Possibility of converting indigenous *Salvadora persica* L. seed oil into biodiesel in Pakistan

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ABSTRACT

In this research study biodiesel has been successfully produced from vegetable seed oil of an indigenous plant *Salvadora persica* L. that meets the international biodiesel standard (ASTM D6751). The biodiesel yield was 1.57 g/5g (31.4% by weight) and the *in-situ* transesterification ester content conversion was 97.7%. The produced biodiesel density was 0.894 g/mL, its kinematic viscosity 5.51 mm^2/s, HHV 35.26 MJ/kg, flash point 210 ^oC, cetane no. 61 and sulphur content 0.0844 %. Thermal analysis of the biodiesel showed 97% weight loss was achieved at 595°C with total oxidation of the biodiesel. The production energy efficiency was 0.46% with a lab scale setup, assuming the volume fraction ratio (volume of the sample/ total volume of the equipment used). The results revealed that single step *in-situ* transesterification method is suitable for the production of biodiesel from *Salvadora persica* seed oil.

Keywords: *Salvadora persica; biodiesel; transesterification; thermogravimetry; energy analysis*

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INTRODUCTION

Renewable energy resources are becoming more attractive because of environmental degradation, air pollution and the scarcity of petroleum reserves. The importance of biodiesel has been realized in the last few decades as a fuel for transportation (Demirbas 2007), due to a number of desirable characteristics such as renewability, biodegradability, better fuel characteristics (e.g., higher cetane number) and environmentally friendly nature, especially as it causes far less emissions of particulate matter, unburnt hydrocarbons and other pollutants e.g. carbon monoxide and sulphur dioxide (Akhtar, et al. 2017).

The environmentally friendly biodiesel fuel can be produced from edible, non-edible feed stocks and waste cooking oils (Kuo, Shaw and Lee 2015; Dogan 2016). It is basically produced by combining methyl alcohol with an acid or base catalyst in vegetable oil, animal fat, or recycled cooking oils containing triglycerides to produce methyl ester (biodiesel) and glycerol as a value added by-product (Demirbas 2008; Ali and Watson 2015).

Pakistan is a developing country, facing an energy shortage with the gap between production and consumption widening every year. Recent statistics showed that the electricity-generation capacity of the country stands at 17000 MW whereas an average demand is 22797 MW, the shortfall lies somewhere between 4,000 and 5,000 MW, which is expected to increase in the coming years as the population expands by almost two percent annually (Zeb 2016). Moreover, Pakistan's current (2016) estimated oil import is around 346,400 barrels/day, with the current approximate price of crude oil at $30/ barrel a total annual bill of about US$ 10.7 billion is payable, with the total petro-diesel consumption in the country of around 8.22 million tons per year. The major portion of energy demand is met by fossil fuels, which are non-renewable

resources and the major source of greenhouse gas emissions, creating environmental issues like climate change and global warming. This resource is also finite and would not last for more than 50 years (Ali 2016). The effect of augmenting the limited energy resources in Pakistan through intense harnessing of the varied biodiesel sources can not only addresses the deficiency issue but also ensure energy security in the country (Chakrabarti, et al. 2012). The Alternative Energy Development Board of Pakistan (AEDB 2016) is continually supporting the development of biodiesel projects and giving initiatives such as waving the custom duty on the machinery to produce biodiesel for motivating the stakeholders to invest in these renewable energy projects. These steps would help to tackle the environmental degradation problem due to air pollution through the transportation sector and helps in mitigating measures. The National Biodiesel Programme has also been launched to reduce the country's dependence on imported crude oil and to meet environmental guidelines by blending 10% biodiesel with petroleum derived diesel for use in the transportation sector by the year 2025 (Ali 2014).

These efforts will support the economic prosperity by saving valuable foreign reserves spent for importing petroleum crude oil. The current daily import of crude oil (346,400 barrels/day) produces 4,156,800 gallons/day of petroleum diesel. It is estimated that from one barrel of crude oil approximately 12 gallons of petro diesel is produced. Using 10 % blended biodiesel fuel with petroleum diesel will proportionately reduce the quantity of diesel consumption by 415,680 gallons/day (saving 34,640 barrels/day of imported crude oil and at $30/barrel, this saves around $1,039,200/day (Ali 2016).

