Production of Biodiesel by Ultrasonic-Assisted Methanolysis of Cantaloupe Seed Oil and its Optimization by Taguchi Method

Taslim Akhtar, Muhammad Ilyas Tariq, Shahid Iqbal*, Nargis Sultana
Muhammad Ahmad and Kim Wei Chan
[1]*Department of Chemistry, University of Sargodha, Sargodha, 40100, Pakistan,*
[2]*Laboratory of Molecular Biomedicine, Institute of Bioscience, University Putra Malaysia, UPM Serdang Selangor Malaysia.*
shahidiqbalrana@uos.edu.pk*

(Received on 24th February 2017, accepted in revised form 28th December 2017)

Summary: Present work is an effort of an agrowaste valorization, whereby the cantaloupe seed residue has been proposed as a potential feedstock for biodiesel production. Oil, from dried cantaloupe seeds, was extracted using *n*-hexane as extraction solvent in three batches. Oil content was found to be 42.8% (w/w) of seed residue. Physicochemical characteristics of oil including density (0.887 g/mL), kinematic viscosity (34.5 cSt), refractive index (1.48), free fatty acid content (0.78%), iodine value (128 g I_2/100 g oil) and saponification value (220 mg NaOH/g), were determined using standard IUPAC methods. Fatty acid composition of both oil/ biodiesel was determined by GC-FID and confirmed by ^{1}H NMR spectra of methyl esters. Ultrasonic-assisted transesterification of cantaloupe seed oil was carried out using KOH as catalyst and optimization of process parameters was done using Taguchi method. Optimized parameters included molar ratio of alcohol to oil (9:1), amount of catalyst (1% w/w of oil) and reaction time (60 min). Major fuel properties of synthesized biodiesel including cetane index, flash point, cloud point, pour point, density, kinematic viscosity, total ash and distillation range were determined according to standard ASTM methods. The values were found to be within ASTM D6751 specifications for biodiesel. On the basis of findings of this study, cantaloupe seed oil may be ranked as a viable feedstock for biodiesel production.

Key words: Cantaloupe, Transesterification, Biodiesel feedstock, Agrowaste utilization.

Introduction

In recent years, consumption of fossil fuels for automobiles and power generation has increased exponentially owing to the rapidly increasing global population. This has led to depletion of natural reserves of these fuels as well as proportional increase in environmental pollution [1-2]. An outcome of this situation is the search for alternate energy sources, which may replace the fossil fuels in future partially or completely. Biodiesel (BD), a first-generation biofuel, is found to be a suitable alternative of petrodiesel and may be employed without any modification in existing compression-ignition engines. Synthesis of BD is carried out by transesterifying vegetable oils or animal fats with short-chain alcohols catalyzed by an acid, a base or an enzyme. BD has number of technical benefits over petrodiesel; as it is renewable, non-toxic, biodegradable, and holds comparatively higher oxygen and lower sulphur contents than that of petrodiesel; offering reduced emission of different pollutants like particulate matter, carbon monoxide, and sulphur dioxide [3-4]. Fuel characteristics of BD e.g. density, viscosity, flash point, and cetane index are found comparable or even better in some cases in comparison to petrodiesel [5].

A number of potential BD resources have been successfully explored from vegetable oils, animal fats and yellow grease; amongst which the vegetable oils have been found to be the most promising due to their abundant global availability. Feedstocks impart major share in production cost of BD [6]. Moreover, most of the vegetable oil sources used for synthesis of biodiesel (soybean, canola, and palm) is edible ones and their application for BD production, on industrial scale, has raised serious concerns about security of food items [7-9]. All these feedstocks do not suffice to fully replace the total volume of petrodiesel; as clear from the fact that annual global consumption of petroleum is upto 4.018 billion tons in comparison to vegetable oil production of 0.107 billion tons. In this scenario, search for some inedible feedstocks, preferably from agrowastes, is becoming increasingly important worldwide that would lessen the strain on edible oilseed crops as well as to improve the production of BD [5]. This is of importance for oil-importing countries like Pakistan, China, Italy and United Kingdom, which import both edible oils as well as mineral oils/petroleum products to meet their needs [10]. Though, more than 350 oil-bearing plant species have been investigated to explore their potential for

---

[*] To whom all correspondence should be addressed.

the synthesis of biodiesel, but very few are found to be the potential feedstocks like *Melia azedarach* [11, 12], *Eriobotrya japonica* [13], *Jatropha curcas, Azardirachta indica, Pongamia pinnata, Moringa oleifera,* rubber seed, neem, silk cotton tree, tall oil and microalgae [1]. These are considered potential feedstocks, as these are available in developing countries and are far more economical as compared to edible oil sources [1, 10].

Cucurbitaceae is a large family containing 120 genera and 825 species, out of which 17 genera and 32 species are found in Pakistan [14]. Different species of this family, especially cucumis and citrullus, commonly called melons, are grown as major food crops in various subtropical and tropical areas of the world [15]. Various studies have shown that many species of the cucurbitaceae family contain quite a large amount of oil in their seeds [16, 17]. *Cucumis melo* var. *cantalopensis* generally known as "cantaloupe", is a variety of Cucumis *melo*. It belongs to cucurbitaceae family and is one of the various melons grown in many areas of Pakistan for their fruits, while their seeds are usually discarded [11].

Cantaloupe is a large-sized oval shaped fruit with a large number of seeds present in the hollow center. Seeds of various melon varieties contain oil, proteins and carbohydrates [12, 14, 18]. Also, the melon seeds have been found to be medicinally important for curing diabetes and chronic eczema. Generally, seeds of various species of cucurbitaceae family are recognized to contain large quantities of oil, which are medicinally helpful for the prevention of some heart diseases [19]. Some of these have been investigated for the preparation of BD as well, like melon [20], *Cucurbita pepo* [21, 22], cantaloupe [23], and *Citrullus colocynth* [24] etc.

