REPUBLIC OF TURKEY
ERCIYES UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

EVALUATION, CHARACTERIZATION AND ENGINE PERFORMANCE OF COMPLEMENTARY FUEL BLENDS OF BUTANOL-BIODIESEL-DIESEL BLENDS FROM *ALEURITES MOLUCCANUS* AS POTENTIAL ALTERNATIVE FUELS FOR CI ENGINES

Prepared
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Supervisor
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MSc Thesis

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KAYSERİ

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SCIENTIFIC ETHICS SUITABILITY

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SUITABILITY FOR GUIDE

The MSc thesis entitled **EVALUATION, CHARACTERIZATION AND ENGINE PERFORMANCE OF COMPLEMENTARY FUEL BLENDS OF BUTANOL-BIODIESEL-DIESEL BLENDS FROM *ALEURITES MOLUCCANUS* AS POTENTIAL ALTERNATIVE FUELS FOR CI ENGINES** has been prepared in accordance with Erciyes University Graduate Education and Teaching Institute Thesis Preparation and Writing Guide.

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ACCEPTANCE AND APPROVAL PAGE

This study entitled "Evaluation, characterization and engine performance of complementary fuel blends of butanol-biodiesel-diesel blends from *Aleurites moluccanus* as potential alternative fuels for CI engines" prepared by Mebrouk MEKAOUSSI under the supervision of Assist. Prof. Dr. Abdulaziz ATABANI was accepted by the jury as MSc. Thesis in Mechanical Engineering department.

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APPROVAL

That the acceptance of this thesis has been approved by the decision of the Institute's Board of Directors with the 08/08/2017 date and 2017/33-04 numbered decision.

08/08/2017

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Erciyes University, Graduate School of Natural and Applied Sciences
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ABSTRACT

Biodiesel has gained worldwide attention due to its renewable aspects. However, biodiesel needs more properties and quality improvement. Compared to methanol and ethanol, butanol has been considered as a favourable alternative fuel or additive CI engines. The objective of the present work is to evaluate butanol-diesel-biodiesel blends as potential alternative fuels. Biodiesel has been produced from *Aleurites moluccanus* oil. Seven blends were prepared with different butanol/diesel/biodiesel percentages/ratios. All samples were tested for some important properties such as kinematic viscosity, density, flash point, cloud point, pour point and cold filter plugging points. Moreover, FT-IR, TGA and DSC of all blends were also analyzed. Important engine and emissions performance parameters such as brake power (BP), brake torque, brake specific fuel consumption (BSFC), carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and exhaust gas temperature (EGT) were also studied in the work to evaluate the blends. Results revealed that the butanol-diesel-biodiesel blends improve the properties of pure biodiesel such as kinematic viscosity and density while keeping acceptable range for cold flow properties and they show similar trends to the properties of Euro-diesel. A reduction in BP, HC and CO was observed for all blends at full load compared to Euro-diesel. However, an increase in BSFC was observed. Overall, the blends appear to be good alternatives to the biodiesel-diesel blends. Thus, butanol-biodiesel-diesel blends can be considered as a potential sustainable fuel to substitutes for fossil diesel.

Keywords: *Aleurites moluccanus*, Biodiesel-diesel-butanol blends, Fatty acid composition, FT-IR, TGA, DSC, Engine and emissions analysis.

DIZEL MOTORLAR IÇIN ALTERNATIF YAKIT OLARAK *ALEURITES MOLUCCANUS*'DEN ÜRETILMIŞ BIYODIZELIN, BÜTANOL-BIYODIZEL-DIZEL KARIŞIMLARININ KARAKTERIZASYONU VE MOTOR PERFORMANSININ DEĞERLENDIRILMESI

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ÖZET

Yenilenebilir özelliğinden dolayı biyodizel, dünya genelinde dikkat çekmektedir. Ancak, biyodizelin özelliğinin ve kalitesinin artırılması gerekmektedir. Son zamanlarda, altrnatif yakıt olarak metanol ve etanolden başka bütanolünde dizel yakıtına karıştırılarak kullanılması olumlu düşüncelerin başlamasına neden olmuştur. Bu tez, bütanol-dizel-biyodizel karışımının potansiyel alternatif yakıt olarak değerlendirilmesi üzerinedir. Biyodizel *Aleurites moluccanus* yağından üretilmiştir. Yedi farklı oranda bütanol-dizel-biyodizel karışımı hazırlanmıştır. Hazırlanan yakıt örneklerinin kinematik viskozitesi, yoğunluk, alevlenme noktası, donma noktası, akma noktası ve soğuk filtre tıkanma noktası gibi birçok özellikleri test edildi. Ayni zamanda, tüm örneklerin FT-IR, TGA ve DSC özellikleri belirlendi. Karışımları değerlendirmek için önemli özelliklerinden olan motor performansı ve egzoz emisyonlarından fren gücü, fren torku, fren özgül yakıt sarfiyatı, karbon monoksit, hidrokarbonlar, azot oksitler ve egzoz gaz sıcaklığı değerlri tespit edildi. Sonuçlar olarak, bütanol-dizel-biyodizel karışımları saf biyodizele göre daha iyi soğuk akış özelliklerine sahip olurken, kinematik viskozite ve yoğunluklar da iyileşmeler ve Euro dizel özellikleri ile benzer özellikler göstermektedir. Testlere göre, tam yükte fren gücü, hidrokarbonlar ve karbon monoksit salınımlarında Euro dizele göre azalma gözlemlenirken, fren özgül yakıt sarfiyatında artış gözlemlendi. Genel olarak, karışım biyodizel-dizel karışımlarına güzel bir alternatif olarak gözükmektedir. Böylece, bütanol-biyodizel-dizel karışımı fosil yakıt yerine kullanılabilecek potansiyel bir sürdürülebilir yakıt olarak düşünülebilir.

Anahtar Kelimeler: *Aleurites moluccanus,* Biyodizel-dizel-bütanol karışımı, yağ asidi birleşeni, FT-IR, TGA, DSC, yanma ve emülsiyon analizleri.

TABLE OF CONTENTS

EVALUATION, CHARACTERIZATION AND ENGINE PERFORMANCE OF COMPLEMENTARY FUEL BLENDS OF BUTANOL-BIODIESEL-DIESEL BLENDS FROM *ALEURITES MOLUCCANUS* AS POTENTIAL ALTERNATIVE FUELS FOR CI ENGINES

CHAPTER 2

MATERIALS AND METHODS

CHAPTER 3

TESTS AND RESULTS

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A_i	Percentage of fatty acid
AMME	*Aleurites moluccanus* methyl ester
B	Biodiesl
But	Butanol
CAMO	Crdue *Aleurites moluccanus* oil
CN	Cetane number
CPEO	Crude Pangium edule oil
D	Diesel
DU	Degree of unsaturation
HHV	Higher heating value
IV	Iodine value
LCSF	Long chain saturated factor
M_i	Molecular weight of fatty acid
N	Number of double bonds of fatty acid
OS	Oxidation stability
PEME	*Pangium edule* methyl ester
SN	Saponification number

INTRODUCTION

The world suffers from many environmental problems such as pollution and global warming, This has caused economic problems for many developed and developing countries. The depletion of energy resources pushed scientists and researchers to try to find alternative energy resources such as wind energy, solar energy, biofuels and hydrogen energy. This thesis aims at studying the feasibility of *Aleurites moluccanus* as a promising non-edible biodiesel feedstock.

Many techniques have been performed before for the production of biodiesel along with the study of its properties (physical and chemical). In this study, esterification and transesterification process (two-step process) were adopted to produce fatty acid methyl ester (Biodiesel). Characterization of *Aleurites moluccanus* methyl ester (AMME) properties and its blends with Euro diesel and butanol was conducted at Alternative Fuels Research Laboratory (AFRL) following the standards specified by both ASTM D6751 and EN 14214 standards. The fatty acid compositions of AMME were determined using gas chromatography. *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends were characterized by FT-IR, TGA and DSC analytical methods. Analysis of engine performance and exhaust emissions parameters were conducted in a single-cylinder, four stroke, naturally aspirated and direct injection.

The importance of this study is to identify the characteristics of different blends, and compare them with various studies in the same field to obtain a renewable fuel, to preserve the environment and to add a value to scientific research in the field of alternative fuels and clean energy.

CHAPTER 1

GENERAL INFORMATIONS

1. Introduction

1.1. Overview

Today, much of the world's energy demands are derived from crude oil, coal and natural gas, while nuclear and hydropower are also utilized. Due to increasing world's population, expected depletion of fossil fuels and the negative impacts of exhaust emissions of fossil-fueled engines on the environment, many countries have started to encourage renewable energy and fuels by various policies such as tax exemption and subsidiaries [1].

Biodiesel has been accepted worldwide as a promising alternative fuel that can be used in CI engines. It was reported that biodiesel blends up to 20% can be burned in CI engines without the need for engine modifications. The wide availability of biodiesel feedstock has promoted biodiesel production worldwide. This availability is subjected to some factors such as regional climate, geographical location and agricultural practices of any country [2].

