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The Effects of the Addition of Dill Oil (*Anethum graveolens)* into Biodiesel-Diesel Blends

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Abstract: The effects of dill oil extract as an antioxidant on the crystallization properties of colza biodiesel were investigated. 3000 ppm dill oil *(Anethum graveolens)* was blended with colza biodiesel-diesel mixtures at certain rates. The chemical antioxidant butylated hydroxytoluene (BHT) was used to compare the effects. For this reason, the samples were prepared and called D100, B20D80, B20D80D, and B20D80BHT. The crystallization temperatures (T_{cr}) of the samples were determined by using a Differential Scanning Calorimetry (DSC) technique. The values of samples with antioxidants were decreased compared to the non-antioxidant biodiesel sample (B100). The order of antioxidant power was D100<B20D80<B20D80BHT<B20D80D. DSC results showed that the crystallization onset temperatures for D100, B20D80, B20D80BHT and B20D80D were −11.37 °C, −13.42 °C, -14.94 °C, and −15.65 °C, respectively. The addition of dill oil extract as a natural antioxidant had a positive effect on biodiesel oxidative stability for 3000 ppm concentration. Natural dill oil showed a similar efficiency with BHT that the synthetic chemical antioxidant. The dill oil can be used as an antioxidant after the complete standard fuel tests.

Keywords: Anethum graveolens oil, Biodiesel, Colza biodiesel, Dill oil, Natural antioxidant, Oxidative stability.

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INTRODUCTION

Energy resources are a crucial factor in the economies of many countries as they are used in many areas. Fossil fuels (such as oil, coal, and natural gas) have been used as the main energy sources around the world for a long time. (Atabani et al., 2019). The high consumption of fossil fuels has increased carbon emissions, which has accelerated the global warming. The CO_2 gas released because of the combustion fossil fuels has a negative impact on the environment. The frequent occurrence of these climate problems encourages countries to develop renewable energy sources (1, 2). Due to the negative effects of fossil fuels on the environment and the decrease in their reserves, environmentally friendly and sustainable alternative fuels are being researched instead of fossil fuels (3).

In new-renewable energy sources, biomass energy such as biofuel has the greatest technical potential. Biodiesel is obtained by esterification reaction of oils/animal fats (4) or waste cooking oils (5,6) with alcohols, and constitutes an alternative to conventional diesel (7). Biodiesel contains various saturated/unsaturated fatty acid esters, mainly fatty acid methyl esters (FAMES) (Boulal et al., 2019). Biodiesel has some advantages such as being biodegradable, having fast dissolution in nature, having an absence of toxic waste, being nonexplosive, and has supply security because of the wide raw material resources available. Since biodiesel is a better lubricant compared to petroleum diesel, it prolongs the life of the engine. Due to the fact that production can be completely domestic, eliminates foreign dependence (8). Besides the advantages, there are also disadvantages in the use of biodiesel, such as high production cost, the tendency to oxidation, and high NO_x exhaust emissions. These disadvantages might prevent the frequent use of biodiesel. NO_x emissions are 10% higher than conventional diesel, but as there is no sulfur in its composition, NO_x emission can be reduced by using a catalytic converter. Compared to diesel biodiesel cold flow properties are worse, and cold weather may cause problems during the first start-up. Biodiesel can be applied as a substitute for conventional diesel, or biodiesel can be blended with diesel (Jain & Sharma, 2011a) or alcohols (Maleki & Ashraf Talesh, 2022) instead of diesel fuels. Biodiesel is generally named as in Table 1.

Table 1. Biodiesel codes and the content of the code (9)

Standard Code	Biodiesel Content (%)	Diesel Content (%)
B5	5	95
B20	20	80
B50	50	50
B100	100	-

There are three different types of biodiesel. These are; FAME (Fatty Acids Methyl Ester), HVO (Hydroprocessed Vegetable Oil), and BTL (Biomass to Liquids). In Europe and America, biodiesel produced in certain proportions can be added to diesel fuel. As fuel stability of the fuel depends on the climatic conditions, oxidation may occur in the fuel due to heat changes and as a result of this oxidation, deposits may occur in the fuel, and this situation can cause storage stability issues. Antioxidants are added to the biodiesel-diesel blend to improve some properties like oxidation stability as well as cold flow, to prevent or delay the oxidation in the fuel (10). The types of antioxidants involved are divided into *Natural and Synthetic* (11). The antioxidant types were classified in Figure 1. The studies about natural antioxidants from plants were represented in Table 2.

