Pyrolysis of Sour Cherry Kernels: Physicochemical Characterization of Pyrolysis Oil in Blends of Diesel and n-butanol

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Abstract: ***Switching from conventional fuels to alternative renewable biofuels offers the possibility of significant reductions in the pollutant emissions of diesel engines. Biofuel can be obtained from biomass through pyrolysis. Although pyrolysis oil (PO) is a suitable alternative biofuel for diesel engines, the direct use of PO in diesel engine is limited due to its insufficient properties. To improve the properties of PO, it can be blended with conventional diesel using n-butanol as a co-solvent. In this study, PO was produced from sour cherry kernels (SCPO) by pyrolysis at optimum operating conditions which were: 450 °C temperature, 0.5 L/min gas flow rate, 10 °C/min heating rate, 15 min residence time and particle size as broken kernels. SCPO was blended with diesel using n-butanol. The miscibility of the blends was assessed by evaluating their homogeneity after 48 hours. The physicochemical properties of SCPO and the blends were measured. Results showed that it was possible to create homogeneous blends of SCPO and diesel using n-butanol. Blends showed reduced density, kinematic viscosity and water content, and increased cetane number, pH and calorific value as compared to SCPO. We concluded that diesel/SCPO/n-butanol blends could be a potential biofuel source for diesel engine applications.***

Keywords: Sour cherry, pyrolysis oil, diesel, homogeneity, characterization

1. Introduction

The replacement of conventional petroleum-based fuels has been of particular interest as the problems of air pollution, global warming, and fossil fuel depletion have become relevant in recent years. To overcome these problems, the development and application of alternative biofuels derived from biomass is essential. Bio-oil or pyrolysis oil (PO) is a clean, sustainable and renewable energy resource derived from biomass [1], [2]. Recent research highlighted the potential of PO as renewable biofuel for internal combustion engine applications [3], [4]. Use of PO as alternative biofuel has grown recently due to its positive effect in diminishing exhaust gas emissions and sustainability [5]–[9]. Among the various types of biofuels, PO derived from sour cherry kernels has been of particular interest as a substitute for conventional petroleum-based fuels, especially in countries with abundant sources of sour cherries [10]. PO can be produced from biomass by pyrolysis, whereby biomass is decomposed at an oxygen-free, high temperature condition generating vapours which after cooling and condensing, leads to a dark liquid referred as PO [11]. The fuel compositions and properties of PO vary with the biomass feedstock and the operating conditions of pyrolysis [7], [12].

Direct use of PO in a diesel engine is limited because of its poor properties, including a low cetane number, low calorific value (lower heating value; LHV), high kinematic viscosity, high acidity (pH 2-3), and high-water content [5]–[8]. Several approaches have been tested to improve the inadequate properties of PO for use in conventional automotive diesel engines [5]–[8], [13]–[20]. The most viable method is to blend PO with conventional hydrocarbon fuels, such as diesel to physically upgrade the fuel properties of PO for reliable combustion in conventional diesel engines [8], [14], [15], [17], [18], [21]–[25].

However, the miscibility of PO with all conventional hydrocarbon fuels has been a problem due to differences in polarities and densities forming an unstable mixture whereby phase separation occurs after a short period of time [5], [7], [8], [20]. Therefore, an additive is required for the miscibility of PO with conventional hydrocarbon fuels.

According to Alcala and Bridgwater, the use of alcohol as an organic solvent allows the miscibility and formation of stable blends over a long time period. They showed that the type and quantity of alcohol used is crucial for blend formation and stability. Using n-butanol gave the widest selection of homogenous stable blends when mixed with PO and bio-diesel [19]. Furthermore, n-butanol has a higher calorific value and better auto-ignitability than ethanol [26]. Therefore, we selected n-butanol as a blend component from among the other alcohol candidates for mixing sour cherry kernel pyrolysis oil (SCPO) with diesel. N-butanol has a kinematic viscosity of 2.2 mm^2/s which is quite similar to the kinematic viscosity value of 2.7 mm^2/s for diesel and can effectively lower the viscosity of the blended fuel [8]. N-butanol can dissolve solid particles in PO and suppress the formation of gummy polymers that is produced by polymerization of tar, thereby improving the fuel properties of PO, engine performance and emission characteristics [5], [19], [27], [28].

Few studies have been performed on the pyrolysis of sour cherries [29]. However, no study has been reported on the physicochemical characteristics of SCPO and its usability as an alternative biofuel in compression-ignition (CI) or diesel engines. In this study, pyrolysis of sour cherry kernels was performed whereby the effect of pyrolysis parameters such as reaction temperature, heating rate, residence time, nitrogen gas flow rate and particle size on the bio-oil yield was investigated. N-butanol was added in blends of SCPO and diesel to evaluate for their miscibility. The blend homogeneity was visually evaluated after 48 hours. SCPO and its blends were physicochemically characterized, and their characteristics were compared to each other and diesel for future use in CI engine experiments. For this purpose, SCPO and diesel/SCPO/n-butanol blends were tested among others for kinematic viscosity, density, water content, cetane number, pH, LHV, flash point and elemental components (C, H, and O) [8], [19], [30]. We show that homogeneous blends of SCPO and diesel can be created with the aid of n-butanol without any phase separation facilitating the use of SCPO in CI engine. Our data also shows that some of the negative physicochemical properties of SCPO were compensated by mixing with n-butanol and diesel.

