Biodiesel from tomato seed oil: transesterification and characterisation of chemical-physical properties

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Abstract. The transesterification process of an oil is influenced by four variables: reaction temperature, reaction time, amount of alcohol and amount of reaction catalyst. The cost of production, yield and chemical-physical characteristics are therefore directly dependent on these variables. In this work, tomato seed oil was transesterified and the influence of the quantities of the alcohol (methanol) and catalyst (potassium hydroxide) was tested. The values of total esters, density, kinematic viscosity, iodine value, acid number, linolenic acid, cetane number and residual glycerides in the different biodiesels produced (Bio from A to F), were studied and compared with the current European regulations EN14214: 2014 (Liquid petroleum products - Fatty acid methyl esters for use in diesel engines and heating applications - Requirements and test methods). The six obtained biodiesels yielded between 72.59 (BioB) and 96.8% (BioE) of the total esters. The presence of non-transesterified oil, besides being a yield index, also negatively affects the viscosity at 40 °C of the produced biodiesel. In fact, the only sample with a value within the legal limit was BioE (4.95 mm^2 s^{-1}), while the others showed viscosity values higher than the 5.00 mm^2 s^{-1} established by the European regulation. The density, however, always remained within the specified limits, with values between 880 kg m^{-3} in BioE and 891 kg m^{-3} in BioB. The presence of linolenic acid was well below the maximum legal limit in all samples, the iodine value ranged between 119 and 122 g I$_2$ 100g^{-1}.

Key words: biodiesel yield, industrial waste, methanol, potassium hydroxide, tomato seed oil, transesterification.

INTRODUCTION

The worldwide demand for energy is increasing day by day, and, consequently, reserves of fossil fuels, which until now have largely satisfied this demand, are becoming depleted. In addition to this problem, there are growing health and environmental concerns, due to fossil fuel emissions. For these reasons, alternative sources of renewable energy are needed (Royon et al., 2007). Some alternatives are different forms of biofuels: liquid or gaseous (Sajjadi et al., 2016) obtained from different types of biomass. Biodiesel is one of the most common biofuels produced from biological resources such as vegetable oils by their transesterification (Kilic et al., 2013). Many studies have been conducted on edible oils: castor oil (Meneghetti et al., 2006), soybean oil (Abrahamsson et al., 2015; Al-Mulla et al., 2015), palm oil (Al-Zuhair et al., 2007; Hameed et al., 2009), peanut oil (Giuffrè et al., 2016a), transformed into biodiesel by transesterification. However, both from an ethical and economic point of view, it would be preferable if

biodiesel was produced from material otherwise considered food industry waste. Tomato seeds, obtained from the waste of canning industries, contain around 18– 23% of oil (Giuffrè & Capocasale, 2015), which could be used for biodiesel production (Giuffrè et al., 2015; Giuffrè et al. 2016b).

The transformation of a vegetable oil into biodiesel occurs by a chemical reaction: transesterification, in which the oil is mixed with an alcohol in the presence of a catalyst and is heated. Four variables (reaction temperature, reaction time, amount of alcohol and amount of reaction catalyst) directly influence the conversion of the vegetable oil's fatty acids into their methyl esters (Gupta, 2016).

The most common alcohol used for transesterification is methanol (Demirbas, 2009; Knothe & Steidley, 2009), which substitutes the functional group of a fatty acid with a methylic functional group, with production of three water molecules (Fig. 1). The higher the molar ratio MeOH/oil, the higher the reaction yield.
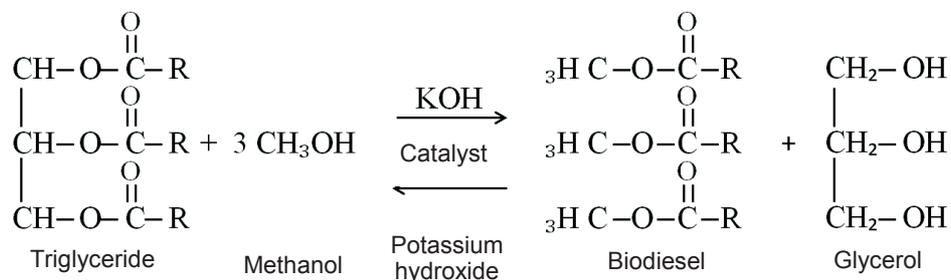
$$
\begin{array}{c}
CH-O-\overset{\overset{O}{\|}}{C}-R \\
CH-O-\overset{\overset{O}{\|}}{C}-R + 3\ CH_3OH \\
CH-O-\overset{\overset{O}{\|}}{C}-R
\end{array}
\underset{\underset{\text{Potassium hydroxide}}{\longleftarrow}}{\overset{\overset{KOH}{\longrightarrow}}{\text{Catalyst}}}
\begin{array}{c}
{}_3H\ C-O-\overset{\overset{O}{\|}}{C}-R \\
{}_3H\ C-O-\overset{\overset{O}{\|}}{C}-R \\
{}_3H\ C-O-\overset{\overset{O}{\|}}{C}-R
\end{array}
+
\begin{array}{c}
CH_2-OH \\
CH_2-OH \\
CH_2-OH
\end{array}
$$