Table 2: Presented studies about natural oil as an antioxidant in the literature.

Antioxidant	Biodiesel	Report
Tert-Butylhydroquinone	Soybean	Longer induction period (12)
Butylated hydroxyanisole Butylated hydroxytoluene	Palm oil	Reduced emissions (13)
Butylated hydroxyanisole	Calophyllum inophyllum	Reduced nitrogen oxide (14)

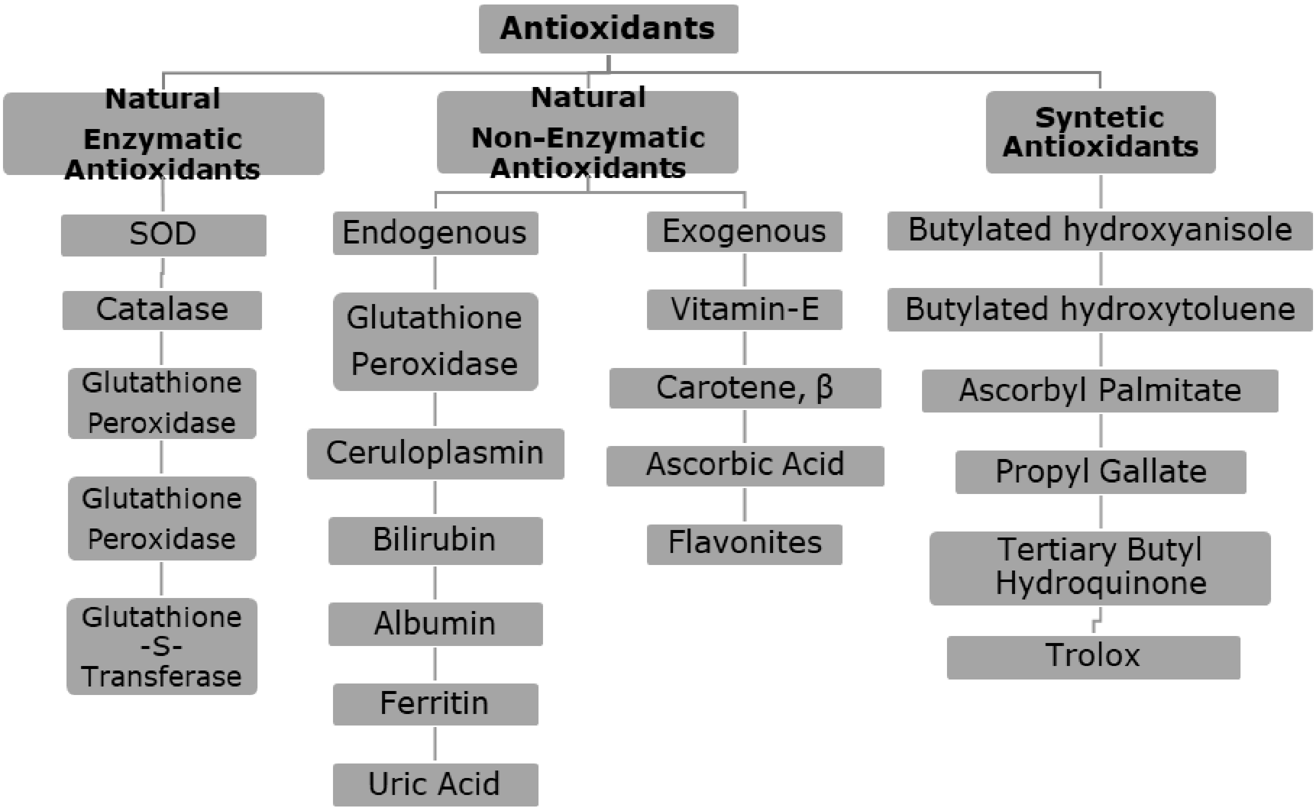
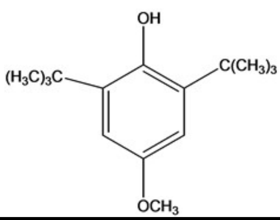


Figure 1: Classification of antioxidants (15).

