

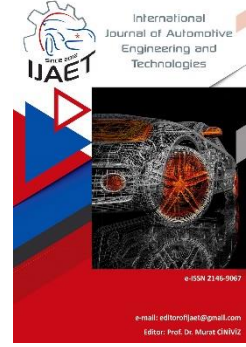


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Original Research Article

Unique fatty acid composition of coriander seed biodiesel



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ABSTRACT

Biodiesel is a renewable and environmentally friendly alternative fuel that can be used in diesel engines without modification. In this study, biodiesel production from coriander seed oil obtained through a two-stage transesterification process using the cold pressing method was carried out in the Konya region. First, the oil's acid value was reduced through acid-catalyzed pretreatment to form coriander seed oil methyl esters, and then biodiesel was produced using standard transesterification with methanol and sodium methoxide catalyst.

Coriander (*Coriandrum sativum*) contains an unusual fatty acid not previously reported as a major component in biodiesel fuels: petroselinic acid (6Z-octadecenoic acid; 68.5% by weight).

Coriandrum sativum seed oil methyl ester was evaluated to have properties suitable for diesel engines, complying with EN 14214 and ASTM D6751 standards, with a unique fatty acid composition and excellent oxidative stability.

Keywords: Biodiesel, Transesterification, Coriander Seed, *Coriandrum sativum* L., Vegetable Oils

1. Introduction

Biodiesel is defined as the mono alkyl esters of long-chain fatty acids prepared from vegetable oils, animal fats, or other lipids [1]. Globally, there are over 350 oil-bearing products identified as potential sources for biodiesel production, and the diversity of feedstocks is one of the most significant advantages of biodiesel production [2-5]. The utilization of energy crops or even technologies for converting them into biodiesel dates back to ancient times and is now widely adopted. In

recent years, the depletion of petroleum-based fuel reserves, increasing environmental concerns, energy costs, and the quest for sustainable and renewable energy have made this field attractive in many aspects.

Biodiesel consists of ethyl or methyl esters containing short to medium-length fatty acid chains [6-8]. Biodiesel derived from used cooking oils, including vegetable, animal, microbial oils, and triglycerides, has been widely accepted as a good alternative to petroleum-based fuels [9-12]. Generally, biodiesel feedstocks can be divided into four

main categories: i) Edible vegetable oils (rapeseed, soybean, peanut, sunflower, palm, and coconut oil, etc.), ii) Non-edible vegetable oils (jatropha, karanja, sea mango, algae, and halophytes), iii) Waste or recycled oils, iv) Animal fats (tallow, yellow grease, by-products from chicken and fish oil) [2, 13-15].

Biodiesel harbors many positive properties due to being produced from renewable raw materials, its superior lubricity, reduced dependence on external sources, biodegradability, lower toxicity, nearly sulfur-free content, high flash point, and reduction in most exhaust emissions [16].

Despite its many advantages, biodiesel also brings some disadvantages compared to fossil fuels, such as high raw material costs, lower energy capacity compared to diesel, higher viscosity and density, lower volumetric energy content, lower storage and oxidative stability, and in some cases, higher NO_x emissions [17-19].

There are four main methods for the use of vegetable oils in engines without the need for any modification; these are i) blending or direct use, ii) microemulsification, iii) pyrolysis, and iv) transesterification. Among these methods, transesterification has been significantly researched and commercially utilized [7, 20-26].

Biodiesel can be produced on an industrial scale through transesterification of its feedstocks, such as solid and liquid oils [27]. Approximately 97% of vegetable and animal oils consist of triglycerides, with 3% being monoglycerides and diglycerides. Triglycerides, also known as triglycerides, are esters formed by the combination of three fatty acids with glycerol [28, 29]. The esterification of fatty acids with glycerol, or in other words, the chemical equation for transesterification, is illustrated in Figure 1.

