Waste cooking oil into sustainable and lucrative bio-diesels and their blend with diesel

Mabusab Pinjari[1], *Babi* Lakkoju[1*], and *Vandana* Vemulapalli[2], *Gunda* Tavanya[3], *Vaibhav* Mittal[4]

[1]Chemistry, Humanities & Sciences Department, KGRCET, India.
[2]School of Sciences, Department of Chemistry, GITAM University, India
[3]Department of CSE, GRIET, Hyderabad, Telangana, India
[4]Lovely Professional University, Phagwara, Punjab, India.

Abstract. The necessity to find an alternate fuel has arisen due to the rapid spike in cost of crude oil. In terms of economics, the alternative fuel should be more appealing than fossil fuels. Vegetable oils are used to make costly yet environmentally beneficial biodiesels. Utilizing leftover cooking oil to produce biodiesel is less expensive than using virgin oil. The bio-diesel have prepared from Waste cooking oil (WCO), collected from GITAM University hostel mess. This reaction has accelerated by the base catalysed the transesterification reaction with using ethanol. ^{1}HNMR and IR spectrum analyses were used to describe the biodiesel that was produced. Numerous physico-chemical characteristics of biodiesels and their mixes with petroleum diesel were examined. The results of the investigation indicate that the blends from B10 to B40 have high flash points, lower pour points, and kinematic viscosity in the range of 2 to 5 cSt at 40 ^{o}C.

Keyword: Waste cooking oil, transesterification, ethyl ester, biodiesel, blends.

1 Introduction

Now a days the alternative fuels are very essential due to the exhausting oil reserves and escalating oil prices together with utilization of fossil fuels. The increase in pollution caused by over combustion of fossil fuels such as petroleum, coal and natural gas, require better alternative fuels as energy source [1-3]. Since last few decades the biodiesel has increased importance as an alternative fuel for diesel engines. Production of biodiesel from different vegetable oil source such as edible oils like sunflower [4], palm [5] and soybean oils [6]. Non-edible oils like rapeseed [7], and castor oil [8] etc. by transesterification method. It is simple process. However, the use of edible vegetable oils for biodiesel generation has raised significant concerns due to the high cost and scarcity of edible oil. Hence, the used edible vegetable oils and non-edible oils can be used for biodiesel production [9]. These are the attractive raw materials, which are available cheaper compared to edible vegetable oils [10, 11]. The WCOs obtained after frying of food. During the deep frying of food, cooking oils

* Corresponding author: babilakkoju@kgr.ac.in

are exposed to a very high temperature leads to formation of free radicals, which are highly reactive molecules that can damage cells and increases the cancer risk. Therefore, the used cooking oils after deep frying need to be disposed. Most of the used cooking oil is thrown directly in environment without proper treatment leading environmental pollution.

The most popular approach to make biodiesel is by transesterification using various alcohols such as methanol and ethanol [12], which refers to conversion of triglycerides to fatty acid alkyl esters and glycerol in presence of catalysts like acid or alkali. Melero et al has worked on the production of biodiesel by transesterification of palm oil in presence of sulphuric acid as catalyst [13], Isam et al has reported on transesterification of WCOs in presence of NaOH [14], Anh et al, has worked on production of biodiesel from WCO in presence of KOH catalyst [15], Liu et al has worked on production of biodiesel from soybean by using CaO as catalyst [16] etc. The main advantage of some biodiesels are that they have almost similar physico chemical properties to that of mineral diesel [17, 18]. Higher viscosity biodiesel derived from some vegetable oils can create engine issues such as inadequate fuel atomization, partial combustion, engine fouling, and lubricant oil contamination. Hence to reduce the viscosity of biodiesel blending with petroleum diesel is preferable [19]. The blending of biodiesel referred to adding petroleum diesels into biodiesel with different proportions [20]. The efficiency of biodiesel blends from vegetable oils like castor [21] and jatropha [22] with petroleum diesel have improved efficiency compared to its virgin oil. Biodiesel can be utilized in its pure form; however, engine modifications may be required to prevent maintenance and performance issues. This paper discusses about the biodiesel preparation from WCO by transesterification with ethanol in presence of NaOH. The biodiesel efficiency was improved by making blends with petroleum diesel. The blends were analysed for various physico chemical properties.