Dill, which was found suitable to be used in the study, is generally preferred as a sedative, antispasmodic, diuretic, and gas blocker in babies, which contains essential oil, fixed oil, and phenolic components. The well-being of dill essential oil is proportional to the percentages of carvon and α-phellandrene in it. Carvone and limonene are the main mixtures in dill essential oil. Dill is preferred in foods as an antioxidant due to its intense taste and essential oil (16).

The data obtained because of the experiment were compared with BHT, a synthetic antioxidant. BHT, or by its chemical name 2,6-di-tert-butyl-p-cresol (DBPC), is a synthetic phenolic antioxidant widely used as a food additive. BHT, due to its phenolic structure, gives hydrogen from phenolic hydroxide groups and prevents the emergence of free fatty acid radicals in the head part of the fatty acid. It has a high antioxidant character. It activates the quality of the oils and prevents the formation of deposits. BTH is used in the food and rubber sectors, metallurgy, cosmetics, pharmaceuticals, embalming liquids, antifreeze, and auto chemistry liquids, and it is also widely used in the fuel industry. The properties of BHT is depicted in Table 3.

Table 3: The properties of BHT.

Chemical structure	Molecular weight (g/mol)	Chemical formula
	220.35	$C_{15}H_{24}O$

Dill (*Anethum graveolens* L.) is an annual or biennial herb belonging to the Apiaceae family. Dill essential oil is used for the treatment of gastrointestinal disorders such as abdominal distension, gastritis, intestinal spasm, and flatulence. The leaf, seed, and essential oil of dill shows good antioxidant activities (17).

Dill was preferred for this study because of the natural antioxidant properties it contains. The essential oil was obtained using soxhlet extraction. The extracted oil was added to 3000 ppm into various prepared biodiesel-diesel fuel mixtures. Biodiesel-diesel fuel mixture containing extract was subjected to various characterization tests. FT-IR is a highly preferred type of characterization test due to its characteristics such as being cheap and giving fast results, so it was preferred for this study. At the stage of determining the crystallization point of the resulting fuel mixture, DSC was used. Because of the tests carried out and the data obtained, improvements in the crystallization point occurred with the addition of dill extract to biodiesel-diesel fuel mixtures. Such a study could open up new directions for the field of biodiesel research in the future (18–20). In this study, the effects of *Anethum graveolens* oil addition to biodiesel-diesel blends. FT-IR and DSC analyses were performed and the obtained data were evaluated.

EXPERIMENTAL SECTION

Materials and Methods

n-Hexane (97%) was purchased from Sigma-Aldrich. Colza biodiesel (B100) and diesel fuel were provided commercially by Biodiesel Company (TBE) and fuel company (OPET) in Turkey, respectively. *Anethum graveolens* were collected manually in the region of Samsun, Turkey. It was cleaned with distilled water to remove surface impurities. Then it was dried in the oven at 70 °C for 48 hours to yield a fine powder. After drying, samples were crushed and sieved by a grinder. This was preserved by storage at the temperature of 4 °C against both light and humidity, until following extractions.

Soxhlet Extraction

Anethum graveolens powder (20 g) was firstly put in a filter paper cellulose cartridge and then extracted for 8 h on a soxhlet apparatus using 300 mL of analytical grade n-hexane as a solvent. After the extraction, the residual solvent was separated from the solid with a rotary evaporator. The remaining substance was kept in a drying oven at 40 °C for 48 hours. Finally, the glass round-bottomed flask containing the substance was sealed and stored at the temperature of 4 °C until following process (21).

Preparations of Biodiesel-Diesel Blends

Standard biodiesel-diesel blends were prepared with 20% biodiesel and 80% diesel. The mixture was called as B20D80. The plant extracts were added into the blends at 3000 ppm level.