2. Materials and Methods

2.1 Sour cherry kernel oil extraction by pyrolysis and parameter optimization

Pyrolysis of sour cherry kernels was conducted in a pyrolysis reactor at the Automotive Engineering Department Laboratory of Afyon Kocatepe University, Turkey. Sour cherry kernels were obtained from a commercial firm in Afyonkarahisar, Turkey. In brief, sun-dried sour cherry kernels were thermally decomposed in the absence of oxygen by pyrolysis (100 grams for each experiment), producing vapour which was cooled and condensed. The condensed liquids were collected in a separate tank, which contain the SCPO product. The non-condensable gases leave the reactor, which contain flammable constituents called pyrolytic gas. Other formed products were solid char which remains in the reactor after the pyrolysis has been completed. The pyrolysis process is schematically viewed in Figure 1.

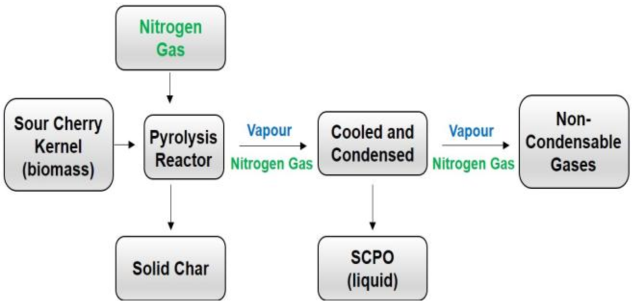

Figure 1: Schematic diagram of the pyrolysis process

SCPO was extracted from the condensed liquids by adding dichloromethane as an organic solvent to the liquid collecting tank. This mixture was allowed to settle in a separating funnel for 30 minutes to ensure good phase separation. An upper dichloromethane insoluble (aqueous) phase and a bottom dichloromethane soluble phase (containing SCPO) was formed. The two phases were then separated from one another by turning the valve. Dichloromethane soluble phase was collected, filtered through cellulose filter paper and then evaporated under a vacuum at 45°C to remove dichloromethane. The remaining SCPO, which is a dark brown free flowing liquid with a smoky aroma was then physicochemically characterized and used for preparing blends. In order to find the optimal parameters leading to maximum bio-oil yield, pyrolysis experiments were conducted under different operating conditions such as reaction temperature, heating rate, residence time, nitrogen gas flow rate and particle size, varied one at a time. The tested operating parameters for pyrolysis are specified in Table 1.

2.2 Diesel, sour cherry kernel pyrolysis oil and n-butanol blends preparation

First, SCPO was added to diesel, however SCPO didn't mix with diesel. Therefore, diesel and SCPO were blended with the aid of n-butanol by using the same methodology as Alcala and Bridgwater [19]. In short, three-component blends were prepared at room temperature at varying wt.% following a simple procedure: first diesel was added in the bottle, then n-butanol, followed by SCPO. The volume of the mixture of diesel, SCPO and n-butanol was fixed at 10 ml. Diesel and n-butanol (CAS No: 71-36-3, purity: 99%) used for this study were purchased from local Petroleum Company and supplier, respectively. The prepared blends in the bottles were capped and lightly shaken. The blends were left to settle for 48 hours at room temperature and thereafter photographed to assess their appearance.

2.3 Physicochemical characterization of SCPO and diesel/SCPO/n-butanol blends

The physicochemical characteristics of SCPO and homogenous blends were measured by an external national accredited laboratory following standard methods (ASTM/EN ISO) which give an indication of fuel's suitability for engine testing. The properties of diesel and n-butanol were obtained from a local Petroleum Company and supplier, respectively.

Table 1: Operating parameters of pyrolysis in different experiments

Experiment no.	Reaction Temperature, °C	Heating rate, °C/min	Residence time, min	Nitrogen gas flow rate, L/min	Particle size (broken, unbroken)
1, 2, 3	400	10, 15, 20	15	0.5	Unbroken
4, 5, 6, 7	400	10	15	0, 0.5, 1, 1.5	Unbroken
8, 9, 10, 11,12	400	10	0, 15, 30, 45, 60	0.5	Unbroken
13, 14	400	10	15	0.5	Broken & unbroken
15, 16, 17, 18, 19, 20, 21	300, 350, 400, 450, 500, 550, 600	10	15	0.5	Broken

3. Results and Discussion

Bio-oil has been the subject of extensive studies in which the main objective is to upgrade the original product into a more stable and desirable fuel via physical, catalytic or chemical techniques [30]. In this study, PO was extracted from sun-dried sour cherry kernels by pyrolysis. Optimization of the operating conditions of pyrolysis was carried out to obtain the maximum pyrolysis oil yield. Optimization experiments were conducted under different operating conditions of pyrolysis such as reaction temperature, heating rate, residence time, nitrogen gas flow rate and particle size, varied one at a time. First, pyrolysis was carried out with different heating rates (10 °C, 15 °C and 20 °C/min) at 400 °C reaction temperature, 0.5 L/min nitrogen gas flow rate, unbroken sour cherry kernels and 15 min residence time. The SCPO yield decreased as the heating rate increased. In these experiments, the optimum SCPO yield (24.4 wt.%) was obtained at 10 °C/min heating rate. The results of the yields for SCPO, water, char and gas at different heating rates are shown in Figure 2.