More recently, application of alcohols such as methanol (C_3HOH), ethanol (C_2H_5OH) and butanol (C_4H_9OH) as additives in compression ignition engines have gained more attention. The addition of ethanol causes a reduction in some proeprties such as calorific value, cetane number, kinematic viscosity and lubricity of diesel fuel. On the other hand, butanol has more similar physical properties close to those of diesel than ethanol and methanol. Butanol has higher heating value (33 MJ/kg), higher density (0.81 g/ml), higher flash point (29 °C), cetane number (33), kinematic visociy (3.6 mm^2/s), miscibility and lower vapor pressure than ethanol and methanol [3, 4]. Thus, butanol is regarded as a more favourable additive for CI engines. The application of butanol-diesel blends in CI engines has been already studied well in literature [5, 6].

1.2. Research Background

Availability of wide biodiesel feedstocks is one of the main factors to realize the production of biodiesel. Oil content of the seeds, the average yield per hectare, low production cost and large production scale are crucial factors for the economy of biodiesel industry. Moreover, regional climate, geographical locations, local soil conditions and agricultural practices of a country are also significant factors. It has been reported in literature that 75% of the total biodiesel production cost is affected by feedstock prices. Therefore, a low-cost biodiesel feedstock is important to guarantee low biodiesel production cost [1].

Aleurites moluccanus is one of suitable feedstocks for biodiesel production. *Aleurites moluccanus* (Candle-nut tree) is a member of the *Euphorbiaceae* family [7, 8] and is native to Southeast Asian countries such as Malaysia, Indonesia and Philippines [9]. Fig. 1.1 shows the geoghraphical location of *Aleurites moluccanus* [10]. The tree of *Aleurites moluccanus* is a medium-sized, up to 20 m tall, with wide-spreading or pendulous branches. Bark grey-brown, fairly smooth with fine vertical lines [10]. The tree produces spherical fruits (5 cm in diameter) with a thick, rough and hard nut shell. The tree can produce 30-80 kg of nuts [7, 10]. The oil content is 15-20% and its oil is rich in polyunsaturated fatty acids with high iodine number [7-9, 11]. The potential of *Aleurites moluccanus* as a biodiesel feedstock has been reported earleir in [7-9, 11-14].

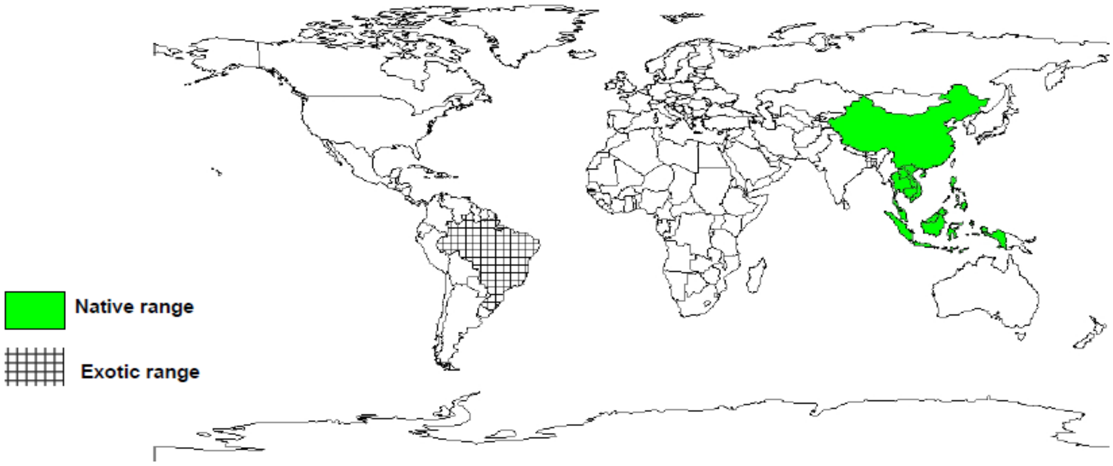


Fig. 1.1. Geoghraphical location of *Aleurites moluccanus* [10]

1.3. Problem Statement

Oil prices are rising due to the gradual decrease of oil reserves in the world. Much of our energy needs comes from oil and its derivatives. As oil reserves are limited, it is expected that this will cause some economic crisis globally.

Another problem that arises besides the daily cost of oil products is environmental pollution. Vehicles produce a lot of air pollution. Vehicles are known to be a cause of polluted emissions such as NO_x, CO, CO_2, and HC. The use of fossil fuels increases the amount of CO_2 in the atmosphere. This increase results in global warming as a result, causing "greenhouse effect" which leads to overheating on the earth.

All these challenges have led scientists to work on development of alternative fuels, especially in the use of vegetable oils for diesel engines. In fact, the use of vegetable oils (rapeseed, linseed, cottonseed, soy, sunflower, hint, coconut, palm, etc.) in diesel engines is not a new idea. In 1900, when Rudolph Diesel was promoting the new engine he developed in Paris, he used one of his engines with peanut oil. In addition, vegetable oil varieties were used in many vehicles in southern France during World War II. Therefore, it is targeted in this thesis to cover the application of biodiesel and alcohols in CI engines.

1.4. Objectives

Biodiesel, natural gas, ethanol, methanol, butanol, hydrogen and LPG are used as alternative fuels in CI diesel engines. In particular, alcohols such as ethanol, methanol and butanol can be used in diesel engines at certain ratios to diesel fuel due to their clean nature.

This research aims to achieve the following objectives:

(a) To select promising potential oil bearing plant (non-edible) for biodiesel production.
(b) To investigate the physical and chemical properties of the selected feedstock followed by production of biodiesel using conventional esterification and transesterification process.

(c) To characterize and determine the physical and chemical properties and fatty acid compositions of the produced biodiesel (methyl ester).
(d) To investigate butanol-biodiesel-diesel blending opportunities to improve the final properties.
(e) To conduct engine performance and emissions analysis of some selected blends.

1.5. Scope of the study

The oxygen in the build-up of alcohols has been considered recently in CI engines. Among alcohols, butanol can be blended with other fuels easily.

However, the application of butanol/diesel/biodiesel ternary fuel blends in diesel engines is still scanty. For instance, the high cetane number and flash point of biodiesel might overcome the problem of blending butanol with diesel. Therefore, this thesis aims to to produce biodiesel from *Aleurites moluccanus* oil. Followed by evaluating the proerties of butanol-diesel-biodiesel blends as potential alternative fuels. This is finalized by studying the effect of biodiesel-butanol fuel blends on engine performance and emissions in a direct-injection single-cylinder diesel engine fuel. For this purpose, 5%, 10% and 20% of butanol were added to diesel fuel. Diesel, biodiesel-diesel and biodiesel-diesel-butanol blends were tested at different speeds and at a constant load. The fuels are compared in terms of performance and emissions.

1.6. Organization of dissertation

This dissertation is divided into four chapters as follows:

Chapter 1 Gives general information about research topic. It starts by giving an introduction to the importance of energy, climate change and alternative fuels, followed by a background that shows the importance of biodiesel and the possible methods to improve the physical and chemical properties of biodiesel, ended by the existing results included in the literature.

Chapter 2 Explains in detail the research methodology and design.

Chapter 3 Is dedicated to show and present all findings of the study.

Chapter 4 Provides a discussion and analysis of these findings besides a summary of the key findings and puts forward some recommendations for the future work.

1.7. Literature Survey

In literature, several studies have focused on biodiesel production and its properties beside its effect on engine and emissions. Moreover, many studies have been conducted on the use of biodiesel and alcohols as fuel in diesel engines.

According to Sarin *et al*. [15], biodiesel properties are influenced by structure (Fatty acid composition), which is influenced by on the oil origin.

Atabani *et al*. [2] studied the concept of biodiesel blending from several edible and non-edible oils available in South East Asia (Malaysia and Indonesia) to improve the physical and chemical properties. It was found that most of the properties such as kinematic viscosity at 40 °C, flash, cloud, pour and cold filter plugging points can be improved by blending and following the standard specified by ASTM D 6751.

Sulistyo *et al*. [11] investigated the production of biodiesel from high iodine number and high FFA (free fatty acids) feedstock; candlenut oil as a case of study. It was found that a pretreatment process (esterification) of 1 hour and 70 °C using acid catalyst is needed to reduce FFA level less than 2%. Afterwards, transesterification process converts the esterified oil to ethyl ester and glycerol within 1 hour, molar ratio of 7.5:1 and 1.50% KOH (as a catalyst). The authors indicated that, transesterification reaction is strongly affected by the molar ratio of ethanol to oil.

Lima *et al*. [16] studied (*Aleurites moluccana*) and tucum (*Astrocaryum vulgare*) oils to produce biodiesel. The oil contents of both oils were found 60% and 30% respectively. In this work, ethanol was used in transesterification process with sodium hydroxide (Catalyst). After the completion of reaction, centrifugation to separate the final products followed by biodiesel washing with distilled water and drying at 60 ºC for 40 minutes under argon flow was done to obtain the final product.