2 Materials and Methods

2.1 Material

The Cooking oil (waste) is gathered from the girls' hostel mess at GITAM in Visakhapatnam (17.6868° N, 83.2185° E). The Diesel fuel was bought from a nearby HP petrol station located in Yendada, Visakhapatnam. Himedia laboratories pvt. Ltd. in Dombivli was the supplier of ethanol. We bought ethyl acetate, hexane, and HCl from Finar, India. Fisher Scientifics in Ahmadabad, India is where the silica gel was acquired. Fisher Scientifics, in Mumbai, India, supplied anhydrous sodium sulphate. $NaHCO_3$ was bought from Merck Specialties Pvt. Ltd. All of the compounds listed above were utilized without additional purification.

2.2 Method

2.2.1 Spectral Analysis

The GC analysis was carried out using an Agilent 6890 N series gas chromatography system with a flame ionization detector. Infrared (IR) spectra were acquired using a 1600 FT-IR Perkin-Elmer spectrometer (Norwalk, CT) with a liquid layer between the NaCl cells at 400-4000 cm^{-1}. 1HNMR were obtained using a Brucker Avance 400 MHz spectrometer in CDCl3. Chemical shifts relative to TMS as an internal standard are expressed as δ values (ppm).

2.2.2 Physico chemical and Lubricant properties

Physicochemical characteristics of synthesized biodiesel and its blends, Such as API gravity, Density, Specific Gravity, Dynamic and Kinetic viscosity at 40 °C, Low & High temperature Properties (cloud & pour point, flash & fire point) and copper strip corrosion were determined by using standard ASTM methods with the Equipment or instrument sourced from GITAM, India.

2.2.3 Preparation of WCO ethyl ester

50 g of WCO, 225 ml ethanol and 2.75 g of sodium hydroxide (1% weight of reactants) were taken in a 3 necked RB-flask equipped with reflux condenser. The reaction mixture was refluxed at 80-90 °C for 5-6 h with continuous stirring. The reaction has been tracked using thin-layer chromatography (TLC) using hexane and ethyl acetate as solvents. After a reaction was completed, the liquid was cooled to a normal temperature and rinsed twice with distilled water to remove the glycerol. The reaction mixture free of glycerol was washed with dil. HCl solution to neutralize the excess NaOH and dried over anhydrous sodium sulphate solution. The crude ester was concentrated by using rotatory evaporator. The crude ethyl esters were purified by using silica gel column chromatography (as 98% of hexane and ethyl acetate solvent) to obtain pure ester and it is characterized by ^{1}HNMR and IR spectral data show in following **Table-1.**

Table-1: Spectral data for the synthesized compound

^{1}HNMR Chemical Shift (δ)	**Multiplicity**	**Assignment**	**IR Absorption Peaks (cm^{-1})**	**Assignment**
0.8-0.9	t	-C<u>H</u>$_3$	3007	-CH$_2$-C=C
1.2-1.4	m	-C<u>H</u>$_2$	2926	-CH$_2$
1.6-1.7	m	-C<u>H</u>$_2$	2855	-CH$_3$
2.0-2.1	m	-C<u>H</u>$_2$-CH=CH	1739	-C=O
2.3-2.4	t	-C<u>H</u>$_2$-CO-	1180	COC
2.7-2.8	m	-O-C<u>H</u>$_2$-CH$_2$-		
4.1-4.2	t	-O-C<u>H</u>$_2$-		
5.3-5.4	m	-C<u>H</u>=C<u>H</u>-		

3 Results and Discussion

WCO was gathered from GITAM hostel mess, Visakhapatnam (17.6868° N, 83.2185° E), Andhra Pradesh, India. To get rid of the muck and moisture, WCO was sieved and heated to 105 °C. The fatty acid composition was analyzed by GC (**Fig.1**). WCO mainly has 56.42 % of linoleic acid 28.23 % of oleic acid, which is mono and di unsaturated fatty acids respectively. It has a lower amount of saturated fatty acids, especially palmitic acid (6.82%) and steric acid (4.43).