Pakistan is an agricultural country and various oilseed crops are cultivated here. However, only a small number of oilseed plants are exploited for the extraction of oil for both edible and inedible purposes. The total consumption of vegetable oils is 27.73 million metric tons (MMT), while the production of various vegetable oils is approximately 6.86 MMT, leaving behind a shortage of 20.87 MMT. Consequently, a huge amount of foreign exchange is to be spent for the import of edible oil or oilseeds from other countries in addition to that required for mineral oil import. It is need of the hour that non-conventional oilseed plants must be explored to evaluate their potential as alternate edible oil source as well as production of biofuels, *i.e.*, biodiesel. This will certainly reduce the volume of oil import and hence saving valuable foreign exchange [25].

To the best of our knowledge, no comprehensive report regarding characterization of cantaloupe seed oil has been presented yet, although a huge area is under cultivation for the production of different varieties of melons worldwide. The present work was carried out to assess the fatty acid composition as well as physiochemical characteristics of oil from cantaloupe seeds in order to establish its suitability as a feedstock option for biodiesel production. Also, a comparison of its fatty acid composition and fuel properties has been done with those of soybean oil and rapeseed oil to verify the said application. Ultrasonic-assisted transesterification of cantaloupe seed oil was attempted and optimization of the process parameters was done using Taguchi method. Utilization of waste cantaloupe seeds, as a BD feedstock, has been done from a residue valorization standpoint. Conversion of such an agro-waste into an added value product will not only contribute to a decrease in such residual by-products but also will be of great economic interest.

Experimental

Materials and Reagents

Cantaloupe seeds were procured from local market, washed with clean water, dried in an oven at 100 ^{o}C and stored in dry, airtight jars before analyses. All the chemicals and reagents (*n*-hexane, methanol, potassium hydroxide, sodium hydroxide, anhydrous magnesium sulphate, sodium thiosulphate, and potassium iodide) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and were used without further purification. All the chemicals were of analytical grade except methanol that was of HPLC grade.

Extraction of Cantaloupe seed oil

Dried cantaloupe seeds were ground with an IKA® all basic mill (IKA Works Inc. Wilmington, USA). For the extraction of oil, ground seeds were subjected to Soxhlet apparatus fitted with a 1 L round bottom flask using *n*-hexane as solvent. The extraction was carried out at the boiling point of solvent in three batches; each of 1.5 h duration using 600 mL of solvent. Freshly ground seeds were used in first batch; while in second and third batches, respective seed residue, were re-subjected to extraction using fresh solvent. After which, solvent containing oil from all the three batches was combined and solvent was separated under vacuum using a rotary evaporator (Laborota 4001, Heidolph, Germany) at 48 ^{o}C to obtain the crude cantaloupe seed oil.

Evaluation of General Properties

State as well as color of cantaloupe seed oil (CSO) was examined visually at room temperature [26,27]. General physical and chemical properties were evaluated that included density (by pycnometer) using the standard IUPAC method 2.101, kinematic viscosity following ASTM method D445, while iodine value (Wij's method), refractive index (Abbe's refractometer), free fatty acid content (FFA %) and saponification number were determined following standard AOCS methods Cd 1-25, Cc 7-25, Ca 5a-40 and Cd 3-25, respectively.

Determination of Fatty Acid Profile

For the preparation of fatty acid methyl esters (FAMEs) of CSO, standard IUPAC method 2.301 was followed [28] and these FAMEs were studied on a SHIMADZU gas chromatograph, model 17-A. It was fitted with a SP-2330 (SUPELCO Inc. Supelco Park Bellefonte, PA, 16823-0048, USA) polar capillary column (30 m × 0.32 mm), coated with methyl lingoserate (having a thickness of 0.25 μm) and a flame ionization detector. Nitrogen served as carrier gas with a flow rate of 0.5 mL min^{-1}. Initial column oven temperature was 180 ^{o}C with a ramp rate of 5 ^{o}C to a final temperature of 235 ^{o}C, while the temperature of injector and detector were maintained at 235 ^{o}C and 250 ^{o}C, respectively. Sample volume injected into the system was 1.5 μL. Identification of FAMEs was done by comparison of their absolute and relative retention times with those of standards (Sigma, St. Louis, MO, USA; 99% purity specific for 168 GLC). Quantification was accomplished using a data-handling program, Chromatography Station for Windows (CSW32). Further confirmation of fatty acid composition was done by ^{1}H NMR spectroscopy, that was performed on a digital NMR spectrometer Avance series, Bruker (Switzerland), operating at 300 MHz, using $CDCl_3$ as solvent.

Production of Biodiesel

Ultrasonic-assisted transesterification of cantaloupe seed oil was carried out using an ultrasonic water bath (ThermoScientific) operated at 35 KHz. Methyl esters of cantaloupe seed oil were prepared with the help of sodium hydroxide and methanol in a 250 mL round bottom glass reactor equipped with a condenser. The reaction temperature was maintained at 40 ^{o}C while frequency of ultrasonication was 35 KHz. After completion of reaction, the contents of reactor were transferred to a separating funnel and allowed to stand overnight for separation of methyl esters from glycerol. 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. 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. The bath was filled with 2.5 L of distilled water (up to 1/3 of its volume). Three experimental variables, namely methanol to oil molar ratio, amount of catalyst and reaction time, were studied at three different levels as shown in Table-1.

Table-1: Selected parameters for ultrasonic-assisted transesterification of cantaloupe seed oil and their levels.