Triglyceride   Methanol   Potassium hydroxide   Biodiesel   Glycerol

Figure1. Diagram of a chemical reaction of a overall transesterification of a vegetable oil.

Potassium hydroxide is one of the common used catalysts (Macario et al., 2013). It can reduce reaction time and, at the same time, the yield of the reaction. Potassium hydroxide is homogeneous catalyst. Although the removal of homogeneous catalyst after reaction is more difficult than heterogeneous catalysts, use of homogeneous catalyst is gaining attention because of its good catalytic activity, faster reaction rate and moderate reaction temperature conditions, between 50 and 70 °C (Vicente et al., 2007; Georgogianni et al., 2009).

In all chemical reactions, the higher the temperature, the faster the product formation. Furthermore, the variables of temperature and time can influence both the yield and the chemical physical parameters of the final product. For the production of biodiesel, these parameters must stay within those values defined by the European regulation EN14214:2014 (Table 1).

The aim of this work was to study the influence of alcohol and catalyst content on biodiesel production from tomato seed oil by transesterification at a fixed temperature and reaction time. This was both to optimise the conversion parameters from tomato seed oil into biodiesel, and to identify the best product in relation to the current European biodiesel legislation.

Table 1. Parameters of biodiesel described in European regulation EN 14124– 2014 analysed

| Characteristics | Unit | Values | | Analysis Method |
		min	max	
Total Esters	% wt.	96.5		EN 14103
Density 15 °C	kg m^{-3}	860	900	ISO 12185:1996
Viscosity 40 °C	mm^2 s^{-1}	3.5	5.0	ISO 3104:1994
Cetane number		51		EN 5165
Acid value	mg KOH g^{-1}		0.5	EN 14104
Iodine value	g I$_2$ 100 g^{-1}		120.0	EN 14111
Linolenic acid methyl ester	% wt.		12.0	EN 14103
Monoglycerides	% wt.		0.8	EN 14105
Diglycerides	% wt.		0.2	EN 14105
Triglycerides	% wt.		0.2	EN 14105

MATERIALS AND METHODS

Tomato seed oil

The oil used for the experiment was obtained from seeds from a mix of tomato cultivars (*Solanum lycopersicum* L.) discarded after tomato sauce processing in an Italian factory. Oil extraction was conducted by pressing after a complete drying of the seeds. The oil was preserved until its utilisation in dark bottles in cool, dark and dry place.

Chemicals

Methanol, potassium hydroxide, chloroform, acetic acid, Wijis reagent, sodium thiosulphate, starch soluble, ethanol, diethyl ether and phenolphthalein, all of analytical grade; *n*-hexane GC grade ≥ 99.5% were from Panreac (Barcelona, Spain). Sigma-Aldrich (Steinheim, Germany) provided the authentic standard samples of methyl heptadecanoate (purity ≥ 99.0%), N-methyl-N-trimethylsilyl- trifluoroacetamide (TMS) synthesis grade, tricaprin (purity ≥ 99.0%), monolein (purity ≥ 99.0%), diolein (purity ≥ 99.0%), triolein (purity ≥99.0%).

