OPTIMIZATION OF BIODIESEL PRODUCTION THROUGH BASE-CATALYZED METHANOLYSIS OF CANTALOUPE SEED OIL

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ABSTRACT: Biodiesel represents a suitable alternative to the petroleum-derived diesel fuel as it is renewable and can be used directly in compression-ignition engines. Present work was aimed at extraction of cantaloupe seed oil and its application to the production of biodiesel through base-catalyzed transesterification using four different basic catalysts viz. NaOH, $NaOCH_3$, KOH and $KOCH_3$. The percent yield of biodiesel afforded by these catalysts was 94.5, 88.0, 85.5 and 89.5%, respectively. The results indicated that NaOH was the best catalyst for transesterification of cantaloupe seed oil. Further, optimization of the process variable, including methanol to oil mole ratio, reaction temperature and amount of catalyst (NaOH) was carried out. The optimum levels of these variables that afforded maximum biodiesel yield were found to be 6:1 molar ratio of methanol to oil, 60 ^{o}C reaction temperature and one percent wt/wt catalyst loading. From the results obtained in this study,it was concluded that cantaloupe seed oil can be successfully utilized for the production of biodiesel as a cost-effective feedstock.

Key words: Transesterification, biodiesel, cantaloupe seed oil, catalyst and optimization.

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INTRODUCTION

Oil and natural gas are the main sources of energy which provide mobility and power for comfortable living as well as the development of any country. In modern era, the economy of a country is totally depended on the availability of cheap fuel; hence fuel demand is increasing constantly throughout the world. Rapid and constant depletion of conventional energy reserves as well as growing environmental concerns regarding pollution have diverted the focus of research towards the development of alternate energy sources for the last many years. Biodiesel represents one of such alternate forms of fuel as it can be used directly as a substitute of petroleum-derived diesel fuel in compression ignition engines (Demirbus, 2009). Major advantages of biodiesel over petroleum-based diesel include its biodegradability, renewability, lower sulphur contents, higher flash point, lower exhaust emissions like NO_x and particulate matter. However, its major drawback lies in its comparatively higher price depending upon the source of oil/s employed for its production, as most of the commercial biodiesel is prepared from food-grade edible oils presently (Singh and Singh, 2010; Demirbus, 2009).

Pakistan being a developing country has to import crude oils for industries, power generation as well as transportation. No doubt, the country is producing fossil oil but its exploration is 60,000 barrel/day which does not meet its domestic requirements. For its domestic consumption, Pakistan has to import crude oil which is continuously increasing with the passage of time. In 2005-2006, State Bank Pakistan paid $6.7 billion for oil imports (Khan and el-Dessouky, 2009). According to bioengineering resources, energy (power and transportation) demand may increase by 50-53% by 2030 (Anonymous, 2008). Recently, auto industry and power sector in Pakistan is growing with an increase of 25% per annum which will expand in future requiring more fuel. To mitigate energy crises, the country has its own natural coal resources but production of energy through coal is not feasible due to production of oxides of Sulphur hence not recommended as such (Khan and el Dessouky, 2009). This is of utmost importance for oil-importing countries, like Pakistan, China, Italy and the United Kingdom, which import both edible oils as well as mineral oil/petroleum products to meet their domestic needs (Demirbus, 2009). A large number of vegetable oils have been explored for production of biodiesel so far including both edible and nonedible ones, with a few sources explored extensively viz. soybean, palm, rapeseed, sunflower, cotton seed, rubber seed, rice bran etc. As clear, most of these feedstocks are edible oils and their utilization for the production of biodiesel will put a stress on their food chain supply. This situation necessitates the exploration of new and nonedible feedstocks for producing biodiesel in an economical way (Moser, 2009; Akhtar *et al*., 2016; 2017). Among the various alternate feedstock options available in Pakistan for the said purpose, availability of biomass resources, that generate agro-waste materials to be disposed of, can be exploited much positively, for example *Melia azedarach* seeds (Akhtar *et al.*, 2016), date seed (Azeem *et al.*, 2016), *Eriobotrya japonica* seeds (Akhtar *et al.*, 2017), etc.