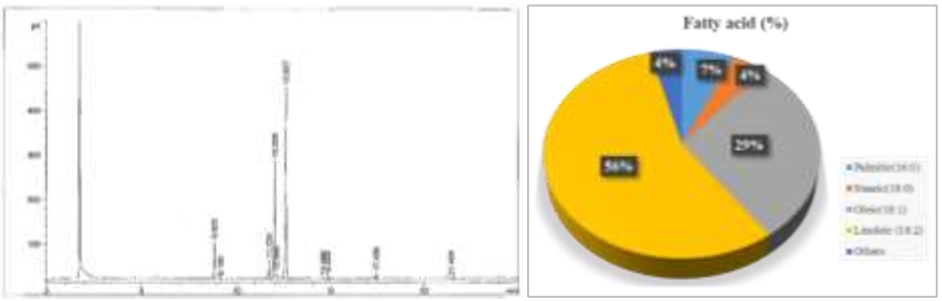
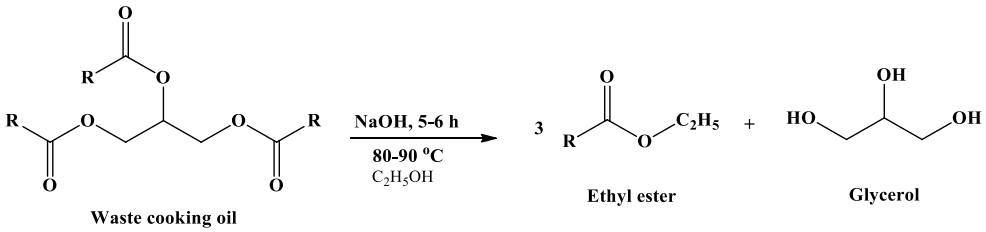


Fig. 1. Fatty acid composition of WCO

Transesterification has been employed to produce WCO biodiesel. WCO was transesterification with ethanol in the presence of aq sodium hydroxide catalyst at refluxed temperature for 5-6 hr. Through the use of TLC, the reaction was observed. After completion of reaction, the reaction mixture was washed with water followed by neutralizing with dil HCl and dried over anhydrous sodium sulphate. The crude biodiesel was concentrated by using rotatory evaporator. The crude ethyl esters were purified by silica gel column chromatography using 98% hexane and ethyl acetate as eluent (Scheme 1). The obtained esters were characterized by ^{1}HNMR and IR spectra.



Scheme 1: Synthesis of methyl and ethyl esters from waste cooking oil

The presence of ester peak in ^{1}HNMR (Fig. 2) a triplet at 2.3-2.4 ppm (-CH_2-CO-) and a tripilet at 4.1-4.2 ppm (-O-CH_2) confirm ethyl ester. Presence of C=O stretching peak in IR (Fig. 3) at 1739 cm-1and COC stretching peak observed at 1180 cm^{-1}confirm ethyl ester.

The petroleum diesel used for blending was purchased from a local HP petrol pump station at Yendada, Visakhapatnam and showed properties such as density 0.8762 g/cc, viscosity 2.0982 cSt at 40oC, flash point 38.3°C, fire point 48.6°C, cloud point -0.2 °C and pour point -19.2°C. Blended oil samples were prepared by mixing waste cooking ethyl ester with petroleum diesel, at 10 – 100%, with 10% increase by volume.