Physico-chemical characterization showed cloud points of (-5 and 5 °C). While their iodine indexes are (150.36 and 14.67 g/100g). This reflects the high level of unsaturation *Aleurites moluccana* methyl ester. The kinematic viscosities were found 4.12 and 4.54 mm^2/s respectively.

The optimized reaction conditions showed that biodiesel production from *Aleurites moluccana* resulted in a high biodiesel yield. While, the same optimized conditions did not apply for *Astrocaryum vulgare* oil.

Ejder [17] reported that canola biodiesel reduced motor torque and motor power at low engine speeds while B5 and B10 mixtures reduced the specific fuel consumption by 1.4% compared to reference at 1500-1800 rpm, B10 mixture has also increased the overall yield on average by 2%.

Palash *et al*. [18] tested 5% and 10% by volume blends of *Aphanamixis polystachya* methyl ester with diesel in a multi-cylinder diesel engine. The results obtained shows reduction in brake power and torque for APME5 and APME10 compared to diesel. Moreover, reduction of CO and HC emissions compared to diesel were observed. However NO and CO_2 emissions increased. The blends APME5 and APME10 increased the BSFC by 0.87% and 1.78%, respectively, compared to diesel fuel.

Eryilmaz *et al*. [19] studied methyl ester production and characterization from safflower oil (SO). The results of cold flow properties of safflower biodiesel indicate that it is suitable for the cold weather regions beside its excellent flash point of 171 °C. These results indicate that safflower biodiesel is a promising future biodiesel source. Furthermore, engine performance, combustion analysis and exhaust emissions tests was demonstrated.

Jaichandar *et al*. [20] investigated performance, emission, and combustion characteristics of Pongamia oil methyl ester. The main findings are:

1. Due to the lower calorific value of Pongamia oil methyl ester, BSFC increases.

2. The increase in percentage of Pongamia oil methyl ester, in the blend, CO emissions and smoke intensity decrease.

3. The high oxygen content in the Pongamia biodiesel causes better combustion and therefore increases the combustion chamber temperature. However, this casues an increase in NO_X emissions compared to diesel.

4. The engine produce the maximum pressure and heat release rate for diesel compared to Pongamia oil methyl ester and its blends.

Altun *et al*. [21] reported the effect of Diesel-Biodiesel-Butanol blends on performance and exhaust emissions in a CI diesel engine. The study was conducted at three engine loads and a constant engine speed. Firstly, B20 was prepared, after that butanol was added at percentages of 10% and 20% (volume basis). Afterwards, fuel consumption and exhaust emissions were measured. The results of B20 showed an increasing trend in brake specific fuel consumption coupled with a decrease in brake thermal efficiency compared to diesel fuel. However, butanol addition to B20 improved brake thermal efficiency. NO_x emissions decreased with all blends. In addition, a remarkable reduction of smoke opacity was reported for all blends.

Zhang *et al*. [22] studied the effect of methanol addition on the exhaust emissions in the intake manifold in a diesel engine. It was observed that with the addition of methanol, HC and CO emissions increased while NO_x emissions decreased.

Çelikten [23] examined the effect of E10 (90% diesel + 10% ethanol) fuel on engine performance and exhaust emissions in a 4-stroke diesel engine. The addition of ethanol causes a reduction in engine torque and brake power and increased the specific fuel consumption. However, as O_2, CO and NO_x emissions increases CO_2, SO_2 and smoke emissions decreased.

Huang *et al*. [24] studied the effect of ethanol and diesel blends on performance and emissions. 10%, 20%, 25% and 30% ethanol were used in the blends. As the ethanol ratio increases, specific fuel consumption and HC increase, CO and NO_x decrease.

Yilmaz *et al*. [25]; examined biodiesel-butanol blends (5%, 10%, and 20% respectively) in a diesel engine. It has been found that the blends increased BSFC, CO and HC emissions. However, the exhaust gas temperature and NO_x emissions decreased when butanol concentration is above 20%.

Mehta *et al*. [26] analyzed butanol-diesel-biodiesel blends for their physic-chemical properties and stability in four-cylinder CI engine. Blends showed similarity in some physical properties such as density, kinematic viscosity, pour point and oxidation stability with euro diesel. However, blends have lower flash point values (due to the presence of butanol). Engine performance parameters such as brake power and brake thermal decreased while BSFC showed an increase. CO and NO emissions also decreased.

The effects of butanol-diesel fuel blends on engine performance and emissions in CI diesel engine was examined by Rakopoulos *et al*. [27]. Diesel was blended with n-butanol at percentages of 8%, 16% and 24% respectively. Soot, NO_x and CO emissions decreased while HC emissions increased with the addition of n-butanol in the blends. Addition of n-butanol also increased the thermal efficiency and specific fuel consumption.

Tüccar *et al*. [28] studied the effect of diesel beside blending of diesel with biodiesel derived from microalgae and butanol on engine performance and exhaust emissions in a four-cylinder diesel engine. The tested blends were D80B20, D70B20But10 and D60B20But20. The main findings showed a reduction in both power and torque when butanol was blended with biodiesel-diesel blends. However, butanol addition improved CO and NO_x emission and smoke opacity. Some properties of biodiesel-butanol-diesel blends such as cetane number, density, kinematic viscosity and pour point were similar with those of diesel.

CHAPTER 2

MATERIALS AND METHODS

2.1 Introduction

Research methodology is an important research element that results in an effective research with credited consequences. It can be defined as procedures, methods and techniques that are applied to collect and integrate all important information related to the specific research.

This chapter explains how the whole research was conducted and shows the methods by which *Aleurites moluccanus* oil collection, crude oil characteristics, biodiesel production, fatty acid composition of biodiesel, physical and chemical properties of biodiesel and its blends with butanol and euro diesel and engine performance and emissions were conducted. The opportunities of biodiesel-diesel and biodiesel-diesel-butanol blending method was adopted in this research to improve some of the properties. All equipment lists and the apparatus used are shown in this chapter.

2.2 Structure of research methodology

This research aims to produce biodiesel from *Aleurites moluccanus*. Therefore, Fig. 2.1 shows the implemented flow chart of this research.

