

Production of Biodiesel from *Pinus Roxburghii* Oil and its Evaluation

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Summary: Biodiesel fuel is an alternative and renewable source of energy. It may help to reduce air pollution and our dependence on fossil fuel for energy. In this study the plant oil was extracted from saw dust of pine tree using methanol as a solvent and acid catalyst (H₂SO₄) was used for transesterification. The effect of reaction time, temperature and catalyst ratio was studied, which presented that the high yield of biodiesel is produced by using 9 mL of catalyst for 1 h reaction time. The physicochemical properties such as density, viscosity, heating value, cetane index, flash point, Conradson carbon residue and distillation behavior of the obtained biodiesel were determined. The results showed that the final fatty acid methyl esters (FAME) product meets with the biodiesel quality standards, and ASTM specification D6751-02. The UV-Visible and FT-IR spectroscopic studies was also performed, which revealed that the synthesized biodiesel consists of aliphatic, olifinic and aromatic hydrocarbons along with fatty acids.

Key words: Biodiesel, Transesterification, Pine oil, FT-IR.

Introduction

Biodiesel (fatty acid alkyl esters or FAME) is a renewable, alternative fuel produced from grease, vegetable oils, or animal fats. It is suitable to blend with petroleum diesel or use directly as fuel in compression ignition engines. It was reported that the biodiesel and its blends with petroleum diesel are environment friendly because biodiesel is biodegradable and contain very little sulfur and metals. The diesel which obtained from petroleum, contain up to 20% polycyclic aromatic hydrocarbons while biodiesel has very little/does not contain polycyclic aromatic hydrocarbons, and as a result it is easy and safe during storage and transportation. It was also reported that the use of biodiesel and its blends with petroleum diesel in diesel engine results in reduced exhaust pollutants as compared to petroleum diesel fuel [1]. While the engine power drop by using biodiesel (especially with pure biodiesel), which is due to the loss of heating value of biodiesel [2].

The biodiesel produced by transesterification of fatty acids or by transesterification of vegetable oils with short-chain alcohols [3]. The transesterification reaction includes the conversion of triglycerides into fatty acid alkyl ester, in the presence of an alcohol, like methanol or ethanol, where alkali or acid are use as a catalyst. During this process, the glycerol is formed as a byproduct. The chemical reaction without any catalyst has also proposed at supercritical conditions [4-6]. Extensive research is going on the production of biodiesel from vegetable oils, or animal fats. Carlozzi *et al* [7]

grown *Rhodospseudomonas palustris* under low to high continuous irradiances value and then produced both bio-H₂ and biodiesel (lipids) using fed-batch conditions. Harrington and D'Arcy Evans [8] used both conventional and *in-situ* methods for transesterification of seed oil from a series of sun flower cultivars to produce acid catalyzed fatty acid methyl esters. After comparism, they were found that both methods are effective to yield high conversion of seed lipids to fatty acid methyl esters. Jeong *et al* [9] studied batch (one- and two-stage) production of biodiesel fuel from rapeseed oil. They performed the transesterification of rapeseed oil in the presence of potassium hydroxide and methanol at about 60 °C. Srinivas and Satyarthi [10] used solid acid double-metal (Fe-Zn) cyanide complex as a catalysts for the production of biodiesel from vegetable oils and animal fat. Chen *et al* [11] used enzymes (immobilized lipase *Rhizopus oryzae*) for the conversion of waste cooking oils into biodiesel. They studied various process parameters such as molar ratio of methanol to waste oils, bio-catalyst load, adding method, reaction temperature, and water content, for the determination of optimal condition for the maximum conversion.

In the present study, we extracted plant oil from saw dust of pine tree using methanol as a solvent, because biodiesel production has also been proposed from indigenus plants [12]. The transesterification of pine oil was performed in the presence of H₂SO₄ catalyst. The various physico-chemical characteristics such as density, viscosity,

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heating value, cetane index, flash point, Conradson carbon residue and distillation behavior of the product was studied. The UV-Visible and FT-IR spectroscopic analyses of the synthesized biodiesel were also performed to confirm its characteristics with that of the petroleum diesel.