Cantaloupe is the common name given to a variety of *Cucumis melo*, (*Cucumis melo var. cantalopensis*) locally known as 'garma'. *Cucumis melo* is a species of cucurbitaceae family and many of its different varieties are grown in Pakistan, generally known as 'melons' (Nazimuddin and Naqvi, 1982). The fruit is utilized as a rich source of food, while the seeds are usually discarded. After a comprehensive literature survey it was found that cantaloupe has neither been studied before this for its seed-oil characterization nor for the preparation of biodiesel.

The present work was designed to carry out the production of biodiesel through transestrification of cantaloupe seed oil, after solvent extraction.

MATERIALS AND METHODS

Cantaloupe seeds were obtained manually from fresh fruits, washed with clean water and dried in sunlight for three days. Dried seeds were stored in airtight bottles until extraction. All the required chemicals i.e *n*-hexane, methanol, sodium hydroxide, potassium hydroxide, anhydrous magnesium sulphate, sodium methanoate and potassium methanoate were procured from Sigma-Aldrich (St. Louis, Missouri, USA).

Extraction of oil: Dry cantaloupe seeds were grinded, weighed in a clean, dry beaker and subjected to extraction of oil using soxhlet assembly fitted with 500 mL round bottom flask, and *n*-hexane as solvent. The process of extraction was carried out for a period of 6 h, followed by separation of the excess solvent with the help of a rotary evaporator (Rashid *et al.*, 2008).

Physicochemical properties of cantaloupe seed oil: Various physiochemical properties of the extracted oil were examined including density, kinematic viscosity, saponification number, free fatty acid (FFA) value and iodine value using the standard AOCS methods(2002). For determining the fatty acid composition of cantaloupe seed oil, fatty acid methyl esters were prepared by standard IUPAC method 2.301, and analyzed on a SHIMADZU gas chromatograph, model 17-A. It was equipped with a polar capillary column, a flame ionization detector and nitrogen as a carrier gas. The separated fatty acids were identified by comparing their relative retention times with those of standards (Akhtar *et al*., 2017).

Transesterification of cantaloupe seed oil: Initially, the methyl esters of extracted cantaloupe seed oil (CSO) were prepared by transesterification following a standard method of 6:1 methanol to oil molar ratio and 1% wt/wt of sodium methoxide as the methylating agent. The oil was preheated up to the desired temperature prior to addition of alcohol-catalyst mixture. The temperature was maintained at levels given in the experimental matrix. After completion of reaction, the reaction mixture was cooled to room temperature followed by separation of cantaloupe seed oil methyl esters (CSOMEs) from glycerol, a by-product, under gravity using a separating funnel. The upper phase comprised of cantaloupe oil methyl esters that also contained traces of unconverted glycerides and glycerol as well as excess of catalyst and methanol. Maximum quantity of methanol was recovered at 65 $^{\circ}$C by distillation, while excess catalyst and contaminants were removed by repeated washing of methyl esters with warm water. The washed product was then dried with anhydrous magnesium sulphate, filtered and stored in air-tight sample bottles. However, keeping in view that this variety of *Cucumis melo* i.e, cantaloupe has not been reported earlier for the preparation of biodiesel, four different homogeneous basic catalysts were reported in literature that furnish maximum yield of biodiesel were also studied, along with three other experimental variables. Various experiments were carried out for finding an optimum set of conditions resulting in maximum biodiesel yield, varying one-factor-at-time reported by (Rashid *et al.*, 2008a). The reaction time and stirring rate were kept constant at 2 h and 600 rpm, respectively, during the whole series of experiments.