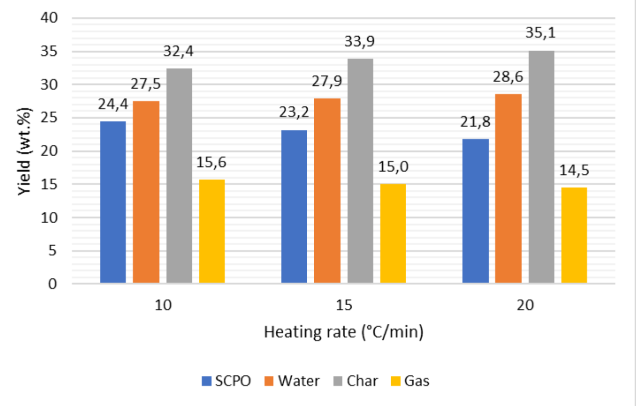

Figure 2: Effect of heating rate on pyrolysis product yields.

Then, the effect of different nitrogen gas flow rates on the yields of pyrolysis products at 400 °C reaction temperature, unbroken sour cherry kernels, 15 min residence time and 10 °C/min heating rate were examined. SCPO yield increased as the nitrogen gas flow rate increased from 0 to 0.5 L/min, then decreased from 0.5 to 1.5 L/min, indicating an optimum SCPO yield at 0.5 L/min. The results of the yields for SCPO, water, char and gas at different nitrogen gas flow rates are shown in Figure 3.

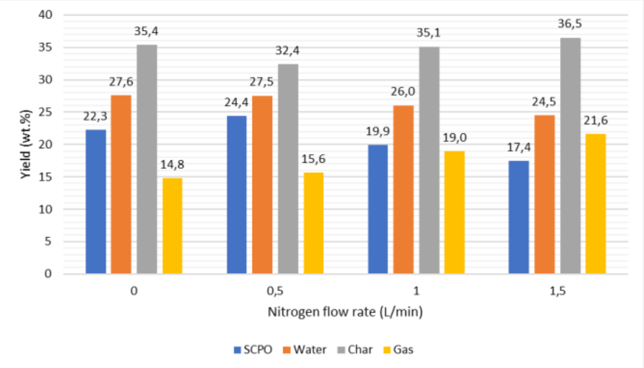

Figure 3: Effect of nitrogen gas flow rate on pyrolysis product yields

Figure 4 shows the effect of residence time on pyrolysis product yields at 400 °C reaction temperature, 0.5 L/min nitrogen gas flow rate, unbroken sour cherry kernels and 10 °C/min heating rate. When the pyrolysis residence time increased from 0 to 15 min, the SCPO yield increased. However, negative effects on SCPO yield was observed at a higher residence time range between 15 and 60 min, indicating a optimum SCPO yield at 15 min residence time.

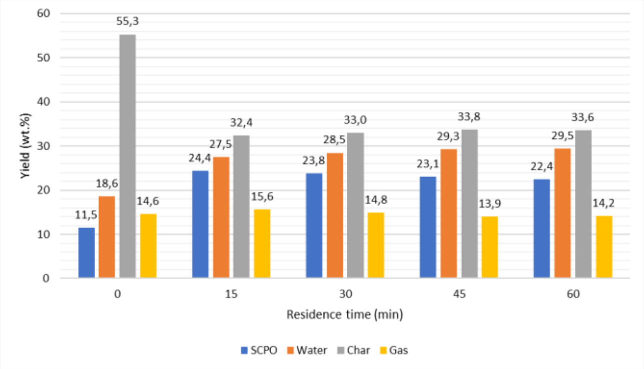

Figure 4: Effect of residence time on pyrolysis product yields

To study the effect of biomass particle size on the pyrolysis product yields, experiments were conducted with unbroken and broken sour cherry kernels at 400 °C reaction temperature, 0.5 L/min nitrogen gas flow rate, 15 min residence time and 10 °C/min heating rate (Figure 5). As the particle size decreased such as in the case of broken kernels, more SCPO yield was observed.