Fourier Transform Infrared Spectroscopy (FT-IR)

The possible chemical functional groups present in *Anethum graveolens* were investigated with FT-IR (Perkin Elmer, Spectrum-Two, USA). The sample surface was scanned in the 650–4000 cm^{-1} range. The ATR FT-IR spectra were recorded at room temperature. The background subtraction, baseline, and data tune-up correction were done.

Differential Scanning Calorimetry (DSC)

To determine the crystallization temperatures of D100, B20D80, B20D80D, B20D803000, and BHT were analyzed by DSC Q-2000 (TA Instrument-Waters, USA). Dynamic DSC measurements were carried out in an aluminum crucible with a small variation in sample mass of approximately 5±0.5 mg and placed in the DSC module with a similar empty pan as reference. The rate of cooling was 10 °C/min between −90 °C and 25 °C with a flow rate of 50 mL/min. The instrument was flushed with nitrogen. Each DSC test took about 16.5 minutes to complete a single sample. The summary of the DSC method is given in Table 4 (18).

Table 4: Summary of DSC method by TA Q-2000 DSC (18).

Instrument	TA Q-2000 DSC
Sample amount	5±0.5 mg
Gas	Nitrogen
Flow rate	50 mL/min
Temperature range	-90 °C-25 °C
Ramp rate	10 °C/min

RESULTS AND DISCUSSIONS

FT-IR

In the FTIR spectra, the spectrum placed between wavenumber (cm^{-1}) vs. transmittance percentage (T %) shows the regions of the spectrum that specific molecular vibrations containing in the D100, B20D80, B20D80D, B20D803000, and BHT. Generally, wavenumber and transmittance percentage were obtained for v(O−H) (3000−3700 cm^{-1}), v(C−H) (2700−3000 cm^{-1}), v(C=O) (1500−1800 cm^{-1}), and v(C−O) (600−1400 cm^{-1}) vibrations. Oxidation stability is shown by v(O−H) and v(CH) vibrations of samples because of the substitution by alkyl functionals in ortho- and para position to develop the electron density around the -OH group. In the FTIR spectra, v(C−O) and v(C=O) vibrations represent in the presence of ether or ester functional groups in a sample (22). The effect of adding natural and synthetic antioxidants to biodiesel samples at 3000 ppm concentration. v(O−H) valence-stretching vibration of an unbounded hydroxyl group is usually quoted as being 3700−3500 cm^{-1}. In addition, IR spectra of function biodiesel samples indicate a decrease in the intensity of the vibrations at v(C−H) (2700−3000 cm^{-1}). Because of increase in saturation represents that there is a lack of possibility in favor oxidative polymerization reaction. Antioxidant activity as D100< B20D80< B20D80300BHT<B20D80300D because phenolic antioxidants can be positioned in the same order (23).Consequently, the increases in the transmittance in the antioxidant effect regions of the FTIR spectrum with the addition of antioxidants are evidence of the effectiveness of the added antioxidant which has carvone and limonene groups. The lists of functional groups identified were shown in Table 5 (24).