Colour	**Light yellow**
Density (g/mL) @ 20 ^{o}C	**0.887**
Kinematic viscosity (cSt) @20^{o}C	**34.5**
Refractive index @30 ^{o}C	**1.48**
%FFA	**0.78**
Iodine value (I_2 g/ 100 g oil)	**128**
Saponification number (mg KOH/g)	**198**

Optimization of ultrasonic-assisted transesterification of cantaloupe seed

Taguchi method presents one of the standard versions of design of experiments (DOE), as developed by Dr. G. Taguchi, which helps us to apply the technique for optimizing product design and investigating production problems. Taguchi method employs orthogonal arrays (OA) for optimizing the influence of various parameters that affect the process and levels to which these may be changed. The OA helps to finalize the number of experiments required and their conditions. The selection of OA type is made on basis of number of parameters and variation levels of each parameter. The least number of experiments (N) is decided from the number of levels (L), number of design and chosen control parameters (P), using the following relationship [29]:

$$N = (L-1)\ P + 1$$

Out of various experimental variables affecting ultrasonic-assisted transesterification process, only three most relevant variables were chosen and three levels were taken into account in this work, i.e. L = 3 and P = 3, as given in Table-1.

Table-2 represents L_9 orthogonal array for DOE with three variables at three levels (3^3) for carrying out a set of nine experiments regarding optimization of ultrasonic-assisted transesterification of cantaloupe seed oil.

Table-2: L9 orthogonal array for DOE with three variables at three levels (3^3) for ultrasonic-assisted transesterification of cantaloupe seed oil.

	Parameters	Levels		
		1	2	3
A	Methanol to oil ratio (in moles)	3:1	6:1	9:1
B	Amount of catalyst (wt. %)	0.5	1	1.5
C	Reaction time (min)	20	40	60

Table 3 Physicochemical characteristics of cantaloupe seed oil

Experiment	Parameters and their levels		
	Methanol to oil ratio (moles)	Amount of catalyst (wt%)	Reaction time (min)
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	2
9	3	3	1

Characterization of Biodiesel

Biodiesel was characterized by evaluating some basic fuel properties following the standard methods of American Society of Testing and Materials (ASTM) D6751. These include ASTM colour, specific gravity, kinematic viscosity, flash point, cloud point, pour point, cetane index and distillation range. ASTM colour was inspected as described in ASTM method D-1500. Specific gravity was determined at 15 °C in accordance with ASTM method D-1293, while kinematic viscosity was obtained at 40 °C by ASTM method D-445. Flash point was measured by Pensky-Marten closed cup-tester according to ASTM method D 93-02a. Cold weather properties (cloud point and pour point) were determined according to ASTM methods D-2500 and D-97, respectively. Cetane index of BD was evaluated by the procedure laid out in ASTM method D-976. The distillation range was determined following the ASTM method D-86. Fatty acid profile was determined by the same procedure as well as conditions described for FAMEs analysis of cantaloupe seed oil.

Results and discussion

Oil characterization

Some fundamental physicochemical characteristics of cantaloupe seed oil are summarized in Table-1. The seeds contain ~ 42.8% (w/w) crude oil that is in agreement with the other studies regarding different varieties of *Cucumis melo* [30]. The difference may be attributed to varying agroclimatic conditions for plant growth [31]. The oil yield was found to be significantly higher than those of commonly used feedstocks for making biodiesel that include soybean (18.3%), palm kernel (44.6%) and sunflower (40.9%) [32] but less than jatropha seed oil; a potential biodiesel source now-a-days [33].

The oil obtained, through solvent extraction, appeared to be clear and light yellow in colour on visual inspection. The density, determined by pycnometer, was 0.887 g/mL at 20 °C, while kinematic viscosity, determined by a viscometer, was found out to be 34.5 cSt @ 20 °C. The refractive index was observed to be 1.48 at 30 °C.

Free fatty acid content of oil was found to be 0.78% that shows its moderate resistance to hydrolysis and is well within the range of % FFA specified by various researchers for the feedstocks to be employed for the production of BD, i.e., 0.5-3% [34-38].

The saponification value represents the mg of KOH that are needed to saponify 1 g of fat/oil, during which the free fatty acids are neutralized. The saponification value for CSO was found to be 198 mg of KOH g^{-1} oil, that is comparable to that of pumpkin seed oil (185-198 mg of KOH g^{-1}) and honeydew melon (210 mg of KOH g^{-1}); both of which are members of family cucurbitaceae [30,39]. The iodine value, which is an estimated level of unsaturation in the oil/fat, was calculated to be 128 g I_2/100 g of oil. This is comparable to the iodine values of melon seed oil (121.8) [20] but higher than pumpkin seed oil (104-107) as reported in literature [21,22].

Fatty acid Composition of Cantaloupe Seed Oil by GC and ^1H NMR

Fatty acid profile of cantaloupe seed oil and derived methyl esters is given in Table-4. Also, the fatty acid composition of soybean and rapeseed oils is given in this Table for comparison [40]. The most remarkable feature of cantaloupe seed oil is presence of ~54.9% linoleic acid ($C_{18:2}$), that constitutes more than 50% of total oil and is very close to its content in soybean oil (55.53%), but much different than rapeseed oil that contains 22.30 % linoleic acid; the two common BD feedstocks. Following this are the oleic, palmitic, linolenic, stearic and arachidic acids that make up 24.7, 9.88, 7.9, 2.1 and 0.02% of the oil, respectively. The total saturated fatty acid content of the oil comes out to be 12%, while monounsaturated and polyunsaturated contents of fatty acids were 24.7% and 62.8%, respectively.

