Study the Fuel characteristics of Ethanol and Waste Engine Oil Pyrolytic oil blends

Nivedita Patel

Veer Surendra Sai University of Technology, Burla

Krushna Prasad Shadangi (✉ krushnanit@gmail.com)

Veer Surendra Sai University of Technology, Burla <https://orcid.org/0000-0002-7716-1668>

Research Article

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Abstract

This study shows the application of pyrolytic oil derived from Waste Engine oil (WEPO) as an alternative fuel by blending with Ethanol. For this, the effect of blending of ethanol at 5 %, 10 %, 15 %, 20 %, 25 %, and 30 % on the compositions and fuel properties were analyzed. The utmost blending was established based on the higher heating value. The pyrolytic oil used for this study was produced at 550 °C which was the optimum pyrolytic temperature. A comparison study of the blended oil was done with commercially available gasoline to observe the similarities in their fuel properties and composition. The study confirmed that ethanol can be blended with WEPO at 20% by volume to obtain a fuel of a higher heating value of about 44.24 MJ/kg that can be used as fuel. Since, WEPO contains 65.80% of C4-C12 (gasoline range) hydrocarbon compounds and the rest 31.48 % C11–C15, 11.84 % C15-C19, and 6.94 % >C19 compounds it can be used as a future fuel.

1. Introduction

The whole World is in trouble due to the scarcity of fossil fuel. The fossil fuel reserves are depleting at an alarming rate globally due to the increase in population and energy demand. Initiatives are taken to meet the energy demand. Alternative fuels are produced to substitute gasoline and diesel because of their calamity, hike in price, and as per emission norms. A billion tonnes of waste materials like biomass, waste oil, and waste plastic are produced annually. The disposal of these waste materials which contain hazardous substances like Poly aromatic hydrocarbons (PAHs), hazardous metals, and toxic chemicals affects badly the living beings and environment (Patel and Shadangi 2020; Patel et al. 2020; Kumar et al. 2013). The increase in the number of automotive vehicles creates a big problem with the disposal of waste engine oil (WEO). WEO is considered as one of the major waste materials among all which spoil the environment severely. It was reported in the literature that around 40 million metric tonnes of engine oil are produced every year and a major portion (around 60%) were discarded as waste and the remaining (only 40%) were recycled (Fuentes 2007; Arpa et al. 2010; Tripathi et al. 2015). The direct exposure of waste engine oil affects badly the living beings and the environment. Now a day the WEO is considered an alternative energy source and received much attention. It is reported in the literature that diesel-like fuel (Arpa et al. 2010) and gasoline-like fuel (Arpa and Yumrutas 2010) can be produced from waste engine oil by using suitable processes. There are varieties of techniques to handle waste engine oil. Different recycling techniques like distillation (Demirbas 2015), clay treatment (Abu-Ellella et al. 2015), hydrogenation (Batov et al. 2018), acidic refining (Osman et al. 2018) etc. are adapted to process waste engine oil. But these techniques are not widely accepted due to certain drawbacks which require further improvement. Processes like gasification, incineration, and pyrolysis are coming under thermochemical conversion technology. Further, in the gasification and incineration process more toxic gases were evolved directly into the environment which affects severely the human health. The emission of oxidized compounds of metals and PAHs are the major hazardous pollutants of the environment. These processes can only able to recover the heating value from wastes except valuable chemicals (Dong et al. 2018). Pyrolysis is one of the suitable thermochemical conversion process which yields pyrolytic oil, gases, and