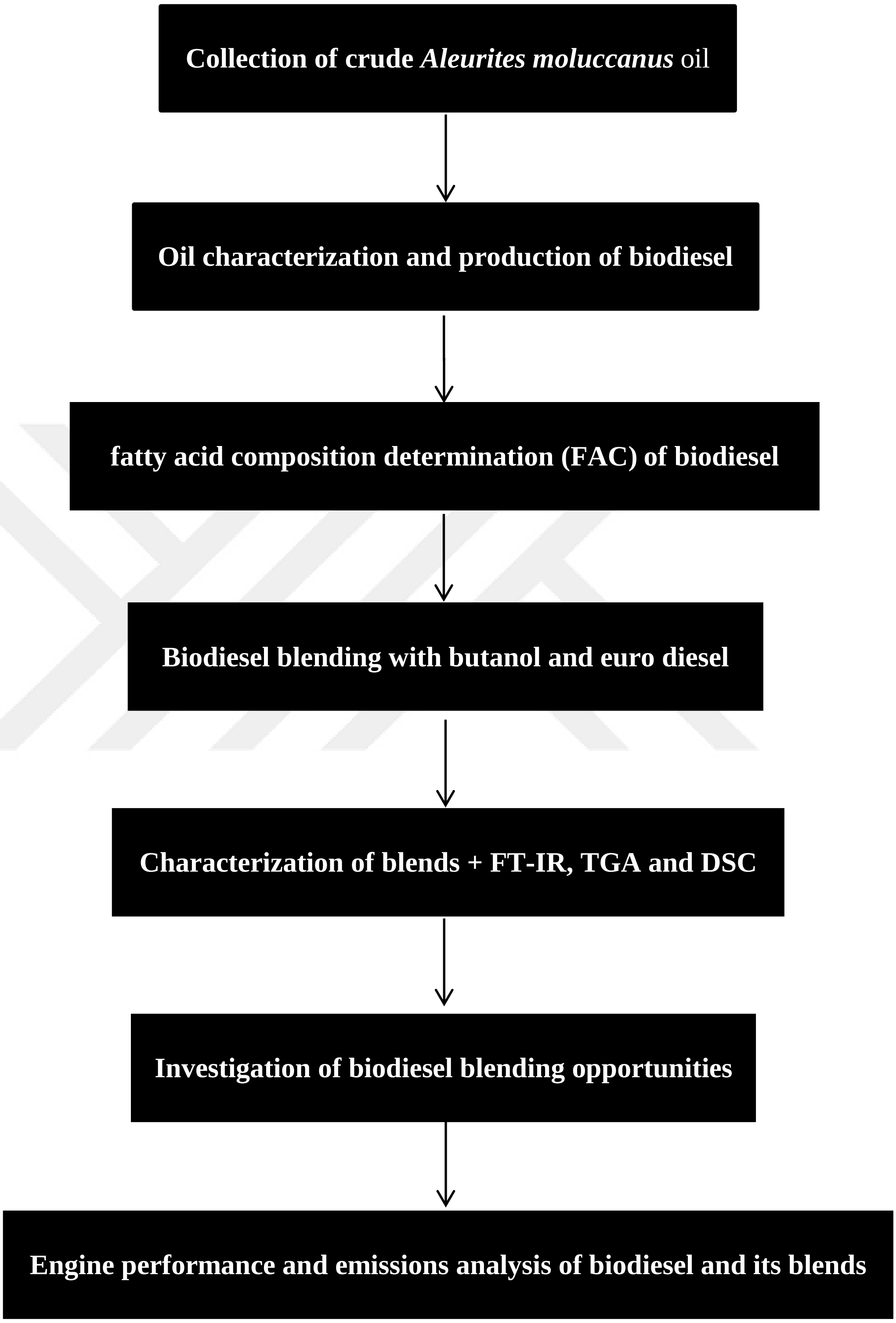


Fig. 2.1. Flow chart of the research methodology

2.3 Materials and chemicals

Crdue *Aleurites moluccanus* oil (CAMO) was obtained through a personal communication. The oil was brownish colour. All chemicals such as methanol (Ch_3OH), sulfuric acid (H_2SO_4), potassium hydroxide (KOH), 2-propanol (C_3h_8O), phenolphthalein ($C_{20}H_{14}O_4$), sodium sulfate (Na_2SO_4) beside quality filter papers were purchased from a local supplier and used as received. Euro diesel was purchased from a local petrol station in Kayseri, Turkey. Table. 2.1 shows the properties of the oil. For the sake of comparison, crude *Pangium edule* oil (CPEO) was added.

Table 2.1. Physical and chemical properties of the crude oil

Property	**CAMO**	**CPEO[1]**
Kinematic viscosity at 40 °C (mm^2/s)	26.906	27.175
Cloud point (°C)	-13	-6
Pour point (°C)	-17	-10
Flash point (°C)	>284	-
Density at 15 °C (g/cm^3)	0.9249	0.8976[2]
Density at 20 °C (g/cm^3)	0.923	-
Acid value (mg KOH/g oil)	10.68	19.62

[1][29], [2]Measured at 40 °C.

2.4 Biodiesel production procedures

The acid value of *Aleurites moluccanus* oil was found 10.68 mg KOH/g oil (Table 2.1). Therefore, a two-step production process has been adopted to convert the crude oil into methyl ester [2]. The reaction was done in a small scale jacketed reactor (Caspacity: 2L) equipped with condenser, circulating bath to control the temperature during the reaction and electrical motor to control the stirring speed. Table 2.2 shows a summary of the biodiesel production procedures from crude *Aleurites moluccanus* oil (CAMO).

Table. 2.2. Biodiesel procduction procedures from crdue *Aleurites moluccanus* oil (CAMO)

Process	**Parameters**
Acid-catalyzed esterification	Methanol: 50% (v/v oil) Acid catalyst: H_2SO_4 (1% v/v oil) Reaction time: 3h Reaction temperature: 60 °C Stirring speed: 400 rpm
Alkanline-catalyzed transesterification	Methanol: 25% (v/v oil) Alkaline catalyst: KOH (1% m/m oil) Reaction time: 1.5h Reaction temperature: 60 °C Stirring speed: 400 rpm

2.5 Measurement of physicochemical properties

Characterization of *Aleurites moluccanus* methyl ester (AMME) and its blends with euro diesel and butanol was conducted at Alternative Fuels Research Laboratory (AFRL) under Energy Division, Department of Mechanical Engineering, Erciyes University. All properties were tested according to ASTM D6751 and EN 14214 standards. Table 2.3 shows the equipment used to measure the physicochemical properties of crude oils, methyl esters and blends.

Table 2.3. Equipment list

Property	**Equipment**	**Origin**
Kinematic viscosity	Tamson TV2000	Netherlands
Flash point	Normalab NPM 450	France
Cloud point	Normalab NTE 450	France
Pour point	Normalab NTE 450	France
Cold filter plugging point	Normalab NTL 450	France
Density	Krüss DS7800 Density meter	Germany

Saponification number of AMME was predicted by the following empirical formula [30]:

$$\mathrm{SN} = \mathrm{SUM}\left(\frac{560 * \mathrm{A_i}}{\mathrm{MW_i}}\right) \quad (1)$$

Where, A_i is the percentage of fatty acid and MW_i is the molecular weight of each fatty acid.

Iodine value (IV), cetane number (CN) and oxidation stability (OS) of AMME were predicted by the following empirical formulas [31]:

$$IV = 1.0617(\mathrm{DU}) - 10.805 \quad (2)$$

$$CN = -0.1268(\mathrm{DU}) + 67.926 \quad (3)$$

$$OS = -0.0518(\mathrm{DU}) + 11.121 \quad (4)$$

Where, DU is the degree of unsaturation (section 3.3).

Higher heating value (HHV) of AMME was predicted by the following empirical formula [32]:

$$\mathrm{HHV} = \left[46.19 - \left(\frac{1794}{M_i}\right) - (0.21 \times N)\right] \quad (5)$$

Where, M_i is the molecular weight of each fatty acid and N is the number of double bonds.

2.6 Chromatography (GC) method of *Aleurites moluccanus* methyl ester (AMME)

The fatty acid compositions of AMME were determined using gas chromatography (GC) (Shimadzu, Japan). The devise was equipped with a flame ionization detector and a RT2560 capillary column. The test was conducted using an optimized in-house GC method [29]. The carrier gas was helium with column flow rate of 1.03 mL per minute at a 50:1 split ratio. Table 2.4 shows GC operating conditions.

Table 2.4. The GC operating conditions

Property	**Specifications**	**Unit**
Sample	1 µL	
Carrier gas	Helium	
Linear velocity	19.10	cm/sec
Flow rate	1.03 (column flow)	mL/min
Detector temperature	250	
Column head pressure	264.4 (flow control made)	kPa
Column dimension	RT2560	100.0mx0.25µmx0.3 mm
Injector column oven	240	ID
Temperature ramp	140 (hold for 2 minutes)	°C
	4 °C/min 165 °C	°C
	2 °C/min 192 °C	
	4 °C/min 240 °C (hold for 5 min)	

Degree of unsaturation (DU) was calculated from the percentages of monounsaturated and polyunsaturated fatty acids (wt %) of AMME by [31]:

$$\mathrm{DU} = (\text{monosaturated } \mathrm{C_n}: 1, \mathrm{wt\%}) + 2(\text{polyunsaturated } \mathrm{C_n}: 2, \mathrm{wt\%}) + 3(\text{polyunsaturated } \mathrm{C_n}: 3, \mathrm{wt\%}) \quad (6)$$

LCSF was calculated from the percentages of the saturated fatty acids (wt%) of AMME and their corresponding melting points (MPn) by [31]:

$$\mathrm{LCSF} = \sum \frac{(\mathrm{MP_n} \times \mathrm{C_{n\ wt\%}})}{100} \quad (7)$$

LCSF was calculated from the percentages of the saturated fatty acids (wt%) of AMME by [33]:

$$\mathrm{LCSF} = (0.1\mathrm{XC16}: 0) + (0.5\mathrm{XC18}: 0) + (1\mathrm{XC20}: 0) + (2\mathrm{XC24}: 0) \quad (8)$$

2.7 Biodiesel-diesel, butanol-diesel and biodiesel-butanol-diesel blending

Blending of AMME with n-butanol and euro diesel was carried out to examine the influence on properties such as density, kinematic viscosity, pour point, cloud point, flash point and cold filter plugging point. In this work, *Aleurites moluccanus* methyl ester (AMME) was blended with n-butanol and diesel at 7 different blends as follow:

B20D80, D75B20But5, D70B20But10, D60B20But20, B95But5, B90But10 and B80But20. All blends were kept in a reagent bottle with a screw cap at the room temperature.

2.8 FT-I R analysis

FT-IR method is an easy modern analytical technique to detect the functional groups and the bands in biodiesel. Both oils and esters are reported as strong absorbers in the infrared region of the electromagnetic spectrum [34]. The ester groups common described as R1-C(OR)=O in oils and as R1-C(OCH_3)=O in biodiesel.R1 represent long chains of hydrocarbons [35]. The position of carbonyl group (C=O) in FT-IR is sensitive to substituent effects and to the molecular structure. Esters have two strong absorption bands arising from carbonyl (C=O) at the range of 1750-1730 cm^{-1} and C-O at the range of 1300-1100 cm^{-1} and 1150-1000 cm^{-1} respectively. The stretching vibrations of $(CH)_n$ (n=3,2,1) can be identified at 2980-2950, 2950-2850 and 3050-3000 cm^{-1} respectively. The bending vibrations of $(CH)_n$ (respectively n=3,2,1 can be identified at 1475-1350, 1350-1150 and 722cm^{-1} respectively [36]. Biodiesels are often blended with petroleum diesel to make biodiesel blends [37].

In this study, *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends were characterized by FT-IR using Perkin Elmer device in the range 4000-650 cm^{-1} and processed with the help of a software program. The resolution was 4 cm^{-1} and 4 scans.