Petroleum-derived diesel fuel consists predominantly of paraffins and aromatics [30]. Vegetable oils, on the other hand, comprise triglycerides, carbohydrate-based compounds, phosphatides, aromatic compounds, coloring matter, free fatty acids, and glycerides. The type and quantity of unsaturated fatty acids are determinant factors in the properties of vegetable oils [31].

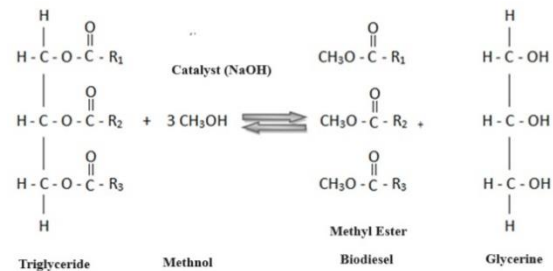


Figure 1. Vegetable oils transesterification.

Fatty acids are monocarboxylic organic acids composed of varying lengths of straight chains, and the chemical structure of the fatty acid affects many characteristics of the fuel. The cold flow properties of oil are related to chain length, degree of branching, and degree of saturation. For example, as the chain length of fatty acids decreases or branching increases in the carbon chain, the cold filter plugging point improves, along with other properties such as flow and cloud point. Additionally, an increase in the saturation ratio of the oil leads to an increase in cetane number [32].

Vegetable oils typically consist of five common fatty acids: i) palmitic (hexadecanoic), ii) stearic (octadecanoic), iii) oleic (9 Z - octadecenoic), iv) linoleic (9 Z, 12 Z - octadecadienoic), and v) linolenic (9 Z, 12 Z, 15 Z - octadecatrienoic) acids. The fuel properties of biodiesel largely depend on the composition of the lipid from which it is prepared [33]. Consequently, biodiesel fuels with different fatty acid compositions exhibit different fuel properties and can serve as models for other oils with similar fatty acid profiles. An economically significant plant containing an unusual fatty acid profile is coriander (Figure 2).



Figure 2. Appearance of coriander plant seeds, leaves, and roots (USDA, 2023)

The scientific name of coriander, also known colloquially as cilantro, is *Coriandrum Sativum*. It belongs to the Apiaceae family of the Apiales order, which encompasses more than 3000 species (Table 1) [34, 35]. *Coriandrum sativum*, originating from the Mediterranean and Middle Eastern regions, is

now widely cultivated and used across various sectors worldwide [36, 37].

Table 1. Taxonomic classification of the coriander plant (USDA, 2023)

Taxonomic classification	Scientific Name
Kingdom	Plantae
Subkingdom	Tracheobionta-vascular plants
Subdivision	Spermatophyta
Division	Magnoliophyta
Class	Magnoliopsida-Dicotyledons
Subclass	Rosidae
Order	Apiales
Family	ApiaceaeLindl
Genus	Coriandrum L.
Species	Coriandrum sativum L.

Naturally occurring exclusively in flowering plant families, the Apiaceae family contains petroselinic acid in its fixed oil, which constitutes approximately 60-70% of coriander (*Coriandrum Sativum*) [38]. Petroselinic acid serves as the primary fatty acid in raw coriander oil and exhibits various biological and health-enhancing properties [39].

Due to its antioxidant, anti-diabetic, mutation-preventing, and antimicrobial activities, along with analgesic and hormone-balancing effects, petroselinic acid is promoted for its numerous health benefits in food applications [40]. Additionally, its preservative effect prolongs the shelf life of food products [37, 41]. Turkey's soil and climatic conditions are highly conducive to coriander cultivation [42].

The medicinal uses of coriander (*Coriandrum Sativum*) have been known since ancient times. Since the 1900s, coriander seed oil has been utilized in the food and fragrance industries. Coriander, especially its roots, leaves, fruits, fresh shoots, and dried powdered seeds, is commonly used as a spice due to its remarkable organoleptic properties [43, 44]. Coriander's volatile oil is employed as a flavor enhancer or preservative in cooking, as a therapeutic agent in the pharmaceutical sector (antimicrobial, antimutagenic, anthelmintic, anticonvulsant, diuretic, gastric mucosa protector), and as a fragrance in perfumery [37]. *Coriandrum Sativum* is rich in linalool, vitamin A, vitamin B12, vitamin C, folate, and phenolics. *Coriandrum sativum* fixed oil is rich in sterols, tocopherols, and bioactive phytochemicals.

