28,0
Fuel 4	3,5	28,7	2,60	941	35,2	58,1	11,9	29,7
Fuel 5	3,8	27,8	2,63	973	37,2	56,8	11,4	31,4
Diesel	2,7	42,9	-	822	52	86,1	13,9	-

3. RESULTS AND DISCUSSION

Many studies have been conducted on the conversion of bio-oils into more stable fuels by physical, catalytic or chemical methods (Bridgwater, 2012). The aim of this study is to investigate the usability of WPO as an alternative fuel in internal combustion engines. There is not enough research on the usability of the mixtures obtained by blending PO obtained from wood sawdust with PEG400, n-butanol and 2-EHN as fuel. Therefore, our study aims to fill this gap.

Although there are many studies in the literature on the production of fuel by pyrolysis of wood chips, the majority of the studies on the usability of these fuels in internal combustion engines have focused on diesel and biodiesel (wood chip pyrolysis oil) mixtures. The fuel mixtures used in this study (combinations of PEG400, wood pyrolysis oil, n-butanol and 2-ethylhexyl nitrate) address a very current and innovative topic within the scope of alternative and environmentally friendly fuel research. Although there are various studies on each of these components in the literature review, studies using these four components together are quite limited. In this respect, the presented study provides an original contribution to the literature. In addition, systematically changing the ratios of these four components (especially increasing the PEG400 ratio and decreasing the n-butanol ratio) aims to provide a new parameter analysis and provide a different perspective on the subject.

The combustion properties of pyrolysis oil blends may be limited by high acidic content and uneven combustion. PEG400, 2-EHN and b-butanol can increase combustion efficiency and improve the combustion properties of pyrolysis oil. Optimizing the mixture ratios can improve combustion performance (Bridgwater, 2012).

WPO cannot be used directly in diesel engines due to its insufficient properties such as high kinematic viscosity and low LHV; therefore, blending PY with diesel offers a solution to improve fuel properties (Lee et al., 2020). However, WPO is known to be incompatible with other additives directly, so an organic solvent such as n-butanol is required (Alcala and Bridgwater, 2013). N-butanol increases the calorific value by reducing the viscosity and acidity of the blends (Yalçın and Mutlu, 2022).

The effect of cetane number on combustion in diesel engines is important, therefore PEG400 and 2-EHN were added to the blends as cetane enhancers to increase cetane numbers (Kim et al., 2015). As seen in Table 4, it was observed that there was an increase in the cetane numbers and oxygen amounts of the blended fuels due to the increase in PEG400 as a weight percent in the blended fuels.

As seen in Table 4, the density and kinematic viscosity of blended fuels containing 10 wt% WPO are close to diesel, but an increase is observed when compared to the increase in PEG400; kinematic viscosity was measured between 2.9-3.8 mm^2/s. Blended fuels show increased calorific values compared to the original WPO. As the PEG400 content increases, the density and kinematic viscosity increase, while the calorific values decrease, which leads to longer injection times and combustion delay (Kim et al., 2015). In addition, blended fuels carry a water content of 2.51-2.63% compared to WPO, and the water content increases as the PEG400 ratio increases (See Table 4). In general, the n-butanol ratio decreases with the increase in the PEG400 ratio, and this reduces the calorific values of blended fuels. The increase in the presence of n-butanol improved the stability of the mixtures, reduced density differences and increased their calorific values.

In Europe, the minimum cetane number is ≥51, and in the USA it is ≥40 (Lapuerta et al. 2009). As the PEG400 content increases, the cetane number increases, which does not improve adverse conditions such as ignition delay and incomplete combustion. To increase the cetane number, PEG400 was added to the blended fuels in 10% weight increments and a fixed 5% 2-EHN, thus increasing the cetane numbers to the range of 27.7-37.2.

The cetane numbers of the blended fuels were improved with PEG400, 2-EHN and n-butanol. Since the cetane number of the fuels containing 40% PEG400 by weight approaches the optimum value compared to diesel, it may be suitable for diesel engine applications. In the present study, by selecting appropriate WPO-mixable additives for WPO blended fuels in a diesel engine, fuel properties such as viscosity and autoignition of WPO blended fuels were improved. As a result, physicochemically improved blended fuels that can be tested in CI engines were obtained. In the future, diesel engine performance and exhaust emissions of these fuels can be compared with pure diesel.

In the study conducted in line with the above-mentioned analyses, it was concluded that the inadequate fuel properties of PO could be improved in terms of physicochemical fuel properties by applying modifications based on the determination of its fuel properties and that it could be used as an alternative fuel in a diesel engine.

4. CONCLUSION

This A WPO was obtained by pyrolysis from wood sawdust. The optimum conditions for maximum 23.4% yield are 10 °C/min heating, 500 °C reactor temperature and 0.5 L/min N2 flow rate. However, the density of WPO is 1100 kg/m³ and its kinematic viscosity is 8.9 mm²/s, which is higher than diesel, which can cause engine deposits and engine problems such as fuel pump and injector wear. WPO, which has a low calorific value, has a low water content of 1.1%. The low water content increases the stability of the fuel, reduces ignition delay and abrasiveness, and can increase the viscosity of the fuel. Due to this situation, modification is required for Po in terms of physicochemical properties.

To improve the fuel properties of PY, it was mixed with PEG400, 2-EHN and n-butanol. To obtain stable mixtures due to polarity, n-butanol was used as a co-solvent. In this way, WPO, PEG400 and 2-EHN were mixed homogeneously.

The increasing n-butanol due to the proportional decrease of PEG400 decreased the kinematic viscosity of the blended fuels and increased the calorific value. The negative properties of PO were reduced by the addition of PEG400, 2-EHN and n-butanol, and the cetane numbers reached the minimum specification of diesel. Thus, the blended fuels can be considered as a potential biofuel source in CI engine applications.

In this study, blended fuels based on n-butanol, PEG 400, 2-EHN and WPO were evaluated as potential alternatives to conventional diesel fuel. It was found that the autoignition properties of blended fuels could be improved with two cetane improvers, PEG400 and 2-EHN. PEG 400, 2-EHN and n-butanol are effective tools to improve the performance of biomass-based fuels. The cetane improving properties of PEG 400 and 2-EHN, the viscosity reducing and polymerization inhibiting abilities of n-butanol enable biomass-based fuels such as WPO to be used more efficiently in diesel engines. The use of these components in appropriate proportions can increase fuel performance and provide a wider range of applications for biomass-based fuels. In addition, determining the effects of blended fuels on long-term performance, combustion characteristics and exhaust emissions in diesel engines is important for the integration of these fuels into practical applications. In addition, comparative evaluation of alternative cetane improvers other than PEG400 and 2-EHN and viscosity modifiers other than n-butanol can contribute to further improvement of fuel properties. Studies to be carried out in this direction will support biomass-based fuels to become a competitive alternative to diesel fuel in terms of sustainability and environmental compatibility.

5. ACKNOWLEDGEMENTS

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6. CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

7. AUTHOR CONTRIBUTION

Arif Hakan YALÇIN contributed to determining the concept and/or design process of the research, data analysis and interpretation of the results, critical analysis of the intellectual content, and final approval and full responsibility. Ercan ŞİMŞİR contributed to managing the concept and/or design process, data collection, preparation of the manuscript, and final approval and full responsibility.

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