2.9 TGA analysis

Thermogravimetric analysis (TGA) determines the amount and rate of mass change in materials such as esters and oils as a function of increasing temperature and time in a controlled atmosphere under nitrogen, argon, oxygen and air etc. TGA is used to determine oxidation and thermal stabilities of biodiesel and biodiesel with antioxidants at different fractions. This information identifies the percentage of mass change and correlate chemical structure [38, 39]. In this study, The thermogravimetric (TG) thermograms of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends were recorded with the help of a Shimadzu DTG 60H thermogravimetric analyzer using platinum pans [40]. 10 mg of each sample was loaded into pans. After each analysis, platinum pans were cleaned well in order to make the pans ready for the next run. In this analysis, temperature ranges of 25-700 °C with a heating rate of 10 °C/min under dry air atmosphere of 100 ml/min to determine the oxidative stability. Each sample takes almost an hour [38, 40]. A maximum temperature of 700 °C was used as the mass remains constant [7]. TGA curves can detect the onset temperature of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends.

2.10 DSC analysis

Differential scanning calorimetry (DSC) determines the low temperature properties of biodiesel and the crystallization onset temperature. It can be plotted on the graph against heat flow. Biodiesel has different carbon chain length and degree of saturation. Therefore, crystallization of esters depends on some parameters such as the interactions between the molecules of fatty acids and their chain length [41]. As a result of saturated fatty acids having higher melting points than unsaturated fatty acids, they crystallize at higher temperature than those unsaturated fatty acids [42]. The DSC curves were recorded by model DSC Q20 with RCS90 coupled with a cooling system, both from TA Instruments. 3 ± 0.5 mg of each sample was loaded to aluminum pan and the heat flow was measured by comparing heat flow of empty pan as a reference. The heating/cooling rate was 10 ˚C min^{-1} between -80 ˚C and 20 ˚C under nitrogen atmosphere (N_2) with a flow rate of 50 mL min^{-1} (Table 2.5).

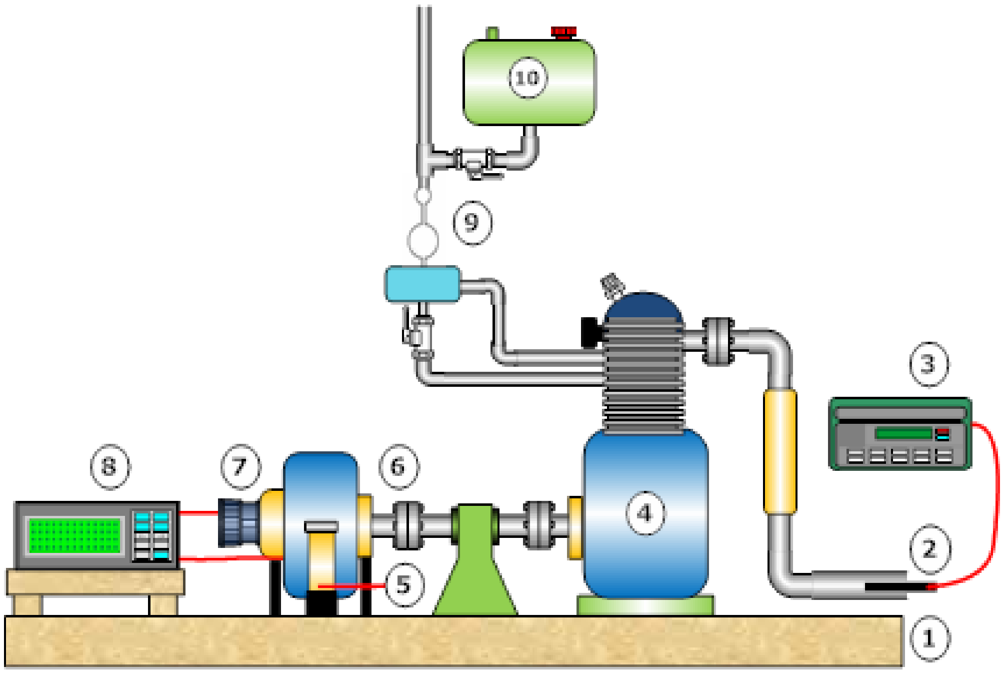
In this study, *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends were analyzed by TA Q-2000 DSC under the flow of nitrogen. Each DSC test takes about 17 mins to complete a single sample. All results were processed with the help of TA Orchestrator Version V7.2.2.1.

Table 2.5. Summary of Differential Scanning Calorimetry method

Instrument	TA Q-2000 DSC
Sample amount	3±0.5 mg
Gas	Nitrogen
Flow rate	50 ml/min
Temperature range	-80 °C to 20 °C
Ramp rate	10 °C/min

2.11 Engine and Emissions tests

Engine performance and exhaust emissions were conducted in a single-cylinder, four stroke, naturally aspirated and direct injection (Antor 4 LD 820 diesel engine). To adjust the load, a water brake dynamometer was coupled to the diesel engine. An electronic control and measurement device were used to display performance data. The accuracy of the speed, fuel measurement and brake power were ±5 rpm%, ±0.5045% and ±0.5055, respectively. Fig. 2.2 shows the engine test rig and exhaust analyzer. The engine specifications are listed in Table 2.6. The experimental investigation was carried out using Euro-Diesel fuel; D80B20 blend (80% Euro-Diesel and 20% *Aleurites moluccanus* methyl ester) and D70B20But10 blend (70% Euro-diesel, 20% *Aleurites moluccanus* methyl ester and 10% Butanol). The engine was firstly run at 1500 rpm with Euro-Diesel fuel for 15 minutes to warm the engine up before testing each blend. Similarly, the engine was operated with Euro-Diesel before shutting it down. The engine was initially run at 3000 rpm without load. Then engine load was increased up to full load by using water brake dynamometer, therefore engine speed was decreased to 2500, 2000, 1500, and 1000 rpm respectively. To measure the emissions parameters of CO, HC, NO_x and exhaust gas temperature, a portable emissions analyzer (model testo 350) was used. Table 2.7 shows the technical specification of emissions analyzer. Each test was repeated three times and all average results were considered.



1) engine chassis, 2) exhaust gas analyzing probe, 3) exhaust gas analyzer, 4) single cylinder diesel engine, 5) load cell, 6) dynamometer, 7) tachometer, 8) control unit, 9) fuel burette, 10) fuel container.

Fig. 2.2. Schematic diagram of the test engine and exhaust analyzer

Table 2.6. Detailed technical specification of the tested engine

Engine model	Antor 4 LD 820
Engine type	Single cylinder, Four stroke
Fuel type	Diesel
Bore	102 mm
Stroke	100 mm
Swept volume	817 cm^3
Compression ratio	17:1
Cooling type	Air cooled
Maximum engine speed	3000 rpm (Limited by manufacturer)
Maximum power	12,7 kW at 3000 rpm
Maximum torque	50 N.m at 1600 rpm
Injection pressure	20 MPa
Specific fuel consumption	255 g/kW.h at 2800 rpm
Engine position	Vertical

Table 2.7. Detailed technical specification of the exhaust gas analyzer (testo 350)

Measurement	**Measurement range**	**Accuracy**
CO	0-10000 ppm	±10 %
HC	100-40000 ppm	± 5 %
NO	0-4000 ppm	±10 %
NO_x	0-500 ppm	± 5 %
Exhaust Gas Temperature (EGT)	-200- +1370 ^oC	±1^oC

CHAPTER 3

TESTS AND RESULTS

3.1. Introduction

This chapter discusses in details the results of crude oils characteristics, physical and chemical properties of methyl ester, fatty acid compositions, biodiesel blending with butanol and Euro-diesel, FT-IR, TGA, DSC and engine and emissions performance.

3.2. Fatty acid composition, DU and LCSF of *Aleurites moluccanus* methyl ester (AMME)

Physical and chemical properties of methyl ester are affected by the fatty acid composition [33]. Therefore, parameters such as chain length, degree of unsaturation and number of double bonds are necessary to predict the properties of FAME. The results of fatty acid composition, DU and LCSF of AMME have been tabulated in Table 3.1. It can be seen that the saturated fatty acids represent only 9.7114%, while monounsaturated fatty acids represent 25.124% and polyunsaturated fatty acids represent 65.1646% of total fatty acid compositions. Based on Eqn 6, 7 and 8 the degre of unsaturation and LCSF for AMME was calculated to be 180.3796, 6.3123 and 2.2449 respectively. These findings are in agreement with [7] but quite different from [8].

3.3. Physicochemical properties of *Aleurites moluccanus* methyl ester (AMME) and its blends with Euro-diesel and butanol

The physicochemical properties of the produced biodiesel beside a comparison with the literature are shown in Table 3.2. The kinematic viscosity of AMME is lower than the crude oil and following the limit prescribed by ASTM D6751 and EN 14214 standards. AMME has also an excellent flash point. The results of CP (-6 °C), PP (-5 °C) and

CFPP (-8 °C) of AMME indicate that the product has a good cold flow properties and, therefore, biodiesel derived from *Aleurites moluccanus* can be utilized in cold flow region. The result of density of AMME was 0.8896 (g/cm^3). This result satisfies the limit prescribed by EN 14214 of 0.86-0.9 (g/cm^3). However, blending with butanol and diesel might further reduce the density and therefore, improve the engine performance of AMME.