Characterisation of the oil

Each vegetable oil has a characteristic fatty acid composition, which influences its molecular weight. Consequentially, it is necessary to know the composition of these fatty acids to calculate the molar ratio of methanol for esterification. Fatty acid composition was determined by the method reported in CONSLEG 2011 (annex Xa) and is reported in Table 2. The oil's molar mass weight (MW Oil) was calculated using its fatty acid methyl ester (FAME) composition by the following formula (1):

$$MW\ Oil = \frac{\sum_{i=1}^{n} x_i \ MWx_i}{100} \qquad (1)$$

where: x_i is the mass fraction (in %) of the individual FAME and MWx_i is the molecular weight of the individual FAME.

Table 2. Acid composition and molar mass weight of the tomato seed oil used in the transesterification

Fatty acid	%	Mass weight g mol^{-1}	Mass fraction G mol^{-1}
C14:0	0.11	228.37	0.30
C16:0	14.66	256.42	35.47
C16:1	0.20	254.40	1.08
C17:0	0.07	270.45	0.25
C17:1	0.00	268.43	0.97
C18:0	4.82	284.47	12.94
C18:1	20.44	282.46	54.89
C18:2	57.42	280.44	163.96
C18:3	1.88	278.42	6.24
C20:0	0.34	312.53	1.15
C20:1	0.06	311.51	0.31
Total molar mass weight			277.56

Oil transesterification

The experiment was conducted in a 500 ml Erlenmeyer flask with glass stopper and with the use of a refrigerant. A 50 gram sample of oil was preheated to 55 °C and kept in continuous agitation. For each esterification test different amounts of methanol and catalyst were added (Table 3), the chemical reaction was conducted for one hour in all the tests. The choice of this experimental plan was supported by the literature (Refaat et al., 2008; Argawal et al., 2012) where different combinations of temperature, time reaction, amount of catalyst and alcohol were studied. After transesterification, the obtained methyl esters were separated from glycerol by decantation using a separating funnel, and were subsequently washed with until a neutral pH was reached, and to remove any excess catalyst. The resulting biodiesel was heated at 95 °C until their clarification and to remove any excess water. Each sample was stored in a dark glass bottle at room temperature until analysis.

Table 3. Experimental plan

Sample name	Tomato seed oil / MeOH (molar ratio)	KOH/Tomato seed oil (% wt. ratio)
BioA	1/4	1.0
BioB	1/4	0.5
BioC	1/5	1.0
BioD	1/5	0.5
BioE	1/6	1.0
BioF	1/6	0.5

Acid value

The acid value was calculated according to the EN 14104 method. A sample of biodiesel was dissolved in 50 ml of an ethanol/diethyl ether mixture (1 : 1) and titrated with a 0.1 N potassium hydroxide solution. The results were expressed as mg of potassium hydroxide per gram of biodiesel.

Iodine value

Using the EN 14111 method, a sample of biodiesel was dissolved in 20 ml of glacial acetic acid and 25 ml of Wijs reagent was added. After 5 minutes, a 15 ml of potassium iodide (10% w/v) solution was added and the mixture was titrated with a 0.1 mol l^{-1} sodium thiosulphate solution.

Density

Density was determined by a glass densimeter as described by the ISO 12185:1996 method. The analysis was conducted at 15 ± 0.5 °C and the results were expressed as kg m^{-3}.

Kinematic viscosity

Kinematic viscosity was determined according to the ISO 3104:1994 method by a Ubbelohde viscometer and a thermostatic bath to maintain temperature at 40 ± 1 °C. The kinematic viscosity was expressed as mm^2 s^{-1}.

Cetane number

Cetane number determination is laborious. Freedman & Bagby (1990) and Geller & Goodrum (2004) proposed a method to estimate the cetane number (CN) on the basis of FAME composition of the vegetable oil used. This method was implemented by Giuffrè et al., (2016b) on the basis of the formula (2) proposed by Viola et al. (2011):

$$CN = \sum_{i=1}^{n} x_i \; CN_i \qquad (2)$$

where: x_i is the mass fraction of the individual FAME and CN_i is the experimental CN of the individual methyl ester (Viola et al., 2011). It was calculated by the experimental determination of the cetane number of each single FAME following the EN ISO 5165 methods and, then, a relationship between them was found.