Results and discussions

Characterization of Pine Oil Extract

The physico-chemical properties of the pine oil extract are shown in Table-1. The values of kinematics viscosity, flash point, and cetane index of the pine oil was 0.0046 (at 20 °C), 45 °C and 53, respectively. The carbon residue (0.1653 g) and ash content (0.015 g) was obtained after the combustion of pine oil extract.

Table-1: Physicochemical properties of crude pine extract.

Properties	Values
Carbon residue (g)	0.1653
Ash contents (g)	0.015
Flash point (°C)	45.00
Density (g/cm ³)	0.90
Viscosity (C.poise)	1.048
K.V at 20°C	0.0046
TAN (mg KOH/g)	1.40
API Gravity	41.009
Cetane index	53.00

Thermal Transesterification

Effect of Temperature on Yield of Glycerol

The methyl esterification of pine oil was carried out at different temperatures in order to study the effect of reaction temperature on methyl ester formation. The yield of glycerol, which was obtained after thermal transesterification, is shown in Table-2. The result showed that the transesterification of pine oil was maximum at 70 and 80 °C (0.01 mL). Table-2 also showed that the glycerol was not formed below 70 °C. The transesterification of pine oil was also carried out at different time intervals at 80 °C and the maximum yield of glycerol was obtained at 1 h reaction time.

Table-2: Yield of Glycerol at Different Temperature without Catalysts.

Temperature (°C)	Yield of glycerin (mL)
50	-
60	-
70	0.01
80	0.01
90	0.001

Physico-Chemical Properties

The physico-chemical properties like density and viscosity of biodiesel obtained by

transesterification of the extract at different temperature and different reaction time are shown in Tables-3 and 4. The results in Table-3 presented that the densities of the products (obtained at different temperatures) do not show a regular pattern. The ranges of densities of the products are in the range of 0.71-0.93 g/cm³. The density of original diesel oil is 0.85g/cm, which is nearly related to the sample treated at 70 and 80 °C. The viscosities range of the products was 1.04-1.26 centipoise at 50-80 °C. The product which obtained at 90 °C, showed lowest viscosity (0.9806 centipoise).

Table-3: Physico-chemical Properties of Treated Sample at Different Temperature.

Reaction time (h)	Amount of sample (mL)	Properties	
		Density (g/m ³)	Viscosity (centipoise)
1	50	0.9	1.1
2	50	0.98	1.2
3	50	1.07	1.3
4	50	1.073	1.339

Table-4: Physico-chemical Properties of Treated Samples for Different Time duration.

Amount of sample (mL)	Temperature (°C)	Properties	
		Density (g/cm ³)	Viscosity (c.p)
Original sample	80	0.75	1.323
50	90	0.71	0.9806
50	80	0.901	1.26
50	70	0.93	1.31
50	60	0.74	1.04
50	50	0.9	1.216

Table-4 shows the results of the densities and viscosities of the product obtained at 80 °C and different treatment time. The data shows that the density of sample obtained at 1, 2, 3 and 4 h is given as 0.9, 0.98, 1.07 and 1.07 g/cm³, respectively. The density of the original biodiesel is 0.85g/cm³, which are compatible to the densities of the samples treated for 1, and 2 h. Table-4 also shows that the 1h is optimum for maximum conversion (at 80 °C) of pine extract to biodiesel.

Effect of Catalysts on Biodiesel Synthesis

The methyl esterification of pine oil was carried out in the presence of H₂SO₄ catalyst at optimized temperature and time. The yield of glycerol with different concentrations of H₂SO₄ catalyst is shown in Table-5. The results show clearly that the yield of glycerol increased as increased the concentration of the H₂SO₄ catalyst and then the yield was constant after addition of 8 mL of catalyst, which means that 8 mL is the maximum amount of catalyst having catalytic activity while addition of more catalyst is non effective.

Table-5: Yield of Glycerol of Catalytically Treated Sample.