Based on Eqn 2, the iodine value of AMME was found extremely high 180.704 (g iodine/100 g). This result does not satisfy EN 14214 standards of maximum 120 (g iodine/100 g). This is due to the lower pecentage of saturated fatty acid in AMME (9.7714%) [33]. The high iodine value influence the oxidation stability, cetane number, NO_x formation and deposit formation in diesel engine injector. Therefore, blending with butanol and diesel might be a proper solution to decrease the high iodine value of AMME. Based on Eqn 3, the cetane number of AMME was found 45.054. This result does not satisfy the limit prescribed by ASTM D6751 and EN 14214 standards of minimum 47 and 51 respectively. This is because increase in DU, decreases CN. The higher the unsaturation fatty acids, the lesser the CN [33]. Based on Eqn 4, the result of oxidation stability of AMME was 1.777 h. This result does not satisfy both ASTM D6751 and EN 14214 of 3 h and 6 h minimum. It is obvious that the high iodine value of AMME negatively influences the oxidation stability. Therefore, blending of AMME with butanol and Euro-diesel leads to a more stabilized product.

Table 3.3 shows the proeprties of *Aleurites moluccanus* methyl ester (AMME) and its blends with euro diesel and butanol. D60B20But20 possesses the lowest kinematic viscosity of 2.414 mm^2/s followed by D70B20But10 (2.559 mm^2/s), D75B20But5 (2.6452 mm^2/s), B20 (2.8359 mm^2/s), B80But20 (3.0007 mm^2/s), B90But10 (3.3621 mm^2/s), B95But5 (3.549 mm^2/s) and finally B100 (3.8494 mm^2/s) compared to 2.3255 mm^2/s of euro diesel. It can be seen that having blends such as D75B20But5, D70B20But10 and D60B20But20 yield a similar or close kinematic viscosity to Euro-diesel. This indicates that blends of diesel-butanol-biodiesel are possible to be used in CI diesel engines and improvement in both engine and emissions performance compared to pure biodiesel or B20 are anticipated. It is obvious that the butanol has a postive effect on kinematic viscosity of biodiesel-diesel blends.

D60B20But20 has the lowest density at 15 °C of 0.8418 g/cm^3 followed by D75B20But5 (0.8454 g/cm^3), D70B20But10 (0.8442 g/cm^3), B20 (0.849 g/cm^3), B80But20 (0.872 g/cm^3), B90But10 (0.882 g/cm^3), B95But5 (0.8846 g/cm^3) and finally B100 (0.8896 g/cm^3) compared to 0.8405 g/cm^3 of euro diesel. It can be seen that having blends such as D75B20But5, D70B20But10 and D60B20But20 yield a similar or close density to euro diesel. This also indicates that blends of diesel-butanol-biodiesel are possible to be used in CI diesel engines. It is obvious that the butanol has a postive effect on density of biodiesel-diesel blends.

The results of cloud point, pour point and cold filter plugging point indicate that having a ternary blends of biodiesel-diesel-butanol yield similar cold flow proeprties as for Euro-diesel. However, the binary blends of biodiesel-butanol yields higher pour and cold filter plugging point than diesel as AMME has higher pour and cold filter plugging points.

The results of flash points indicate that only B20 has a similar flash point to euro diesel. However, all result for biodiesel-diesel-butanol blends shows much lower value compared to Euro-diesel. This is attributed to the lower flash point if butanol.

Table 3.1. Fatty acid compositions, DU and LCSF of *Aleurites moluccanus* methyl ester (AMME)

Fatty acid	**Molecular weight**	**Structure**	**Systematic name**	**Formula**	**AMME**	**AMME[1]**	**AMME[2]**
Myristic	228.3709	14:00	Tetradecanoic	$C_{14}H_{28}O_2$	0	0	0.1
Palmitic	256.4241	16:00	Hexadecanoic	$C_{16}H_{32}O_2$	6.527	7.0	8.3
Palmitoleic	254.414	16:01	9-hexadecenoic	$C_{16}H_{30}O_2$	0	0	0.1
Stearic	284.4772	18:00	Octadecanoic	$C_{18}H_{36}O2$	3.1844	2.7	4.0
Oleic	282.4616	18:01	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	25.124	27.1	45.2
Linoleic	280.4455	18:02	Cis-9-cis-12 Octadecadienoic	$C_{18}H_{32}O_2$	40.2382	36.6	39.3
Linolenic	278.43	18:03	Cis-9-cis-12	$C_{18}H_{30}O_2$	24.9264	26.3	2.5
Arachidic	312.538	20:00	Eicosanoic	$C_{20}H_{40}O_2$	0	0	0.2
Gondoic	310.552	20:01	11- Eicosanoic	$C_{20}H_{38}O_2$	0	0	0.3
Saturated	**-**	**-**	**-**		**9.7114**	**9.7**	**12.6**
Monounsaturated	**-**	**-**	**-**		**25.124**	**27.1**	**45.6**
Polyunsaturated	**-**	**-**	**-**		**65.1646**	**62.9**	**41.8**
Total	**-**	**-**	**-**		**100**	**99.7**	**100**
DU	**-**	**-**	**-**		**180.3796**	**179.2**	**131.7**
LCSF[3]	**-**	**-**	**-**		**6.3123**	**6.2741**	**8.1435**
LCSF[4]	**-**	**-**	**-**		**2.2449**	**2.05**	**3.03**

[1] [7], [2] [8], [3] Calculated using Eqn (7), [4] Calculated using Eqn (8).

Table 3.2. Physical and chemical properties of the produced biodiesel

Property	**AMME**	**AMME[1]**	**AMME[2]**	**AMME[3]**	**AMME[4]**	**PEME[5]**
Kinematic viscosity at 40 °C (mm^2/s)	3.8494	4.12	4.819	4.56	4.8	5.2296
Cloud point (°C)	-6	-5	-	-	6	-6
Pour point (°C)	-5	-	6.66	-	6.84	-4
Cold filter plugging point (°C)	-8	-	-	-	-	-8
Flash point (°C)	>224	-	160	159	161	-
Density at 15 °C (g/cm^3)	0.8896	-	-	-	-	871[6]
Density at 20 °C (g/cm^3)	0.8859	0.8789	0.8869	-	0.8857	-
Iodine value (g iodine/100 g)	180.704	150.36	-	-	-	119
Cetane number	45.054	-	-	-	-	47
Saponification number	200.815	-	-	-	-	201
Oxidation stability (h)	1.777	-	-	-	5.9	0.57
HHV (MJ/kg)	39.38	-	-	-	-	39.625

[1][12], [2][43], [3][44], [4][8], [5][29], [6]Measured at 40 °C.

Table 3.3. Physical and chemical properties of the blends

Property	**Diesel**	**B100**	**D80B20**	**D75B20But5**	**D70B20But10**	**D60B20But20**	**B95But5**	**B90But10**	**B80But20**
Kinematic viscosity at 40 °C (mm^2/s)	2.3255	3.8494	2.8359	2.6452	2.559	2.414	3.549	3.3621	3.0007
Cloud point (°C)	-7	-6	-8	-7	-7	-7	-8	-8	-9
Pour point (°C)	-26	-5	-22	-24	-24	-26	-9	-10	-11
Cold filter plugging point (°C)	-25	-8	-20	-20	-19	-20	-9	-11	-11
Flash point (°C)	65	>224	68	41	39	36	52	46	41
Density at 15 °C (g/cm^3)	0.8405	0.8896	0.849	0.8454	0.8442	0.8418	0.8846	0.882	0.872
Density at 20 °C (g/cm^3)	0.8295	0.8859	0.8445	0.8418	0.8404	0.8382	0.881	0.8778	0.8678

3.4. FT-I R analysis

Fig. 2 displays the infrared spectra of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends. In FT-IR, there are units that use an integration of the side (1750-1760 cm^{-1}) of the ester carbonyl group stretching shows strong bands at nearly ~ 1744 cm^{-1} to screen the reaction progress [43, 44] .The esteric –COC vibration at 1171 and 1207 cm^{-1} reveals medium intensity bands, and the presence of the $(CH_2)_n$ group vibration band is seen at nearly 722 cm^{-1}. Fingerprint spectrum region is the main region that allows for chemical discrimination between 1500-900 cm^{-1} [43, 44]. The peak at nearly 1361 cm^{-1} correspond to the asymmetric stretching of –CH_3. The stretching of O-CH_3, represented by the absorbance at 1196 cm^{-1}, is typical of biodiesel [44]. 3550-3200 cm^{-1} broad peaks indicate O-H stretching in alcohols and phenols compounds. The 3332 cm^{-1} broad strong peak indicates O-H stretching in butanol (BUT100). Moreover, 1073 cm^{-1} indicates C-O strong stretching vibration in butanol (BUT100) [45]. The detailed results of FT-IR are shown in APPENDIX A.