Table 4 Fatty acid profile of cantaloupe seed oil/cantaloupe seed oil methyl esters, soybean and rapeseed oils

Fatty acid (No. of carbon atoms: No. of unsaturated bonds)	Relative proportion of fatty acids (%)		
	CSO/CSOME	Soybean oil[a]	Rapeseed oil[a]
Palmitic acid ($C_{16:0}$)	9.88	11.75	3.49
Stearic acid ($C_{18:0}$)	2.1	3.15	0.85
Oleic acid ($C_{18:1}$	24.7	23.26	64.40
Linoleic acid ($C_{18:2}$)	54.9	55.53	22.30
Linolenic acid ($C_{18:3}$)	7.9	6.31	8.23
Arachidic ($C_{20:0}$)	0.02	-	-
Saturated fatty acids	12	14.9	4.34
Monounsaturated fatty acids	24.7	23.26	64.40
Polyunsaturated fatty acids	62.8	61.84	30.53

[a] Ma and Hanna [40]

Table-5 Percentage yield and SNRs for the experiments designed by L_9 orthogonal array for ultrasonic-assisted transesterification of cantaloupe seed oil

Experiment #	A	B	C	% yield			Mean yield (%)	SNR
				Trial 1	Trial 2	Trial 3		
1	3:1	0.5	20	68.5	69	70.2	69.23	36.80
2	3:1	1.0	40	72.42	73	71.9	72.44	37.20
3	3:1	1.5	60	74.5	73.8	74	74.1	37.39
4	6:1	0.5	40	80.5	81.2	81.5	81.06	38.18
5	6:1	1.0	60	84.2	85.0	84.5	83.57	38.54
6	6:1	1.5	20	80.5	81	80.75	80.75	38.18
7	9:1	0.5	40	92.0	92.5	93	92.5	39.32
8	9:1	1.0	60	94.5	94	93.8	94.1	39.47
9	9:1	1.5	20	92	91.5	92.5	92	39.28
					SNR_T = 38.26			

Additional confirmation of fatty acid composition was obtained by ^1H NMR analysis of the oil as well as its fatty acid methyl esters, as shown in Fig. 1. The presence of C_{18} fatty acids (oleic, linoleic and linolenic) in oil and in their esters was confirmed by the signals at 2.77 ppm, which are a combine measure of triene (linolenate) and diene (linoleate), and those at 2.05 ppm that relate to all these esters. The presence of linolenate in CSO or cantaloupe seed oil methyl esters (CSOMEs) is additionally confirmed by noticeable signals at 0.89 ppm that is used, in routine, to distinguish it (that is n-3 esters) from all other esters. Also, the presence of bis-allylic protons is confirmed by the signals at approximately 2.8 ppm that points out the presence of polyunsaturated fatty acids in CSO/CSOMEs [32,41]. Apart from the confirmation of fatty acid composition of CSO, ^1H NMR spectrum also shows the maximum conversion of triglycerides into fatty acid methyl esters as shown by virtual absence of NMR signals at 4.1-4.3 ppm that are caused by the glycerol moiety of any of the mono-, di-, or triglycerides, and presence of a strong singlet at nearly 3.7 ppm corresponding to the methyl esters.

As clear from the above discussion, fatty acid profile of the cantaloupe seed oil/methyl esters is very much similar to that of soybean oil, especially in terms of the amount of polyunsaturated fatty acids that point out towards the suitability of cantaloupe seed oil as a feedstock for biodiesel synthesis.

Estimation of optimum conditions of process parameters by Taguchi method

Table-5 shows the experimental yields of CSOMEs as a result of ultrasonic-assisted transesterification of cantaloupe seed oil, as well as SNR calculated for each experimental run and their mean. Objective of present work was to sort out the experimental conditions that result in maximum yield of biodiesel, and this required 'larger the better' SNR model to be adopted. As is clear from the data given in Table-5, experiment number 8 shows the maximum yield of CSOMEs up to 94.1 % with a corresponding SNR value of 39.5. The least mean yield (69.23) resulted from experiment number 1 with SNR value up to 36.80. The set of experimental conditions corresponding to highest yield may not be the optimum set of conditions and needs to be confirmed further.

Table-6 represents the SNR_L (level mean SNR) values of each experimental variable for each of its specified level, separately, for ultrasonic-assisted transesterification of cantaloupe seed oil. For instance, the SNR_L for parameter A at level 1 has been computed to be '37.13' using the values of SNR for the experiment No. 1, 2 and 3, at level 2 it is '38.3' using the SNR values from experiment No. 4, 5 and 6, and at level 3 it is '39.36' using SNR values for experiment No. 7, 8 and 9. Similarly, SNR_L values for parameters B and C were also computed. The SNR_L values for each parameter, at its different levels, show its influence on CSOMEs yield. Higher the value of SNR_L, greater the influence of a particular parameter at that level. The optimum level of each parameter corresponds to maximum value of SNR_L that is directly related to maximum yield of CSOMEs. In this way, the optimum levels for parameters A, B and C were 3, 2 and 3, that are methanol to oil ratio of 9:1, catalyst amount of 1 % w/w and reaction time of 60 min, respectively.

