Biodiesel Production Through Base Catalyzed Transesterification of Peach (*Prunus persica* L.) Kernel Oil

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Abstract

The peach (*Prunus persica* L.) is related to the Rosaceae family. It may occur in temperate regions and subtropical climates across the world. In terms of output and planted area, it is the second-largest stone fruit in Pakistan, trailing only apricot. The peach kernel is a high-oil source that is not edible. Its biodiesel-producing properties can be commercially utilized. Peach kernel crude oil was extracted using n-hexane and contained 29.36%. Physical extraction yielded 32.43 % crude oil extracted from peach kernels. The moisture content in peach kernels was 4.24 %. The main parameters that influence biodiesel yield include the molar ratio, the moisture and water content, the temperature of the reaction, and the reaction interval, among others. The oil has an acid rate of 1.53, a catalogue temperature of 1.47 at 30 degrees Celsius, and a definite magnitude of 0.91 at 30 degrees Celsius. The most abundant fatty acid was oleic acid (63.7%), followed by linoleic acid (26.0%). Biodiesel was made with the help of peach oil by trans-esterifying it with methanol in the presence of a base (KOH) catalyst. Vital biodiesel fuel parameters, such as thickness, flash point, specific gravity, and so on, were calculated and associated with ASTM standards. The fuel characteristics of biodiesel are equivalent to those of fossil diesel. This study supports biodiesel generation from peach kernel oil as a viable substitute for diesel production. Additional stability is needed to make biodiesel at the lowest possible price.

Keywords: Base catalyst; Crude oil; Peach kernel; Rosaceae, Transesterification

1. Introduction:

Biodiesel is a possible answer for the current situation due to the paucity of energy supplies (Ahmad *et al.,* 2007). Developing countries, such as Pakistan, want more energy to support rapid economic expansion and to lessen reliance on imported crude oil and gas; therefore, producing ethanol and biodiesel from indigenous sources is preferable. Recently, the use of eatable vegetable oils for biodiesel manufacture has been concerning since they conflict with food materials. So, one cost-cutting alternative is to create biodiesel from leftover fats and oils (Refaat *et al.,* 2008). Biodiesel made from plant seeds or other plant components, such as flowers, is easy to use, recyclable, non-hazardous, and devoid of sulphur and aromatics. These biodiesel qualities are so compelling that development has begun in both industrialized and underdeveloped nations like Pakistan (Karmee &

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Chadha, 2005). It has no effect on the side-by-side ratio of CO_2 in the air (Barnwal & Sharma, 2005). Transesterification of triglycerides present in oil is a common method for producing biodiesel, and it has advantages over pyrolysis, dilution, and micro-emulsion formation as a result of its high conversion productivity and low rate (Pedro et al., 2014). Transesterification is the primary step in the production of biodiesel, with trans-esterification aiming to complete organic reactions in which an ester is changed into another (Fig. 1). This is an orderly process, and the alteration takes place primarily by combining two reactants. The existence of a catalyst quickens the process; additional alcohol is needed to gain a great return on product (Otera, 1993).

The transformation happens by combining two reagents in an equilibrium reaction. The activated carbon (a strong acid or base) speeds up the reaction, and an excess of alcohol is required to achieve a high product yield (Otera, 1993). Catalysts of similar or dissimilar character are utilized, and the reaction is used to match their efficacy. The NaOH, KOH, HCl, H_2SO_4, and HNO_3 are utilized as liquid-phase catalysts (Hattori, 2004). Metals, organometallics, alteration metal complexes, solid origins, and inorganic compounds such as SiO_2, Al_2O_3, ZrO_2, TiO_2, and alkaline earth metal oxides can all be employed as heterogeneous catalysts (Salvi & Panwar, 2012; Umdu *et al.,* 2012; Borges *et al.,* 2011; Castro *et al.,* 2011; Alonso *et al.,* 2010). Even under moderate settings, basic catalysts favour faster reaction rates (Marciniuk *et al.,* 2010). Furthermore, because they have the benefit of rescue and recycling, they open up a new field of search for the best-suited basic heterogeneous catalyst (Bazi *et al.,* 2006). Triacylglyceride is the primary ingredient used to make biodiesel. In addition to triacylglycerides, oils and fats include a variety of additional compounds, such as free fatty acids. It is thus better to examine the chemistry involved in transe-sterification and the effect of catalysis on substrates using pure esters (Castro *et al.,* 2011).