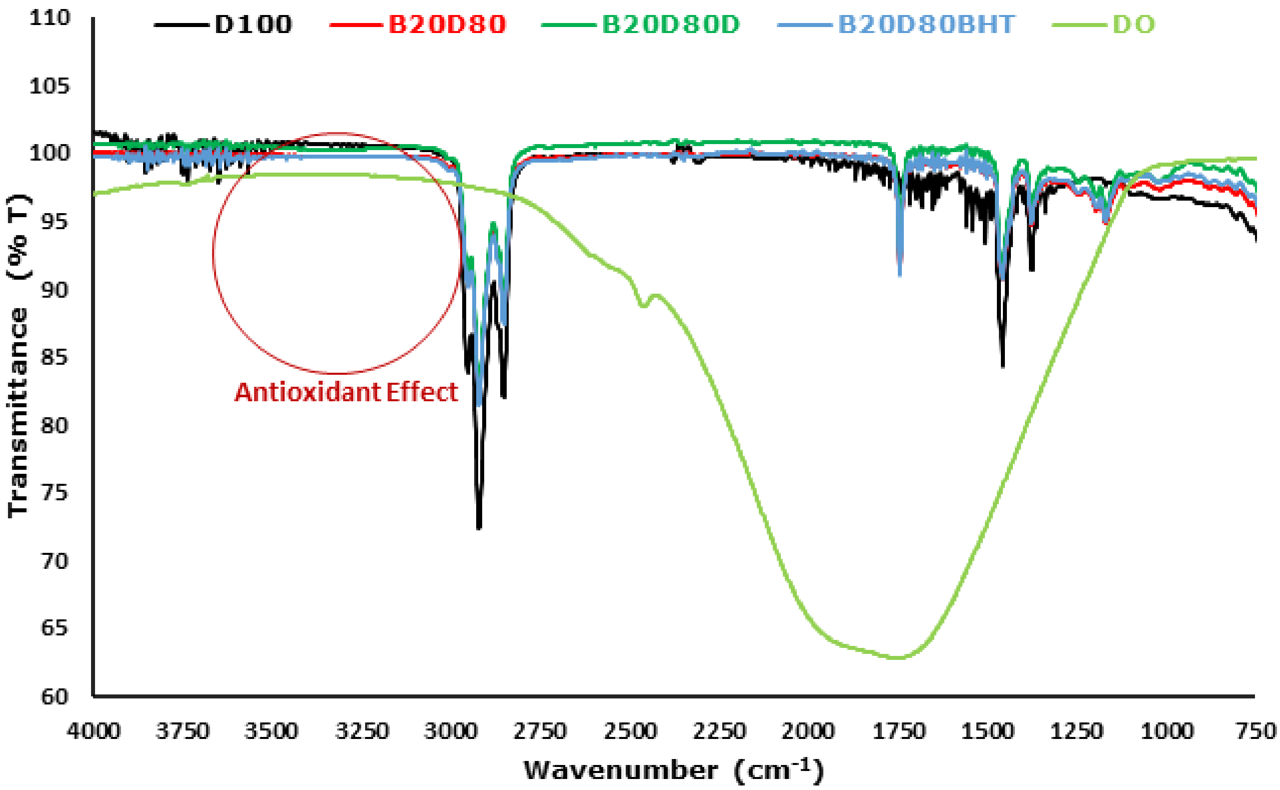


Figure 2: FT-IR spectra of D100, B20D80, B20D80D, DO, and B20D80BHT between 750-4000 cm^{-1} range.