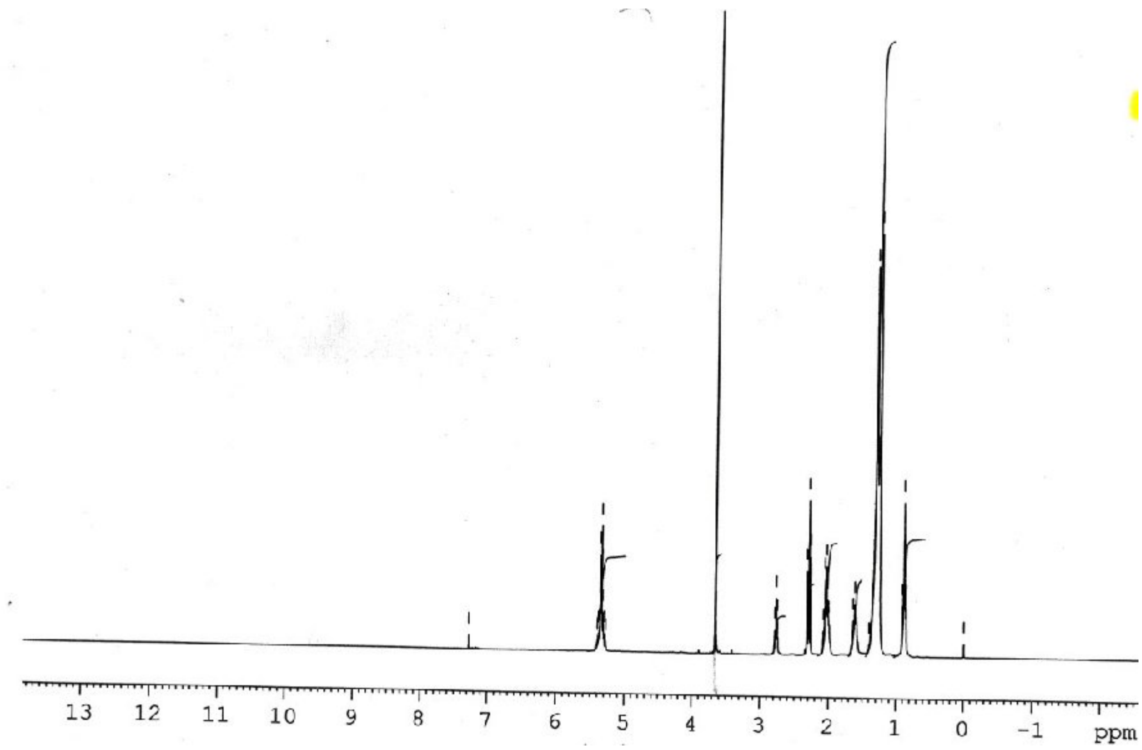

Fig. 1 H^{1}NMR of CSOMEe with characteristic peaks at nearly 3.7ppm corresponding to methyl esters, while the presence of bis-allylic protons is confirmed by the signals at approximately 2.8ppm that point out the presence of polyunsaturated fatty acids.

Table 6 Level mean signal-to-noise ratios (SNR_L) for different parameter levels for ultrasonic-assisted transesterification of cantaloupe seed oil

Parameter	**Levels**		
	1	**2**	**3**
A. Molar ratio of alcohol to oil (in moles)	**37.13**	**38.30**	**39.36**
B. Amount of catalyst (% wt/wt of oil)	**38.10**	**38.40**	**38.28**
C. Reaction time (min)	**38.08**	**38.28**	**38.41**

Analysis of Variance (ANOVA)

Ultrasonic-assisted transesterification of cantaloupe seed oil:

Table-7 represents the computed sum of squares (SS) and % contribution of each process parameter as studied for ultrasonic-assisted transesterification of cantaloupe seed oil. These results are helpful to identify the most significant parameter i.e, the parameter that influences the CSOMEs yield the most. It is clear that methanol to oil molar ratio was the most influential parameter with a contribution as great as 96.0%, followed by the reaction time and catalyst amount with a contribution of 2.14 and 1.76 %, respectively. This little contribution can be correlated to slight variation in SNR_L values for three levels of each of these two parameters, as shown in Fig. 2. In other words, difference between maximum and minimum SNR_L values for a particular parameter (ΔSNR) directly determine % contribution of that parameter towards mean yield of final product i.e, biodiesel. According to ΔSNR calculations, ranks can be assigned to these parameters with the highest rank for the parameter showing largest value of ΔSNR. So, methanol to oil molar ratio comes up to rank 1, followed by the reaction time and catalyst amount, in accordance with the data shown in Tables 6 and 7.

Table-7: Percentage contribution of selected process variables for ultrasonic-assisted transesterification of cantaloupe seed oil

Parameter	**SS_f**	**% contribution**
A. Molar ratio of alcohol to oil	**2.4885**	**96.1**
B. Amount of catalyst	**0.0456**	**1.76**
C. Reaction time	**0.0553**	**2.14**

