BIODIESEL PRODUCTION FROM STRAWBERRY POMACE SEED OIL

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Strawberry pomace is the beverage industry waste and should be utilized as circular economy feedstock, animal feed, or a fertilizer following environmental regulations. This work aimed to characterize and implement strawberry pomace oil in the biodiesel industry. Oil was extracted from the strawberry seed by a maceration method for physicochemical characterization. Two seed/solvent ratios were used to achieve the maximum oil yield. The yield of strawberry seed oil by *n*-hexane extraction at the seed/solvent ratio of 1:3 was 0.11 g/g. Extracted strawberry oil was used for biodiesel production by a two-step process that included the acid (H_2SO_4)-catalyzed pre-esterification of strawberry oil, followed by the base (KOH)-catalyzed transesterification of the pre-esterified strawberry oil. Further, the methanolysis ensured a biodiesel content of 97.2% in 30 min. However, the low yield of this technology's final product and physicochemical characterization showed that strawberry oil should be used in a mixture with other oils (hybrid oil) for biodiesel production, or in the cosmetics and food industry.

Keywords: waste, biodiesel, strawberry pomace, seeds.

Introduction

The energy demand for electricity production, transport, and many branches of the industry at the world level is constantly increasing. Most of the energy consumed is obtained from fossil fuels. However, due to limited quantities, high prices, and massive demand for fossil fuels, increasing attention is paid to alternative renewable fuels. Among them, biodiesel, a mixture of alkyl esters of fatty acids (FAs), stands out as the best potential replacement for diesel fuel. Edible, nonedible, waste, used oils, and animal fats with a high triacylglycerol (TAG) content can be used as feedstocks for biodiesel production. Raw vegetable oils are the most commonly used feedstock for the industrial production of biodiesel, but the largest share in biodiesel production costs is the price of vegetable oil, with 60–80% of the total costs. In addition, waste oils from the food processing industry and low-cost used cooking oils from food preparation in the food industry, restaurants, and households are other appropriate oil feedstock. This way, the cheap feedstock is used, and the waste oil disposal problem is solved. However, waste and used cooking oils usually contain a higher content of free fatty acids (FFAs), water and solid impurities, complicating their use in biodiesel production [1]. For example, only the oils having an FFA content of up to about 1% (corresponding to an acid value less than 0.5 mg KOH/g) can be directly transesterified to biodiesel in the presence of a base catalyst [2]. However, the oils with higher acid values must be pre-esterified in the presence of an acid catalyst (usually H_2SO_4) to reduce the FFA content before the base-catalyzed transesterification [3].

According to the Food and Agriculture Organization [4], about 91 million tons of berries, such as strawberries, raspberries, blackberries, currants, blueberries, cranberries, and grapes, were produced worldwide in 2018. However, their processing creates large amounts of waste. Residues after berry fruit processing can be up to 60% of the fruit mass, which is currently used in animal feed production or disposed of in landfills. The latter represents a serious environmental problem that can be reduced or solved by decreasing or processing berries waste into energy or other chemicals for everyday use [5]. For example, berry seeds can be a cheap oily feedstock in biodiesel production.

Strawberry (*Fragaria ananassa*) is adapted to grow in different conditions and climates [6]. According to the Food and Agriculture Organization (FAO) data, almost 9 million tons of strawberries were produced worldwide in 2019. Strawberries are used industrially to obtain the juice, while the pomace (minimum 20%) with oil-rich seeds remains in the residual pomace as waste that can be used as animal feed or secondary raw material [7]. The dry pomace matter comprises about 40% of the

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seed, with an average oil content of 9.8% [6].

So far, the oil has been recovered from strawberry seeds by cold pressing [8–10], solvent [6,11], supercritical CO_2 extraction [12–14], and characterized chemically [8–10,12,14–18]. It is used as a moisturizing and skin-softening agent [17]. Also, as a source of FAs and bioactive compounds, it is tested for health implications on rats [15] and humans [10]. The most abundant FAs in strawberry oil are linoleic (39.5–48.7%), *α*-linolenic (29.0–37.98%) and oleic (14.5–28.5%) acid [8,9,12,13,15]. So far, strawberry oil has not been used as an oily feedstock for biodiesel production.

This study aimed to recover the oil from strawberry pomace by solvent extraction, to characterize it physicochemically, and to use it as a biodiesel feedstock. Also, the physicochemical properties of the obtained biodiesel were characterized. Finally, the material balance of the biodiesel production process from the strawberry pomace was analyzed.

Materials and methods

Materials

All chemicals were of analytical reagent grade quality: *n*-hexane, methanol (HPLC purity; J.T. Baker, Deventer, Netherlands), H_2SO_4 (96%; Lach-Ner, Czech Republic), KOH (Centrochem, Stara Pazova, Serbia), anhydrous Na_2SO_4 (Zorka Pharma, Šabac, Serbia), absolute ethanol (HPLC purity; Panreac AppliChem, Germany), 2-propanol (HPLC grade; Fisher Scientific, UK), ethyl acetate (≥99.5), diethyl ether (≥98.0%; Sigma-Aldrich, USA), acetic acid (99.5%; MosLab, Serbia), and phenolphthalein (Carl Roth GmbH Co KG, Germany).

Methods

Deseeding strawberries pomace

The fruit processing company "Fruvita" d.o.o (Belgrade, Serbia) donated strawberry pomace. It was stored in a freezer until used to slow down the rotting. The strawberry pomace dewatering was in an oven (DRYSC136, COLO, Slovenia) at 105 °C. The pomace moisture and dry matter were calculated from the masses before and after drying from 10 random samples. The dried strawberry pomace was crushed in a porcelain mortar with a pestle and sieved by mechanically shaking sieves (Labdex Ltd, UK). The mean equivalent seed diameter was calculated by Eq. (1):

$$d_e = \frac{1}{\frac{m_{0.63}/m_{seeds}}{0.63} + \frac{m_{0.8}/m_{seeds}}{0.8} + \frac{m_{1.0}/m_{seeds}}{1.0}} \quad \text{.....(1)}$$

where $m_{0.63}$, $m_{0.8}$, and $m_{1.0}$ – the mass of the seed fractions remained by the 0.63, 0.8, and 1.0 mm sieves, respectively, and m_{seeds} – the total mass of seeds.