char as the products. The yield of pyrolytic oil is optimum. Based on the residence time of vapour and rate of heating, the pyrolysis can be either fast pyrolysis process or slow pyrolysis process (Basu 2018). The char and gas yield increases with increase in residence time of vapour and slow rate of heating (Lam et al. 2012) while the oil yield increases with small residence time of vapour and high rate of heating (Kim and Kim 2000). In fast pyrolysis of waste engine oil, the higher hydrocarbon compounds are thermally decomposed to lower hydrocarbon compounds in the form of pyrolytic oil and non-condensable gases which can be used as alternative fuel or chemical feedstock. The yield of char is very less and contains a very minute quantity of hazardous metal (Patel and Shadangi 2020). The main purpose is to produce as an alternative fuel, pyrolysis of WEO was found to be the environmentally acceptable and proper way to handle this waste (Lam et al. 2018). Many researchers reported the engine performance of pyrolytic oil blended with diesel, gasoline, or ethanol. Bert et al. 2018 had reported that when a four-cylinder, 50kW diesel engine (4C) was fuelled with Fast Pyrolysis Bio-Oil was blended with 20 % mass fraction of ethanol (FPBO20) shows the optimum performance with 80 % power output (Bert et al. 2018), while Gadwal et al. 2019, studied the performance and emission characteristics of CRDI diesel engines fuelled with plastic pyrolysis oil (PPO) blended with ethanol and diesel. The blend of 70PPO+15D+15E shows the engine performance similar to diesel (Gadwal et al. 2019). Kareddula and Puli 2018, investigated the emission and performance of multi-cylinder spark-ignition engines fuelled with plastic oil blended with ethanol and gasoline. It was concluded that 15PPO5E shows high BSFC and low BTE of the engine as compared to an engine run with pure gasoline (Kareddula et al. 2018). But till today, the study of fuel characteristics of Ethanol and Waste Engine Oil Pyrolytic oil blends (WEOP) was not reported in any literature. In this study, WEO was pyrolyzed at different temperatures and the optimum yield of pyrolytic oil at the lowest temperature was determined. The chemical composition and fuel properties of the various blending of ethanol with pyrolytic oil derived from Waste engine oil were analyzed. The utmost blending was established based on the higher heating value.

2. Materials And Method

2.1 Feedstock

The prime feedstock for the pyrolysis experiment was WEO. It was gathered from Yash Honda servicing centre, Sambalpur, Odisha, India and Analytical Grade Ethanol was procured from LOBA Chemie. The solid impurities present in WEO were discarded by using vacuum filtration. Both the feedstock was kept safely at room temperature for future usage.

2.2 Pyrolysis Process

A reactor with furnace arrangement was used to perform all the pyrolysis experiments in the temperature range of 450 °C to 575 °C. In the previous work (Patel and Shadangi 2020), the representation of the experimental setup used was mentioned. The heating rate was maintained at 25 °C min⁻¹ with a 25 mL min⁻¹ flow rate of nitrogen for all the experiments. The optimum yield of pyrolytic oil at the lowest temperature was determined on a weight basis. The yield of char was calculated at the end of the

process while the yield of non-condensable gases was determined by subtracting the sum of the yield of pyrolytic oil and char from the feed.

2.3 Blending of Ethanol with pyrolytic oil

Bending of ethanol and pyrolytic oil obtained at optimum temperature was executed using a magnetic stirrer. Ethanol was blended with the pyrolytic oil in variable volume percent and the samples were named as E5, E10, E15, E20, E25 and E30. The blended sample E5 represents the blending of 5 volume % of ethanol with 95 volume % of pyrolytic oil. Fig. 1 shows the picture of E20 and pyrolytic oil. The appearance of pyrolytic oil was dark brown but it changes to light brown with the addition of ethanol. No phase separation was observed in the blended samples.

2.4 Characterization of Blended oil samples and pyrolytic oil

The Penskey Marten apparatus and Engler's Viscometer were used to determine the flashpoint and kinematic viscosity of all blended oil samples and pyrolytic oil as per ASTM standards. The higher heating value was estimated by an automatic Bomb calorimeter (IKON instruments). The presence of functional groups was analysed by a FTIR analyzer (Bruker, Germany) in 4500-300 cm^{-1} wave no. range. The attendance of different compounds was studied using a GC-MS analyzer (Shimadzu, JAPAN).