Pakistan is an agriculture country with 70% of its population earning their living from the agriculture sector. The most abundant edible oil bearing seed crops in Pakistan are: soybean, corn, cotton, canola/rapeseed and sunflower (Khan and Dessouky 2009). **Table 1** shows the

non-edible indigenous crops jatropha, pongame (*Pongamia pinnata*), castor and taramira (*Eruca sativa*) are a potential candidate that can be cultivated on the marginal land in the country to produce renewable biodiesel fuel (Chakrabarti, et al. 2012). There are numerous other untapped wild plants that can serve this purpose very well. The growers can uplift their standard of living by cultivating oil seed crops utilizing their marginal and saline lands. Small scale biodiesel production facilities can be designed with less investment and will be helpful in providing biodiesel fuel to run agriculture machinery on the farm lands (Khan and Dessouky 2009).

Among many local, widely distributed plants in arid and semiarid areas of Sindh province, Pakistan, that can be used as renewable biodiesel fuel source, Salvadora *persica* L. (local name peelu or meswak, belonging to *Salvadoraceae* family) is one of them (Tahir, Rajput and Korejo 2010). Salt tolerant *S. persica* can be cultivated in highly saline black soils where arable farming is not possible for economic and ecological benefits (Reddy, Shah and Patolia 2008). The seeds of *S. persica* yield a pale yellow solid fat (oil) containing 40–45% oil, rich in lauric (C12) and myristic (C14) acids which are used in making soaps, illuminants, varnishes, paints and in the food industry. *S. persica* is also a medicinally important plant, used traditionally in the treatment of rheumatism, leprosy, gonorrhoea, ulcers, scurvy, tumours and dental diseases (Kumar, Rani and Mangal 2012). The antimicrobial toothbrush stick (meswak) for oral hygiene and to treat gum inflammation, is a chewing stick prepared from its stings and roots, which maintains the dental hygiene and ultimately the potential and safely use as dental remedy (Ahmad and Rajagopal 2014). It is also a good source of feed, fodder, lipids, gum and resins and thus provides an income for farmers inhabiting the highly saline soil areas. Cultivation of *S. persica* on highly saline black soils though gives marginal per hectare returns. However, profits

apart this is an ideal plant species for the arid saline land restoration programs (Rao, et al. 2004) and represents environmental greening advantage.

With many developing countries such as Pakistan, focusing on alternative fuel production to reduce crude oil imports and related expenditure, offering significant financial incentive, it is timely to explore different untapped local flora to produce biodiesel as a petroleum substitute or to blend with conventional fuels. *Salvadora persica* oil has not being explored in the past in detail as a potential feedstock to produce biodiesel in Pakistan, therefore this research study has been undertaken to investigate its oil yield and characterization (physical, chemical and thermal properties) of the biodiesel produced from its seeds . Furthermore, thermal and energy analyses were also conducted to find out the biodiesel thermal behavior and production energy feasibility based on a bench-scale setup to pilot scale by introducing a volume fraction factor that considers the volume of the equipment used.

MATERIALS AND METHODS

Salvadora persica L. fruit (~ 500g) was procured from the experimental field of Plant Tissue Culture Lab, Pakistan Council of Scientific and Industrial Research (PCSIR) Complex, Karachi. The seeds were separated from their fruit manually and dried under the sun for 24 h (at 30 ± 1 ^{o}C). The seeds were then further dried at 80 $^{\circ}$C for 12 h in an oven to reduce its moisture content to around 1 % by weight, the method of (Kartika, et al. 2013) was followed for oil extraction). 10 g of seeds were ground into a powdered form with a coffee grinder (A10, Tekmar, Germany) and sieved with mesh size of 16 (i.e. 1.19 mm nominal sieve opening) to provide consistent results for oil extraction and biodiesel yield. All the experimental work was carried out at the Department of Environmental Engineering, NED University of Engineering

and Technology, Karachi. There were two experiments repeated three times, one was to study oil extraction and the de-oiled cake yield, while the other assessed *in-situ* biodiesel production, glycerine and de-oiled cake yields.