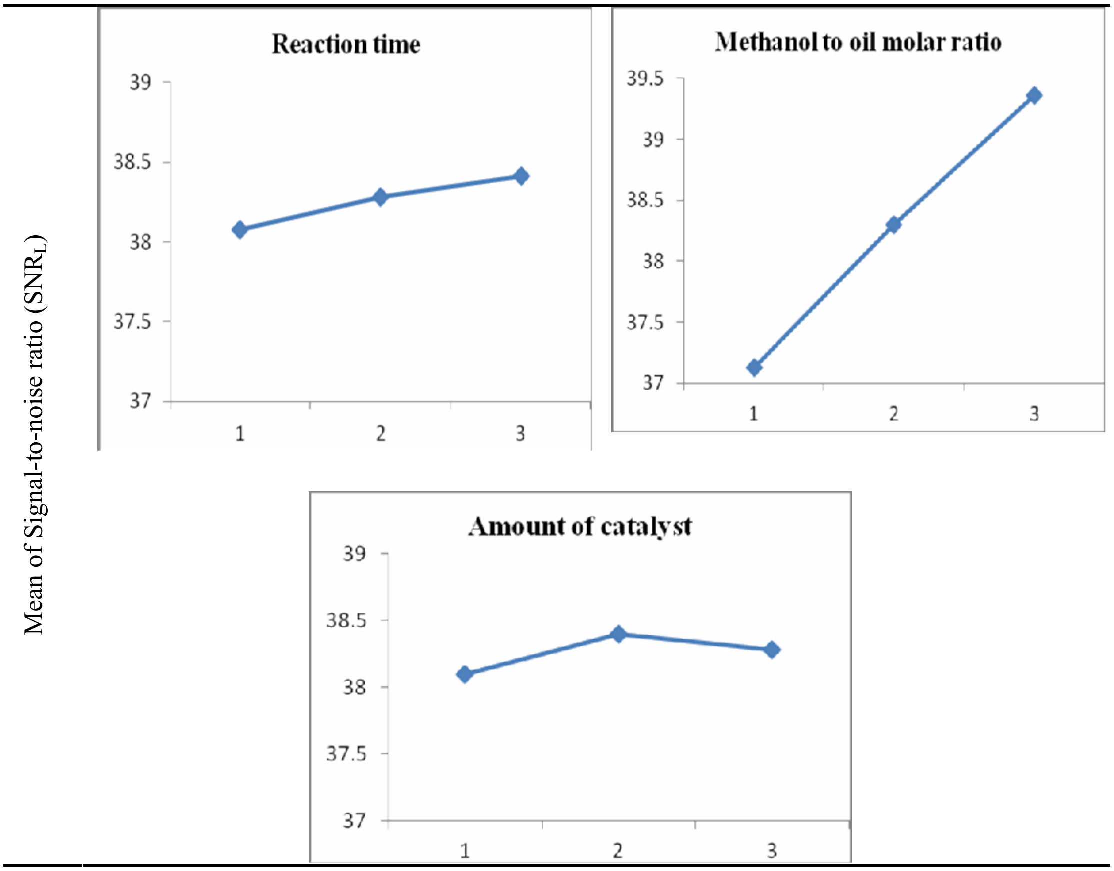

Fig. 2 SNR$_L$ of selected parameters at pre-set levels for ultrasonic-assisted transesterification of cantaloupe seed oil.

Optimum levels of all the parameters were used to find out the percentage yield of CSOMEs, in three replicate trials. The mean % yield of biodiesel was found to be 93.99 % that is quite close to value obtained in experiment number 8.

Fuel properties of CSOMEs

Table-8 represents the basic fuel properties along with ASTM specifications for the given samples.

Table 8: Fuel characteristics of cantaloupe oil methyl esters (CSOMEs).

Property	CSOMEs	ASTM limit	Units
ASTM colour	L 1.5	-	
Density	0.8781		
Kinematic viscosity @ 40°C	3.92	1.9-6.0	mm^2/sec
Water %	0.01	0.05	% vol
Cloud point	-3	Report	°C
Pour point	-6		
Flash point P.N.C.C	120	130min	°C
Cetane index	48.68	47min	-
Cu strip corrosion	1	No. 3max	-
T. Ash % wt.	NIL	0.05max	% wt.
Distillation (90% vol. recovery)	340	360max	°C

As compared to diesel fuel, all the FAMEs have higher density and lower compressibility [42], which are the two very important features since they have an influence on the injection system of engine. Both of these parameters i.e., density and compressibility, affect fuel's injected amount, timing for injection and spray pattern, directly [43]. The density of CSOME was determined to be 0.8781 g/mL that is lower than those of soybean methyl esters (0.884 g/mL) and rapeseed methyl esters (0.882 g/mL), which are the most common biodiesels used in USA and Europe [44].

Injection process is interfered by high values of kinematic viscosity leading to improper atomization of the fuel. Incomplete combustion results from improper mixing of fuel and air. The kinematic viscosity of CSOMEs was found to be 3.92 mm^2/s that is again quite lower than those of soybean and rapeseed oil methyl esters, i.e.4.08 and 4.83 mm^2/s, respectively. The ASTM limit specified for FAMEs to be employed as BD is 1.9-6.0 mm^2/s, and kinematic viscosity of CSOMEs meets the specified limit of this crucial parameter quite satisfactorily.

Two important experimental parameters that determine the tendency of a fuel (BD) to solidify at low temperatures and, hence, its cold weather performance is 'cloud point' (CP) and 'pour point' (PP) [45]. Cold-weather properties of BD are greatly affected by its fatty acid profile [46]. The CP and PP of CSOMEs were found to be -3 °C and -6 °C, respectively. Although no specific value/range is given in ASTM standards for biodiesel but for evaluation of these properties, the values were compared with those of soybean and rapeseed methyl esters. The CP of CSOME was lower, and hence better, than that of soybean methyl esters (-0.5 °C) but higher than that of rapeseed methyl esters (-4 °C). Similarly, PP of CSOMEs was lower than that of soybean methyl esters (-4 °C) but higher than that of rapeseed methyl esters (-10.8 °C).

Cetane number (CN) is a measure of the ignition delay time, which is the time between start of the injection and the onset of the combustion. For biodiesel, ASTM specified limit (minimum) of CN is 47, while CN of CSOMEs was determined to be 48.68. It is well within the required lower limit for BD and is comparable to soybean methyl esters (50.9) and sunflower methyl esters (49).

Flash point (FP) is an important feature of a fuel during its storage and transportation. Usually, FP of the most commonly employed BD feedstocks (soybean, rapeseed and sunflower oils, which are 131, 155 and 183 °C, respectively) is far above than petro-diesel (55 °C). [44]. The FP of CSOMEs, on the other hand, was found to be lower than all of these common BD feedstocks i.e, 120 °C.

The evaluation of total ash content of a fuel product, may suggest its suitability for a given application. In CSOME, negligible ash (%) was found as given in Table-3, showing the absence of above-mentioned materials in it. Similarly, water content was also found to be at trace level (0.01%) that is well within ASTM specifications. Copper strip corrosion test is basically designed to evaluate the relative degree of corrosivity of a fuel product and shows how much wearing of the engine system may occur by that product [47]. The ASTM requirement for Cu strip corrosion is No. 3 max., while it was found to be No. 1 for CSOMEs. The evaluation of distillation (volatility) range of a fuel is important regarding its safety and performance. It provides information about its properties and behavior, while under use or storage [48]. The ASTM maximum limit for the distillation range of BD at 90% recovery of volume is 360 °C, while it was found to be 340 °C for CSOMEs. This value of distillation at 90% recovery is lower and hence better than common BD feedstocks like soybean, sunflower, canola and cottonseed methyl esters (357-359 °C) [49].