3. Results And Discussion

3.1 Impact of pyrolysis temperature on yield

The variation in the yield of char, gases, and pyrolytic oil related to operating temperature is shown in Fig. 2. It was observed that the yield of gas was optimum (74.54 wt. %) at 500 °C. With the hike in the temperature to 550 °C, the yield of gas was decreased from 74.54 % to 21.53 %. It was due to the long pyrolytic vapours residence time in the reactor. However, the yield of WEPO was utmost (76.73 %) at 550 °C. Further, by increasing the temperature to 575 °C, the pyrolytic oil yield decreased from 76.73 % to 65 % and the gas yield increased from 21.53 % to 33.47 %. At temperature above 550 °C, secondary cracking of hydrocarbons took place which was responsible for decreasing the yields in pyrolytic oil and increasing the yield of gases.

3.2 Impact of ethanol blending on Higher heating value

Fig. 3 shows the variation in calorific value when ethanol was blended with WEPO. The higher heating value has reached a maximum of 20 % blending of ethanol with WEPO. The higher heating value of the E20 blended oil sample was 44.24 MJ/kg which was very near to petrol and greater than other blended samples. It was confirmed that E20 can run either diesel engines or SI engines. Martin et al. reported that the mixture of 80 % ethanol and 20 % biomass pyrolytic oil can be an alternative fuel for residential boilers (Martin and Boateng 2014). It was also observed that the pyrolytic oil produced from eucalyptus (low nitrogen content) blended with ethanol gives less NO_x emission on combustion. However, the higher

heating value of pyrolytic oil generated from proteinaceous biomass blended with ethanol was found to be very high. The experimental results showed that the higher heating value of the blended sample decreased with an increase in the concentration of pyrolytic oil (Martin and Boateng 2014). On the other hand, the wood pyrolytic oil has 1/3th the calorific value of fossil fuel due to high oxygen content. Only 20-40 % wood pyrolytic oil can be blended with ethanol to prevent lower viscosity and polymerization. Less NO_x and PM emission was observed on the combustion of blended oil in diesel engines (Lee and Kim 2015). It confirmed that ethanol can be added as an additive to improve the performance of a SI engine and control NO_x emission (Kareddula and Puli 2018). Gadwa et al. 2019 concluded that the blend of 70 % plastic pyrolytic oil, 15 % diesel, and 5 % ethanol could be the best suitable fuel for the CRDI diesel engine (Gadwa et al. 2019), while M Patel et al. verified that DP95 E5 (95 % of 85 % diesel and 15 % tyre pyrolysis oil and 5 % ethanol) provided the best performance results for a single-cylinder diesel engine without any modification (Patel and Patel 2012). Hence, it was confirmed that the % blending of ethanol with pyrolytic oil mainly depends upon pyrolysis process and feedstock of the pyrolysis oil.

3.3 Fuel Properties

The fuel properties such as density, absolute viscosity, flash point, and higher heating value of pyrolytic oil and all blended samples are shown in Table 1. These fuel properties at all blending conditions were compared with the petrol. The density of pyrolytic oil was 795 kg/m³ which were higher than the petrol. However, with increasing the volume % of ethanol in the pyrolytic oil, it was perceived that the density of all blended samples was decreased from 782 kg/m³ to 737 kg/m³. Though, the density of the E20 blended sample was 751 kg/m³ which were approximately the same as petrol. A similar trend was also perceived for absolute viscosity. The absolute viscosity of the blended samples was declined from 15.34 cSt to 5.26 cSt with an increase in volume % of the ethanol from 5% (E5) to 30% (E30), while the absolute viscosity of petrol was very less (only 0.71 cSt) as compared to pyrolytic oil and all blended samples. It was confirmed from the literature that on the blending of ethanol with biomass pyrolytic oil, both density and viscosity were decreased for increasing volume % of ethanol (Bert et al. 2018; Martin and Boateng 2014). A falling tendency was also detected for Flash point of all blended samples.