Oil extraction

After drying, the moisture content of the seeds was 3.41 ± 0.22 % (on dry basis). Three replicates of seed samples of 1 g were mixed and soaked overnight with 6 mL of analytical grade ethyl alcohol (Merck, Germany) in the ratio of 1:6 (g/mL), in a conical flask (100mL), with a reflux apparatus attached (Ali and Watson 2014). The mixture was placed on a hot plate magnetic stirrer (Wise stir, MSH-20A, Daihan Scientific, Korea) and heated at the boiling point of ethyl alcohol (80° C) for 8 h. The mixture was allowed to cool down to room temperature (26 ± 1° C) and filtered with a 0.45 µm size filter (Whatman, England) to separate powder seed residue from the mixture. The filtrate was heated in oven at 80° C to evaporate the solvent. The recovered oil yield was measured by weight with an electronic weighing balance (AB 304-S, Mettler Toledo, Switzerland).

Characterization of *Salvadora persica* oil

The fatty acid composition of the extracted *Salvadora persica* oil was determined by GC analyzer (7890B, GC systems, Aligent Technologies Inc., USA) fitted with a flame ionization detector (FID) at the International Center for Chemical and Biological Sciences, University of Karachi, Pakistan.

The density of the extracted oil was measured by using a density meter (DA-130N, Kyoto Electronics, Japan), while the kinematic viscosity of the extracted oil was measured with an

Ostwald viscometer (China). The flash point of the vegetable oil was calculated with the following equation having known kinematic viscosity (Demirbas 2008);

$$Flash\ point(℃) = 1.8512 \times kinematic\ viscosity\ \left(\frac{\mathrm{mm}^2}{\mathrm{s}}\right) + 462.66 \quad (1)$$

The iodine value (IV) was calculated from the fatty acids percentage area covered by palmitoleic acid, oleic acid, linoleic acid and linolenic acid in the GC profiles. While, the saponification value (SV) was determined by fatty acid profile analysis according to AOCS method No. cd 3A-94 i.e. calculated by multiplying molecular weight of each individual fatty acid with its % peak area and then dividing by 100 following (Firestone, 1994). The higher heating value of the extracted oil was measured using an oxygen bomb calorimeter (C-200, IKA, Germany) at the Department of Chemical Engineering, NED University, Pakistan.

The free fatty acid content of the oil was determined using a standard titration method. The acid value of the biodiesel was calculated with the help of the free fatty acid concentration present in the sample as oleic acid and by using the following relationship (Akiko, *et al*. 2006);

$$Acid\ value = \%\ free\ fatty\ acid \times 1.99 \quad (2)$$

The ash content was measured by heating a small quantity of extracted oil (0.5 g) up to 550˚C for 3 h in an oxidizing atmosphere. All the carbon content is combusted under these conditions, leaving behind only the ash, which was measured by weight.

***In-situ* transesterification**

Powdered sieved seeds (5 g) were mixed with a prepared solution of 30 mL methyl alcohol (Merck, Germany) and anhydrous potassium hydroxide (KOH) (Merck, Germany) in a 500 mL round bottom flask, attached to a distillation column assembly to reflux the methanol at its boiling point. The optimum methanol to powdered seed ratio (v/w, expressed in mL/g) and the amount of KOH in methanol was 6:1 i.e. 0.075 moles of KOH/L (Kartika, et al. 2013). Based on this ratio, the amount of KOH used was 0.126 g. In order to increase the oil miscibility in the mixture and to facilitate the extraction of oil from the seeds, 5 mL of n-hexane (Merck, Germany) was added in the ratio (seed to n-hexane w/v, 1:1) g/L. The mixture was then heated to 60° C on a hot plate magnetic stirrer for 4 h. After the reaction the mixture was allowed to cool down to room temperature and filtered to separate crude methyl ester with methanol from the residual powdered seeds. The miscella (mixture of solvents and methyl ester) was heated in an oven at 60° C for 3 h to evaporate methanol and n-hexane to recover the top layer of methyl ester (biodiesel produced yellow in colour) and the dark brown layer of glycerol settled at the bottom. The *in-situ* biodiesel produced was washed with de-ionized water (at 70° C) for neutralization and to remove impurities with a volumetric ratio of 3:1 and then it was dried in an oven at 80°C for 1 h. The yield of *in-situ* transesterified biodiesel, glycerol and the *in-situ* residual cake recovered as a by-product were measured gravimetrically by weight in grams.