Catalyst concentration (mL)	Yield of glycerol (mL)
6	0.3
7	0.4
8	0.6
9	0.6
10	0.6

Table-6 shows the physico-chemical properties like densities and viscosities of FAME, obtained with different concentrations of catalyst. The results showed that the density of the products obtained after using 8 and 9 mL catalyst concentration (0.90, 0.96 g/cm³, respectively) are comparable with that of original diesel fuel oil (0.85g/cm³). Table-6 also shows that the viscosities trend of the product is not in regular pattern. The viscosities of the products using 9 and 10 mL H₂SO₄ catalyst (2.64 and 2.68 centipoises, respectively) are nearly equal to the viscosity of the original diesel fuel oil (2.6 centipoises) (table 7).

Table-6: Physico-chemical Properties of FAME Obtained with concentrations of catalyst.

Volume of H ₂ SO ₄ (mL)	Properties	
	Density (g/cm ³)	Viscosity (c.p)
6	1.18	2.40
7	1.03	2.30
8	0.9	1.65
9	0.969	2.683
10	1.04	2.64

The various physico-chemical properties of pine biodiesel and pure diesel oil are shown in table 7. The results presented that the pine biodiesel had comparable fuel properties with those of diesel fuel. The viscosity of catalytically obtained biodiesel (2.68 centipoises) is higher than thermally obtained biodiesel (1.216 centipoises) and are comparable with that of petroleum diesel e.g. 2.60 cp. It was reported that the higher viscosity biodiesel does not burn completely and as result blockage/deposition occur in the fuel injector of diesel engines [13]. The calorific value of the catalytically and thermally obtained biodiesels is 37 and 34 MJ/kg, respectively which is close to 100% petro-diesel (42 MJ/kg). It means that the obtained biodiesel has good fuel properties. Table-7 also shows that the flash point, water contents and acid value of the catalytically obtained biodiesel are lower than thermally obtained biodiesel. The higher flash point of thermally obtained biodiesel means that its storage, handling and transportation are safer than catalytically obtained biodiesel and petro-diesel. The ash contents of catalytically obtained biodiesel is higher than petrobased diesel, which mean that biodiesel contains more mineral matter compared with that of petroleum diesel.

Table-7: Physico-chemical Properties of Thermally and Catalytically Obtained Biodiesel and Petroleum Based diesel oil.

Property	Unit	Thermally treated oil	Biodiesel catalytically treated	Diesel oil
Density	g/cm ³	0.901	0.900	850
Viscosity @20°C	C.p	1.216	2.68	2.60
Flash point	°C	70	53	68
Water contents	%	1.6	0.04	0.02
Ash contents	%	0.23	0.99	0.17
Carbon residue	%	0.45	0.10	0.25
Acid value	ppm	2.4	1.4	0.35
Calorific value	Mj/kg	34	37	42

FT-IR Study

The FT-IR spectra of pine extract and catalytically obtained (H₂SO₄ catalyst) biodiesel samples are shown in Fig. 1. The FT-IR spectrum of pine extract (Fig. 1a) showed a broad peak at 3400cm⁻¹, which show alcoholic or carboxylic O-H group. The peaks appeared at 2950 and 2800 cm⁻¹ are due to the stretching vibration of C-H (methyl and methylene). The spectrum also showed peaks at 1620 and 1210-1100 cm⁻¹. The weak peak indicates olfinic C=C and C-O linkage of ester or ether, respectively. The FT-IR spectrum of pine oil extract also show peak at about 1050 cm⁻¹, which are due to the stretching vibration of C-O in alcohols [14]. The FT-IR spectra of catalytically obtained biodiesel samples show similarities with that pine oil extracted sample. However, the catalytically obtained biodiesel presented new peaks at the ranges of 1700 to 1780 and 1310-1250 cm⁻¹. The peaks appeared at 1700 to 1780 cm⁻¹ corresponds to carbonyl C=O of ketones, carboxylic acids and esters. The peaks appeared at 1310-1250 cm⁻¹ is due to the stretching vibration of C-O-C ether and esters, which shows that trans esterification occur in pine oil [15].