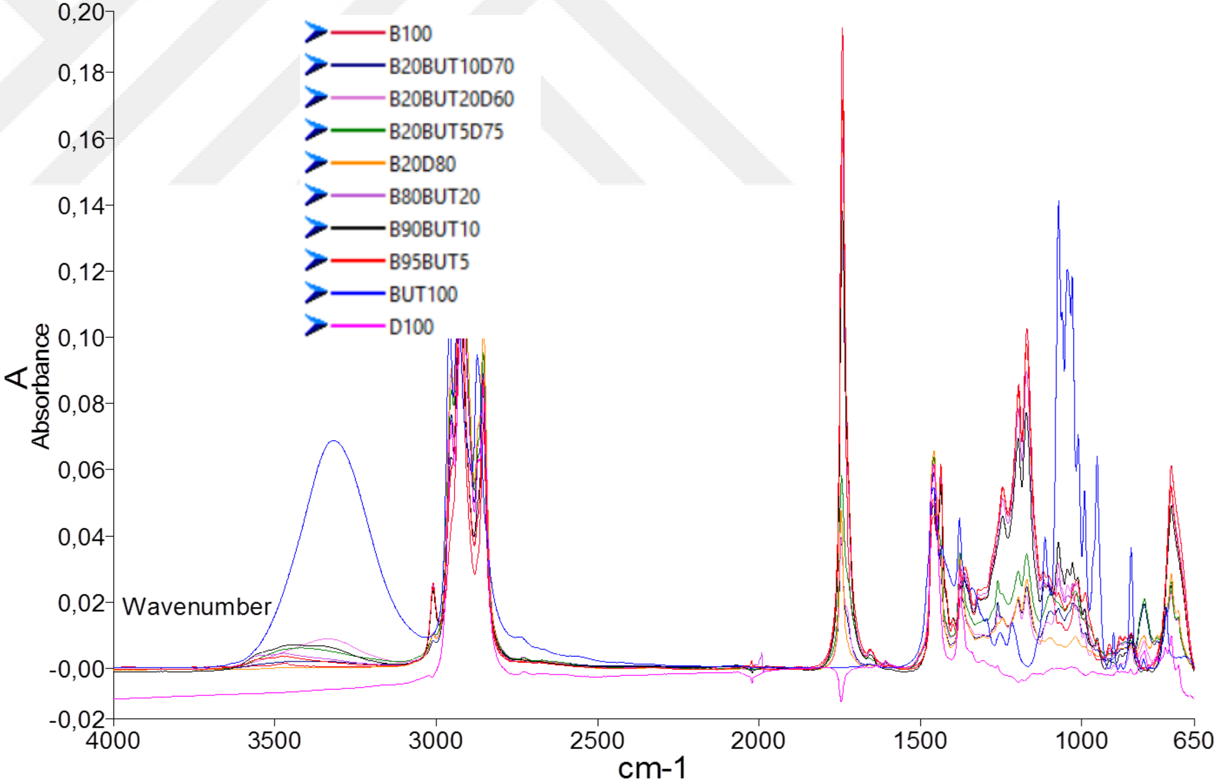


Fig. 3.1a. Infrared spectra of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends

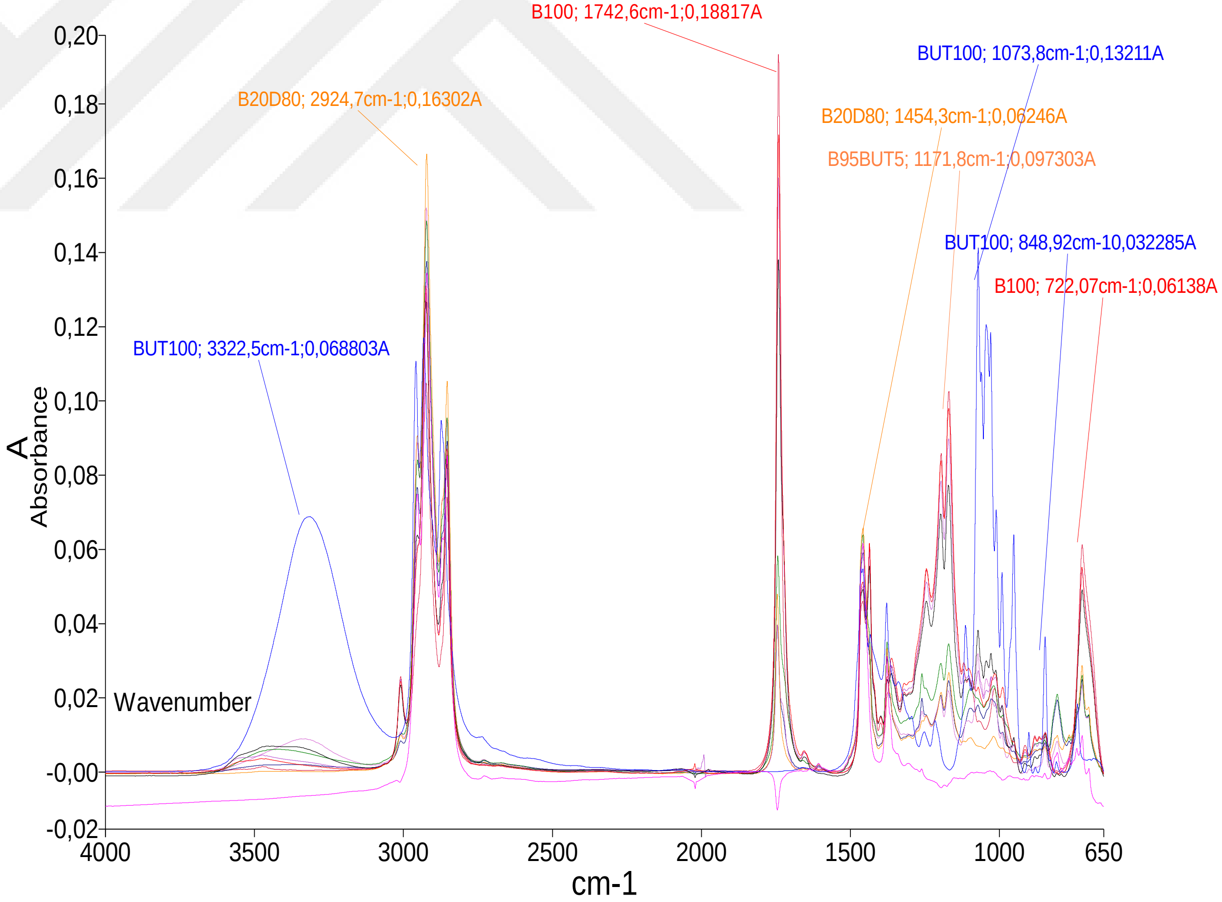


Fig. 3.1b. Infrared spectra of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends

3.5. TGA analysis

Oxidative stability of *Aleurites moluccanus* methyl ester and its blends with diesel were quantified by Thermogravimetric analysis (TGA). This was expressed as weight change as a function of increasing temperature. Thermogravimetric curves (TGA) show the weight loss in different temperatures and the first derivative of the weight loss in relation to the temperature curves. TGA/DTGA curves show that oxidative degradation for *Aleurites moluccanus* methyl ester and its blends took place in the temperature range 130-220 °C (Fig. 3.2a, Fig. 3.2b). In these ranges, the mass losses were recorded at levels of 95.1-98.5% for *Aleurites moluccanus* biodiesel and its blends. While oxidative degradation occurred at 75 °C for butanol (BUT100) and 117 °C for diesel (D100). In these ranges, the mass losses were recorded at levels of 99.3 % and 96.0 % for butanol and diesel respectively. The oxidation onset temperatures were represented in Table 3.4. The degradation temperatures of it are possible to observe the great similarity between the curves, with small variations of T_{onset} between the blends, with those that had the highest concentration of biodiesel being more thermally stable. The detailed results of TGA are shown in APPENDIX B.