Biodiesel characterization

Gas Chromatography was used to determine the percentage of methyl esters of fatty acids present in the *in-situ* biodiesel sample according to EN ISO 5508. The density, specific gravity, kinematic viscosity of the *in-situ* biodiesel and glycerol recovered were measured as explained earlier in ***section 2.2.*** The higher heating value of the in-situ biodiesel, glycerine produced and the *in-situ* residual cake recovered were determined with an oxygen bomb calorimeter. The ash

content percentage of the biodiesel fuel was measured with a standard method as explained earlier in ***section 2.2***.

The following relationship was used to calculate the flash point of the biodiesel with the help of a known kinematic viscosity (Demirbas 2008);

$$Flash\ point(℃) = 32.641\ \times kinematic\ viscosity\ \left(\frac{\mathrm{mm}^2}{\mathrm{s}}\right) + 305.02 \qquad (3)$$

The cetane number of biodiesel was estimated using the given fatty acid concentration (Saravanan and Chanrasekar 2013);

$$Cetane\ number = (61.03 + 0 \times X1\ + 0.1025\ \times X2\ + 0.133\ \times X3\ + 0.152\ \times X4\ - 0.001\ \times X5 - 0.037\ \times X6\ - 0.243\ \times X7\ - 0.395\ \times X8) \qquad (4)$$

Where, X1= Lauric acid (C12:0); X2=Mystic acid (C14:0); X3= Palmitic acid (C16:0); X4= Stearic acid (C18:0); X5= Palmitoleic acid (C16:1); X6=Oleic acid (C18:1); X7=Linoleic (C18:2); X8=Linolenic acid (C18:3). The concentrations are percentage of the fatty acid composition.

Thermal analysis

The thermogravimetric analysis of the *Salvadora persica* L. biodiesel was conducted using a thermal analyzer (SDT Q600, TA Instruments, USA) at the International Center for Chemical and Biological Sciences, University of Karachi. Using an alumina pan, with a sample

weight of 15 mg, dry nitrogen was flushed over balance at a flow rate of 50 mL /min to maintain an inert atmosphere. The thermo-balance was equilibrated at 50^{o} C and then the temperature was increased to 600^{o} C with ramp rate of 10^{o} C/ min (Rashid, et al. 2010).

Scanning electron microscopy (SEM) analysis of de-oiled and *in-situ* cake

A scanning electron microscope (Model JSM5910, JEOL, Japan) at the Centralized Resource Laboratory, University of Peshawar was used to capture the micrographs to investigate the microstructural changes that took place in the de-oiled cake and the *in-situ* transesterified cake after the extraction process and compared with the raw powdered seeds.

***In-situ* transesterification energy consumption analysis**

The energy consumption analysis of *in-situ* transesterification of *Salvadora persica* seeds was conducted to find the feasibility of the biodiesel production in Pakistan. The term volume fraction ratio was introduced (Ali and Watson 2014) to take account of the volume used of each process in an attempt to identify the system scalability; this was multiplied with the power consumption of each equipment and its operating time to provide an energy usage; the volume fraction = volume of sample vessel/ volume of the equipment . The seeds were dried in an oven (volume of an oven 32768 cm^3) and for 12 h in a petri dish with volume 95 cm^3 and then dried seeds were ground in a coffee grinder for 1 min. The power consumption of the oven (0.836 kW) and grinder (0.300 kW) were multiplied with their respective operating times to get the kWh and then multiplied with the volume fraction of the oven (2.89 x 10^{-3}); the grinder volume fraction was taken as unity, meaning that the entire volume of the grinder was effectively used. The powdered, sieved seeds were transesterified in a round bottom flask attached to a distillation column on a hot plate magnetic stirrer, the power consumption (0.650 kW) of a hot plate

magnetic stirrer was multiplied with its reaction time (4 h) with volume fraction of 1 assumed. After the reaction, the mixture in a 100 mL beaker was placed in an oven used for solvent evaporation, its power consumption was multiplied with 3 h drying time and volume fraction ($3.05 \times 10^{-3,}$ i.e. 100 /32768. The collected biodiesel (methyl ester) was washed to remove impurities and placed in a 100 mL beaker and oven dried at 105°C for 1 hr. Finally the energy input required was calculated by multiplying the power consumption of the oven by its operating time and volume fraction. The methanol (30 mL) and hexane (5 mL) volume consumption were multiplied by their respective production energies required to produce the solvent per liter i.e. 43.55 MJ/L and 24.71 MJ/L, respectively. The potassium hydroxide (KOH) which was used as a catalyst was not included in the energy input due to its negligible heat capacity (Ali and Watson 2014) and recyclabilty. The total energy demand to produce the *in-situ* biodiesel was calculated by adding up the energy required for each equipment and processes. The total output energy was calculated by adding the biodiesel yield (kg/kg seeds), glycerol yield (kg/kg seeds) and *in-situ* cake (kg/kg seeds) multiplied by their respective HHV's i.e. 41.52 MJ/kg, 19.0 MJ/kg and 12.66 MJ/kg respectively. The energy ratio of the *in-situ* biodiesel produced was calculated by dividing the total energy output by the total energy input of the process.