Strawberry seeds were grounded (e-mill, Alpina 2813, Switzerland) for 1 min before the further extraction step.

Strawberry seeds oil extraction

Strawberry seed oil extraction was carried out by a maceration method. The apparatus for maceration was a round-bottom glass flask equipped with a condenser in a thermostatic water bath (70±2 °C). The ground seeds and *n*-hexane in the mass ratio of 1:3 or 1:10 were poured into it and kept for 1 h. Then, a GF3 glass microfiber filter (Chmlab Group, Spain) was placed in a Büchner funnel, and the suspension was filtered under a vacuum. Washing of the filter cake was done using 30 ml of *n*-hexane. Finally, the obtained liquid extract was subjected to a vacuum evaporation (Heidolph, Germany) performed at 40 °C.

Biodiesel production

Strawberry oil was converted into biodiesel in two steps. Due to a high FFA content, the strawberry oil was first esterified, and then the pre-esterified oil was transesterified.

Strawberry oil esterification

The apparatus for esterification was a three-necked round-bottom flask equipped with a condenser in a thermostatic water bath on a magnetic stirrer (1200 min^{-1}). The reaction conditions (atmospheric pressure, 45 °C, and a molar ratio of methanol: oil of 8.5:1 for 1 h) were chosen based on some optimization studies of the esterification reaction of other types of oils [19]. Methanol (36.2 g) and H_2SO_4 (2.3 g) were mixed and pre-heated in a flask to 45 °C and added to thermostated strawberry oil (116.0 g). Upon completion of the reaction, centrifugation (Sigma Germany, 3900 min^{-1}, 10 min) and decantation were used to separate the oil-ester from the alcohol phase (a separation funnel). Again, a separation funnel was used to wash (distilled water, room temperature, 15% based on the mass of the oil-ester phase) the residual catalyst. Anhydrous Na_2SO_4 was then added to the dry oil-ester phase. Then, a GF3 glass microfiber filter (Chmlab Group, Spain) was placed in a Büchner funnel, and the mixture was filtered under a vacuum. The pre-esterified strawberry oil was used in the next stage of methanolysis.

Pre-esterified strawberry oil methanolysis

The methanolysis was performed using the same apparatus as the esterification. Methanol (4.4 g) and KOH (0.2 g) were mixed and pre-heated in a flask to 60 °C and added to thermostated pre-esterified strawberry oil (20.0 g). The reaction conditions (atmospheric pressure, 60 °C, mixing rate of 400 min^{-1}, and a molar ratio of methanol: oil of 6:1 for 30 min) were chosen based on most optimization studies of the methanolysis reaction of other types of oils [20–22]. At specific intervals during the methanolysis, 100 µl of the reaction mixture was taken to monitor the kinetics of biodiesel synthesis and the reaction end.

Biodiesel purification

Upon completion of the methanolysis, centrifugation (Sigma Germany, 3900 min^{-1}, 10 min) and decanting (separation funnel) were used to separate the biodiesel from the methanol-glycerol phase. Again, a separation funnel was used to wash (distilled water, room temperature, 10% based on the mass of the biodiesel phase) the residual catalyst. Anhydrous Na_2SO_4 was then added to dry the biodiesel phase. Then, a GF3 glass microfiber filter (Chmlab Group, Spain) was placed in a Büchner funnel, and the mixture was filtered under a vacuum. Finally, using the following equation, the biodiesel yield was calculated as follows:

The biodiesel yield (%) = mass of biodiesel obtained / mass of oil used.....(2)

Physicochemical characteristics of strawberry oil

Acid value

A measured amount of strawberry oil and a diethyl ether: ethanol mixture (1:1 v/v) was stirred until the oil was wholly dissolved. Then, titration of the dissolved oil mixture and a few drops of 1% phenolphthalein ethanol solution was done using a 0.1 mol/l KOH solution. Titration was stopped when a pale pink color appeared stable for a minute. The value of acid value was calculated by Eq. (2):

$$K_b = \frac{A \cdot 5.61}{O_k} \quad \text{.....(3)}$$

where: A – the KOH consumption (ml), and O_k – the sample (g) measured amount.

Fatty acid profile

The fatty acid composition of strawberry oil was carried out by a gas chromatography-mass spectrometry (GC-MS) standard methodology [23,24]. The GC-MS apparatus included an Agilent Technologies (Palo Alto, CA, USA) gas chromatograph 7890B, a 5977A mass selective detector, autosampler 7693, and a capillary column DB-23 (0.25x60 mm, a film thickness of 25 µm, Supelco, USA). The temperature program was: 50 °C (1 min), increase at 5 °C/min up to 200 °C (0 min), and then increase by 3 °C/min to the final temperature of 230 °C, maintained for 7 minutes. The injector temperature and volume were 250 °C and 1.0 µl, while the split ratio was 1:80. Helium (1.0 ml/min) was the carrier gas. The corrected peak area normalization method calculates each fatty acid content (mass percentage). The correction factors were defined using a standard solution (37 component fatty acid methyl esters (FAMEs) Mix, 47885-U, Supelco).

HPLC

The HPLC method was used to quantitatively analyze the reaction ester-oil phase. The HPLC apparatus included the chromatograph (Agilent Technologies 1100 Series, Germany), a degasser, binary pump, thermostated Zorbax Eclipse XDB-C18 column (4.6×150 mm, 5 µm), and UV/VIS detector. A previously filtered (Millipore, 0.45 µm) solvents of methanol (solvent A) and 2-propanol/n-hexane mixture (solvent B) were used in column (40 °C) as a mixture (1 ml/ min) with a linear gradient from 100% A to 40% A + 60% B in 15 minutes. Injected sample (20 µl) was the ester-oil phase sample, previously dissolved (1:200 ratio) in a mixture (2-propanol: *n*-hexane, 5:4 v/v) and filtered (Millipore, 0.45 µm).

The components (TAGs, diacylglycerols (DAGs), monoacylglycerols (MAGs), and FAMEs) were detected at a wavelength of 205 nm. Their content (%) was the corresponding chromatogram area peaks per total area of all reaction mixture components peaks. At the same time, their concentrations were calculated from the calibration curves (dependence of the chromatogram peaks area on the analyte mass). The TAG conversion degree (x_A) was calculated as follows:

$$x_A = 1 - \frac{TAG}{TAG_0} \quad \text{.....(4)}$$

where: TAG_0 – the TAG content (%) at the beginning of the reaction; TAG – the TAG content (%) at a given time.