Petroselinic acid is the main fatty acid in *Coriandrum sativum* fixed oil [45]. Although petroselinic acid has not been widely reported as the main component in biodiesel fuels, the high cost of fossil fuel feedstocks, pollution caused by exhaust emissions, and the anticipated decline in fossil fuels in the future have prompted scientists to search for alternative fuels. The aim of this study was to produce biodiesel from the oils extracted from coriander, a plant species rarely used in fuel production, by purifying them from fatty acids and employing transesterification.

2. Material and Method

2.1. Material

Coriander seeds were obtained through cold pressing method using the apparatus shown in Figure 3 (Tazemiz Doğal Ürünler İşletmesi Erdemli/MERSİN). Coriander seeds, obtained from growers in the Konya region, were passed through a sieve to separate them from stems and debris. Oil was extracted from coriander seeds using pressing technique without applying heat treatment, yielding an average of 10-13% oil.



Figure 3. Process of extracting coriander seed oil using the cold pressing method.

2.2. Composition and properties of coriander seed oil

The primary fatty acid identified in coriander oil is petroselinic acid (constituting approximately 68.5% by weight), along with linoleic acid (13.0% by weight) and oleic acid (7.6% by weight), which together make up the majority of the remaining fatty acid profile (Table 5). Minor components include palmitic acid (5.3% by weight), stearic acid (3.1% by weight), and vaccenic acid (11 Z -octadecenoic acid, 1.0% by weight), with trace amounts of palmitoleic acid (0.3% by weight) also identified. Coriander oil is characterized by a high content of monounsaturated fatty acids (77.4% by weight), primarily due to the

combined petroselinic and oleic acid content. It contains a moderate amount of polyunsaturated fatty acids (13.0% by weight) and saturated fatty acids (8.4% by weight).

Table 2. Fatty acid profile of coriander oil (% by weight) [46].

Fatty Acids	Coriander
C16:	5,3 (0,5) ^b
C16:1 c9	0,3 (0,2)
C18:0	3,1 (0,1)
C18:1 c6	68,5 (0,8)
C18:1 c9	7,6 (0,2)
C18:1 c11	1,0 (0,1)
C18:2 c9, 12	13,0 (0,1)
C18:3 c9, 12, 15	–
Unknown (total)	1.2
Σ Sat ^c	8.4
Σ Monounsaturated ^d	77.4
Σ Polyunsaturated ^e	13.0

For instance, C18:1 9c indicates an 18-carbon fatty acid chain with a cis double bond at carbon 9 (9 Z -octadecenoic acid; oleic acid).

^a The number within parentheses represents the standard deviation. ($n = 3$).

^c Σ Sat = C16:0 + C18:0.

^d $e\Sigma$ Monounsaturated = C16:1 + C18:1.

^e Σ Polyunsaturated = C18:2 + C18:3.

2.3. Biodiesel production

To produce coriander seed oil methyl esters, the acid value of the oil was first reduced through an acid-catalyzed pretreatment. Then, standard transesterification procedure was carried out using methanol and sodium methoxide catalyst to produce biodiesel.

2.4. Acid-catalyzed pretreatment of coriander oil

The acid-catalyzed pretreatment of coriander seed oil, with an initial acid value of 2.66 mg KOH g⁻¹, was conducted in a 500 mL round-bottom flask connected to a reflux condenser and a magnetic stirrer set at 1200 rpm. Initially, coriander oil (224g, 250 mL) and methanol (70.72 g, 88 mL) were added to the flask, followed by the slow addition of sulfuric acid (2.50 mL). The contents were then heated for 1 hour under reflux. After cooling to room

temperature, the phases were separated, and the oil phase was washed with distilled water until a neutral pH was achieved.