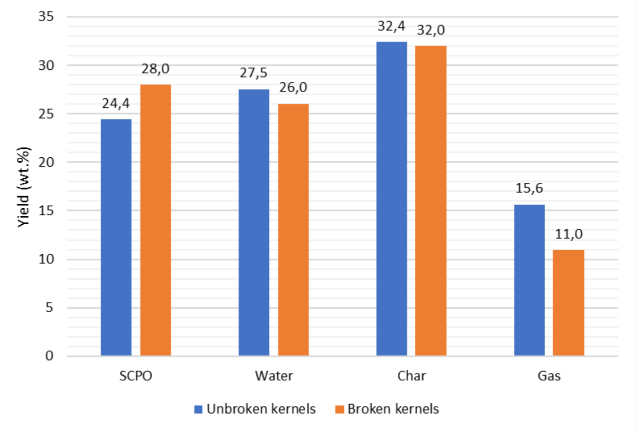

Figure 5: Effect of particle size on pyrolysis product yields

Finally, the effect of pyrolysis reaction temperature on the pyrolysis product yields at 0.5 L/min nitrogen gas flow rate, broken sour cherry kernels, 15 min residence time and 10 °C/min heating rate was studied (Figure 6). As the reaction temperature increased from 300 to 450 °C the SCPO yield increased. As the reaction temperature increased from 450 to 600 °C the SCPO yield decreased. After conducting all experiments, the optimum operating conditions for pyrolysis with maximum SCPO yield were obtained at 450°C reactor temperature, 0.5 L/min nitrogen gas flow rate, 10 °C/min heating rate, 15 min residence time and particle size as broken kernels. The product yields under these optimum operating conditions on weight basis were: 29.7 wt.% SCPO, 29.1 wt.% aqueous phase, 28.5 wt.% char and 12.7 wt.% of gas. Hence, these operating pyrolysis parameters were used for SCPO production.

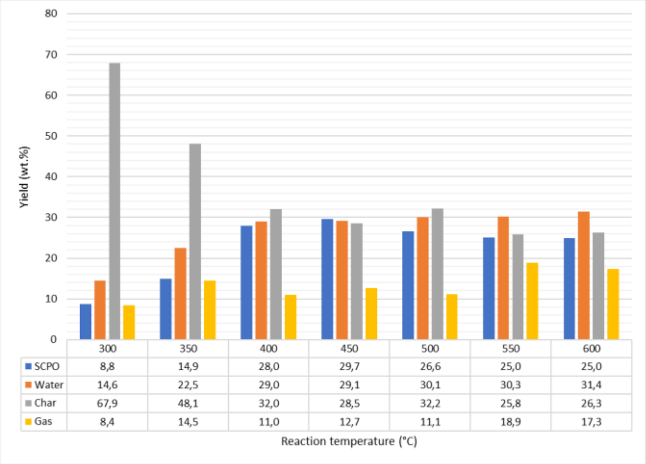

Figure 6: Effect of reaction temperature on pyrolysis product yields

The physicochemical properties of the produced SCPO such as kinematic viscosity, calorific value (LHV), water content, element (C, H, O) content, density, pH, cetane number and flash point were determined in an external laboratory following standard methods. Multiple measurements were done and averaged in order to ensure the repeatability. The results are shown in Table 2. The properties of SCPO were compared with conventional diesel. As shown in Table 2, SCPO is different from diesel and n-butanol in terms of chemical composition and physicochemical properties. The kinematic viscosity of SCPO at 40°C was found to be 8.4 mm^2/s which was approximately 3 times higher than that of conventional diesel. The high viscosity renders it inappropriate for direct use as an alternative fuel for conventional diesel engines. A fuel with a high viscosity increases engine deposits, requires more energy to pump the fuel and increases wear to fuel pump elements and injectors [31]. In addition, the density of SCPO was found to be 1089 kg/m^3 which is higher than that of conventional diesel. This density difference partially explains immiscibility of the two liquids [20]. The pH of SCPO was 3.8, which indicates that it is acidic and may cause major issues with corrosion [30]. Blending SCPO with less acidic components may help to partially diminish the corrosivity of SCPO. The calorific value (LHV) of SCPO is about 25.6 MJ/kg, which was 1.7 times lower than that of conventional diesel, signifying that the energy density of SCPO is lower than that of diesel. Low energy density of the fuel may cause ignition delay and retardation of the combustion phase [6]. Flash point, which is a measure of the ease of ignition of the liquid is defined as the lowest temperature at which the material will ignite from an open flame [30]. The flash point of SCPO was estimated to be 98 °C, which was approximately 1.8 times higher than that of conventional diesel. Higher flash point may lead to ignition delay [9], indicating that the ignition delay of SCPO is higher than diesel which may hence deteriorate the combustion [32], [33]. The water content within PO originates from the water contained in the original feedstock plus water generated from pyrolysis reactions [19], [30]. PO is unstable and separates into oily aqueous phases due to high water content [8]. The water content within PO reduces the heating value of the liquid [34]. Water content in PO also plays a role in lowering combustion temperature by its large latent heat of vaporization [5]. The presence of water in PO causes ignition delay and corrosion problems in injectors and fuel supply [5], [34], [35]. The longer ignition delay of PO can be mainly attributed to the lower in-cylinder temperature [36]. Therefore, water content in the blend is not desirable as it reduces the stability, does not yield any energy and can cause corrosion and combustion issues. Likely, the low water content (1.5 wt.%) of SCPO may not cause corrosion and combustion problems, and may make our SCPO stable for long-term. The contents of carbon (C), hydrogen (H), and oxygen (O) in SCPO were determined on weight basis and were 75.8 wt.%, 9.1 wt.% and 12.6 wt.%, respectively. Our elemental analysis indicated that SCPO contained higher amount of O than conventional diesel. The low calorific value of SCPO may be attributed to its high O content [5], [9].