Density

The strawberry oil density (20 °C) was calculated by Eq. (5):

$$\frac{\rho_{oil}}{\rho_{water}} = \frac{m_3 - m_1}{m_2 - m_1} \quad \text{.....(5)}$$

where ρ_{oil} and ρ_{water} are the densities of strawberry oil and water (1000 kg/m^3), respectively, m_1 is the mass of the empty pycnometer, and m_2 and m_3 are the masses of the pycnometer filled with distilled water and strawberry oil, respectively.

Dynamic viscosity

The apparatus for measuring the strawberry oil dynamic viscosity (20 °C) was a rotary viscometer (Visco Basic Plus v. 0.8. Fungilab S.A., Spain) at 100 s^{-1}.

Physicochemical characteristics of biodiesel

Density

Eqs. (6) and (7) calculated the strawberry oil density (20 °C, g/cm^3) [25]:

$$\rho_b = \sum_{i=1}^{n} z_i \cdot \rho_i \quad \text{.....(6)}$$

$$\rho_i = 0.8463 + \frac{4.9}{M_i} + 0.0118 \cdot N \quad \text{.....(7)}$$

where: ρ_b - biodiesel density, ρ_i - i^{th} FAME density [26], z_i - strawberry oil i^{th} fatty acid mass fraction, M_i - i^{th} fatty acid molecular mass [27], and N - the double bonds number

of the i^{th} FAME (0, 1, 2, or 3).

Cetane number

Eqs. (8) and (9) calculated the biodiesel cetane number [25]:

$$\phi_b = \sum_{i=1}^{n} z_i \cdot \phi_i \quad \text{.....(8)}$$

$$\phi_i = -7.8 + 0.302 \cdot M_i - 20 \cdot N \quad \text{.....(9)}$$

where: ϕ_b - biodiesel cetane number, ϕ_i - the i^{th} FAME cetane number [26], z_i - the strawberry oil i^{th} fatty acid mass fraction, M_i - the i^{th} fatty acid molecular mass [27], and N - the double bonds number of the i^{th} FAME (0, 1, 2, or 3).

Kinematic viscosity

Eqs. (10) and (11) calculated the biodiesel kinematic viscosity (40 °C, mm^2/s) [25]:

$$\eta_b = \sum_{i=1}^{n} z_i \cdot \eta_i \quad \text{.....(10)}$$

$$\ln(\eta_i) = -12.503 + 2.496 \cdot \ln(M_i) - 0.178 \cdot N \quad \text{.....(11)}$$

where: η_b - the biodiesel kinematic viscosity, η_i - the i^{th}-FAME kinematic viscosity [26], z_i - the strawberry oil i^{th} fatty acid mass fraction, M_i - the i^{th} fatty acid molecular mass [27], and N - the double bonds number of the i^{th} FAME (0, 1, 2, or 3).

Higher heating value

Eqs. (12) and (13) calculated the biodiesel higher heating value (MJ/kg) [25]:

$$\delta_b = \sum_{i=1}^{n} z_i \cdot \delta_i \quad \text{.....(12)}$$

$$\delta_i = 46.19 - \frac{1794}{M_i} - 0.21 \cdot N \quad \text{.....(13)}$$

where: δ_b - the biodiesel higher heating value, δ_i - the i^{th} FAME higher heating value [26], z_i - the strawberry oil i^{th} fatty acid mass fraction, M_i - the i^{th} fatty acid molecular mass [27], and N - the double bonds number of the i^{th} FAME (0, 1, 2, or 3).

Oxidation stability

Eq. (14) calculated the biodiesel oxidation stability (h) [25]:

$$Y = \frac{117.9295}{X} + 2.5905 \quad \text{.....(14)}$$

where: Y – is the oxidation stability and X – is the sum of linoleic and α- linolenic acid content (wt.%, 0<X<100).

Iodine value

Eqs. (15) and (16) calculated the biodiesel iodine value [25]:

$$I_b = 0.6683 \cdot DU + 25.0364 \quad \text{.....(15)}$$

$$DU = \left(\sum MUFA, C_n : 1\right) + 2 \cdot \left(\sum PUFA, C_n : 2\right) + \\ + 3 \cdot \left(\sum PUFA, C_n : 3\right) + 4 \cdot \left(\sum PUFA, C_n : 4\right) \quad \text{.....(16)}$$

where: I_b is the value of iodine value, *DU* is the degree of unsaturation, *ΣMUFA* C_n:1 is the mass fraction of monounsaturated FAs, *ΣPUFA* C_n:2 is the mass fraction of polyunsaturated FAs with 2 double bonds, *ΣPUFA* C_n:3 is the mass fraction of polyunsaturated FAs with 3 double bonds, and *ΣPUFA* C_n:4 is the mass fraction of polyunsaturated FAs with 4 double bonds.

The cold filter plugging point (CFPP)

Eqs (17) and (18) calculated the CFPP (K) [25]:

$$CFPP = 3.1417 \cdot FZ - 16.477 \quad \text{.....(17)}$$

$$FZ = 0.1 \cdot C16 + 0.25 \cdot C17 + 0.5 \cdot C18 + \\ + 1 \cdot C20 + 1.5 \cdot C22 + 2 \cdot C24 \quad \text{.....(18)}$$

where *FZ* - the long-chain FAs saturation factor, and *C16 – C18, C20, C22*, and *C24* - the strawberry oil saturated FAs amount (wt.%).

Results and discussion

Strawberry pomace and seed characterization

The average moisture content of strawberry pomace was 81.66 ± 1.34%. Higher values (92.30% and 91.79%) were published for two strawberry varieties grown in Serbia [28]. However, much lower 55% and 52.2% values were reported for Polish [10] and Italian [11] varieties, respectively. A higher moisture proportion made seed separation difficult and the processing more expensive because of the high drying costs. The mass fraction of seeds in the dry pomace was 50.42 ± 4.17% (based on six dry pomace samples). The rest consisted of stalks, dry pulp, and other impurities. The seed fractions after crushing were retained by the 1.0, 0.8, and 0.63 mm sieves. The average equivalent diameter of the seed powder was 0.87 ± 0.03 mm. A similar result was obtained by Juskiewicz *et al*. [29], who collected fractions in the range of 0.5–1.0 mm.