2.5. Methanolysis

Standard transesterification procedure with methanol and sodium hydroxide (NaOH) catalyst was employed to obtain coriander seed oil methyl esters. Weighing of the oil, alcohol, and catalyst was done on a precision balance. After weighing methanol and catalyst (NaOH) into a glass beaker, the mixture was heated to approximately 30°C in a magnetic stirrer with heating, and NaOH was completely dissolved in alcohol with stirring using a glass rod. Methanolysis of the oil was conducted in a 1 L round-bottom flask. To ensure uniform temperature distribution on the magnetic stirrer with heating, water was placed in a container (as seen in Figure 4.a), and the container was placed on the magnetic stirrer with heating. The glass flask containing coriander seed oil was placed into the water. Once the desired temperature was reached, the previously prepared alcohol + catalyst mixture was added to the heated oil to initiate the reaction.

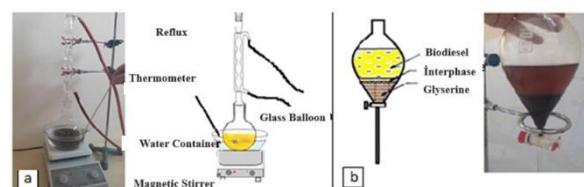


Figure 4. a) Reaction setup for transesterification b) Phase separation

Glass reflux condenser connections were made in the prepared setup to minimize methanol evaporation during the reaction. The mixture was stirred at approximately 800 rpm at 60°C for 1 hour. After the reaction time elapsed, the magnetic stirrer with heating was turned off, and the mixture was allowed to cool to room temperature. Once cooled, the mixture was transferred to a separation flask (Figure 4.b). The reaction process with transesterification is illustrated in Figure 5.

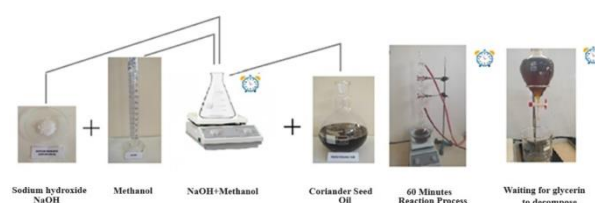


Figure 5. Reaction process with transesterification.

The biodiesel-glycerin mixture was allowed to settle until a distinct separation line formed. After the separation process, the glycerin collected at the bottom of the separating funnel was drained into an Erlenmeyer flask by opening the valve.

The remaining portion in the separating funnel is biodiesel. To separate biodiesel from glycerin particles, a washing process was conducted five times. Distilled water was added onto the biodiesel, the cap of the separation flask was closed, and the water-biodiesel mixture was shaken to repeat the washing process. In the separating funnel, due to the difference in density, the distilled water collected in the lower phase. Biodiesel accumulated in the upper part of the separation flask. The distilled water collected at the bottom was drained out through the valve of the separation flask. For methanol recovery, a reflux distillation process was conducted at

75°C. Coriander seed oil methyl ester was obtained by drying with Magnesium Sulfate $MgSO_4$ (94% by weight) at 100°C for one hour. Finally, the obtained biodiesel underwent filtration using Whatman filter paper.

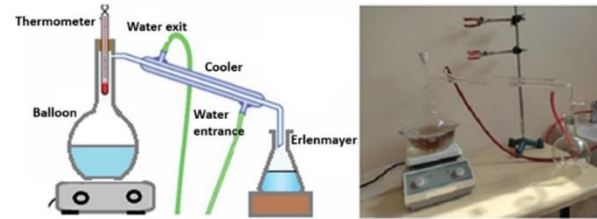


Figure 6. Methanol Recovery by Distillation Process.