Since our SCPO has unsatisfactory fuel properties such as high kinematic viscosity, density and flash point, and low LHV and pH, SCPO cannot be used directly in conventional diesel engines. Therefore, blending of SCPO with diesel may be a solution in improving the fuel properties of SCPO. Diesel can, among other things, improve the self-ignitability of the fuel by increasing the cetane number of the fuel [8]. However, our data showed that even minimal amount of SCPO was not miscible with diesel (See Figure 7A).

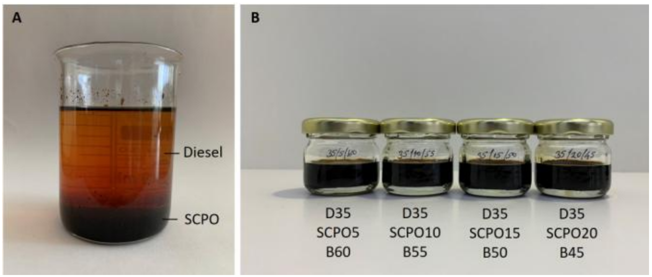

Figure 7: Phase-separated diesel (90 wt.%) - SCPO (10 wt.%) mixture (A). Homogeneous ternary blends (wt.% D, diesel/ wt.% SCPO/ wt.% B, n-butanol) (B).

Table 2: Composition and fuel properties of diesel, SCPO and n-butanol

	Diesel	SCPO	n-butanol
Kinematic viscosity (mm^2/s) at 40°C	2.7	8.4	2.2
LHV (MJ/kg)	42.9	25.6	33.1
Water content (wt.%)	0	1.5	0
C (wt.%)	86.1	75.8	64.8
H (wt.%)	13.9	9.1	13.6
O (wt.%)	0	12.6	21.6
Density (kg/m^3)	822	1089	810
pH	5.5-8.0	3.8	7.0
Cetane number	52.0	-	15.9
Flash point (°C)	55.0	98.0	35.0

Therefore, an organic solvent was required to mix SCPO with diesel. Alcala and Bridgwater reported that usage of n-butanol as an organic solvent allows the formation of homogeneous stable blends of PO and bio-diesel over a long time period [19]. Furthermore, n-butanol, has the capacity to reduce the acidity and viscosity, and to increase the calorific value of bio-oil blended fuel so that it is possible to use directly in a conventional diesel engine [5],

[8], [19], [27], [28]. To improve the miscibility of SCPO with diesel and the properties of SCPO, blends of diesel, SCPO and n-butanol were prepared using proportions as indicated by S. Lee et al [8]. The proportions used were 35 wt.% for diesel, 5-10-15-20 wt.% for SCPO and 60-55-50-45 wt.% for n-butanol (See Figure 7B). The blends were investigated in terms of homogeneity and physicochemical properties. All prepared blends displayed no phase separation and were homogeneous after 48 hours of observation. The physicochemical properties of these ternary blends are shown in Table 3. All properties of blends were compared with SCPO and conventional diesel. As shown in Table 3, the kinematic viscosity and density of 35 wt.% diesel, 0-20 wt.% SCPO and 65-45 wt.% n-butanol blends were decreased compared to SCPO and close to that of conventional diesel. The kinematic viscosities of the blends were between 2.4-3.6 mm^2/s, which are close to that of conventional diesel. The blends showed increased LHVs when compared to the original SCPO, which were lower than diesel. In addition, the densities and kinematic viscosities of the blends increased, whereas the LHVs decreased with increasing SCPO content. A high-water content in the fuel is not desirable. As expected, our blends contained much lower water content (0-0.30 wt.%) when compared to the original SCPO which was negligible. The water content of the blends increased with increasing SCPO content. C contents in the blends were in the range of 72.3-74.5 wt.% which were lower than that of conventional diesel. H contents of the blends (12.8-13.7 wt.%) were close to that of conventional diesel. C content increased, whereas H content decreased with increasing SCPO content in the blends. The O contents in the blends (12.2-14.0 wt.%) were higher than conventional diesel, which reduced with decreasing n-butanol contents in the blends. Furthermore, the pH values of the blends (5.0-6.5) were increased by the presence of n-butanol and diesel when compared to original SCPO, but decreased as the SCPO content increased in the blends. The flash point temperatures of the blends were approximately 37.3 °C, which were lower than that of original SCPO and conventional diesel, but quite similar to that of n-butanol. In order to successfully utilize the blends in diesel engines it should meet the 37.8 °C (100 °F) minimum flash point requirement for low temperature operability. Fuels which have a flash point less than 37.8 °C (100 °F) are called flammable, whereas fuels having a flash point at or above 37.8 °C (100 °F) and below 93.3 °C (200 °F) are called combustible [37]. However, the flash points of our blends were below 37.8 °C, which indicates to a risk of fire hazard. The cetane numbers of the blends were between 25.1-27.5, which were lower than that of conventional diesel. The minimum cetane number of diesel fuel in the European Union is specified at ≥51 and in the United States at ≥40 [38]. The higher the SCPO content, the lower the cetane number. Low cetane number values are undesirable because of lowering the auto-ignitability of the blend causing ignition delay [9], [32], [39], eventually delaying the start of combustion which may result in incomplete combustion [32]. In summary, we showed that some of the physicochemical properties of the blended fuels, such as their density, kinematic viscosity, water content, LHV, pH and self-ignitability as measured by cetane number, were improved by the presence of n-butanol and diesel in the blends. Accordingly, we have obtained blended fuels with improved physicochemical properties which can be tested in CI engine experiments. The use of PO blended with diesel has been tested successfully in a number of engines [8], [15], [18], [21], [22], [24]–[26], [40].