Peach (*Prunus persica*) is a Rosaceae plant that blooms in the spring. Peaches are a prominent summer fruit crop. It may be found in temperate and subtropical climates across the world. Peach is the next most significant stone fruit in Pakistan, after apricot, with a cultivated area of 15,657 hectares and a yield of 94,490 metric tonnes (Anonymous, 2010). Punjab domain pays 5,000 tonnes, 57,800 tonnes in KPK and Balochistan 25,400 tonnes for areas of 1000, 6200, and 9500 ha., respectively. Peaches are grown in Muree, Attock, Peshawer, Khushab, Mingora, Swat, North Waziristan, Hazara, Quetta, Chitral, Loralai, Pishin, Qilla Abdullah, Mastung, Kalat, and Qilla Saifullah in Pakistan. The Box-Behnken experimental design was used to explore the primary parameters that drive

biodiesel alteration from vegetable oil using the reaction surface approach (RSM) (triglycerides) (Anonymous, 2010). The model yields and trial outcomes revealed that this technique may be used to optimize biodiesel synthesis from beauty leaf oil in an industrial process (Jahirul *et al.,* 2014).

1.1. Objectives:

- To assess the effectiveness of nominated non-eatable oil seed of peach plant.
- To explore in biodiesel construction, associate the assets of produced biodiesel, and optimize biodiesel making from peach oil.

2. Materials and Methods:

2.1. Collection of Peach Kernels:

Peach kernels were gathered from the canteen, the University of Gujrat, and Food Street Lahore, as well as some seeds from a peer group.

2.2. Solvent:

After being collected, the seeds were dried for two weeks in direct sunlight before being crushed with a gun and pestle. Oil was extracted using the Soxhlet technique (AOCS, 1997), and n-hexane was utilized as the solvent (Umer & Farooq, 2008) (Fig: 2). The following equations were used to compute the percentage of oil (Mebrahtu, 2014).

Contents of Oil = Weight of extracted oil (g) / Weight of desired samples (g) × 100 %

2.3. Physical Extraction:

Physical extraction was done through an electric oil expeller.

2.4. Moisture Content:

The peach seed kernels were oven dried at 100 °C to determine humidity, then cooled in desiccators, and water content was calculated using the procedure (Mebrahtu, 2014).

M= W1-W2/W1 × 100 %

2.5. Physico-Chemical Properties of Oils:

Initial experiments were carried out to characterize the biochemical and mechanical

characteristics of oil and biodiesel using AOCS standard procedures (1997).

2.6. Physical Parameters:

Physical oil properties like density and specific gravity were determined using the AOCS standard technique, and the refractive index was determined using an Abbe's refractometer. The flash and fire points of oil were established using ASTM standards.

2.7. Chemical Parameters:

Chemical characteristics like Acid, Peroxide, and saponification value by standard methods (AOCS, 1997). Preparation of potassium and sodium methoxide solutions, the essential quantity of alcohol was calculated and placed in a 100-ml beaker. A measured number of tablets was added to the alcohol and agitated for 30 minutes to liquify all of the catalyst. Wrap the beakers with aluminum foil to prevent alcohol loss due to dehydration.

2.7.1. Biodiesel Preparation:

To eliminate any air and water, the stored oil was warmed to 110–120°C. The oil was air-conditioned to a temperature of 55°C. The catalyst-alcohol combination was transported to a three-neck round-bottom bottle with a thermometer and a condenser holding hot oil (Fig. 3). At this point, the reaction begins, and the heated oil aids it. The mixture was agitated with a magnetic stirrer at 500 rpm for 60 minutes, while the oil-to-methanol ratio (1:6) was maintained (Fig. 2).

2.7.2. Biodiesel Spilt-up from Derivatives:

To evaporate the surplus alcohol, the reaction mixture was left in open air and allowed to settle overnight. Whereas soap and glycerol were formed as byproducts of the process, three discernible layers of soap, methyl or ethyl ester, and glycerol were seen. A separating funnel was used to split the layers.