Strawberry oil recovery by maceration

Maceration with *n*-hexane at seed-to-solvent mass ratios of 1:10 and 1:3 gave the average oil content of 12.16 ± 1.65% and 11.04 ± 0.51%, respectively, which were lower than reported for cold pressing (14.61% [8] and 18.5% [10]), supercritical CO_2 extraction (18.9%) [12], and Soxhlet extraction with petroleum ether

(19.3%) [6]. Compared to other plant seeds, the maceration of strawberry seeds provides a higher oil yield than Moss-rose purslane (*Portulaca oleracea*) seeds (15.41% under optimal conditions) [30] but a significantly lower yield than Gmelina (*Gmelina arborea*) seeds (49.90%) [31]. However, the oil yield depends not only on the type of extraction but also on the seed characteristics and the extraction conditions. For example, Soxhlet extraction of *Jatropha curcas* using *n*-hexane yields a 95–99% extraction degree for 24 h [32]. In contrast, the oil extraction degree from the same material by the aqueous enzymatic extraction was 73% for 2 h at 60 °C [32].

Physicochemical properties of strawberry oil

Table 1 compares the fatty acid profiles of strawberry seed oils from different regions. In the present study, the most abundant strawberry oil FAs are linoleic acid (47.43%), α-linolenic acid (29.36%), and oleic acid (16.27%). The retention times and elution order of nine FA peaks from C16:0 to C22:0 typically found in strawberry oil samples are shown in Figure 1. This fatty acid profile follows the previously reported profiles [8–10,12,14–18] with slight differences due to the extraction method, extraction time, strawberry variety, and growing conditions.

The strawberry oil acid value of 2.72 mg KOH/g is similar to the oil obtained by cold-pressed raw seed but

Table 1. Fatty acid profiles of strawberry oil.

	This study	[8]	[9]	[10]	[15]	[12]	[17]	[18]	[14]	[16]
Seeds origin	Serbia					Poland			Finland	Turkey
Extraction conditions	n-hexane maceration, 70±2 °C, 60 min		cold pressing			sc CO_2 extraction, 100 MPa, 100 °C, 240 kg/hr, 180–225 min	sc CO_2 extraction, 30 MPa, 50 °C, 80 kg/hr	Folch, Chloroform, methanol	sc CO_2 extraction, 35 MPa, 50 °C, 21 kg/h, 120 min	Bligh and Dyer, chloroform, methanol
(8:0)								0.13		0.01—0.04
(10:0)				0.01						0.01—0.50
(12:0)								0.47		0.05—0.60
(14:0)		0.04						0.42		0.15—1.72
(14:1)										0.02—0.09
(15:0)										0.09—0.27
(16:0)	4.16	3.76—3.92		6.20	6.23	2.80—4.30	3.70	13.71	4.50	5.75—10.71
(16:1)	0.13	0.04—0.07	0.04—0.07	0.25	0.25		0.20	0.33		0.15—0.85
(17:0)										0.06—0.15
(17:1)										0.03—0.09
(18:0)	1.28	1.18—1.25		1.89	0.89	0.90—1.50	1.40	4.66	1.50	1.44—2.54
(18:1 n-9)	16.27	14.55—14.56	14.55—14.56	15.51	15.07	15.00—17.20	15.70	17.36	17.80	16.96—28.48
(18:1 n-7)									0.60	
(18:2)	47.43	48.48—48.66	48.48—48.66	45.45	39.54	47.90—48.70	46.30	48.88	41.20	31.17—40.62
(18:3)	29.36	30.28—30.81	30.28—30.81	29.05	37.98	29.70—31.70	31.50	5.55	33.30	22.35—36.67
γ(18:3)				0.04						
(20:0)	0.92	0.75—1.11		0.91			0.80	3.65	0.80	0.40—1.55
(20:1)	0.24	0.24—0.28	0.24—0.28	0.27			0.30	0.47	0.30	0.12—0.49
(20:2)				0.11				0.31		0.07—0.30
(20:4)										0.02—0.10
(20:5)								0.05		0.03—0.13
(22:0)	0.21			0.12			0.20	3.03		0.13—0.71
(22:1)				0.08						
(22:5)				0.10				0.72		
(22:6)					0.011			0.11		
(24:0)										0.11—0.75
ΣSFA	6.57	5.73—6.28	5.87—6.16	9.14	7.12	3.70—5.80	6.10	26.07	6.80	8.77—15.26
ΣMUFA	16.64	14.83—14.91	14.84—14.90	14.83	15.33	15.00—17.20	16.20	18.16	18.70	17.59—29.87
ΣPUFA	76.79	78.76—79.47	78.94—79.29	74.83	77.54	77.60—80.40	77.80	55.62	74.50	55.26—73.08
Total Σ	100	99.32—100.66	99.65—100.35	98.80	99.99	96.30—103.40	100.10	99.85	100	81.73—118.96

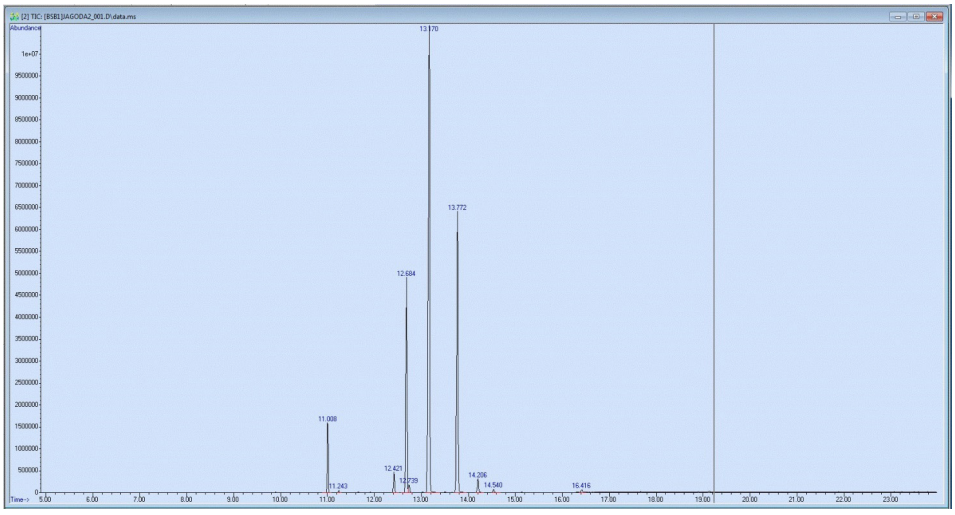

Figure 1. The resulting chromatogram of FAs found in the strawberry oil sample.