Determination of Total Esters and Linoleic acid methyl ester

Gas chromatography-FID analysis was used to determinate the conversion yield after transesterification of each oil sample. The EN 14103 method was applied to verify the yield conversion in Total Esters (TE) in the biodiesel sample and to quantify the single linoleic acid methyl ester. A 250 mg sample of each sample was weighed in a 10 ml glass vial and they were added 5 ml of methyl heptadecanoate in *n*-hexane (10 mg ml^{-1}) was added as an internal standard. A 1 µl sample of this solution was injected in split mode. A Varian GC Thermo 1300 instrument was used, equipped with a fused silica capillary column VARIAN WCOT specific for FAME analysis: length 25 m, ID 0.32 mm and film thickness 0.30 µm. The analytical conditions of the oven were: 140 °C held for 2 minutes, increased by 2 °C min^{-1} to 180 °C held for 5 minutes, increase 5 °C min^{-1} to 230 °C and held for 8 minutes. The injector and detector temperatures were 250 and 280 °C, respectively, with a carrier gas (helium) set at a flow rate of 2.7 ml min^{-1} in constant flow. The TE content was expressed as a percentage and was calculated using the formula (3):

$$TE = \frac{\sum A - AC_{17}}{AC_{17}} \frac{C \times V}{m} 100 \qquad (3)$$

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where: $\sum A$ is the sum of all the FAME peak areas; AC_{17} is the area of the methyl heptadecanoate; C is the concentration in mg ml^{-1} of the methyl heptadecanoate; V is the volume in ml of the methyl heptadecanoate solution and m is the mass in mg of the sample.

The linoleic acid methyl ester (L) content was expressed as a percentage and was calculated using the formula (4):

$$L = \frac{A_L}{\sum A - AC_{17}} 100 \qquad (4)$$

where A_L is the area of linoleic acid methyl ester.

Residual glycerides

The determination of mono-, di- and triglycerides non-transesterified into methyl esters, but residual in the biodiesel sample, was carried out using the EN 14105 method modified as follows: 100 mg of the sample was weighed in a 10 ml glass vial and 200 µl of TMS solution, was added. The vial was hermetically sealed and mixed. After 15 minutes, 2 ml of *n*-hexane were added and 1 µl of the obtained solution was injected in splitless mode into a GC-FID Thermo 1300 trace instrument equipped with a pre-column Restek RXI Guard Column with a length of 5 m, ID of 0.53 mm, and a capillary column Restek Rxi-5HT with a length 15 m, ID of 0.32 mm and film thickness of 0.10 µm. The oven ramp was as follows: 50 °C held for 1 minute, increased to 180 °C at 15 °C min^{-1}, increase to 230 °C at 7 °C min, finally increase to 380 °C at 30 °C min^{-1} and held for 5 minutes. The detector and injector temperatures were 390 °C and 300 °C, respectively, with helium as a carrier gas (4 ml min^{-1} flow rate). The residual glyceride quantity was calculated after injection of mono-, di- and triglyceride standard solution (1,000 mg l^{-1} in *n*-hexane), with tricaprin as an internal standard. This procedure was adopted to calculate the response factor (RF) by the formula (5):

$$RF = \frac{(A_{st} \; C_{st})}{(C_i \; A_i)} \qquad (5)$$

where: A_{st} is the area of the reference standard; C_{st} is the concentration in mg ml^{-1} of the reference standard; C_i is the concentration mg ml^{-1} of the glyceride standard; and A_i is the area of the glyceride standard. RF is necessary to correct the area (A) of the glycerides in the sample and to obtain the corrected area of each peak (A_c) by the formula (6):

$$A_c = A \; \times \; RF \qquad (6)$$

Statistical analysis

The analyses were conducted in triplicate and the results are reported as the mean ± SD, Excel for Windows software (2010 version) was used. The analysis of variance was conducted by one-way ANOVA to study the significant differences and a Tukey's test was applied at $p < 0.05$ by the software SPSS version 17.0 (SPSS Inc., Chicago, IL, U.S.A.).

RESULTS AND DISCUSSION

Yield of biodiesel

Table 4 shows that the highest conversion into biodiesel was obtained from the sample BioE with a content of total esters of 96.80%, the only sample that gave a value above the minimum limit set by European legislation. The other samples showed a lower rate of conversion. This indicates that methanol values lower than the molar ratio 1/6 and an amount of potassium hydroxide lower than 1% does not yield acceptable conversions, at the temperature and for the time used in this experiment. Refaat et al., 2008 using the same conditions as our best result but using a different vegetable oil (fried sunflower oil) and a different reaction temperature (65 °C) obtained a conversion of 96.10%. A 98.20% yield, from a mix of waste cooking oil, was found under the same transesterification conditions, using only a different temperature of 70 °C (Argawal et al., 2012).