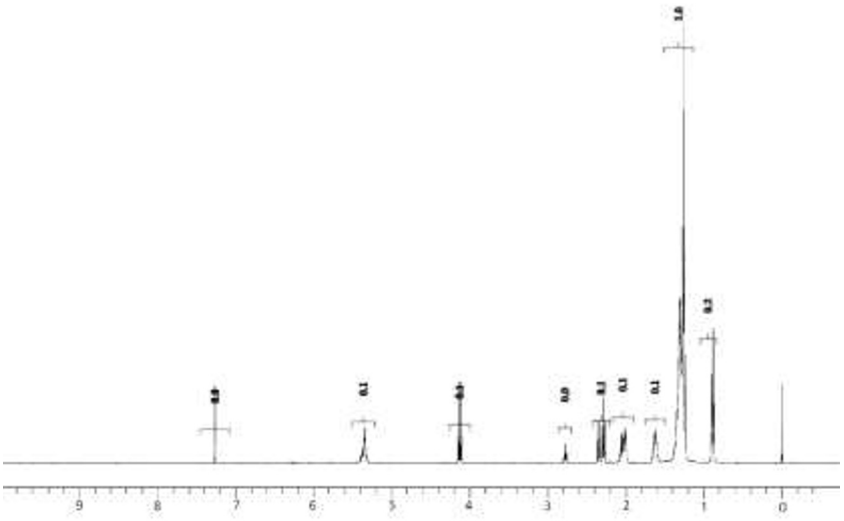


Fig. 2: ^{1}H NMR δ (ppm) of WCO ethyl ester

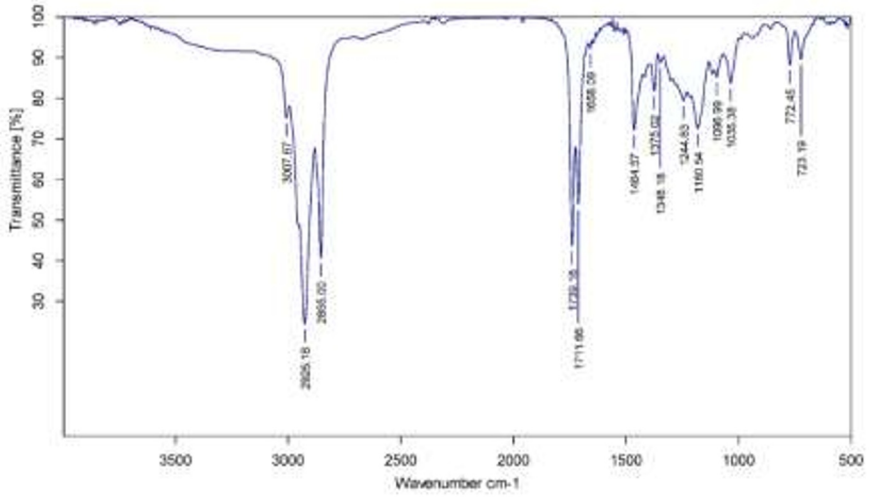


Fig. 3: IR (cm^{-1}) of WCO ethyl ester

Using ASTM standard procedures, the physico-chemical and fundamental lubricating characteristics of WCO ethyl ester and their blends were assessed. The following parameters were measured three times: density, specific gravity, kinematic and dynamic viscosity, cloud point, pour point, flash point, fire point, and copper strip corrosion. The average results are shown in **Table 2.**

Table 2: Physico-chemical properties of biodiesel from WCO and its blends.

Properties	ASTM Methods	Petroleum Diesel	B10	B20	B30	B40	Ethyl-bio-diesel
Density (g/cc)	-	0.876	0.888	0.890	0.889	0.890	0.883

Specific Gravity	-	0.823	0.834	0.836	0.835	0.836	0.829
API Gravity	-	40.47	38.13	37.81	38.00	37.81	39.15
kinematic Viscosity (cSt)	D 445	2.098	2.287	2.421	2.636	2.825	7.586
Dynamic viscosity (mPa.S)	D 445	1.837	2.030	2.155	2.344	2.514	6.698
Cloud Point (ºC)	D 2500	-0.2	-7.3	-4.5	-2.0	-0.6	4.0
Pour Point (ºC)	D 97	-19.2	-19	-16.3	-14.1	-12.8	0.2
Flash Point (ºC)	D 92	36.3	47.7	49.8	65.8	71.2	146
Fire Point (ºC)	D 92	48.6	55.6	66.9	73.7	83.4	153
Copper Strip Corrosion	D 130	1a	1a	1a	1a	1a	1a

All properties were done thrice and an average was tabulated.

The results indicate that the densities of WCO ethyl ester and its blends with petroleum diesels are almost similar, ranging between 0.875-0.890 g/cc. Specific gravity is ratio of weight of given volume of oil to the weight of same volume of water at same temperature. The specific gravity of WCO ethyl ester and its blends with petroleum diesels are in range of 0.823-0.836. The relative masses of oils are expressed in API (American Petroleum Institute). It could be calculated by following mathematical equation.

$$API = \frac{141.5}{Specific\ Gravity} - 131.5$$

The higher API gravity indicates lighter crude oil and lower API value of heavier oils. Here the waste cooking biodiesel and its blends are having higher API gravity range from 38.13 – 40.71.

The kinematic viscosity of WCO ethyl ester and its blends are increasing from B10-B40 at 40ºC. The kinematic viscosities at 40ºC are in the range of 2.287 – 2.825 cSt for B10-B40, B10-B40 blends viscosities are in ASTM standard (ASTM D6751) limits. The remaining viscosity of pure biodiesel has 7.586 cSt. The dynamic viscosities at 40ºC of WCO ethyl ester and its blends are in range from 2.030-2.825 and 6.69 m Pa.S and showed graphically in Fig. 4.