Table 1. Fuel properties of pyrolytic oil, blended samples and petrol

PROPERTIES	PO	E5	E10	E15	E20	E25	E30	Petrol
Density (kg/m ³)	795	782	774	768	751	745	737	750
Absolute viscosity (cSt)	18.21	15.34	12.53	10.06	8.03	6.47	5.26	0.71
Flash point (°C)	33	30	29	25	23	22	21	-43
Higher Heating Value (MJ/kg)	42.40	42.87	43.16	44.18	44.24	43.75	42.62	45.8

3.4 FTIR analysis

The FTIR spectra of WEOP, E20, and Gasoline are shown in Fig. 4 (a), (b) and (c). The absorbance peaks mainly appear in 2800-3000 and 1300-1500 wavenumber ranges in all three cases. In the case of Gasoline, the peak height was reduced while higher peaks were observed in WEOP and E20 spectra. The three medium peaks at 2952 cm^{-1} , 2920 cm^{-1} and 2854 cm^{-1} in WEOP represent the attendance of aliphatic C-H stretching vibrations. Similar peaks are observed in E20 and Gasoline. In all three spectra, a common peak was observed at 2920 cm^{-1} . The weak peak at 2646 cm^{-1} shows the presence of O-H stretching vibrations. The weak peak at 1647 cm^{-1} and 1605 cm^{-1} appeared in both WEOP and gasoline which shows the presence of alkenes while the peak was absent in E20. Further, the presence of C-H bending was confirmed by the peak at 1457 cm^{-1} and 1378 cm^{-1} signified the C=O stretching vibration in WEOP. The attendance of C=O stretching vibrations are also present in E20 and gasoline spectra but appeared at 1462 cm^{-1} and 1371 cm^{-1} wave number in E20 and 1461 cm^{-1} and 1380 cm^{-1} in gasoline.

3.5 GC-MS analysis

Table 2 represents the detailed GC-MS analysis of E20 oil. The retention time, area % and respective compound name are listed in the Table 2. Table 3 shows the presence of hydrocarbon groups in WEOP, E20 oil and gasoline. It was observed that WEOP contains alkanes, alkenes, cycloalkanes, aromatics, acid and PAH compounds and cycloalkenes, acid ester, alcohol, ester hydrocarbon groups were not present. While E20 oil contains mainly alkanes (31.90 %), alkenes (18.89 %), aromatics (30.79 %) with small amount of cycloalkanes (1.12 %), cycloalkenes (7.39 %), acid ester (3.08 %), alcohol (3.63 %), ester (0.16 %) and PAH (2.49 %). The formation of new hydrocarbon compounds like cycloalkenes, acid ester, alcohol and ester were noticed in E20 oil. But in case of Gasoline these compounds were absent along with alkenes, cycloalkanes, acid and PAH. The major area % was contributed by aromatics (95.33 %) and minor amount of alkanes (0.19 %) and cycloalkenes (4.48 %) were present in gasoline. This analysis also inveterate that chemical reaction happened between ethanol and pyrolytic oil during blending.

Table 2. GC-MS analysis of E20 oil

RT	Area %	Compound name
6.236	5.51	1-Vinyl-1,3-Cyclohexadiene
6.411	2.09	Nonane
6.567	0.18	Cis-2-Nonene
7.100	0.24	Isopropylbenzene
7.386	0.28	Octane, 2,6-Dimethyl-
7.797	0.78	1-Dodecene
8.012	1.78	Octane, 1-Chloro-
8.258	9.21	Benzene, 1,3,5-Trimethyl
8.785	1.17	Benzene, 1-Ethyl-3-Methyl-
8.984	1.99	2-Methyl-1-Nonene
9.198	2.56	1-Decene
9.310	5.33	Mesitylene
9.464	2.68	Decane
9.610	0.34	1-Dodecanol
9.875	0.47	1-Octanol, 2-Methyl-
10.339	1.06	4,4-Dimethyl-1-Hydroxy-2-Cyclopentene
10.457	0.36	1-Hexanol, 2-Ethyl-
10.528	0.61	Indane
10.767	0.05	Cyclopropane, 1-Butyl-2-(2-Methylpropyl)-
10.942	0.74	Benzene, 1,3-Diethyl-
11.049	1.16	Benzene, 1-Methyl-3-Propyl-
11.202	1.34	Tetradecane, 1-Chloro-
11.267	1.33	Benzene, 1-Ethyl-2,4-Dimethyl-
11.480	0.74	Benzene, (1-Methylpropyl)-
11.646	0.46	Nonane, 5-(2-Methylpropyl)-
11.827	0.89	Benzene, 2-Ethyl-1,4-Dimethyl
11.910	1.12	Benzene, 1-Methyl-3-(1-Methylethyl)-
12.104	3.97	P-Cymene