Table 4. Total ester content. Data as expressed as means of three measurement ± DS

	% Total Esters
BioA	76.32 ±1.46 c
BioB	72.59 ± 1.96 d
BioC	87.08 ± 1.45 b
BioD	79.77 ± 1.35 c
BioE	96.80 ±0.12 a
BioF	93.73 ±0.07 a
Sign.	**

Means with different letters are statistically different (**, $p < 0.001$).

Parameters of biodiesel quality

Biodiesel quality is characterised by its chemical-physical properties (Table 5). The density ranged from 880 to 891 kg m^{-3}: within the range established by European regulations (Table 1). This parameter varied significantly, in particular it is lower in the samples in which a higher yield was obtained. This is due to the fact that the oil has a higher density than the esters of its fatty acids.

Table 5. Qualitative characteristics of biodiesel samples. Data are expressed as means of three measurements ± DS

	Density kg m^{-3}	Kinematic viscosity mm^2 s^{-1}	Cetane Number	Iodine value g I$_2$ 100 g^{-1}	Acid value mg KOH g^{-1}
BioA	883 ± 1.2 c	7.55 ± 0.16 b	53.2 ± 0.13 c	122 ± 0.1 a	0.14 ± 0.03 a
BioB	891 ± 0.1 a	8.62 ± 0.04 a	53.3 ± 0.12 c	120 ± 1.0 b	0.11 ± 0.01 ab
BioC	881 ± 0.4 d	6.04 ± 0.02 c	53.6 ± 0.09 bc	122 ± 0.4 a	0.11 ± 0.00 ab
BioD	887 ± 0.2 b	7.62 ± 0.07 b	53.6 ± 0.06 bc	119 ± 0.3 b	0.09 ± 0.03 b
BioE	880 ± 0.7 d	4.95 ± 0.03 d	54.2 ± 0.20 a	119 ± 0.3 b	0.06 ± 0.01 b
BioF	886 ± 0.4 b	5.97 ± 0.03 c	54.4 ± 0.15 a	119 ± 0.3 b	0.09 ± 0.03 b
Sign.	**	**	**	**	**

Means in the same column with different letters are statistically different (*, $p < 0.01$; **, $p < 0.001$).

Petrodiesel fuel has a lower density than biodiesel (Lalvani et al., 2015). The density of diesel oil is important because it gives an indication of the delay between the injection and combustion of the fuel in a diesel engine (ignition quality) and the energy per unit mass (specific energy). This can influences the efficiency of the fuel atomization for airless combustion systems.

Kinematic viscosity, expressed as mm^2 s^{-1}, describes a fluid's internal resistance to flow and is influenced by the temperature: an increase in temperature becomes less viscous a liquid. It refers to the thickness of the oil, and is determined by measuring the amount of time in seconds taken for a given measure of oil to pass through an orifice of a specified size (Raj & Sahayaraj, 2010). The viscosity of petrodiesel is often lower than biodiesel (Ramkumar & Kirubakaran, 2016), Kinematic viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel (Demirbas, 2009). Moreover, high viscosity may lead to the formation of soot and engine deposits due to insufficient fuel atomization.

BioE was the only sample showing a kinematic viscosity within the legal limit (4.95 mm^2 s^{-1}), significantly lower and different from the other samples. This was due to the presence in the other samples of unconverted oil, which adversely affects the kinematic viscosity.

Another qualitative parameter of a fuel is the cetane number. The cetane number measures the ignition delay of an engine: a lower cetane number produces higher ignition delay. Moreover fuel with low cetane number tend to cause diesel knocking and show increased gaseous and particulate exhaust emissions due to incomplete combustion. Sometimes petrodiesels have lower cetane numbers than biodiesel fuels.

The studied biodiesel samples showed a cetane number from 53.2 to 54.4, therefore all of them were above the minimum limit stated by the EN 14124:2014, which is 51.0.