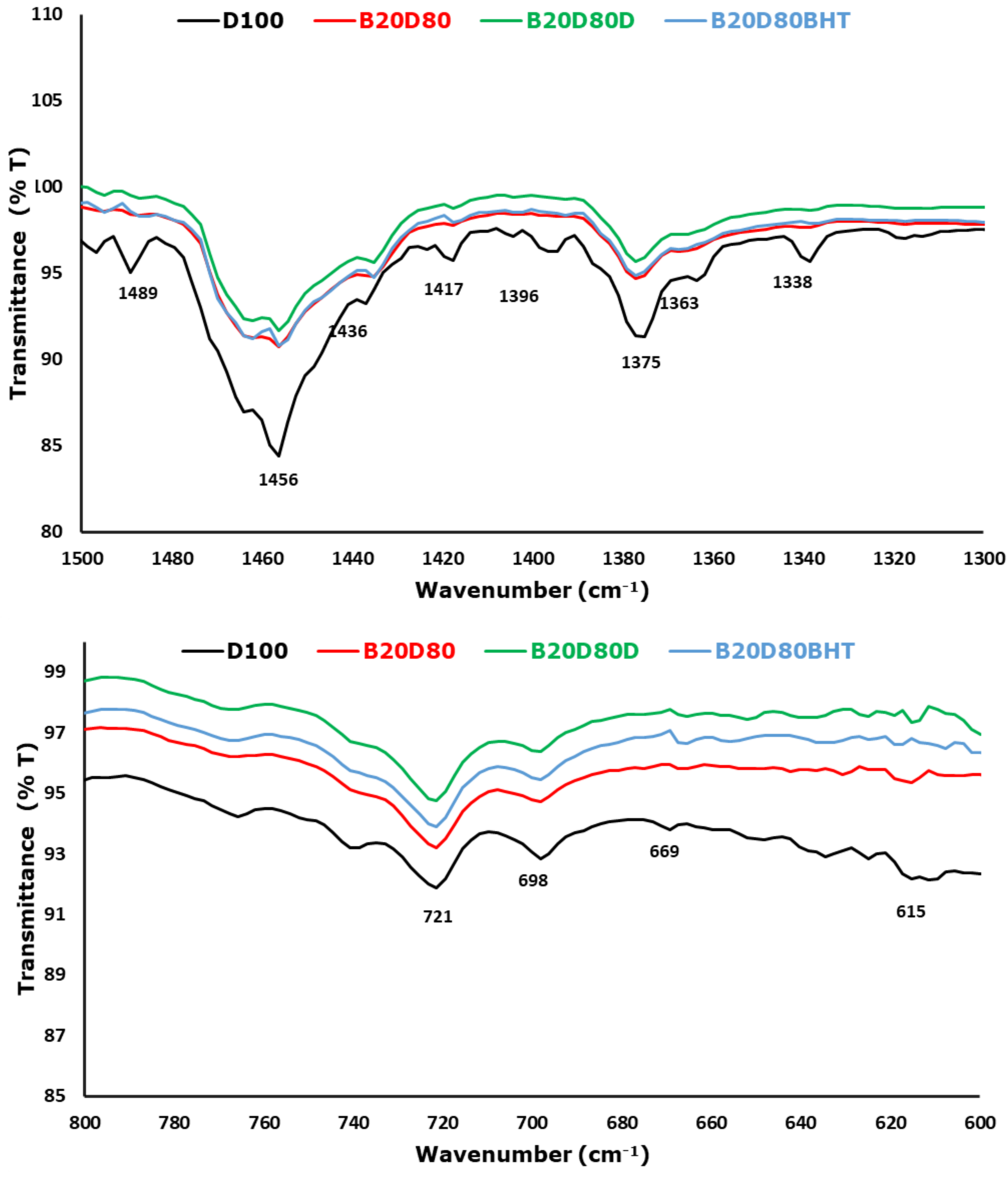


Figure 3: FT-IR spectra of D100, B20D80, B20D80D, and B20D80BHT between 600-800 cm^{-1} range