lower than cold-pressed roasted seeds (4.65 mg KOH/g) [8] or seed oil obtained by supercritical extraction (3.7 mg KOH/g) [8]. The measured dynamic viscosity and density values for strawberry oil are 41.7 mPa s and 922.6 kg/m^3, respectively. Although at slightly higher temperatures, the density of strawberry oil (925 kg/m^3) obtained by Sikora *et al*. [17] agreed with the results of this study. As proved earlier [33], the density is directly proportional to the oil unsaturation degree. The same trend was observed with other berry fruit oils. For example, raspberry and blackberry oil densities were 926.3–929 kg/m^3 [34] and 925.6 kg/m^3 [35], respectively. On the other hand, raspberry oil dynamic viscosity is of the lower value (26 mPa s, [36]) while strawberry values were 41.7 mPa s, at 20 °C using a rotary viscometer (this study) and 300 mPa s, at 20 °C and a shear rate of 50 s^{-1} [17] determined with a rheometer.

Biodiesel production from strawberry oil

The strawberry oil acid value was 2.72 mg KOH/g, so a strawberry oil pre-esterification was necessary to conduct transesterification. After esterification, strawberry oil had an acid value of 0.73 mg KOH/g to be transesterified in the presence of a base catalyst. Figure 2 shows how the FAME content changed during the transesterification of the pre-esterified strawberry oil. Three periods can be observed with the progress of the transesterification reaction. In the initial period, the FAME content increases exponentially with time (up to about 2.5 min from the start of the reaction), indicating a high chemical reaction rate. Intensive mixing of the reaction mixture (400 min^{-1}) and the formation of the emulsifiers (FAMEs, MAGs, and DAGs) ensure a large interfacial area between immiscible strawberry oil and methanol, thus increasing the mass transfer rate. In the medium period of the reaction (3–10 min), the FAME content increases more slowly due to the decrease in the concentrations of the reactants and the increase in the reaction products concentration. After that, the content of FAMEs remains unchanged, indicating the achievement of the equilibrium state of the reaction system. A similar observance has been reported for the transesterification of different vegetable oils catalyzed by KOH [37,38]. The FAME content rose with time with the decrease in TAG content, while the variations of MAG and DAG contents are minor and do not change significantly during the reaction (Figure 2). The final FAME content in the purified biodiesel was 97.2% in 30 min, thus fulfilling the specification of the biodiesel quality standard.

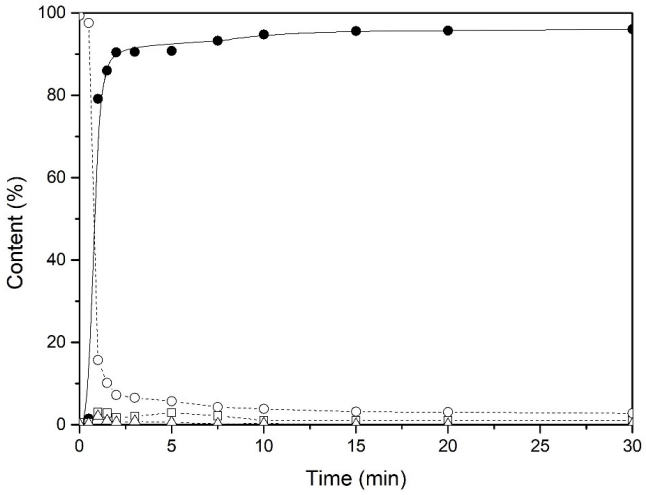

Figure 2. The variation of FAME, TAG, DAG, and MAG contents with time during the KOH-catalyzed transesterification of strawberry oil (methanol-to-oil molar ratio: 6:1, KOH dosage: 1% of the oil mass, and temperature: 60 °C; TAGs – ○, DAGs – □, MAGs – Δ, and FAMEs – ●).

Process of biodiesel production from strawberry pomace

Material balance

Figure 3 provides an insight into the material balance of the strawberry pomace. Strawberry seeds comprise 9.2% and 50% of the wet and dry pomace, respectively.

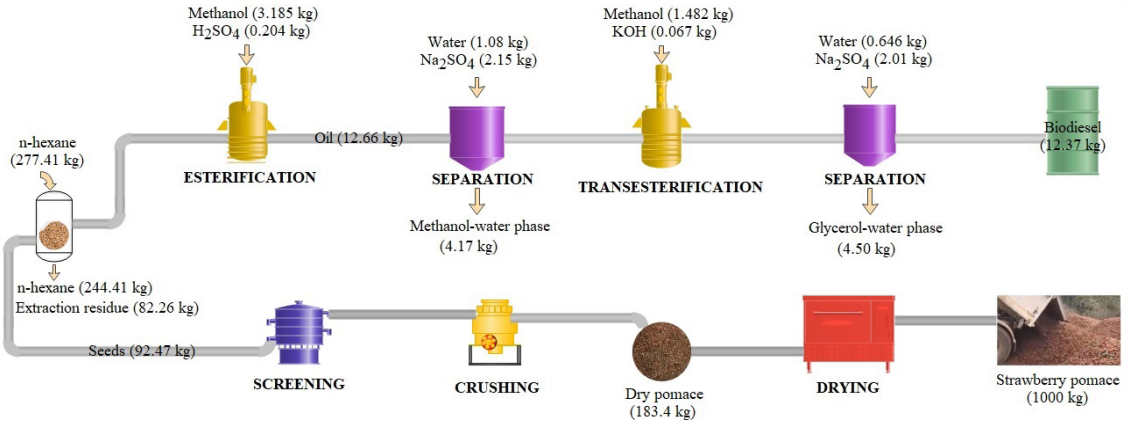

Figure 3. Process diagram of obtaining biodiesel from strawberries pomace with a material balance.