Different fuels are characterised by a different unsaturated fatty acid composition, which influences some of their important characteristics such as the oxidation stability: the higher the saturation, which means less double bonds, the higher the fuel stability. Moreover, the oxidation stability negatively affects some engine components such as nozzles, piston rings and piston ring grooves because of the formation of deposits. The iodine value is the parameter used to quantify total unsaturation and is expressed by g I_2 100 g^{-1} of sample.

The current European legislation states that the iodine value of a biodiesel must not exceed 120 g I_2 100 g^{-1} (Table 1). Transesterification significantly affects this parameter. However, tomato seed oil has a high degree of unsaturation, which is then reproduced in biodiesel. In this study, three samples BioD, BioE and BioF did not exceed the legal limit, while the other three were over the legal limit (Table 5).

The acid value is used to evaluate fuel acidity over time. It is expressed as mg of KOH g^{-1} of biodiesel. According to EN 14124:2014 the acid value must not exceed 0.5 mg KOH g^{-1} of biodiesel (Table 1).

The lowest acid value was found in the BioE sample (0.06%), while the highest was in BioA (0.14%). Therefore, all samples were well below the maximum legal limit (Table 5).

Regarding the iodine value, the presence of linolenic acid increases the instability of biodiesel and thus worsens the biofuel quality, since its three double bonds are easily oxidizable. The legal limit is set at 12% of the total FAME composition, considerably higher than the values found in our samples. The content of linolenic acid was always well below the legal limit (the highest content of 1.88% was found in BioA), as shown in Table 2. This reflects the composition of tomato seed oils. Similarly low figures for tomato seed oils are found in the literature: 1.98% (Zuorro, 2013) and 2.06% (Zuorro et al., 2014).

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The vegetable oil was not completely converted into biodiesel. For this reasons, in biodiesel a residual of triglyceride and mono- and diglyceride partially esterified could be found. The presence of these compounds, not only adversely affects the quality parameters of the final product, (i.e. kinematic viscosity and yield), but also causes an engine malfunction because they are not suitable for the diesel cycle. So, the allowed amount of these molecules in biodiesel is regulated, and a maximum limit has been set at 0.8%, 0.2% and 0.2%, respectively, for monoglycerides, diglycerides and triglycerides (Table 1). As reported in Table 6, only BioE respected this statement.

Table 6. Residual of non-transesterified oil. Data are expressed as means of three measurements ± DS

	Monoglyceride %	Diglyceride %	Triglyceride %	Linolenic acid methyl ester %
BioA	2.34 ± 0.03 c	3.16 ± 0.07 c	5.11 ± 0.50 b	1.88 ± 0.05 a
BioB	8.40 ± 0.28 a	5.65 ± 0.52 a	6.29 ± 1.27 a	1.84 ± 0.04 ab
BioC	2.67 ± 0.73 c	1.02 ± 0.33 d	2.22 ± 0.54 cd	1.71 ± 0.10 bc
BioD	4.61 ± 0.21 b	4.46 ± 0.03 b	9.45 ± 1.22 b	1.79 ± 0.09 abc
BioE	0.30 ± 0.01 d	0.11 ± 0.02 e	0.05 ± 0.01 d	1.65 ± 0.03 c
BioF	0.12 ± 0.01 d	0.43 ± 0.02 de	0.15 ± 0.01 c	1.71 ± 0.01 bc
Sign.	**	**	**	*

Means in the same column with different letters are statistically different (*, $p<0.01$; *, $p<0.001$).

CONCLUSIONS

This study showed that the esterification of tomato seed oil could lead to the production of biodiesel. The biodiesel yield very significantly increases both with increasing amounts of methanol and catalyst, and in one case the biodiesel yield complied with the European legislation, which regulates its conversion. However, other combinations of variables - time reaction, temperature reaction, alcohol and catalyst amount -, should be studied to further improve the yield.

Biodiesel Bio E, which was obtained by trans-esterification of tomato seed oil, at 55 °C for one hour of reaction time with an oil/MeOH ratio molar 1/6 and 1% wt. of catalyst in oil, showed the best yield and had the best chemical-physical parameters. These results confirm the possibility that biodiesel could be economically processed from tomato seed oil with characteristics compliant with the European regulation EN14124:2014. Therefore, such biodiesel could be used as an alternative, or in addition, to fossil fuels, which would also help existing energy sources.

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