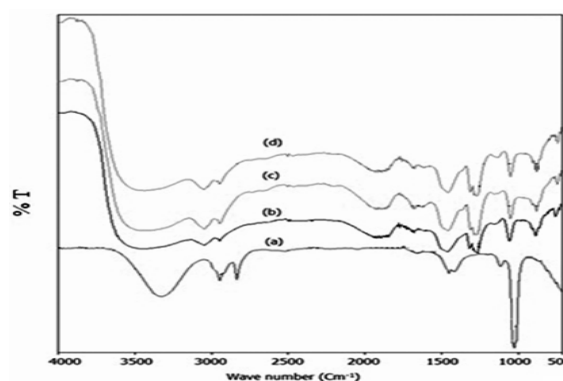


Fig. 1: FT-IR Spectra of Original Sample and treated in the presence of different concentrations of H₂SO₄ as catalyst, (a) Original Sample (b) 7 mL (c) 8 mL (d) 9 mL.

UV-visible Spectrophotometric Study

Fig. 2 shows the UV spectra of pure pine extract and catalytically obtained biodiesel. The spectrum of pure pine extract showed various absorption bands. The absorption band at 210 nm presents the olifinic conjugation in the presence of non bonding system. The absorption band at 238 and 245 nm shows a high degree of conjugation of olifinic double bonds accompanied by other chromophore containing non bonding system. The spectrum also shows absorption bands at 261 and 269 nm, which indicates the presence of condense aromatic configuration accompanied by carbonyl and olifinic chromophores [16, 17]. Fig. 2 also shows absorption bands at 280 and 297 nm, which indicates the presence of carbonyl compounds. The UV analysis presented that pure pine extracts contains olifinic conjugation accompanied with carbonyl chromophores, unsaturated ketones, esters or carboxylic acids.

The UV spectrum of catalytically (8 mL H₂SO₄) obtained biodiesel is shown in the Fig. 3. The spectrum shows strong absorption in the range of 238 and 237 nm, which indicate olifinic double bond in conjugation with chromophores due to non bonding system. It presented that catalytically obtained biodiesel contain nitrogen, oxygen and sulfur. The band arise at 286 nm, which might be due to the presence of ketone, ester and carboxylic. The spectrum also shows absorption in the range of 277-275 nm, which shows the presence of condensed aromatics. The band appears at 211 nm shows the presence of substituted carbonyl or carboxyl system accompanied by auxochromes [18].

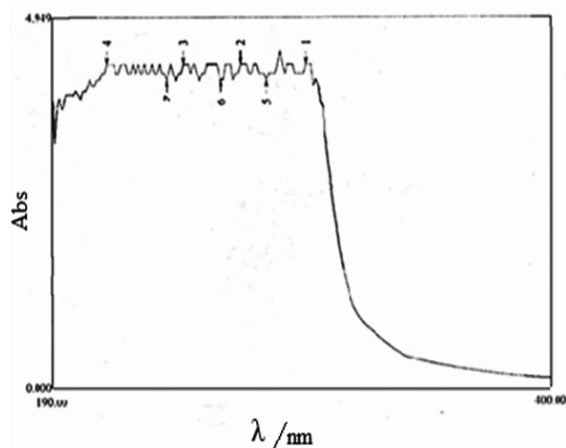


Fig. 2: UV Spectrum of pure pine oil extract.

Experimental*Materials*

The analytical (AR) grade methanol, H₂SO₄ and HCl were used without any further purification.

Sample Collection

The pine trees (*Pinus Roxburghii*) are available in the Northern areas (Kashmir, Swat, Dir, Kohistan) of Pakistan. The pine saw dust sample was collected from a general wood cutter machine situated at Charasada, Khyber Pakhtunkhwa, Pakistan. All the sawdust was obtained from one type of wood. The material was free of dust and collected in cloth bags. The saw dust was dried in shade for about two weeks and then soaked in the solvent for 8 days.

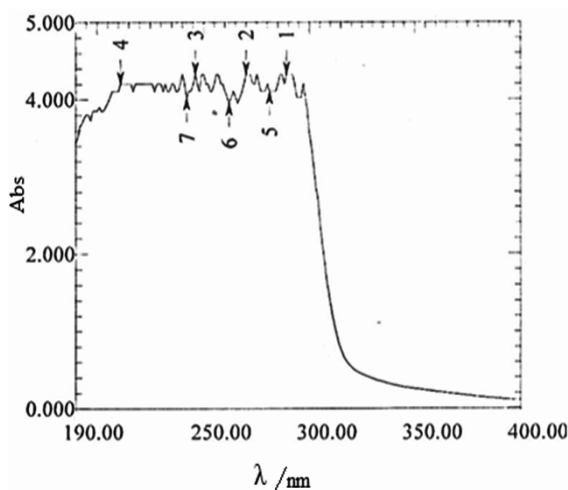


Fig. 3: UV Spectrum of catalytically (8 mL H₂SO₄) obtained biodiesel.