4. Conclusion

The following conclusions were drawn from our research, PO can be extracted from sour cherry kernels by pyrolysis. The optimum parameters of pyrolysis leading to maximum SCPO yield (29.7 wt.%), were obtained at a 450°C reactor temperature with 10 °C/min heating rate, 0.5 L/min nitrogen gas flow rate, and broken kernels. The physicochemical properties of SCPO were determined using standard methods, and found to be unsatisfactory when compared to conventional diesel, which indicated that SCPO should be upgraded before use in conventional diesel engines. In order to improve the fuel properties of SCPO, we mixed SCPO with conventional diesel. However, the polarity of SCPO makes it difficult to create stable blends with diesel without the addition of an organic solvent. Therefore, we prepared blends of SCPO and diesel using n-butanol as a co-solvent. In accordance with the study of Alcala and Bridgwater, we showed that homogeneous blends of SCPO and diesel can be prepared without any phase separation using n-butanol. The prepared blends were physicochemically characterized.

Table 3: Kinematic viscosity, density, LHV, water content, elemental composition (C, H, O), flash point, pH and cetane number of the blends, (wt.% D, diesel/ wt.% SCPO/ wt.% B, n-butanol).

Blends	Kinematic viscosity (mm2/s) at 40°C	Density (kg/m^3)	LHV (MJ/kg)	Water (wt.%)	C (wt.%)	H (wt.%)	O (wt.%)	Flash point (°C)	pH	Cetane number
Diesel	2.7	822	42.9	0	86.1	13.9	0	55	5.5-8.0	52.0
D35/SCPO0/B65	2.4	814	36.5	0	72.3	13.7	14.0	37.3	6.5	27.5
D35/SCPO5/B60	2.7	828	36.2	0.08	72.8	13.5	13.6	37.3	6.2	26.8
D35/SCPO10/B55	3.0	842	35.8	0.15	73.4	13.3	13.1	37.3	5.3	26.6
D35/SCPO15/B50	3.3	856	35.4	0.23	73.9	13.0	12.7	37.3	5.1	25.8
D35/SCPO20/B45	3.6	870	35.0	0.30	74.5	12.8	12.2	37.3	5.0	25.1

Our results show that some of the SCPO properties can be upgraded by blending with diesel and n-butanol, which represent a significant advantage over the use of SCPO on its own. In summary, our study showed that diesel/SCPO/n-butanol blends could be a potential biofuel source for diesel engine applications. Addition of cetane improvers are required to enhance the cetane number of our blends to meet the minimum cetane number specification and to improve the auto-ignition properties of the blends [8]. Hence, it becomes necessary to assess the combustion, performance and exhaust emission characteristics (NO_x, CO, HC and particulate matter) of the diesel engine fueled with our blends, and compare with that of pure diesel operation.

5. Acknowledgments

This research was supported by the Scientific Research Projects Coordination Unit of Afyon Kocatepe University, Turkey [Project No. BAP.16.FEN.BIL.08].

6. Disclosure statement

No conflicts of interest are reported by the authors.

References

[1] T. Bridgwater, D. Meier, and D. Radlein, “An Overview of Fast Pyrolysis of Biomass,” *Org. Geochem.*, vol. 30, pp. 1479–1493, 1999, doi: 10.1016/S0146-6380(99)00120-5.

[2] Q. Zhang, J. Chang, T. Wang, and Y. Xu, “Review of biomass pyrolysis oil properties and upgrading research,” *Energy Convers. Manag.*, vol. 48, no. 1, pp. 87–92, 2007, doi: 10.1016/j.enconman.2006.05.010.

[3] S. Jones *et al.*, “Production of Gasoline and Diesel from Biomass Via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case,” *Richland, WA Pacific Northwest Natl. Lab.*, 2009, doi: 10.2172/950728.

[4] T. Barth and M. Kleinert, “Motor Fuels From Biomass Pyrolysis,” *Chem. Eng. \& Technol.*, vol. 31, no. 5, pp. 773–781, 2008, doi: https://doi.org/10.1002/ceat.200800122.

[5] T. Y. Kim and S. H. Lee, “Combustion and emission characteristics of wood pyrolysis oil-butanol blended fuels in a DI diesel engine,” *Int. J. Automot. Technol.*, vol. 16, no. 6, pp. 903–912, 2015, doi: 10.1007/s12239-015-0092-4.