2.8. Purification and Drying Process of Biodiesel:

Warm water was used to clean the biodiesel. The ester phase was put in a separate funnel and gently covered with warm water from the funnel's top. The water and biodiesel layers were separated using this separating funnel. The rinsing process was done multiple times until the biodiesel was clear. To dry the biodiesel, anhydrous sodium sulphate was used. The biodiesel was then purified with Whatman filter paper.

2.9. Variable Optimization of Biodiesel Production:

For optimal biodiesel yield, parameters such as oil to methanol percentage (1:4, 1:6, and 1:8), temperature (55, 65, and 75 °C), catalyst KOH (0.5, 1.0, and 1.5%), and reaction time (60, 80, and 120 min) were investigated. ASTM 2003 was used to establish the fuel and ignition points.

2.10. The Flash, Fire, Flow and Haze Point:

The ASTM flash and fire point equipment from Cleveland was utilized to get the flash and fire point. The cup was loaded to the fill mark with biodiesel, a thermometer was placed inside, and the contraption was supported by a flame. The temperature goes up by 1 to 2 °C for every 1 °C increase in temperature. Flow point and haze were assessed using the cloud and pour point gadgets based on established procedures, ASTM D2500 and ASTM D97, correspondingly (ASTM, 2003).

2.11. Ash and Calorie/ High Heating Rate Content:

The ash content was determined using the ASTM D874 technique, and the percentage ash content was calculated using the formula below.

Ash percentage= (Bulk of residue /Weight of sample) × 100

Demirbas (2009) provided the higher heating value relationship, which was utilized to determine the higher heating values of samples using the standard technique ASTM D4868 (ASTM, 2003).

$$HHV = 0.6154 VS + 38.998$$

Where VS indicates the density of biodiesel

2.12. Density, Specific Gravity, and Refractive Index:

The density (mass per unit volume) and specific gravity of biodiesel samples vary with temperature and were determined using a specific gravity bottle based on the ASTM standard procedure.

2.13. Kinematic Viscosity:

Immerse the spindle of the viscometer into the sample. Allow the spindle to rotate, then stop the motor and note the dial reading. Calculate the viscosity with the help of the spindle factor (given in the manual).

2.14. Carbon Residue:

Weigh required amount of sample in crucible. Place the crucible in carbon residue apparatus and cover the apparatus. Heat with strong flame until blue flame appears. Ignite these vapours with flame. Then heat the apparatus for 7-8 mins. Remove the burner and allow the apparatus to cool. Take out crucible and weigh it to find the carbon residue.

2.15. Gas Chromatography:

The methyl ester content (Knothe, 2001) was evaluated using GLC with N_2 gas as the mobile phase after esterification. PEG was used as the stationary phase (polyethylene glycol). The beginning temperature of the column was 180°C, and the ultimate temperature was 210°C, with a temperature programmed rate of 3°C/min. The injector temperature was 230°C, while the sensor temperature was 260°C. FID was the detector's name. Peaks were detected by comparing the residence fatty acids 'time and their oil methyl esters to standards. The information was computed as a weight percentage of fatty acids.

3. Results:

3.1. Characterization of Oil:

The peach with acid value of 1.53 mg KOH/g. The current study calculated the saponification value to be 168.75 mg KOH/g. The *Prunus persica* oil has a specific gravity of 0.9108 at 30 °C. The refractive index at 30 °C was 1.468. Oil has flash and fire points of 147 and 162°C, respectively (Table 1).

Table 1: The Peach Kernel Oil Properties Used in Biodiesel Production

S. No	Observed Properties	Oil of Peach Kernel
1.	Specific gravity at 30°C	0.9108
2.	Acid value at mg KOH/g	1.532
3.	Refractive index at 30°C	1.468
4.	Peroxide value at meq/kg	6.50
5.	Saponification at mg KOH/g	168.75
6.	Fire point (°C)	162
7.	Flash point (°C)	147