RESULTS AND DISCUSSION

Physiochemical properties of cantaloupe seed oil: The oil content recovered by soxhlet extraction was calculated, as percentage difference between weight of ground seeds and the oil obtained, was 41% which was in agreement to the studies on *Cucumis melo* seed oil by (Fokuo *et al.*, 2009). It appeared to be clear and golden yellow in color. The density and kinematic viscosity was found to be 0.888 g/mL and 34.1 cSt, respectively. Free fatty acid (FFA) contents were calculated to be 0.87 in the fresh oil sample that predicted its suitability for a single-step base-catalyzed transesterification in order to prepare biodiesel. Saponification number was found to be 195 mg KOH/g oil and resembled that of honeydew melon (210 mg KOH/g oil) which was also a variety of *Cucumis melo* found by (Yanty *et al.*, 2008). The fatty acid composition, as determined by gas chromatography is given in Table-1, showed that a brief proportion of saturated fatty acids (12%) was found in cantaloupe seed oil along with a larger proportion of unsaturated fatty acids (87.8%). Out of this, 25% was contributed by monounsaturated fatty acids that was oleic acid ($C_{18:1}$) and 62.8% comprised of two polyunsaturated fatty acids viz. linoleic acid ($C_{18:2}$) which was found in largest proportion (56%) and linolenic acid ($C_{18:3}$) that was present up to 6.8%. The composition of fatty acids in cantaloupe seed oil was found to resemble that of *Cucumis melo var. inodorus* that was reported to contain 8.4, 4.6, 16.8, 69.0 percent traces of palmitic, stearic, oleic, linoleic and linolenic acids, respectively. The difference in fatty acid composition of the cantaloupe seed oil and the *Cucumis melo var. inodorus* may be attributed to the varying agro-climatic conditions (Moser, 2009)

Table 1. Physiochemical properties of cantaloupe seed oil.

Properties		Values
Density (g/mL) @ 20 ^oC		0.888
Kinematic viscosity (cSt) @ 20 ^oC		34.1
Saponification value (mg KOH/ g Oil)		195
% FFA		0.87
Iodine value (I_2 g/100 g Oil)		130
Fatty acids (%):		
Cucumis melo var. cantaloupensis	*Cucumis melo var. cantaloupensis*	*Cucumis melo var. inodorus**
$C_{16:0}$	10.0	8.4
$C_{18:0}$	2.0	4.6
$C_{18:1}$	25	16.8
$C_{18:2}$	56	69.0
$C_{18:3}$	6.8	Traces
Saturated fatty acid	12.0	13.0
Unsaturated fatty acids:	87.8	77.0
Monounsaturated	25	16.8
Polyunsaturated	62.8	69.0

* (Yanty *et al.*, 2008)

Optimization of conversion of cantaloupe seed oil into biodiesel: Experimental matrix showing different levels of experimental variables have been studied with the aim to find optimum experimental conditions for maximum conversion of cantaloupe seed oil to its methyl esters (CSOMEs) i.e., biodiesel **(**Table-2). Although different type of catalysts i.e., alkalis, acids, or enzymes including NaOH, KOH, sulphuric acid, sulfonic acids, hydrochloric acid and lipases were in use for transesterification of oils; amongst them, alkali was considered to be the more favorable catalyst than acidic catalyst being less corrosive than the acidic catalysts as well as had higher yield of the biodiesel (Khan and El Dessouky, 2009; Ma and Hanna, 1999). In an experiment, four different catalysts (alkali) were studied, using same conditions of all the experimental variables including methanol to oil molar ratio, reaction time and catalyst amount which resulted in maximum amount of biodiesel production with NaOH as a catalyst.

Effect of catalyst type: Four alkali catalysts including NaOH, $KOCH_3$, $NaOCH_3$ and KOH were used for transesterification of the oil under same conditions of other variables i.e, 6:1 molar ratio of alcohol to oil, 60 ^oC temperature and 1 % wt/wt catalyst. It was clear from the CSOMEs yields, that NaOH showed maximum catalytic activity for transesterification the cantaloupe oil had 94.5 % yield, followed by $KOCH_3$, $NaOCH_3$ and KOH as 89.5, 88 and 85.5 % yield, respectively **(**Fig-2**)**. As maximum yield was obtained by NaOH; further experiments were conducted using NaOH as catalyst, varying only one parameter at a time.

Effect of alcohol to oil molar ratio: Alcohol to oil molar ratio affected the biodiesel yield most significantly as reducing the ratio to 3:1 decreased the biodiesel yield by 29 % almost. This was due to the fact that transesterification was an equilibrium reaction that takes place in three steps, as is shown in (Fig-1). According to this equation, three moles of alcohol and one mole of triglyceride were required to react stoichiometrically in order to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, in order to shift

Table 2. Mean cantaloupe seed oil methyl esters (CSOMEs) yield in base-catalyzed transesterification of cantaloupe seed oil under different set of conditions.