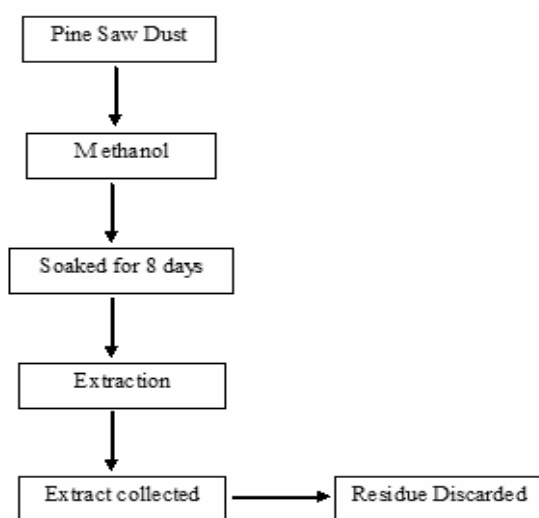
Extraction of Fatty Acids from Plant Material

500 g saw dust was soaked in 3400 mL methanol for 8 days and then the extract was separated from solid saw dust. The scheme for the extraction of fatty acids from pine saw dust is shown in scheme 1.

Preparation of Biodiesel

The Pine extract was heated above 100 °C for about 1 h in order to remove water and other impurities. The transesterification reaction of pine extract was carried out in methanol in the presence of

H₂SO₄ catalyst (used different catalyst ratios). The liquid solution was heated and stirred at a constant rate of 66 rpm and after reaching the desired temperature, the contents were allowed to react for time duration of 1, 2, 3, and 4 h. After the completion of reaction, the mixture was allowed to stand and the two phases (one rich in glycerin and the other one in methyl ester) were separated by centrifugation. The methyl ester (biodiesel) was then washed thrice with HCl solution (0.5 mol/L) until a clear phase biodiesel was obtained, which was collected and stored for further analyses. The same procedure was followed to study the effect of time, temperature and catalyst concentration on transesterification.



Scheme 1: Extraction of Oil Pine saw dust.

Characterization

The physico-chemical characterization of Pine saw dust extracts and biodiesel were characterized by standard methods, like viscosity was determined by (IP-71), density (IP/249), flash point (ASTM D 56-05 / IP 34/87), Conradson carbon residue (ASTM D 189-01 / IP 13/92), Total Acid Number (IP method I), Specific gravity, API Gravity (IP method 160 or 190).

FT-IR Spectroscopic Analysis

FTIR spectra of the samples were recorded using Bruker (Tensor27) FT-IR. The samples were dropped on KBR pellet and the spectra were recorded using in the range of 4000 and 500cm⁻¹. A minimum

of 5 scan was signal averaged with a resolution of 2cm⁻¹ in the range 4000-500cm⁻¹.

UV-Visible Spectrophotometric Analysis

UV-Visible spectra of the sample were recorded on UV/visible spectrophotometer 2550 company Shimadzu, Japan. The biodiesel samples were diluted in methanol and then UV-Visible spectra were obtained.

Conclusion

In this study, the transesterification of methanol extracted pine oil was performed via thermally and catalytically. It was found that the higher reaction temperature speed-up the reaction and shorten the reaction time. The optimum temperature and time was 80 °C and 1 h, respectively. It was also found that the yield was decrease as increased the reaction temperature (above 80 °C), which might be due to decomposition of glycerol. The physico-chemical characteristics of the biodiesel produced in the presence of H₂SO₄ catalysts are very close to those of petro-diesel. The UV/visible and FT-IR studied showed that the obtained biodiesel consists of aliphatic, olifinic and aromatic hydrocarbons along with some fatty acids. The present investigation shows that the extracted oil from saw dust of pine trees as highly promising feedstock for biodiesel industries.

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