Biodiesel production was 27.02 and 24.12 g/g when alkaline catalysts KOH and NaOH were used under optimal circumstances. The greatest yield (1%) was obtained from potassium methoxide. Under ideal circumstances, biodiesel production from alcohol types CH_3OH and C_2H_5OH was 27.02 and 24.60 g/g, respectively (Fig. 1). Alkaline transesterification created FAMEs. The oil or alcohol molar ratio (1:4, 1:6, and 1:8), catalyst/oil mass ratio (0.5, 1.0, and 1.5 wt %), reaction duration (60, 80, and 120 min), and reaction temperature (55, 65, and 75°C) were all tuned (55, 65 and 75°C) and1:6 had the greatest yield. The greatest yield was obtained after 60 min of reaction time (Fig. 2).
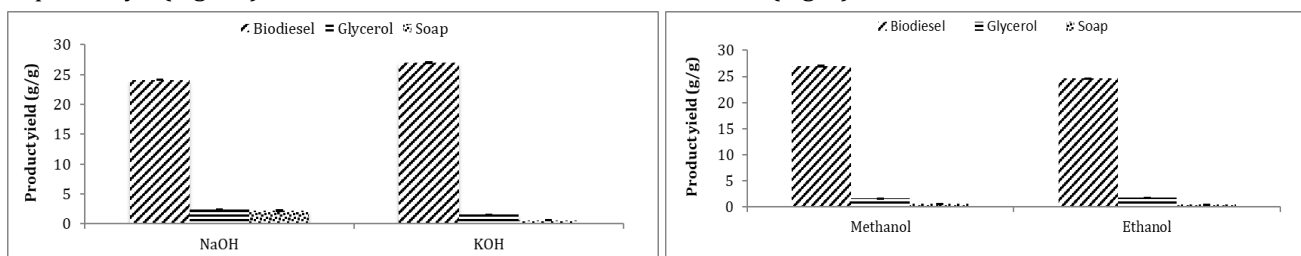

Figure 1: Assessment of Alkaline Catalyst and Alcohol Influence on Product Yield of Peach Oil
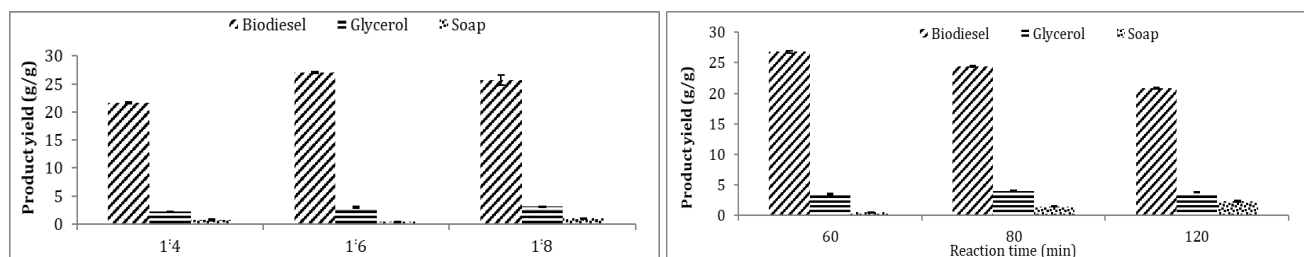
Figure 2: Influence of Oil / Methanol Molar Ratio and Influence of Reaction Time on Product Yield of Peach Oil.

At 55°C, the highest yield of 90% was attained. Odin *et al.* (2013) discovered that as the reaction temperature increased, the percentage of Quassia oil converted to biodiesel increased. The maximum temperature was 60°C. The conversion rate decreased at or above the methanol boiling point (65°C). Perhaps it is because methanol heats at this temperature, causing evaporation and, eventually, solvent loss, decreasing the conversion of oil to biodiesel. The 1.0% catalyst produced the most biodiesel (Fig. 3).
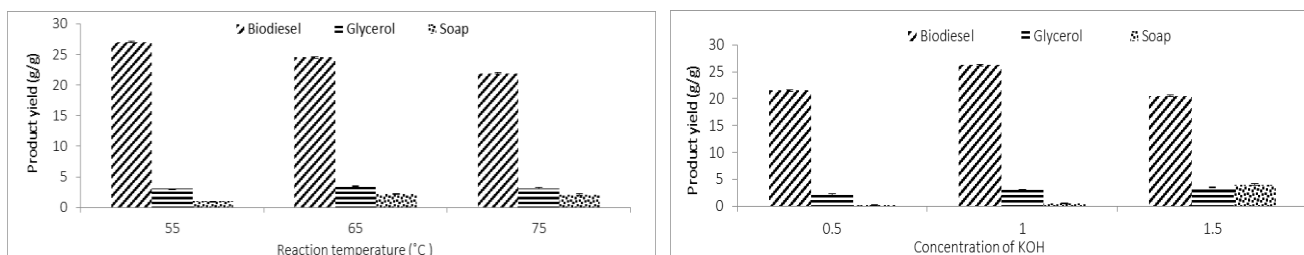