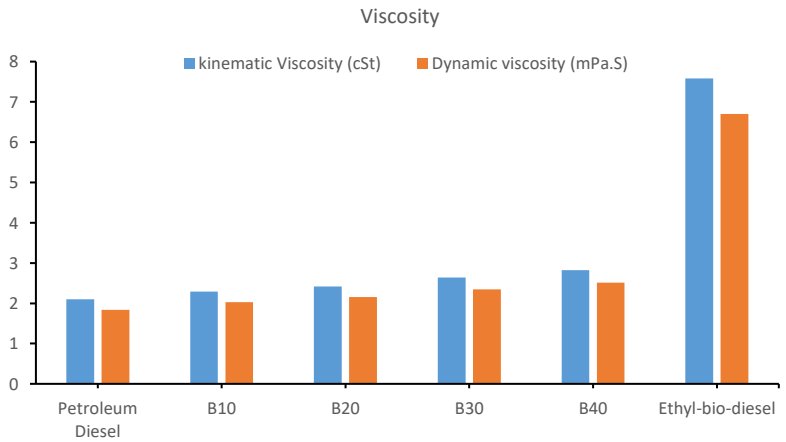


Fig. 4: viscosities of WCO ethyl ester and their blends

Cloud point of WCO ethyl ester and its blends decreases from B10-B40 and are the in range of -7.3 to 4.0ºC. The pour point of WCO ethyl ester and its blends are increasing from B10-B40 and are in the range of -19.2 to 0.2ºC (Fig. 5).

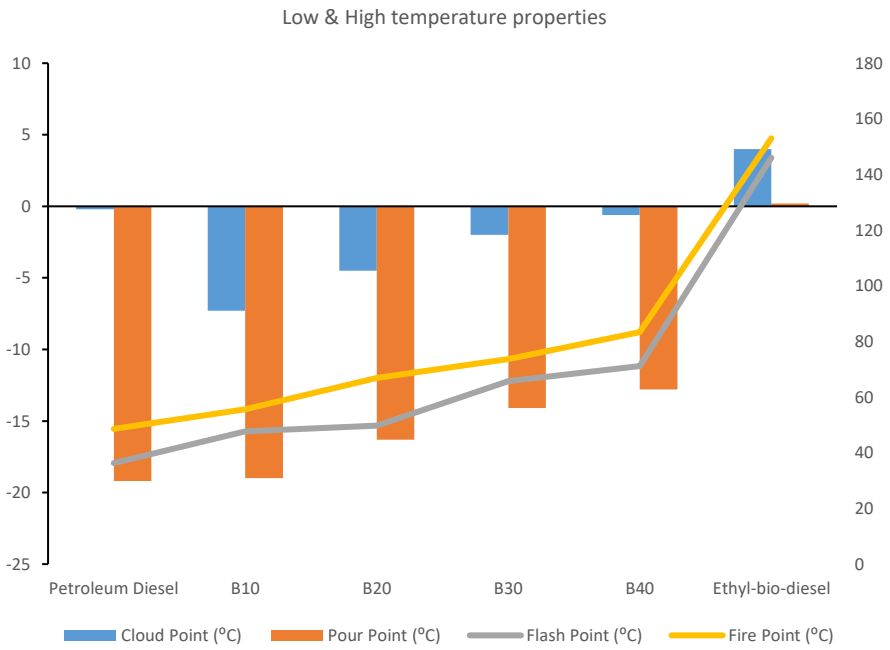


Fig. 5: Flash, fire points and Cloud, pour points of WCO ethyl ester and their blends

The flash and fire point of petroleum diesel is 36.3 and 48.6oC, the WCO ethyl ester and its blends are showing better flash and fire point. The flash point and fire point range from 47.7 – 71 ºC and 55.6 – 83.4 ºC. The WCO ethyl ester and its blends are having less corrosion 1a.

Based on the observation, the physicochemical properties of biodiesel were improved for its blend B10-B40 with petroleum diesel. These blends of biodiesel from WCOs are agreed with ASTM blend (ASTM D-6751) standard diesel properties.

4 Conclusion

Biodiesel and derived economically from Waste Cooking Oil (WCO) and effectively repurposes waste into energy. Studies validate its efficiency and compliance with ASTM standards and showing that biodiesel from WCO and blends ranging from B10 to B40 with petroleum diesel and perform optimally in diesel engines. This underscores its versatility and potential as a sustainable alternative fuel source. By utilizing WCO and biodiesel production not only mitigates environmental concerns but also offers a cost effective solution and reducing reliance on fossil fuels. Its compatibility with existing diesel engines further highlights its practicality and signaling a promising avenue for reducing carbon emissions and promoting a greener energy future.

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