Conclusion

Present study deals with the characterization of cantaloupe seed oil in order to evaluate its potential as a biodiesel feedstock as well as optimization of the ultrasonic-assisted transesterification of the cantaloupe seed oil for synthesis of FAMEs, using Taguchi Method. The high oil yield (42.8%) obtained by solvent extraction and good conversion rates (93.99%) are two major supporting factors in this regard. The fatty acid profile of cantaloupe seed oil was found to be quite satisfactory being similar to that of soybean oil, as it also contains the highest proportion of linoleic acid (54.9%). It imparts a major share to low viscosity and hence cold flow properties like pour point and cloud point found to be -6 °C and -3 °C, respectively, as determined for the methyl esters derived from cantaloupe seed oil. This can be attributed to its lowest melting point (-43°C) among the commonly found fatty acids in different vegetable oils. The presence of 24.7% of monounsaturated acids among other fatty acids is another remarkable characteristic of the cantaloupe seed oil as it is considered as the ideal constituent of biodiesel from a fuel quality standpoint. In addition to aforementioned fuel properties, other properties that were determined during the course of this study included cetane number, flash point etc. that also meet the relevant ASTM specifications. The optimum levels for selected parameters were methanol to oil ratio of 9:1, catalyst amount of 1 % w/w and reaction time of 60 min, respectively, that afforded a % age yield of CSOMEs upto 93.99%. In the light of above study, cantaloupe seed oil can be expected to be a viable feedstock for biodiesel production.

References

1. S. P. Singh and D. Singh, Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review, *Renew. Sust. Energ. Rev.* **14**, 200 (2010).
2. A. P. Vyas, J. L. Verma and N. Subrahmanyam, A review on FAME production processes, *Fuel* **89**, (2010).
3. D. Ayhan, *Biodiesel: a realistic fuel alternative for diesel engine*, Springer, London, (2008).
4. G. Knothe, J. V. Gerpen and J. Krahl (eds.). *The biodiesel handbook,* AOCS Press, Champaign, IL (USA), (2005).

5. B. R. Moser, Biodiesel production, properties and feedstocks. *In Vitro Cell. Div. Biol-Plant.* **45**, 229, (2009).
6. P. T. Vasudevan and B. Fu, Environmentally sustainable biofuels: Advances in biodiesel research. *Waste Biomass Valor.* **1**, 47 (2010).
7. N. A. Khan and H. Dessouky, Prospects of biodiesel in Pakistan. *Renew. Sust. Energ. Rev.* **13**, 1576, (2009).
8. D. Pimentel, A. Marklein, M. A. Toth, M. N. Karpoff, G. S. Paul, R. McCormack, J. Kyriazis and T. Krueger, Food versus biofuels: Environmental and economic costs, *Hum. Eco.* **37**, 1 (2009).
9. S. Srinivasan, The food v fuel debate: a nuanced view of incentive structures. *Renew. Energ.* **34**, 950 (2009).
10. A. Demirbus, Progress and recent trends in biodiesel fuels. *Energ. Convers. Manage.* **50**, 14 (2009).
11. T. Akhtar, M. I. Tariq, S. I. Rana, Production of biodiesel from *Melia azedarach* seed oil: a non-edible feedstock for biodiesel. *Sci. Int. (Lahore).* **28**, 3805 (2016).
12. C. E. Stavarache, J. Morris, M. Vinatoru, Y. Maeda, I. Oeyan, Syringa (*Melia azedarach* L.) berries oil: a potential source for biodiesel fuel. *Revista de Chimie*. **59**, 672 (2008).
13. T. Akhtar, M. I. Tariq, S. Iqbal, N. Sultana and C. K. Wei, Production and characterization of biodiesel from *Eriobotrya japonica* seed oil: an optimization study. *Int. J. Green Energ.* **14**, 569 (2017).
14. A. Perveen and M. Qaiser, Pollen flora of Pakistan – LVI. Cucurbitaceae. *Pak. J. Bot.* **40**, 9 (2008).
15. M. B. Mabaleha, Y. C. Mitie and S. O. Yeboah, A comparative study of the properties of selected melon seed oils as potential candidates for development into commercial edible vegetable oils. *J. Am. Oil Chem. Soc.* **84**, 31 (2007).
16. E. Fokou, M. B. Achu, G. Kansci, M. Fotso, C. Tchiegang and F. M. Tchouanguep, Chemical properties of some cucurbitaceae oils from Cameroon. *Pak. J. Nutr.* **8**, 1325 (2009).
17. A. S. Al-Khalifa, Physicochemical characteristics, fatty acid composition, and lipoxygenase activity of crude pumpkin and melon seed oils. *J. Agric. Food Chem.* **44**, 964 (1996).
18. L. Yu, J. W. Parry and K. Zhou, *Oils from herbs, spices and fruit seeds.* In: F. Shahidi (ed) Bailey's industrial oil and fat products. John Wiley and Sons, Inc. UK (2005).
19. S. Sorho, S. Yaya, A. A. Augustin and L. Laurent, Fatty acids and unsaponifiable composition of *Cucumis amaris* seeds oil. *J. Appl. Sci.* **6**, 3167 (2006).
20. P. M. Ejikeme, C. A. C. Egbounu, I. D. Anyaogu and V.C Eze, Fatty acid methyl esters of melon seed oil: characterization for potential diesel fuel application. *Leonardo J. Sci*. **18**, 75 (2011).
21. A. Mariod, S. Klupsch, H. Hussein and B. Ondruschka, Synthesis of alkyl esters from three unconventional Sudanese oils for their use as biodiesel. *Energ. Fuel*, **20**, 2249 (2003).
22. P. Schinas, G. Karavalakis, C. Davaris, G. Anastopoulos, D. Caronis, F. Zannikos, S. Stournas and F. Lois, Pumpkin (*Cucurbita pepo L.*) seed oil as an alternative feedstock for the production of biodiesel in Greece. *Biomass Bioenerg.* **33**, 44 (2009).
23. T. Akhtar, H. Akhtar, M. I. Tariq, S. Iqbal, N. Sultana, M. Ahmed, Optimization of biodiesel production through base-catalyzed methanolysis of cantaloupe seed oil. *Pak. J. Sci.* **69**, 174 (2017).
24. S. Giwa, L. C. Abdullah and N. M. Adam, Investigating "Egusi" (*Citrullus colocynthis L.*) seed oil as potential biodiesel feedstock. *Energies* **3**, 607 (2010).
25. S. Iqbal, S. T. H. Sherazi and M. I. Bhanger, The vegetable oil industry in Pakistan. *Inform* **16**, 526 (2005).
26. M. Zia-ul-haq, M. Ahmad, S. Iqbal, S. Ahmad and H. Ali, Characterization and compositional studies of oil from seeds of desi chickpea (*Cicer arietinum* L.) cultivars grown in Pakistan, *J. Am. Oil Chem. Soc.* **84**, 1143 (2007).
27. P. C. Branco, P. C. Castilho, M. F. Rosa and J. Ferreira, Characterization of *Annona cherimola* Mill. Seed oil from Madeira Island: a possible biodiesel feedstock. *J. Am. Oil Chem. Soc.* **87**, 429 (2010).
28. U. Rashid, F. Anwar, B. R. Moser and G. Knothe, *Moringa oliefera* oil: A possible source of biodiesel. *Bioresour. Technol.* **99**, 8175 (2008).
29. R. S. Kumar, K. Sureshkumar, R. Velraj, Optimization of biodiesel production from *Manilkara zapota* (L.) seed oil using Taguchi method., *Fuel,* **140**, 90 (2015).
30. N. A. M. Yanty, O. M. Lai, A. Osman, K. Long and H. M. Ghazali, Physicochemical properties of *Cucumis melo* var. *inodorus* (honeydew melon) seed and seed oil. *J. Food Lipids*, **15**, 42 (2008).
31. I. A. Nehdi, S. Hassen, C. P. Tan and S. I. Al-Resayes, Garden cress (*Lapidium sativum* Linn.) seed oil as a potential feedstock for biodiesel production. *Bioresour. Technol.* **126**, 193 (2012).