Figure 3: Influence of Temperature and Catalyst (KOH) % on Product Return of Peach Oil.

3.2. Fuel Properties:

Biodiesel fuel characteristics were evaluated and related to ASTM biodiesel standards (D6751) (Table 2). A biodiesel's primary class standard is density. Biodiesel made from peach kernel oil has a density of 0.874. The definite gravity of the biodiesel generated from peach oil in the recent study was 0.887. The ASTM specification for biodiesel-specific gravity specifications is 0.87–0.90. The cloud point and pour point of the peach kernel oil biodiesel generated in this study were -10°C and -18°C, respectively. There is no identified boundary for cloud point and pour point in the ASTM standard (D 6751), however, it is a significant fuel feature. The flash point of biodiesel made from peach oil was 112 °C. The flash point of biodiesel is better than that of diesel fuel (Ali *et al.,* 1995). Peach kernel oil's researched fire point is 119°C. The shade of the peach kernel oil biodiesel created has a 0.5 range. Biodiesel generated by base-catalysed trans-esterification of peach kernel oil meets the ASTM D6751 specifications.

Table 2: Fuel Properties of Peach Oil Biodiesel Compared to ASTM Standards

S. No.	Fuel properties	Testing Procedure	ASTM Biodiesel Standards 6751	Biodiesel
1.	P1	ASTM-D2500	---------	-10
2.	P2	ASTM-D97	---------	-18
3.	P3	ASTM-D93	Min. 130	112
4.	P4	ASTM-D93	----------	119
5.	P5	ASTM-D1298	---------	0.874
6.	P6	ASTM-D1298	0.87-0.90	0.887
7.	P7	ASTM-D874	Max. 0.02	0.025
8.	P8	ASTM-D445	1.9–6.0	5.3925
9.	P9	ASTM-D974	Max.0.5	0.009
10.	P10	ASTM-D976	48 – 65	46

11.	P11	ASTM-D95	0.05	0.025
12.	P12	ASTM-D240	--------	44.6
13.	P13	Visual	---------	Yellowish
14.	P14	ASTM-D1500	0.5-1.5	0.5
15.	P15	ASTM-D189	Max. 0.05	0.06
16.	P16	ASTM-6751	--------------	1.456

Key: P1 = cloud point (°C), P2 = pour point (°C), P3 = flash point (°C), P4 = fire point (°C), P5= Density, P6 = specific gravity (30°C), P7 = ash content, % Wt., P8 = Kinematic viscosity at 400C, mm2/s, P9 = acid value (mg KOH/g), P10 = cetane index, P11 = Water content (%) Vol. P12 = Calorific value (MJ/kg), P13 = Appearance, P14 = Color, ASTM, P15 = Conradson Carbon, P16 = % Wt