The previously published papers reported seed content of only 1% of the mass of the wet pomace [13]. Therefore, the first problem in strawberry pomace processing is its large water amount, which would significantly increase the cost of the potential industrial application. The seed oil and biodiesel yields in wet strawberry pomace were only 0.11 g/g and 0.13 g/g, respectively. On the other hand, for just 12 kg of biodiesel, the process generated 7.6 times higher (about 91 kg) waste amount. Waste consisted of extraction residues, unpurified methanol, glycerol, and hexane water mixture and had to be sent for further purification.

Physicochemical properties of strawberry oil-based biodiesel

Due to the high polyunsaturated linoleic acid content, the calculated cetane and iodine values differ from those standardized values (Table 2). The same is with red currant, gooseberry, and pomegranate seed oil biodiesel [25]. However, the stability of biodiesel does not depend only on the iodine value, i.e. the number of the double bonds in the molecules, but also on their position, as well as on the presence of natural antioxidants in the oil and can be increased by the addition of additives [39–41]. In addition, the cetane number is influenced by other physical properties of the fuel, such as, viscosity, density, and boiling range [42]. The biodiesel feedstock's suitable suitability is driven by low CFPP values [25,43]. However, the U.S. and EN biodiesel standards exclude this specification since it depends on seasonal and geographic temperature changes. In this study, strawberry oil biodiesel CFPP value was much lower (-16.5 °C) than previously recorded values of various berries, from -7.7 °C to -11.8 °C [25], since strawberry oil was rich in monounsaturated FAs. In addition, the higher the long carbon chain saturated methyl esters, the higher the CFPP values [25,43].

Table 2. Strawberry seed oil biodiesel's physicochemical characteristics.

	This study	ASTM D6751 [2]	EN 14214 [2]
Density (15 °C), kg/m^3	886.5[a]	860—900	860—900
Cetane number	41.0	min. 47	min. 51
Kinematic viscosity (40 °C), mm^2/s	3.8	1.9—6.0	3.5—5.0
Oxidation stability, h	4.1	min. 3 h	min. 8 h
Iodine value	158.4	-	max. 120
The higher heating value, MJ/kg	39.7	-	-
CFPP, K	256.7	depending on location and season	

[a]- at 20 °C

High acid value and viscosity resulted in poor quality of strawberry oil as biodiesel feedstock. However, mixing at least two oils (creating hybrid oil) in appropriate proportions improves the quality of the various physicochemical properties [44]. Adjusting low with high acid value oil or viscosity makes the feedstock hybrid suitable for producing good-quality biodiesel. For example, strawberry oil should be mixed with feedstock having low acid value and viscosity (such as canola oil and plum kernel oil). Since the iodine value of strawberry oil is high, it is optimal to use oil that will reduce its value during mixing.

Conclusion

This work aimed to study the potential of strawberry pomace as feedstock for biodiesel production. The process was performed at a laboratory scale using "non-green" chemicals (i.e. hexane, H_2SO_4, methanol, Na_2SO_4, KOH) since the aim was to obtain maximum yields in each process phase. Considering this technology's low final product yield and the necessity to improve the quality of obtained biodiesel, strawberry oil should be used in a mixture with other oils for biodiesel production or in the cosmetics and food industry. Decisions on the possible valorization of strawberry oil for biodiesel production, cosmetics, or the food industry should be based on techno-economic and environmental impact analysis results.

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List of abbreviations

FAs	Fatty Acids
CFPP	Cold Filter Plugging Point
DAGs	Diacylglycerols
FAMEs	Fatty Acid Methyl Esters
FAO	Food and Agriculture Organization
FFAs	Free Fatty Acids
GC-MS	Gas Chromatography-Mass Spectrometry
MAGs	Monoacylglycerols
TAG	Triacylglycerol

References

[1] Girard P, Fallot A. Review of existing and emerging technologies for the production of biofuels in developing countries. *Energy for Sustainable Development.* 2006, 10, 92–108. https://dx.doi.org/10.1016/S0973-0826(08)60535-9.

[2] Rizwanul Fattah IM, Ong HC, Mahlia TMI, Mofijur M, Silitonga AS, Ashrafur Rahman SM, Ahmad A. State of the art of catalysts for biodiesel production. *Frontiers in Energy Research.* 2020, 8, 101. https://dx.doi.org/10.3389/FENRG.2020.00101.

[3] Pruszko R. Biodiesel production. In: Dahiya A, ed. *Bioenergy: Biomass to Biofuels and Waste to Energy.* 2nd ed. Cambridge, Massachusetts, Academic Press, 2020, 491–514. https://dx.doi.org/10.1016/B978-0-12-815497-7.00023-3.

[4] FAOSTAT. http://www.fao.org/faostat/en/#home. Accessed March 14, 2021.

[5] Ravindran R, Jaiswal AK. Exploitation of food industry waste for high-value products. *Trends in Biotechnology*. 2016, 34, 58–69. https://dx.doi.org/10.1016/j.tibtech.2015.10.008.

[6] Sójka M, Klimczak E, Macierzyński J, Kołodziejczyk

K. Nutrient and polyphenolic composition of industrial strawberry press cake. *European Food Research and Technology.* 2013, 237, 995–1007. https://dx.doi.org/10.1007/S00217-013-2070-2.

[7] Mildner-Szkudlarz S, Różańska M, Gaca A, Jeleń HH. Changes in volatile compound profiles of cold-pressed berry seed oils induced by roasting. *LWT.* 2021, 148, 111718. https://dx.doi.org/10.1016/J.LWT.2021.111718.

[8] Mildner-Szkudlarz S, Różańska M, Siger A, Kowalczewski PŁ, Rudzińska M. Changes in chemical composition and oxidative stability of cold-pressed oils obtained from by-product roasted berry seeds. *LWT*. 2019, 111, 541–547. https://dx.doi.org/10.1016/j.lwt.2019.05.080.

[9] Różańska MB, Kowalczewski PŁ, Tomaszewska-Gras J, Dwiecki K, Mildner-Szkudlarz S. Seed-roasting process affects oxidative stability of cold-pressed oils. *Antioxidants.* 2019, 8, https://dx.doi.org/10.3390/ANTIOX8080313.