12.320	2.00	1-Undecene
12.588	2.94	Undecane
12.992	0.15	Cyclopropane, 1,2-Dibutyl-
13.096	3.20	Benzene, 1,2,3,4-Tetramethyl
13.642	0.26	Tricyclo[4.2.1.1 2,5]Dec-3-En-9-One
13.786	0.56	1H-Indene, 2,3-Dihydro-5-Methyl-
14.041	0.73	Hexanoic Acid, Octadecyl Ester
14.361	0.29	Undecane, 4-Methyl-
14.516	0.62	Hexadecane
14.697	0.49	Undecane, 3-Methyl-
14.817	0.01	Benzene, 1-Methyl-4-(1-Methylpropyl)-
15.135	0.98	1-Undecene, 2-Methyl-
15.214	0.92	Naphthalene
15.346	1.56	1-Dodecene
15.598	1.88	Dodecane
15.955	0.40	Undecane, 2,6-Dimethyl-
16.553	0.48	1-Octanol, 3,7-Dimethyl
16.716	0.14	Dodecane, 4-Cyclohexyl
16.814	0.19	1-Undecene, 7-Methyl-
16.922	0.23	Acetic Acid, Trifluoro-, 3,7-Dimethyloctyl Ester
17.055	0.25	Acetic Acid, Trifluoro-, 3,7-Dimethyloctyl Ester
17.256	0.17	Dodecane, 4-Methyl-
17.414	0.76	Heptadecane
17.600	0.87	Tridecane, 2-Methyl-
17.881	0.26	Benzene, 1,4-Dimethyl-2-(1-Methylethyl)-
18.009	1.02	2-Methyl-1-Dodecene
18.218	2.46	1-Tridecene
18.443	3.21	Tridecane
18.866	0.86	Naphthalene, 1-Methyl

19.575	0.11	2-Undecene, 6-Methyl-
19.686	0.47	Sulfurous Acid, Cyclohexylmethyl Pentadecyl Ester
19.781	0.43	Tetradecane
20.155	1.00	Eicosane, 10-Methyl
20.442	0.19	Hexadecane, 2,6,10,14-Tetramethyl-
20.719	1.14	2-Methyl-1-Octadecene
20.912	1.55	1-Tetradecene
21.033	0.17	Cyclopropane, 1-Ethyl-2-Heptyl-
21.126	1.84	Tetradecane
21.735	0.20	Naphthalene, 1,2-Dimethyl
22.156	0.38	1-Decanol, 2-Hexyl
22.364	0.97	1-Octanol, 2-Butyl-
22.731	0.38	Hexacosane
22.903	0.32	Tetradecane, 3-Methyl
23.280	0.46	2-Methyl-1-Tetradecene
23.458	0.89	1-Pentadecene
23.651	3.39	Hexadecane
24.568	0.35	Trifluoroacetic Acid,N-Tridecyl Ester
24.754	0.31	Decane, 5-Propyl-
25.023	0.42	Pentadecane, 4-Methyl-
25.171	0.35	Octacosane
25.339	0.30	Pentadecane, 3-Methyl
25.695	0.40	Cyclopentane, 3-Hexyl-1,1-Dimethyl-
25.867	0.50	1-Tetradecanol
26.883	0.20	Pentadecafluorooctanoic Acid, Tetradecyl Ester
27.109	0.40	Pentadecane, 2,6,10-Trimethyl
27.322	0.78	Benzene, (3-Octylundecyl)-
27.484	0.26	Heneicosane, 11-(1-Ethylpropyl)-
27.675	0.42	Sulfurous Acid, Cyclohexylmethyl Pentadecyl Ester