RESULTS AND DISCUSSION

Oil, biodiesel and glycerol yield

The extracted oil, de-oiled cake, biodiesel, glycerol and *in-situ* cake yields are shown in **Figure 1** as (mean ± standard deviation, n=3). The figure shows that around 0.918 g/ 5 g powdered seeds i.e. around 18 % oil yield (w/w) was achieved, which is lower than the oil yield

mentioned in the literature (40-45 % by w/w) (Reddy, Shah and Patolia 2008). However, the lower oil yield might be due to the climatic conditions of the country and the quality of soil with different compositions of minerals and nutrients having direct impact on the plant growth and seed quality. The biodiesel yield was found to be around 1.57 ± 0.35; glycerol 0.053 ± 0.01 and the *in-situ* residual cake recovered was 3.42 ± 0.079 g/5 g powdered seeds respectively.

Fatty acid compositional analysis

Figure 2 shows the fatty acid profile of the extracted *Salvadora persica* oil showing different peaks of fatty acids detected at different retention time intervals. **Table 2** depicts the presence of major fatty acids in the range C8-C22 in the sample and is in agreement with published work (Marriod, Matthaus and Hussein 2009; Kaul, et al. 2007). However, the presence of major saturated fatty acids such as C12 (lauric acid), C14 (myristic acid), C16 (palmitic acid) and C18 (stearic acid) were observed, with a total content of around 64.44 % as compared 30.43% area occupied by the mono and poly unsaturated fatty acids such as: C16:1 (palmitoleic acid), C18:1 (oleic acid), C18:2 (linoleic acid) and C18:3 (linolenic acid), which are the most common unsaturated fatty acids present in vegetable seed oils (Ali and Watson 2014).

Physical and chemical properties of *Salvadora persica* oil and biodiesel produced

The measured physical and chemical properties of the *Salvadora persica* oil and biodiesel are depicted in **Table 3**. The density and the specific gravity of the extracted *Salvadora persica* oil were 0.916 and 0.920 g/mL respectively, while for the *in-situ* biodiesel were measured as 0.894 and 0.898 g/mL. The density of the oil was found comparable to that of sunflower seed

oil, while its biodiesel density is equal to rapeseed biodiesel (0.894 g/mL) which looks compatible and complies with the ATSM D 6751 standard (Demirbas 2008).

The ester content was 97.77 %, as determined from the percentage of methyl ester of fatty acids present in the *in-situ* biodiesel sample, which is above the minimum permissible limit prescribed by the European biodiesel standard EN-14214 (i.e. 96.5 %). The kinematic viscosity of the extracted oil and the biodiesel produced were measured as 30.70 and 5.51 mm^2/sec. The kinematic viscosity of the biodiesel was within the permissible range of ASTM D 6751 standard and it can be used in compression ignition engines without making any complication in the atomization and spray formation with fuel injection systems.

The flash points of the extracted oil and *in-situ* biodiesel were 210.49 and 178.50^o C respectively. The flash point of the biodiesel value is close to rapeseed oil biodiesel (Demirbas 2008) and it is therefore advantageous in terms of safer handling and fuel storage. The higher heating value of the extracted oil, biodiesel, glycerol and *in-situ* cake recovered were 39.48 and 35.26, 16.57 and 15.92 MJ/kg respectively. The higher heating value of the *in-situ* biodiesel was low compared to petroleum diesel fuel (45 MJ/kg); however, it is higher than the minimum value quoted in the European biodiesel standard EN-14214 (i.e. 35 MJ/kg).