32. F. D. Gunstone, *The chemistry of oils and fats – Sources, composition, properties and uses*, Blackwell publishing, CRC Press, UK, (2004).
33. A. Emil, Z. Yaakob, M. N. S. Kumar, J. M. Jahim and J. Salimon, Comparative evaluation of physicochemical properties of Jatropha seed oil from Malaysia, Indoniesia and Thailand, *J. Am. Oil Chem. Soc.* **87**, 689 (2010).
34. Y. Zhang, M. A. Dube, D. D. McLean and M. Kates, Biodiesel production from waste cooking oil. *Bioresour. Technol*. **89**, 1 (2003).
35. B. Freedman, E. H. Pryde, T. L. Mounts, Variables affecting the yield of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.* **61**, 1683 (1984).
36. A. K. Tiwari, A. Kumar and H. Raheman, Biodiesel production from jatropha oil (Jatropha curcus) with high free fatty acids: an optimized process. *Biomass Bioenerg*. **31**, 569 (2007).
37. P. K. Sahoo, L. M. Das, M. K. G. Babu, S. N. Naik, Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. *Fuel*, **86**, 448 (2007).
38. M. Canakci and J. V. Gerpan, Biodiesel production via acid catalysis. *Trans ASAE*, **42**, 1203 (1999).
39. J. B. Rossell, *Vegetable oils and fats*. In: J. B. Rossell, J. L. R. Pritchard (eds), *Analysis of oilseeds, fats and fatty foods*. Elsevier Applied Science, New York, p261 (1991).
40. F. Ma and M. A. Hanna, Biodiesel production: a review. *Bioresour Technol*, **70**, 1 (1999).
41. G. Knothe, Analytical methods used in the production and fuel quality assessment of biodiesel. *Trans ASAE*, **44**, 193 (2001).
42. M. Canakci and J. V. Gerpen, Comparison of engine performance and emissions for petroleum diesel fuel, yellow grease biodiesel and soybean oil biodiesel. *Trans ASAE*, **46**, 937 (2003).
43. S. Lee, D. Tanaka, J. Kusaka and Y. Daisho, Effects of diesel fuel characteristics on spray and combustion in a diesel engine. *JSAE*, **23**, 407 (2002).
44. M. Canakci and H. Sanli, Biodiesel production from various feedstocks and their effects on the fuel properties. *J Ind Microbiol Biotechnol,* **35**, 431 (2008).
45. C. Y. Choi and R. D. Reitz, A numerical analysis of the emissions characteristics of biodiesel blended fuels. *J Eng Gas Turbines Power*, **121**, 31 (1999).
46. T. A. Foglia, L. A. Nelson, R. O. Dunn and W. M. Marmer, Low-temperature properties of alkyl esters of tallow and grease. *J. Am. Oil Chem. Soc.* **74**, 951 (1997).
47. Annual book of ASTM Standards, vol 05.03.
48. Annual book of ASTM Standards, vol 05.01.
49. A. Alptekin and M. Canakci, Characterization of the key fuel properties of methyl esters-diesel fuel blends. *Fuel*, **88**, 75 (2009).