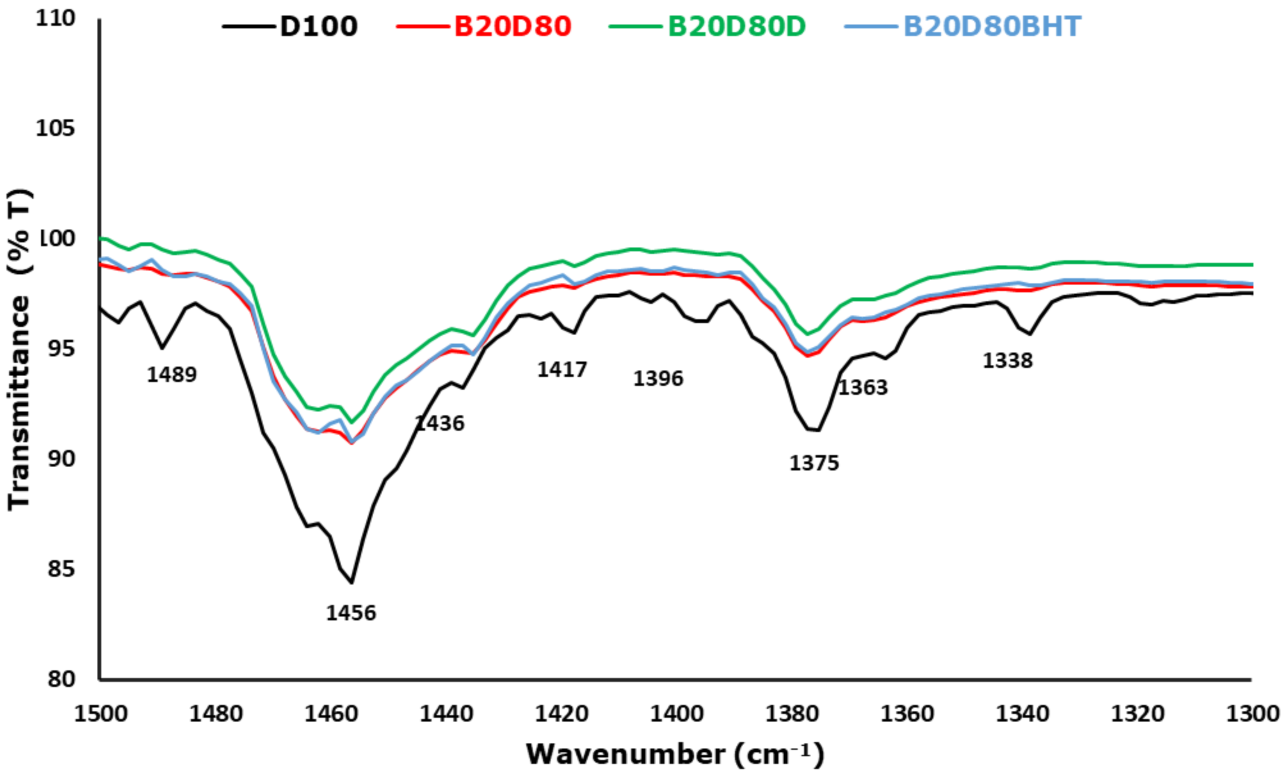


Figure 4: FT-IR spectra of D100, B20D80, B20D80D, and B20D80BHT between 1300-1500 cm^{-1} range.

Table 5: Functional group frequencies of the fuel samples (24).

Wavenumber cm^{-1}	Types of vibration	Functional Groups
3300-3750	Stretching 1	O−H of alcohols
2950	Asymmetrical stretching 2	=C−H of alkenes
2930	Asymmetrical stretching 3	C−H of alkanes
2860	Symmetrical stretching 4	C−H of methylene
1755	Stretching 5	C=O of ester carbonyl functional group
1240-1030	Stretching	C−O of alkoxy esters, ethers, and C−O−C
710	Bending of alkenes and overlapping of rocking vibration of methylene 7	=C−H and −(CH_2)n methylene groups of cis-disubstituted alkenes and aromatic
690	Out of plane bending 8	=C−H of cis-disubstituted alkene and aromatics

DSC

This study increased the crystallization temperature of the natural antioxidant blend fuel from -11.37 °C to -15.65 °C as a consequence of comparing three distinct samples and DSC measurements of natural, synthetic antioxidant blended fuel, and diesel fuel (Table 6).