27.991	0.23	2-Methyl-1-Octadecene
28.150	0.43	1-Heptadecene
28.786	0.45	3-Butynylbenzene
28.907	0.21	Malonic Acid, 2-Heptyl Tetradecyl Ester
29.075	0.13	Heptadecyl Heptafluorobutyrate
29.247	0.24	Hexacosane
29.681	0.19	Heneicosane, 11-(1-Ethylpropyl)-
30.322	0.36	1-Octadecene
31.332	0.50	Nonadecane
33.022	0.28	Hexadecanoic Acid, Methyl Ester
33.929	0.28	N-Hexadecanoic Acid
34.482	0.46	Eicosane
36.352	0.26	2-Methylhexacosane
39.805	0.19	Glycidyl Palmitate
42.199	0.19	1,2-Propanediol, 3-Benzyloxy-1,2-Diacetyl-
42.714	0.16	Glycidyl Oleate
43.641	0.51	Bis(2-Ethylhexyl) Phthalate

Table 3. Presence of Hydrocarbon Groups in pyrolytic oil, E20 blended oil and Gasoline

Hydrocarbon compounds	WEOP (Area %)	E20 (Area %)	Gasoline (Area %)
Alkanes	32.97	31.90	0.19
Alkenes	11.9	18.89	–
Cycloalkanes	7.97	1.12	–
Aromatics	41.21	30.79	94.21
Cycloalkenes	-	7.39	4.48
Acid Ester	-	3.08	-
Alcohol	-	3.63	-
Ester	-	0.16	-
Acid	1.17	-	-
PAH	4.78	2.49	-

Fig. 5 shows the chemical composition of E20 oil and gasoline based on carbon number. E20 blended oil contains C7 to C28 hydrocarbon number compounds while gasoline contained compounds having a carbon number in the range of C8-C11. It was reported in the literature that C4-C12 carbon number compounds are present in gasoline (Teng et al. 1994). However, the presence of C12 to C28 hydrocarbon compounds was confirmed in E20 blended oil by GC-MS analysis which may be due to the blending of pyrolytic oil with ethanol. It confers that during the blending of ethanol with pyrolytic oil chemical reactions took place. Further, it was detected that gasoline had 100 % C4-C12 composition while E20 blended oil comprises 65.80 % C4-C12 compounds. Table 2 and 3 represents the GC-MS analysis of E20 oil and with respect to the various groups of hydrocarbon presents in the oils respectively.

4. Conclusions

This study concluded that the fuel properties of pyrolytic oil were not similar to gasoline. Its density and kinematic viscosity are very high with low calorific value and cannot be used as a fuel for SI engines. While on the blending of 20 % ethanol by volume with pyrolytic oil provided the highest calorific value around 44.24 MJ/kg and considered as the utmost blending of ethanol to pyrolytic oil. At 20 % blending condition, the density of the oil is very near with gasoline. So, with the improved fuel properties of E20 blended oil can be used in SI engines. Further investigation is required to study the engine performance and emission characteristics of SI engines fuelled with E20 blended oil.

Declarations

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Availability of data and materials: Not applicable (This is an experimental research done by us)

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Authors' contributions:

Author	Contribution
Nivedita Patel Department of Chemical Engineering, Veer Surendra Sai University of Technology, Burla, Sambalpur-768018, Odisha, India	Performed the complete experiment, discussed the results and prepared the manuscript.
Krushna Prasad Shadangi Department of Chemical Engineering, Veer Surendra Sai University of Technology, Burla, Sambalpur-768018, Odisha, India	The idea and guidance provided by this author. The manuscript was corrected by this author. This author helps in every respect to finish this manuscript.

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Figures

Figure 1

Image of (A) E20 blended oil and (B) Gasoline

Figure 2

Effect of temperature on yield of char, gas and oil.

Figure 3

Impact of ethanol blending on higher heating value

Figure 4

FTIR spectra of (a) WEOP (b) E20, and (c) Gasoline

Figure 5

GC-MS analysis based on carbon number