Biodiesel must meet acceptable values for specified properties according to recognized fuel standards. In 2008, the current versions of EN 14214 and ASTM D6751 were published, replacing the previous standards [47]. When comparing coriander oil biodiesel with these widely used standards, it is generally found to be compatible with standard values (Table 3).

Table 3. Physical Properties of Coriander Oil Methyl Esters Compared to Biodiesel Fuel Standards [46].

Property	Unit	Biodiesel Standards		Coriander Seed Biodiesel	
		EN 14214	ASTM D6751		
Efficiency ^a	wt%	-	-	94	
MW ^{calculation}	g mol ⁻¹	-	-	294.80	
Gardner color	-	-	-	10	
AV	mg g ⁻¹	0.50 max	0,50 max	0.10 (0.01) b	
Free glycerol	wt%	0.020 max	0,020 max	0.005	
Total glycerol	wt%	0.250 max	0,240 max	0.119	
Low temperature:					
CP	°C	-	Report	n/d c	
PP	°C	-	-	-19 (0)	
CFPP	°C	Variable d	-	-15 (1)	
Oxidative stability:					
IP, 110 °C	h	6.0 minutes	3.0 minutes	14,6 (0,7)	
OT	°C	-	-	205.2 (1.1)	
Kinematic viscosity	40 °C	mm ² /s	3.50–5.00	1,90–6,00	
	Wear scar, 60 °C	micron	- e	- e	
	Sulfur	ppm	10 max	15 max	4,21 (0,01)
	Phosphorus	wt%	0.0004 max	0,001 max	4
	DCN		51.0 minutes	47.0 minutes	0.0000
	Calorific value:				53.3 ^f
	HHV	MJ/kg	-	-	
LHV	MJ/kg	-	-		
IV	g I2/100g	120 max	-	40,10 (0,07)	
a	Efficiency (% mass) = observed product mass divided by the max. theoretical value.				
b	The number in parentheses represents the standard deviation (n = 3).				
c	Not determined.				
d	Varies depending on location and time of year.				
e	Maximum wear scar values of 520 and 460 μm are specified in the petrodiesel standards ASTM				
f	Maximum wear scar values of 520 and 460 μm are specified in the petrodiesel standards ASTM D975 and EN 590.				
g	From reference [48].				

3. Conclusions

Coriander (*C. Sativum* L.) seed oil methyl esters were evaluated as an alternative biodiesel fuel, and a standard transesterification procedure was prepared using methanol and sodium methoxides. Before transesterification, pretreatment with acid catalysis was applied to reduce the acid value of the oil, followed by the standard transesterification procedure. General research findings from the study are given below. Coriander seed oil methyl esters properties have been determined according to the international biodiesel standard, which states that it is an acceptable fuel in diesel engines.

- Coriander seed oil methyl ester meets ASTM D6751 and EN 14214 biodiesel fuel standards. Its kinematic viscosity (4.21 mm²/s), sulfur rate (4 ppm) and phosphorus (0.000) contents are at a satisfactory level.
- Cold filter clogging and flow points are -15°C and -19°C, respectively.
- It also exhibits good additional properties such as heat of combustion (40.10 MJ kg⁻¹) and lubricity (HFFR 163 microns).
- Coriander oil contains high levels of petroselinic acid (68.5% by weight), which has not previously been identified as the main fatty acid component in biodiesel fuels.
- Coriander seed oil methyl esters have superior oxidative stability (14.6 hours 110 °C). However, fatty acid profile alone cannot explain the high oxidative stability of coriander seed oil methyl esters and should be further investigated.
- In conclusion, Coriander (*C. Sativum*) seed oil methyl ester shows interesting fuel properties with its unique fatty acid composition.

As a suggestion for future studies, the relationship of petroselinic acid with oxidative stability can be investigated in detail.

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CRedit authorship contribution statement

Suleyman Simsek: Conceptualization,

Investigation, Methodology, Writing – original draft, Writing – review & editing. **Esra Koc:** Investigation, Conceptualization, Writing – original draft, Writing – review & editing. **Aysegul Can:** Investigation, Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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