[10] Pieszka M, Migdał W, Gąsior R, Rudzińska M, Bederska-L, Ojewska D, Pieszka M, Szczurek P. Native oils from apple, blackcurrant, raspberry, and strawberry seeds as a source of polyenoic fatty acids, tocochromanols, and phytosterols: A health implication. *Journal of Chemistry*. 2015, 2015, https://dx.doi.org/10.1155/2015/659541.

[11] Campalani C, Amadio E, Zanini S, Dall'Acqua S, Panozzo M, Ferrari S, De Nadai G, Francescato S, Selva M, Perosa A. Supercritical CO_2 as a green solvent for the circular economy: Extraction of fatty acids from fruit pomace. *Journal of CO2 Utilization.* 2020, 41, 101259. https://dx.doi.org/10.1016/j.jcou.2020.101259.

[12] Milala J, Grzelak-Błaszczyk K, Sójka M, Kosmala M, Dobrzyńska-Inger A, Rój E. Changes of bioactive components in berry seed oils during supercritical CO_2 extraction. *Journal of Food Processing and Preservation*. 2018, 42, e13368. https://dx.doi.org/10.1111/JFPP.13368.

[13] Korus J, Juszczak L, Ziobro R, Witczak M, Grzelak K, Sójka M. Defatted strawberry and blackcurrant seeds as functional ingredients of gluten-free bread. *Journal of Texture Studies.* 2012, 43, 29–39. https://dx.doi.org/10.1111/J.1745-4603.2011.00314.X.

[14] Yang B, Ahotupa M, Määttä P, Kallio H. Composition and antioxidative activities of supercritical CO_2-extracted oils from seeds and soft parts of northern berries. *Food Research International.* 2011, 44, 2009–2017. https://dx.doi.org/10.1016/j.foodres.2011.02.025.

[15] Pieszka M, Tombarkiewicz B, Roman A, Migdał W, Niedziółka J. Effect of bioactive substances found in rapeseed, raspberry and strawberry seed oils on blood lipid profile and selected parameters of oxidative status in rats. *Environmental Toxicology and Pharmacology.* 2013, 36, 1055–1062. https://dx.doi.org/10.1016/j.etap.2013.09.007.

[16] Kafkas E, Gunaydin S, Ercisli S, Ozogu Y, Unlu MA. Fat and fatty acid composition of strawberry cultivars. *Chemistry of Natural Compounds.* 2009, 45, 861–863. https://dx.doi.org/10.1007/S10600-010-9489-5.

[17] Sikora E, Michorczyk P, Olszańska M, Ogonowski J. Supercritical CO_2 extract from strawberry seeds as a valuable component of mild cleansing compositions. *International Journal of Cosmetic Science.* 2015, 37, 574–578. https://dx.doi.org/10.1111/ICS.12234.

[18] Pieszka M, Gogol P, Pietras M, Pieszka M. Valuable components of dried pomaces of chokeberry, black currant, strawberry, apple and carrot as a source of natural antioxidants and nutraceuticals in the animal diet. *Annals of Animal Science.* 2015, 15, 475–491. https://dx.doi.org/10.2478/aoas-2014-0072.

[19] Kostić MD, Veličković AV, Joković NM, Stamenković OS, Veljković VB. Optimization and kinetic modeling of esterification of the oil obtained from waste plum stones as a pretreatment step in biodiesel production. *Waste Management.* 2016, 48, 619–629. https://dx.doi.org/10.1016/J.WASMAN.2015.11.052.

[20] Stamenkovic O, Kostic M, Jokovic N, Veljkovic, V. The kinetics of base-catalyzed methanolysis of waste cooking oil. *Advanced Technologies.* 2015, 4, 33–41. https://dx.doi.org/10.5937/savteh1501033S.

[21] Kostic M, Jokovic N, Stamenkovic O, Veljkovic V. Dobijanje biodizela iz ulja semena magarećeg trna (*Onopordum acanthium* L.). *Advanced Technologies.* 2014, 3, 35–45. https://dx.doi.org/10.5937/savteh1402035K.

[22] Kostic M, Stamenkovic O, Veljkovic V. The influence of fatty acid composition on the kinetics of the vegetable oil methanolysis reaction. *Advanced Technologies.* 2021, 10, 24–31. https://dx.doi.org/10.5937/savteh2102024K.

[23] ISO 12966-1: Gas chromatography of fatty acid methyl esters – Part 1: Guidelines on modern gas chromatography of fatty acid methyl esters, 2014.

[24] ISO 12966-2: Animal and vegetable fats and oils – Gas chromatography of fatty acid methyl esters – Part 2: Preparation of methyl esters of fatty acids, 2017.

[25] Górnaś P, Rudzińska M. Seeds recovered from industry by-products of nine fruit species with a high potential utility as a source of unconventional oil for biodiesel and cosmetic and pharmaceutical sectors. *Industrial Crops and Products.* 2016, 83, 329–338. https://dx.doi.org/10.1016/j.indcrop.2016.01.021.

[26] Ramírez-Verduzco LF, Rodríguez-Rodríguez JE, Jaramillo-Jacob ADR. Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. *Fuel.* 2012, 91, 102–111. https://dx.doi.org/10.1016/j.fuel.2011.06.070.

[27] Compilers' Toolbox. http://toolbox.foodcomp.info. Accessed January 20, 2022.

[28] Tumbas Šaponjac V, Gironés-Vilaplana A, Djilas S, Mena P, Ćetković G, Moreno DA, Čanadanović-Brunet J, Vulić J, Stajčić S, Vinčić M. Chemical composition and potential bioactivity of strawberry pomace. *RSC Advances.* 2014, 5, 5397–5405. https://dx.doi.org/10.1039/C4RA14296A.

[29] Juskiewicz J, Krol B, Kosmala M, Milala J, Zdunczyk Z, Zary-Sikorska E. Physiological properties of dietary ellagitannin-rich preparations obtained from strawberry pomace using different extraction methods. *Polish Journal of Food and Nutrition Science*. 2015, 65 (3), 199–209. https://dx.doi.org/10.1515/pjfns-2015-0007.