The cetane number of a fuel has a direct relationship with its capacity to ignite. The ASTM D6751 minimum cetane index is 48 - 65. The cetane index of the generated kernel oil biodiesel was 46. This cetane index was rather similar to ASTM D6751. The energy released during full combustion helps determine the competency of biodiesel to be used as a substitute for fossil fuels. A fuel's calorific value is the amount of heat produced by its burning. The calorific values for peach kernel oil biodiesel were 44.6 in the current study (ASTM 240). The ash content of a fuel represents its inorganic pollutants. The ash concentration of the biodiesel studied in this study was 0.025. The ash content average boundary established by ASTM D6751 for biodiesel is 0.02 maximum, and the ash relaxed value of biodiesel was demonstrated to be within the approved limits. Biodiesel's refractive index of peach oil was 1.456. The high carbon residue of biodiesel may cause engines to produce heavy smoke (Rao and Gopalkrishnan, 1991). The carbon residue level of biodiesel produced during the present study was 0.06%, which is in accordance with the ASTM documented level of no more than 0.05. Viscosity has a remarkable influence on the mechanism of spray atomization of fuel (Adinew, 2014). Trans-esterification is a common method for reducing viscosity. The viscosity estimated in the present study (5.3925) falls within the prescribed range of the ASTM D6751 standard (1.9–6.0) mm2/s for biodiesel. Acid value determines the free fatty acids of fuel (Adinew, 2014). The acid value of the present study was 0.009 mg KOH/g, which links with the ASTM D6751 standards. The water content of the present study was 0.025, within the prescribed value of ASTM D6751 standards.

3.3. Gas Chromatographic Analysis:

The fatty acid profile (%) was obtained using gas chromatographic analysis. Biodiesel is a combination of C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3, and C20:0. Oleic (63.7%) was the richest fatty acid, followed by linoleic (26.0%).

4. Discussion:

In literature it is noted that KOH provided the highest ester production for the methanolysis of *P. pinnata* oil and used frying oil, respectively (Dorado *et al.,* 2004; Encinar *et al.,* 1999). However, according to Umer and Farooq (2008), $NaOCH_3$ produced the highest levels of esters.

Triglycerides are trans-esterified with low-molecular-weight alcohols such as methanol and ethanol to form fatty acid alkyl esters (FAAE) (Sharma *et al.,* 2009; Demirbas *et al.,* 2009; Demirbas *et al.,* 2011). Methanol is recommended as it is inexpensive and readily available (Leung *et al.,* 2010). In trans-esterification, an excess of catalyst creates surplus soap over time, reducing yield (Chinmoy *et al.,* 2009). The results of this research are consistent with those of Umera and Farooq, (2008). The oil/methanol stoichiometric ratio (1:3) produced the lowest conversion (Fig. 3). Higher methanol concentrations (over 1:6) had adverse impacts, as seen by reduced yields as the molar ratio increased from 1:6 to 1:18. Esters split up from glycerol develop difficulties at molar ratios of oil/methanol above 1:6 (Umer & Farooq, 2008). This study found results that were consistent with Kang and Wang's, (2013) conclusions that esterification is an equilibrium reaction, and that prolonged reaction time causes a drop in product yield, resulting in a loss of esters and the conversion of additional fatty acids to soap (Kang & Wang, 2013). Our findings are similar to those of Hossain and Mazen, (2010), who investigated biodiesel income at various concentrations of NaOH as an example catalyst and found that a 1.0% NaOH concentration produced the highest output. According to Dorado *et al.* (2004), trans-esterification processes catalysed by too much alkaline catalyst may reduce biodiesel output. It is most likely caused by the development of undesirable soap (Ma *et al.,* 1999; Zhang *et al.,* 2003). It might be because the world's weather conditions differ significantly, affecting the demands of biodiesel consumers in a certain location (Umer & Farooq, 2008). The flash point of a fuel is the temperature at which a fuel is essentially heated to ignite a combination of vapours and air above the fuel (Ullah *et*

al., 2009). Lazos, (1991) reported the fatty acid profile (%) of peach kernel oil. The dominant fatty acid was oleic (69.0%), followed by linoleic (22.0%). Lower concentrations revealed hints of C12:0, C14:0, C14:1, C15:0, C15:1, C16:0, C16:1, C17:0, C17:1, C18:0, C18:3, C20:0, and C20:1. The result of the present study is rather comparable to that proposed by Lazos, (1991).

5. Conclusion:

It was concluded that the properties of peach biodiesel showed very similar relationships to those of fossil diesels and that it could be used efficiently in diesel engines. This research work also relates back to the creation of peach kernel oil-containing biodiesel, which might be utilized as a substitute fuel after being blended. The sample was submitted to the Attock oil refinery in Rawalpindi for analysis of different parameters, which included calorific value, cetane index, appearance, colour, and Conradson carbon. Gas chromatography was performed at the PCSIR in Lahore*.*

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