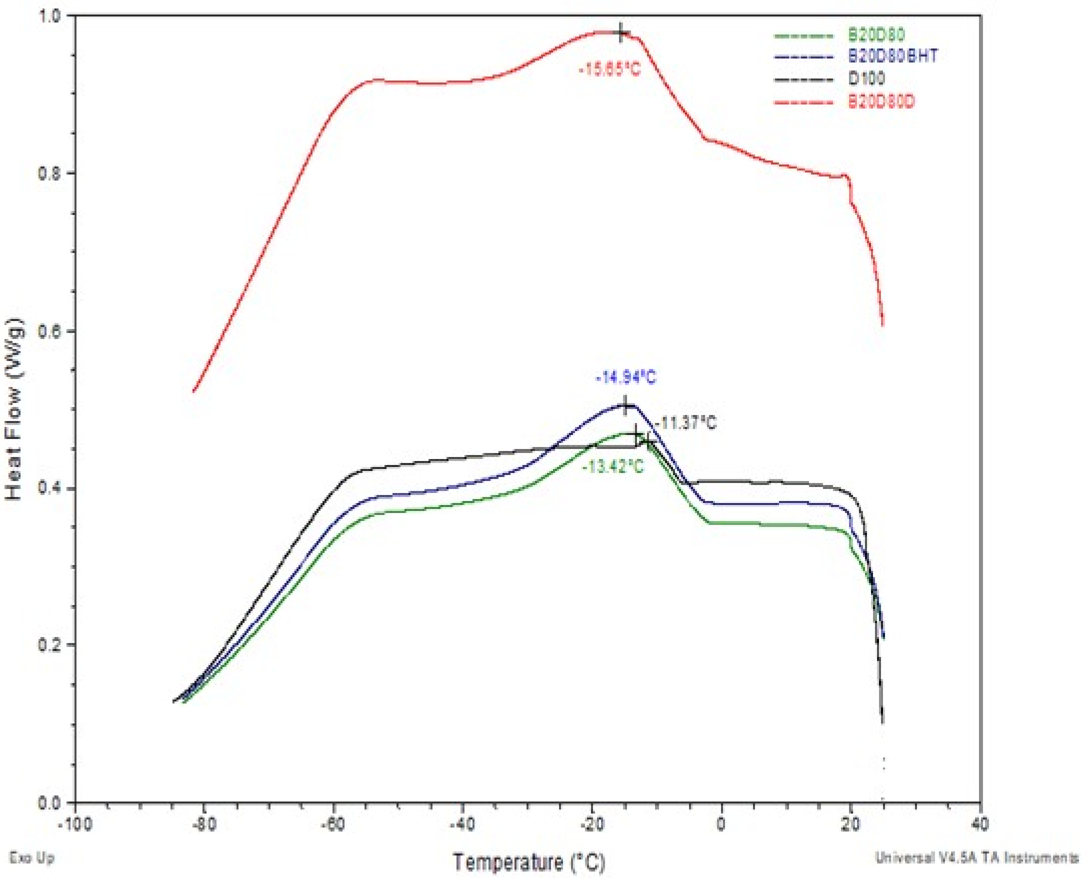


Figure 5: DSC thermograms of B20D80, B20D80D, B20D80BHT, and D100.

Table 6. The crystallization temperature of B20D80, B20D80D, B20D80BHT, and D100.

Sample code	Crystallization temperature (℃)
D100	-11.37
B20D80	-13.42
B20D80D	-15.65
B20D80BHT	-14.94

As a result of the study, the crystallization points of the biodiesel-diesel mixture, in which dill extract was added as a natural antioxidant were determined. Crystallization points of biodiesel-diesel fuel with natural and synthetic antioxidant mixture were determined by the DSC device. As a result, it was found that dill extract increased the crystallization point in the fuel by about 17% better than other samples. When the FT-IR results were examined for biodiesel-diesel fuel mixtures, it was seen that the % permeability values increased with the antioxidant effect.

Recommendation: Dill extract has shown improvement in the fuel mixture as an antioxidant, but other standard tests of the fuel should also be performed.

CONCLUSIONS

This work was intended to examine how natural antioxidants (dill oil extract) affected the performance of biodiesel and biodiesel-diesel blends. It examined the impact of dill oil extract on oxidative stability as well as the temperature at which colza biodiesel crystallizes. The crystallization point is a crucial characteristic of biodiesel and diesel fuels because, at low temperatures, the saturated chemicals that are present in these solutions start to crystallize and produce wax, which can clog filters and pipes and cause engine malfunction. In this study, dill oil extract was used as a natural antioxidant, and for comparative purposes, BHT was used as the synthetic antioxidant.

To carry out this study, four samples were prepared, which are, D100, B20D80, B20D80D, and B20D80BHT. FT-IR, and DSC techniques were used to characterize the samples. The presence of possible functional groups in the samples were determined using FT-IR, and the crystallization temperatures of the simples determined by using DSC. According to the FT-IR graphics, the biodiesel-diesel blend with 3000 ppm of dill oil extract, designated B20D80D, has fewer functional groups than other simples, such as B20D80BHT, which indicates that the dill oil extract increased the oxidative stability of the mixture. On the other hand, from the DSC results, it was found that the dill extract increased the crystallization point in the fuel by 17% better than other samples.

Although dill oil extract has shown excellent results as an antioxidant for biodiesel-diesel blends, more studies and tests should be conducted to determine what its other effects are in biodiesel-diesel blends and whether or not it can be used on a large scale by the fuel industry.

CONFLICT OF INTEREST

Not applicable.

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