Experiment #	Catalyst	Catalyst amount (% wt/wt)	MeOH : oil (moles)	Reaction temperature (^oC)	CSOMEs yield* (%)
1	KOH	1.00	6:1	60	85.5±0.11
2	$KOCH_3$	1.00	6:1	60	89.5±0.12
3	NaOH	1.00	6:1	60	94.5±0.10
4	$NaOCH_3$	1.00	6:1	60	88.0±0.09
5	NaOH	1.00	3:1	60	65.4±0.10
6	NaOH	1.00	9:1	60	93.5±0.13
7	NaOH	0.75	6:1	60	90.6±0.12
8	NaOH	0.5	6:1	60	70.4±0.11
9	NaOH	1.00	6:1	50	92.5±0.14
10	NaOH	1.00	6:1	45	91.8±0.12

*****values given as average for three replicates ± standard deviation

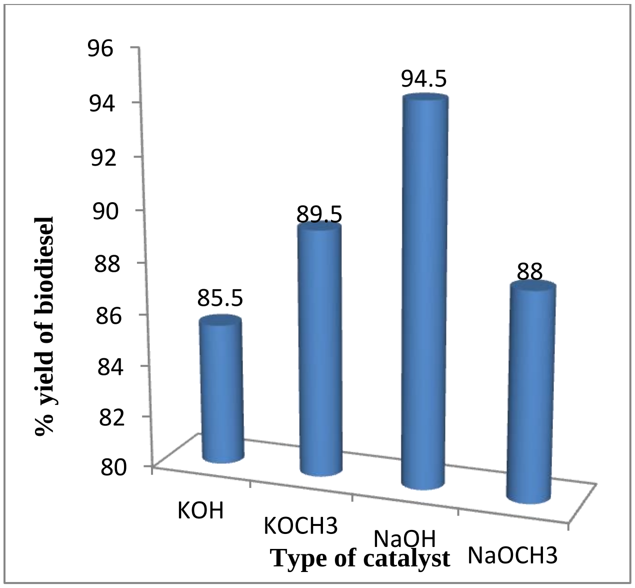

Figure 2: %age yield of biodiesel demonstrating the effect of catalyst type, under same experimental variables (Methanol to oil molar ratio of 6:1, catalyst amount of 1 % wt/wt, reaction temperature of 60 ^{o}C, reaction time of 2 h and stirring speed of 600 rpm)

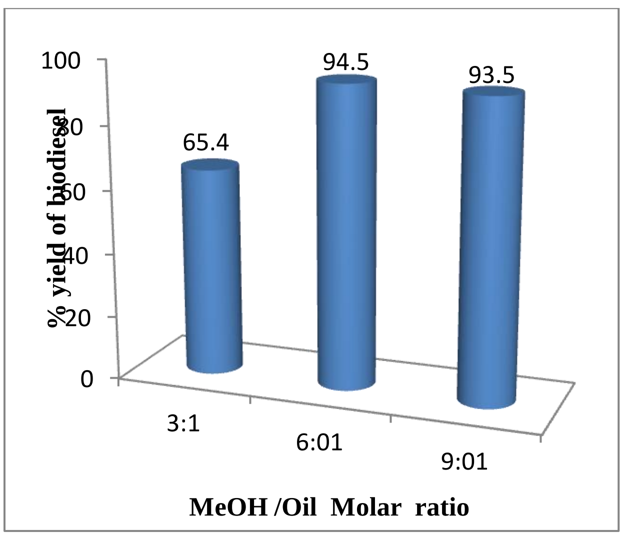

Figure 3: %age yield of biodiesel demonstrating the effect of Methanol to oil molar ratio, under same experimental variables (catalyst amount of 1 % wt/wt, reaction temperature of 60 ^{o}C, reaction time of 2 h and stirring speed of 600 rpm)

the reaction towards product side, an excess amount of alcohol was favorable. The results obtained by this reaction were in line with the work done by (Freedman *et al*., 1984) that the ratio of alcohol to oil beyond 6:1 did not increase the yield of biodiesel. Due to this reason, the remaining two factors i.e, catalyst amount and reaction temperature were studied using this molar ratio.