The oleic acid concentration was 1.67 %, while the acid value of the extracted oil was measured at 3.35 mg/g KOH, lower than *Jatropha curcas* (5.31 mg/g KOH), while slightly higher than *Salvadora oleoides* (2.53 mg/g KOH) (Kaul, et al. 2007). *J. curcas* oil with its higher free fatty acid content needs two steps i.e. esterification and transesterification to convert it into its methyl ester (biodiesel). But in the present investigation for the *S. persica* oil with lower free fatty acid content than *J. curcas oil*, needs only single step transesterification reaction.

The cetane number is an indicator of the fuel's ignition quality and a higher value helps the engine to start up quickly due to the shorter ignition delay. The *in-situ* biodiesel cetane number was 61, which is much higher than the minimum value (35) required in the EN-14214 standard. Ash content is an important parameter directly affecting the higher heating value of the fuel, due to the presence of certain amount of metals and other inorganic elements. In the present study, the ash content of the oil by weight % was 0.003, which is comparable to the value quoted by other researchers (Kaul, et al. 2007). The iodine value is a measure of the unsaturated fatty acid double bonds (C = C) present in the oil and it was calculated to be 36.09 g I_2/100g and the saponification value was calculated as 229.28 mg KOH/ g.

Salvadora persica oil contains sulphur (0.18 % in the current case), at higher concentrations than other seed crops; while its biodiesel produced via *in-situ* transesterification had 1200 ppm of total sulphur present compared to less than 1 ppm in Jatropha and Pongamia biodiesel fuels (Kaul, et al. 2007). Another research study (Sultana, et al. 2016) showed that the biodiesel could emit lower SOx upon combustion in diesel engines if the sulphur content is within the permissible limit of the standard (ASTM D 6751). The work showed that the percentage of sulphur in welted thistle oil biodiesel was very low (0.0112 % wt) compared to the specification limit (0.05 % wt) for environmental air pollution benefits.

However, the sulphur content present in the *in-situ Salvadora* biodiesel produced was measured at 844.16 ppm, which is higher than the conventional petroleum derived diesel (500 ppm), which is a major drawback for this feedstock. The weight loss due to corrosive effects on diesel engine parts in *Salvadora* biodiesel is ten times higher than that from biodiesel from *J. curcas* oil (Kaul, et al. 2007). The *salvadora* biodiesel showed remarkable corrosive effects on engine piston metal and piston liner parts because of the high sulphur content, as compared to

e.g. *Pongamia* (karanja) with no corrosive effects (Hua , et al. 2012). The higher sulphur content is a major drawback for *Salvadora* biodiesel production which also pollutes the air creating acid rain issues due to the formation of oxides of sulphur in the atmosphere. Remedial measures to reduce the extraction of sulphur containing compounds from the *salvadora* oil seeds are mechanical expeller extraction, which leaves the sulphur containing compounds in the de-oiled residual cake after pressing as compared to organic solvent extraction which leads to a higher sulphur content in the oils (He, Gerpen and Thompson 2009). Vacuum distillation is also used to separate the methyl esters (biodiesel) from sulphur species where the light end sulphur species, H_2S and SO_2, will flash out of the liquid phase. In petroleum industries, hydro-desulfurization or HDS technologies are used to remove sulphur from the petroleum crude oil. Simply described, hydrogen is added to a Co-Mo or Ni-Mo charged catalytic column at high temperature and pressure, liberating the sulphur as hydrogen sulphide (H_2S) (Privitera and Borgese 2005).

Scanning electron microscopy analysis

Scanning electron microscopy was conducted to capture images of the seeds during different stages of processing investigate the physical changes on the surface of de-oiled cake and *in-situ* transesterified cake due to solvent extraction and heating as compared to the raw powdered seeds. **Figure 3**, shows the scanning electron micrographs of three samples, (a) raw seeds without any treatment which were found to have smooth surfaces, (b) the de-oiled cake which showed wrinkled and shrunken seeds with few ruptures due to the solvent extraction with addition heat treatment and (c) after *in-situ* transesterification, where the *in-situ* residual cake showed a high degree of perforation (tiny pores) and many ruptures were visible on the surface compared to the de-oiled cake.