[6] T. Y. Kim, S. Lee, and K. Kang, “Performance and emission characteristics of a high-compression-ratio diesel engine fueled with wood pyrolysis oil-butanol blended fuels,” *Energy*, vol. 93, pp. 2241–2250, 2015, doi: https://doi.org/10.1016/j.energy.2015.10.119.

[7] S. Lee, Y. Choi, and K. Kang, “Application of blended fuel containing coffee ground pyrolysis oil in a diesel generator,” *Fuel*, vol. 256, p. 115998, Nov. 2019, doi: 10.1016/j.fuel.2019.115998.

[8] S. Lee, S. H. Woo, Y. Kim, Y. Choi, and K. Kang, “Combustion and emission characteristics of a diesel-powered generator running with N-butanol/coffee ground pyrolysis oil/diesel blended fuel,” *Energy*, vol. 206, p. 118201, 2020, doi: 10.1016/j.energy.2020.118201.

[9] K. Midhun Prasad and S. Murugavelh, “Experimental investigation and kinetics of tomato peel pyrolysis: Performance, combustion and emission characteristics of bio-oil blends in diesel engine,” *J. Clean. Prod.*, vol. 254, p. 120115, 2020, doi: https://doi.org/10.1016/j.jclepro.2020.120115.

[10] N. N. Ivanova, L. M. Khomich, I. B. Perova, and K. I. Eller, “[Sour cherry juice nutritional profile],” *Vopr. Pitan.*, vol. 87, no. 4, p. 78—86, 2018, doi: 10.24411/0042-8833-2018-10045.

[11] A. Bridgwater, “Fast pyrolysis of biomass for the production of liquids,” *Biomass Combustion Science, Technology and Engineering*. Elsevier Inc., pp. 130–171, 2013, doi: 10.1533/9780857097439.2.130.

[12] X. Yuan *et al.*, “Applications of bio-oil-based emulsions in a DI diesel engine: The effects of bio-oil compositions on engine performance and emissions,” *Energy*, vol. 154, pp. 110–118, 2018, doi: https://doi.org/10.1016/j.energy.2018.04.118.

[13] D. Chiaramonti *et al.*, “Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines - Part 1: Emulsion production.,” *Biomass and Bioenergy*, vol. 25, no. 1, pp. 85–99, 2003.

[14] M. Ikura, M. Stanciulescu, and E. Hogan, “Emulsification of pyrolysis derived bio-oil in diesel fuel,” *Biomass and Bioenergy*, vol. 24, no. 3, pp. 221–232, 2003, doi: https://doi.org/10.1016/S0961-9534(02)00131-9.

[15] S. Lee, T. Kim, and K. Kang, “Performance and emission characteristics of a diesel engine operated with wood pyrolysis oil,” *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, vol. 228, no. 2, pp. 180–189, 2014, doi: 10.1177/0954407013502951.

[16] X. Jiang and N. Ellis, “Upgrading Bio-oil through Emulsification with Biodiesel: Mixture Production,” *Energy & Fuels*, vol. 24, no. 2, pp. 1358–1364, Feb. 2010, doi: 10.1021/ef9010669.

[17] Q. Lu, Z.-B. Zhang, H.-T. Liao, X.-C. Yang, and C.-Q. Dong, “Lubrication Properties of Bio-Oil and Its Emulsions with Diesel Oil,” *Energies*, vol. 5, no. 3, pp. 741–751, 2012, doi: 10.3390/en5030741.

[18] Y. Huang, X. Han, S. Shang, and L. Wang, “Performance and emissions of a direct-injection diesel engine operating on emulsions of corn stalk bio-oil in diesel,” *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, vol. 226, no. 8, pp. 1119–1129, 2012, doi: 10.1177/0954407012438295.

[19] A. Alcala and A. V Bridgwater, “Upgrading fast pyrolysis liquids: Blends of biodiesel and pyrolysis oil,” *Fuel*, vol. 109, pp. 417–426, 2013, doi: 10.1016/j.fuel.2013.02.058.

[20] B.-J. Lin, W.-H. Chen, W. M. Budzianowski, C.-T. Hsieh, and P.-H. Lin, “Emulsification analysis of bio-oil and diesel under various combinations of emulsifiers,” *Appl. Energy*, vol. 178, pp. 746–757, 2016, doi: https://doi.org/10.1016/j.apenergy.2016.06.104.

[21] S. Murugan, M. C. Ramaswamy, and N. Govindan, “Assessment of pyrolysis oil as an energy source for diesel engines,” *Fuel Process. Technol.*, vol. 90, pp. 67–74, Jan. 2009, doi: 10.1016/j.fuproc.2008.07.017.

[22] J. Martínez, Á. Ramos, O. Armas, R. Murillo, and T. Garcia, “Potential for using a tire pyrolysis liquid-diesel fuel blend in a light duty engine under transient operation,” *Appl. Energy*, vol. 130, p. 437, May 2014, doi: 10.1016/j.apenergy.2014.05.056.

[23] D. Honnery, J. Ghojel, and V. Stamatov, “Performance of a DI diesel engine fuelled by blends of diesel and kiln-produced pyroligneous tar,” *Biomass and Bioenergy*, vol. 32, no. 4, pp. 358–365, 2008, doi: https://doi.org/10.1016/j.biombioe.2007.10.004.