Effect of catalyst amount: In a study it was reported that amount of catalyst played a vital role in the production of biodiesel (Tariq *et al*., 2012). The catalyst amount at various levels has been experimented varying from 0.5 to 1 % wt/wt of feedstock (oil). The amount of catalyst below 0.75 % wt/wt was found to exert detrimental effects on biodiesel yield while increasing it upto 1 % wt/wt resulted in slightly better yield. The percentage yield of biodiesel at different catalyst amounts is shown in Fig-4.

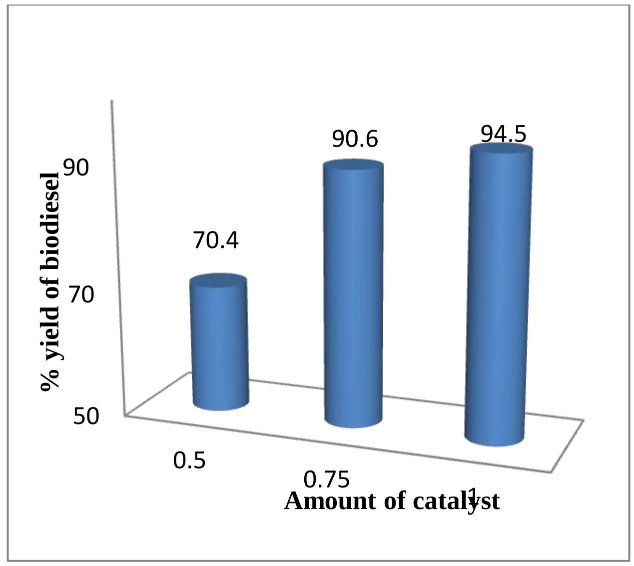

Figure 4. %age yield of biodiesel demonstrating the effect of catalyst amount, under same other experimental variables (Methanol to oil molar ratio of 6:1, reaction temperature of 60 ^{o}C, reaction time of 2 h and stirring speed of 600 rpm)

Effect of temperature: Although transesterification could take place even at an ambient temperature, however, increase in reaction temperature resulted in better yield and shorter reaction time (Moser, 2009). Hence, the reaction was carried out at three different temperatures i.e 45 ^{o}C, 50 ^{o}C and 60 ^{o}C while keeping all other factors constant like methanol to oil molar ratio at 6:1, catalyst amount at 1 %wt/wt, and stirring speed and reaction time as mentioned earlier. Although percentage yield of biodiesel was observed to increase slightly from 45 ^{o}C to 50 ^{o}C , however, at 60 ^{o}C it was increased quite significantly, as is shown in Fig-5. The studies carried out earlier on effect of temperature also supported the present results, that beyond 60 ^{o}C there was no significant increase in the percentage yield of biodiesel by (Hoque *et al*., 2011).

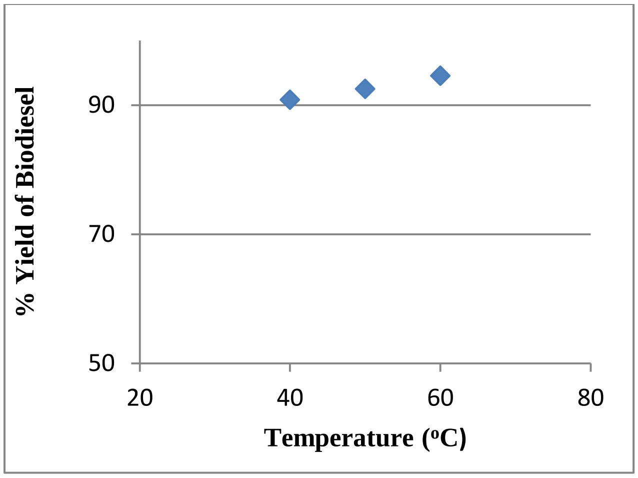

Figure 5: %age yield of biodiesel demonstrating the effect of reaction temperature, under same other experimental variables (Methanol to oil molar ratio of 6:1, catalyst amount of 1 % wt/wt, reaction time of 2 h and stirring speed of 600 rpm)

Conclusion: The present study is an effort to convert waste biomass i.e, cantaloupe seeds, into a value-added product i.e.; biodiesel. 95.6% biodiesel was produced successfully from cantaloupe seed oil after optimization of process variables.

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