Thermal analysis of biodiesel produced

Thermogravimetric analysis of the *S. persica* biodiesel was conducted to investigate its thermal behavior and variation in weight loss versus temperature resulting in vapourization of volatiles, degradation, decomposition, oxidation (in an oxygen atmosphere) and pyrolysis (in an inert atmosphere of nitrogen) of the methyl ester sample (Misutsu, et al. 2015). Thermal analysis of the biodiesel produced showed onset (at which the weight loss begins) and offset (the point at which the weight is consistent and there will be no change in weight) temperatures as 150 ^{o}C and 400^{o} C respectively. During the first step negligible weight loss was observed due to evaporation of volatiles, degradation and attributed to the boiling point of biodiesel (Rashid, et al. 2010). However, in the second step as shown in **Figure 4,** approximately 2.5 % weight loss at 50.8^{o} C was observed, while the weight loss starts to increase rapidly due to both degradation and decomposition at 162^{o} C with 18.6 % weight loss, this increases to 90% at 365^{o} C. The third step, attributed to the combustion and oxidation of the biodiesel, occurred at 595.3^{o} C, where a total of 97 % weight loss was observed. The curve remains relatively flat after 460^{o} C showing no further change taking place in the composition of the methyl ester sample, attributed to vaporization and pyrolysis in an inert nitrogen atmosphere due to the presence of methyl oleate and methyl linoleate. The TGA curve shows three steps (degradation, decomposition and oxidation) of the fuel and its negative first derivative of biodiesel decomposition suggests that the overall process is following first order kinetics reaction as mentioned in previous studies (Dwivedi and Sharma 2016; Jain and Sharma 2012). The derivative of the weight loss percentage as a function of temperature (**Figure 5)** shows initially that the biodiesel sample weight loss was higher i.e. 5.33 % weight loss at 130^{o} C, while with increasing temperature, due to decomposition and degradation, it was found to be only 0.54 % at 316^{o} C.

In-situ transesterification energy consumption and mass performance analysis

The energy balance of the *in-situ* biodiesel produced in the laboratory was 0.46 % (**Table 4**). Although it is a positive value it is very low compared to other research work (Ali and Watson 2014). The input energy value was 4.6 MJ for a batch scale transesterification which considered seed grinding, drying, hot plate magnetic stirring, oven drying and methanol, hexane, potassium and hydroxide consumption, while the output value was only 0.021 MJ, which included the HHV from each component, i.e. biodiesel, glycerol and cake yields. But it seems that the low oil yield extracted (~18% w/w) and conversion into biodiesel during the reaction is the major factor that needs to be addressed in future by optimising variables such as reaction time, mixing speed and temperature to find the most optimum conditions; this optimization was not part of this current study. Futhermore, e.g. solar thermal energy can be utilized for drying operations and solvent recovery by distillation during the production, reducing the energy expenditure and favourably increasing the energy balance.

CONCLUSION

Indigenous *Salvadora persica* seed oil was converted successfully into biodiesel by *in-situ* transesterification meeting the international biodiesel standard (ASTM D6751). The oil extraction and biodiesel production yields were found to be 0.918 g/5g powdered seeds (18 % oil yield by weight) and 1.57 g/5g (31.4 % methyl ester yield by weight) powdered seeds respectively. The *S. persica* oil contains C10-C18 fatty acids, which is a good indicator for successful biodiesel production. The single step *in-situ* transesterification (conversion of vegetable oil into biodiesel) produced an ester content of ~ 98 %. In this study the sulphur content present in the *Salvadora persica* biodiesel was measured as 844.16 ppm (i.e. 0.084 %

wt), which may cause corrosion of internal metal components of an engine. It is recommended to investigate in future mitigation measures to reduce sulphur in *Salvadora persica* biodiesel by using genetically modified crops with low sulphur content or oil extraction by a mechanical expeller, which leaves the sulphur containing compounds in the de-oiled residual cake after pressing. The SEM analysis showed the microstructure on the surface of the *in-situ* cake (with many tiny pores and ruptures) as compared to the raw powdered seeds and the de-oiled cake. The thermal behaviour of the biodiesel produced reflects its potential for its fuel use, such as oxidation and decomposition (instability). The major weight loss was found between 162 to 395^{o} C, with 18.6 to 90 percent respectively. Furthermore, the maximum total weight loss of 97 % was achieved at 595^{o} C, with complete oxidation of the biodiesel. The low energy balance is likely due to the lower yield of biodiesel produced and no account taken of solvent recovery. Of course it can be improved by subsequent increase in biodiesel yield, reducing heat energy losses, maximizing the amount of solvent recovery for recycling and using solar energy in drying operations during the biodiesel production.

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