[30] Stroescu M, Stoica-Guzun A, Ghergu S, Chira N, Jipa I. Optimization of fatty acids extraction from *Portulaca oleracea* seed using response surface methodology. *Industrial Crops and Products*. 2013, 43, 405–411. https://dx.doi.org/10.1016/j.indcrop.2012.07.051.

[31] Uzoh CF, Onukwuli OD, Nwabanne JT. Characterization, kinetics and statistical screening analysis of gmelina seed oil extraction process. *Materials for Renewable and Sustainable Energy.* 2014, 3, 1–12. https://dx.doi.org/10.1007/S40243-014-0038-1.

[32] Keneni YG, Marchetti JM, Keneni YG, Marchetti JM. Oil extraction from plant seeds for biodiesel production. *AIMS Energy 2017* 2:316. 2017, 5, 316–340. https://dx.doi.

org/10.3934/ENERGY.2017.2.316.
[33] Ohlson R. Structure and physical properties of fats. In: Perkins EG, Visek WJ, eds. *Dietary fats and health*. 1st ed. Champaign - Illinois, American Oil Chemists' Society, 1983, 44–54. https://books.google.rs/books?hl=en&lr=&id=pvXuKSTy3BAC&oi=fnd&pg=PA1&dq=Dietary+Fats+and+Health,+American+Oil+Chemists%E2%80%99+Society&ots=dpRYsGrZHQ&sig=tyWMN_H-ovrVKlhf-5iU6gKHFhA&redir_esc=y#v=onepage&q=Dietary%20Fats%20and%20Health%2C%20American%20Oil%20Chemists%E2%80%99%20Society&f=false
[34] Šućurović A, Vukelić N, Ignjatović L, Brčeski I, Jovanović D. Physical-chemical characteristics and oxidative stability of oil obtained from lyophilized raspberry seed. *European Journal of Lipid Science and Technology.* 2009, 111, 1133–1141. https://dx.doi.org/10.1002/EJLT.200900022.
[35] Krist S. Blackberry seed oil. In: Vegetable fats and oils. 1st ed. Basel-Switzerland, *Springer Nature,* 2020, 125–129. https://link.springer.com/chapter/10.1007/978-3-030-30314-3_18
[36] Oomah BD, Ladet S, Godfrey DV, Liang J, Girard B. Characteristics of raspberry (*Rubus idaeus* L.) seed oil. *Food Chemistry.* 2000, 69, 187–193. https://dx.doi.org/10.1016/S0308-8146(99)00260-5.
[37] Bokhari A, Yusup S, Kamil RNM, Junaid A. Blending study of palm oil methyl esters with rubber seed oil methyl esters to improve biodiesel blending properties. *Chemical Engineering Transactions.* 2014, 37, 571–576. https://dx.doi.org/10.3303/CET1437096.
[38] Georgogianni KG, Kontominas MG, Pomonis PJ, Avlonitis D, Gergis V. Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. *Fuel Processing Technology.* 2008, 89, 503–509. https://dx.doi.org/10.1016/J.FUPROC.2007.10.004.
[39] Li SY, Stuart JD, Li Y, Parnas RS. The feasibility of converting Cannabis sativa L. oil into biodiesel. *Bioresource Technology.* 2010, 101, 8457–8460. https://dx.doi.org/10.1016/j.biortech.2010.05.064.
[40] Pešić R, Davinić A, Veinović S. Određivanje motorskih karakteristika biodizel goriva. In: 13. Simpozijum Termičara Srbije, Soko Banja - Srbija, 2007, pp. 13. https://scholar.google.com/scholarlookup?author=Pešić+R.&author=Davinić+A.&author=Veinović+S.&publication_year=2007&title=Određivanje+motorskih+karakteristika+biodizel+goriva
[41] Knothe G, Dunn RO. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *Journal of the American Oil Chemists' Society.* 2003, 80, 1021–1026. https://dx.doi.org/10.1007/S11746-003-0814-X.
[42] Bogojević S, Pavlović PJ. Trend razvoja kvaliteta motornih benzina i dizel goriva u svetu i kod nas. *Hemijska Industrija.* 2001, 55, 79–89. https://scindeks.ceon.rs/article.aspx?artid=0367-598X0102079B.
[43] Hoekman SK, Broch A, Robbins C, Ceniceros E, Natarajan M. Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews.* 2012, 16, 143–169. https://dx.doi.org/10.1016/J.RSER.2011.07.143.
[44] Brahma S, Natha B, Basumatary B, Das B, Saikia P, Patir K, Basumatary S, Biodiesel production from mixed oils: A sustainable approach towards industrial biofuel production. *Chemical Engineering Journal Advances.* 2022, 10, 100284. https://doi.org/10.1016/j.ceja.2022.100284.

Izvod

PROIZVODNJA BIODIZELA IZ ULJA SEMENA TROPA JAGODE

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Trop jagode je otpad koji se dobija iz industrije prerade sokova i trebalo bi da se koristi kao sirovina za cirkularnu ekonomiju, stočna hrana ili đubrivo u skladu sa ekološkim propisima. Ovaj rad je imao za cilj da karakteriše i primeni ulje iz tropa jagode u industriji biodizela. Ulje je ekstrahovano iz semena jagode metodom maceracije za fizičko-hemijsku karakterizaciju. Za postizanje maksimalnog prinosa ulja korišćena su dva odnosa seme/rastvarač. Prinos ulja semena jagode ekstrakcijom *n*-heksanom u odnosu seme/rastvarač 1:3 bio je 0,11 g/g. Ekstrahovano ulje jagode je korišćeno za proizvodnju biodizela postupkom u dva stupnja koji je uključivao pre-esterifikaciju ulja jagode katalizovanu kiselinom (H_2SO_4), a zatim bazom (KOH) katalizovanu transesterifikaciju pre-esterifikovanog ulja jagode. Takođe, metanoliza je obezbedila prinos biodizela od 97,2% za 30 min. Međutim, nizak prinos finalnog proizvoda ove tehnologije i fizičko-hemijska karakterizacija su pokazali da ulje jagode treba koristiti u mešavini sa drugim uljima (hibridno ulje) za proizvodnju biodizela, ili u kozmetici i prehrambenoj industriji.

Ključne reči: otpad, biodiezel, trop jagode, semena.