[24] M. Karagöz, “Investigation of performance and

emission characteristics of an CI engine fuelled with diesel – waste tire oil – butanol blends," *Fuel*, vol. 282, p. 118872, 2020, doi: https://doi.org/10.1016/j.fuel.2020.118872.

[25] O. Doğan, M. B. Çelik, and B. Özdalyan, "The effect of tire derived fuel/diesel fuel blends utilization on diesel engine performance and emissions," *Fuel*, vol. 95, pp. 340–346, 2012, doi: https://doi.org/10.1016/j.fuel.2011.12.033.

[26] D. Nguyen and D. Honnery, "Combustion of bio-oil ethanol blends at elevated pressure," *Fuel*, vol. 87, no. 2, pp. 232–243, 2008, doi: https://doi.org/10.1016/j.fuel.2007.04.023.

[27] S. Lee, *A Feasibility Study of Using Pyrolysis Oil/Butanol Blended Fuel in a DI Diesel Engine*, vol. 2015. 2015.

[28] C. Jin, M. Yao, H. Liu, C. F. Lee, and J. Ji, "Progress in the production and application of n-butanol as a biofuel," *Renew. Sustain. Energy Rev.*, vol. 15, no. 8, pp. 4080–4106, 2011, doi: https://doi.org/10.1016/j.rser.2011.06.001.

[29] G. Gözke and K. Açıkalın, "Pyrolysis characteristics and kinetics of sour cherry stalk and flesh via thermogravimetric analysis using isoconversional methods," *J. Therm. Anal. Calorim.*, 2020, doi: 10.1007/s10973-020-10055-9.

[30] K. J. Chong and A. V Bridgwater, "Fast Pyrolysis Oil Fuel Blend for Marine Vessels," *Environ. Prog. \& Sustain. Energy*, vol. 36, no. 3, pp. 677–684, 2017, doi: https://doi.org/10.1002/ep.12402.

[31] E. Alptekin and M. Canakci, "Determination of the density and the viscosities of biodiesel–diesel fuel blends," *Renew. Energy*, vol. 33, no. 12, pp. 2623–2630, 2008, doi: https://doi.org/10.1016/j.renene.2008.02.020.

[32] A. K. Hossain *et al.*, "Combustion of fuel blends containing digestate pyrolysis oil in a multi-cylinder compression ignition engine," *Fuel*, vol. 171, pp. 18–28, 2016, doi: https://doi.org/10.1016/j.fuel.2015.12.012.

[33] R. Sakthivel, K. Ramesh, S. Joseph John Marshal, and K. K. Sadasivuni, "Prediction of performance and emission characteristics of diesel engine fuelled with waste biomass pyrolysis oil using response surface methodology," *Renew. Energy*, vol. 136, pp. 91–103, 2019, doi: https://doi.org/10.1016/j.renene.2018.12.109.

[34] A. K. Hossain and P. A. Davies, "Pyrolysis liquids and gases as alternative fuels in internal combustion engines – A review," *Renew. Sustain. Energy Rev.*, vol. 21, pp. 165–189, 2013, doi: https://doi.org/10.1016/j.rser.2012.12.031.

[35] A. Oasmaa, B. van de Beld, P. Saari, D. C. Elliott, and Y. Solantausta, "Norms, Standards, and Legislation for Fast Pyrolysis Bio-oils from Lignocellulosic Biomass," *Energy & Fuels*, vol. 29, no. 4, pp. 2471–2484, Apr. 2015, doi: 10.1021/acs.energyfuels.5b00026.

[36] I. Park, Y. Kim, and S. Lee, "Morphological Change and Number-Size Distributions of Particulate Matter (PM) from a Diesel Generator Operated with Wood Pyrolysis Oil-Butanol Blended Fuel," *Int. J. Automot. Technol.*, vol. 19, no. 3, pp. 413–420, 2018, doi: 10.1007/s12239-018-0040-1.

[37] R. Ogle, S. E. Dillon, and J. Ramirez, "Flash fire from a hot combustible liquid," *12AIChE - 2012 AIChE Spring Meet. 8th Glob. Congr. Process Safety, Conf. Proc.*, 2012.

[38] M. Lapuerta, J. Rodríguez-Fernández, and E. F. de Mora, "Correlation for the estimation of the cetane number of biodiesel fuels and implications on the iodine number," *Energy Policy*, vol. 37, no. 11, pp. 4337–4344, 2009, doi: https://doi.org/10.1016/j.enpol.2009.05.049.

[39] C. Kaewbuddee, K. Wathakit, and J. Srisertpol, "The effect of n-butanol to waste plastic oil fuel blends utilization on engine emissions of a single cylinder diesel engine," in *2018 IEEE International Conference on Applied System Invention (ICASI)*, 2018, pp. 1224–1227, doi: 10.1109/ICASI.2018.8394510.

[40] S. Murugan, M. C. Ramaswamy, and N. Govindan, "Use of tyre pyrolysis oil in diesel engines," *Waste Manag.*, vol. 28, pp. 2743–2749, Jun. 2008, doi: 10.1016/j.wasman.2008.03.007.