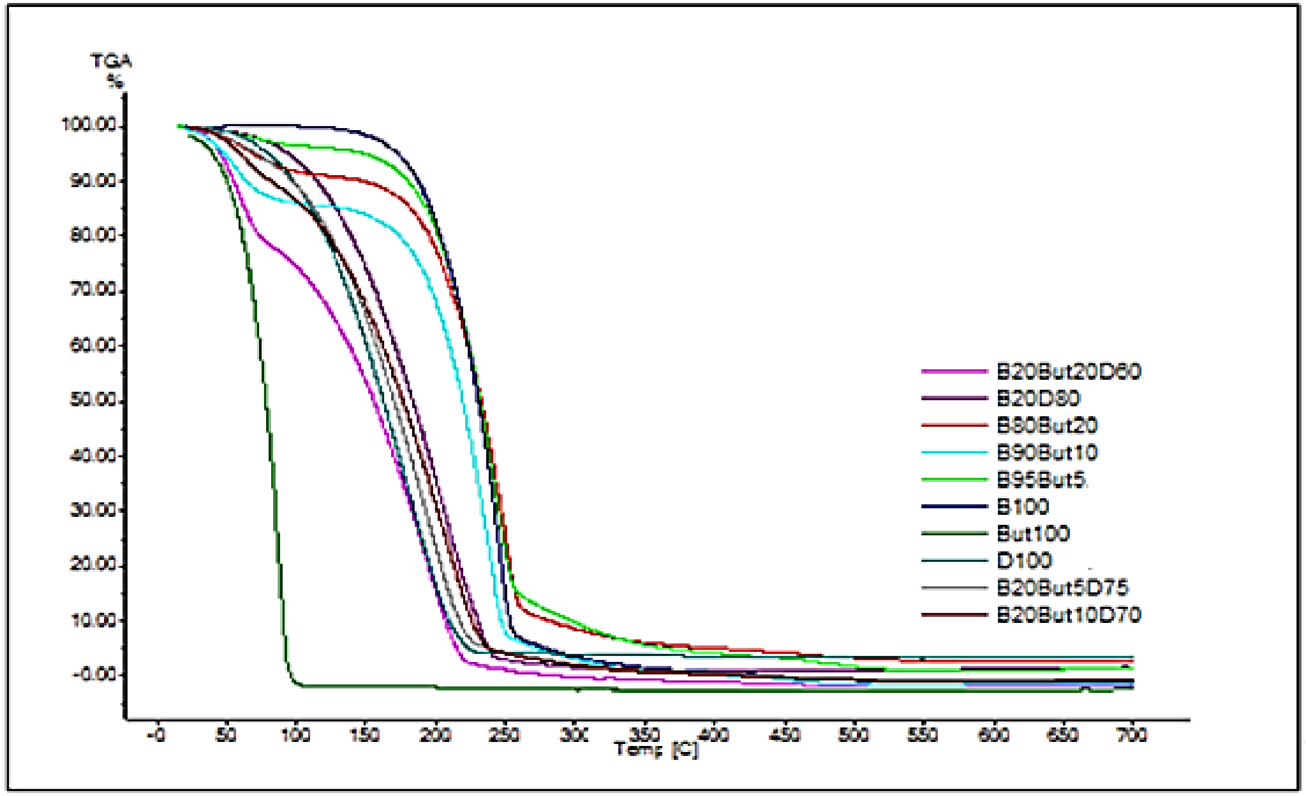


Fig. 3.2a. Thermogravimetric analyzes (TGA) of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends for oxidative stability

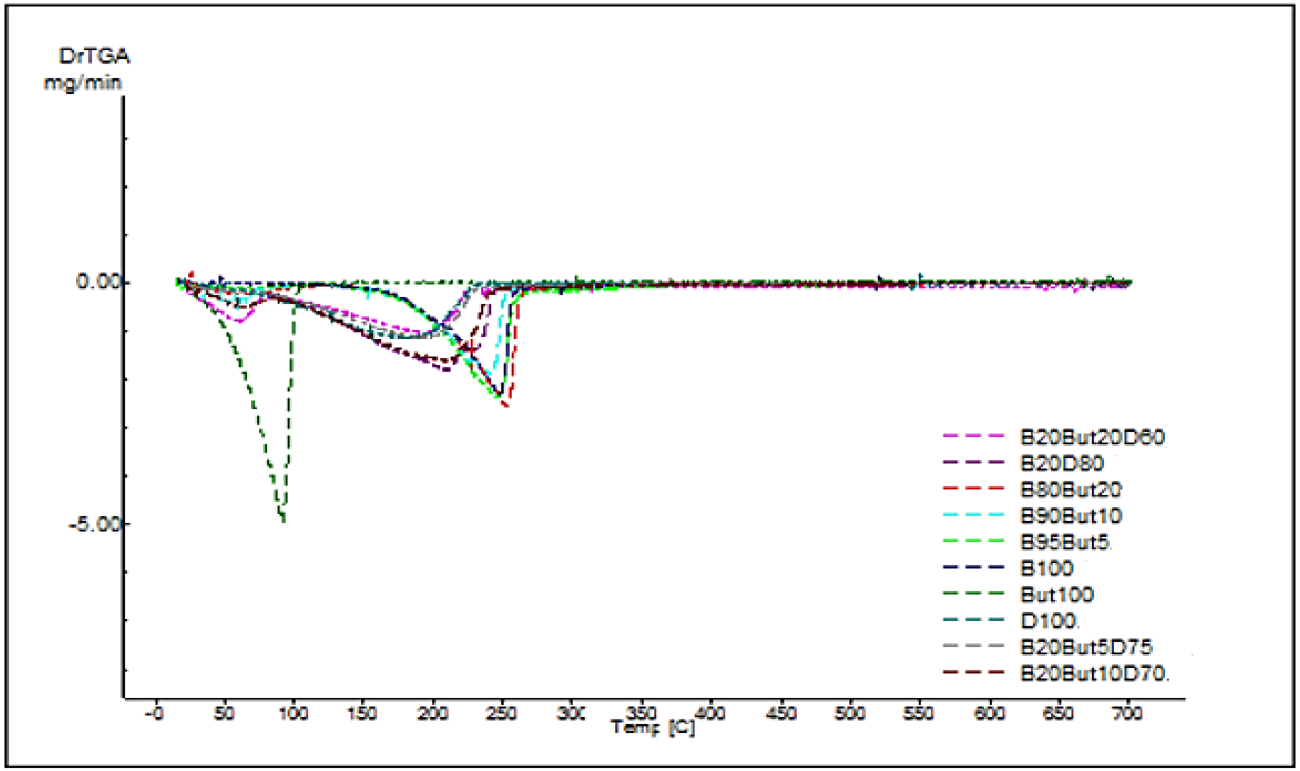


Fig. 3.2b. Derivative thermogravimetric analyzes (DTGA) of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends for oxidative stability

Table 3.4. TGA analysis of *Aleurites moluccanus* methyl ester and its blends

Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20BUT5D75	10	30-200	144.7	96.0
B20BUT10D70	10	30-275	130.7	96.7
B20BUT20D60	10	30-240	134.3	97.1
B20D80	10	30-255	151.0	96.8
B80BUT20	10	30-350	212.9	95.9
B90BUT10	10	30-345	206.5	97.7
B95BUT5	10	30-375	207.2	95.1
B100	10	30-350	219.8	98.5
BUT100	10	30-120	75.3	99.3
D100	10	30-320	117.7	96.0

3.6. DSC analysis

The crystallization onset temperatures of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends under N_2 atmosphere were studied using Differential Scanning Calorimetry (DSC) and presented in Table 3.5. The onset temperatures for B100, D100 and BUT100 are -9.96 °C, -11.49 °C and 15.13 °C respectively. Biodiesel crystallizes faster than diesel and butanol. The crystallization onset temperatures of B20BUT5D75, B20BUT10D70, B20BUT20D60 and B20D80 are -10.60 °C, -10.79 °C, -10.89 °C and -10.59 °C respectively, below B100 which signifies that the adding diesel and butanol lowers the crystallization temperature of biodiesel [52]. The crystallization onset temperatures of B80BUT20, B90BUT10 and B95BUT5 are -11.28 °C, -11.93 °C and -10.39 °C respectively, above BUT100 which represent that addition of biodiesel increase the crystallization temperature of butanol. The crystallization temperature of *Aleurites moluccanus* methyl ester (-9.96 °C) [53] is in a good agreement with macauba ethyl ester (-9.9 °C) and macauba methyl esters (-6.1 °C) [54], higher than coriander methyl ester (-19 °C) [55] and castor methyl ester (-26 °C) [56] and lower than Jatropha methyl ester (-1 °C) [6]. The detailed results of DSC are shown in APPENDIX C.

Table 3.5. Crystallizations onset temperature (°C) of *Aleurites moluccanus* methyl ester (B100), butanol (But100), diesel (D100) and their blends under N_2 atmosphere

Sample	Crystallizations onset temperature (°C)
B20BUT5D75	-10.60
B20BUT10D70	-10.79
B20BUT20D60	-10.89
B20D80	-10.59
B80BUT20	-11.28
B90BUT10	-11.93
B95BUT5	-10.39
B100	-9.96
BUT100	-15.13
D100	-11.49

3.7. Engine performance

Brake torque, brake power (BP) and brake specific fuel consumption (BSFC) of three selected fuel samples namely Euro-diesel, D80B20 and D70B20but10 have been studied in this study. The following sections discuss the detailed results of these parameters.

3.7.1. Brake power (BP)

The variations of brake power at full load with respect to the tested fuels at various engine speeds are shown in Fig. 3.3. For all tested fuels, the maximum brake power was obtained at 2500 rpm. The maximum brake power of 11.22 kW was recorded for Euro-Diesel at 2500 rpm. The average brake power for Euro-Diesel, D80B20 and D70B20But10 are 8.29, 7.92 and 7.74 kW respectively. D80B20 and D70B20But10 reduced the average brake power of 4.5% and 6.66% respectively.

It can be seen that the brake power output values reduced with biodiesel and butanol addition. Butanol addition further reduced brake power compared to biodiesel-diesel blends. The reduction in brake power values is mainly attributed to the lower calorific values, higher viscosities and higher oxygen content of both biodiesel and butanol. These parameters influence the combustion. Furthermore, uneven combustion characteristics of blended fuels decreased the engine brake power [28, 45, 46].

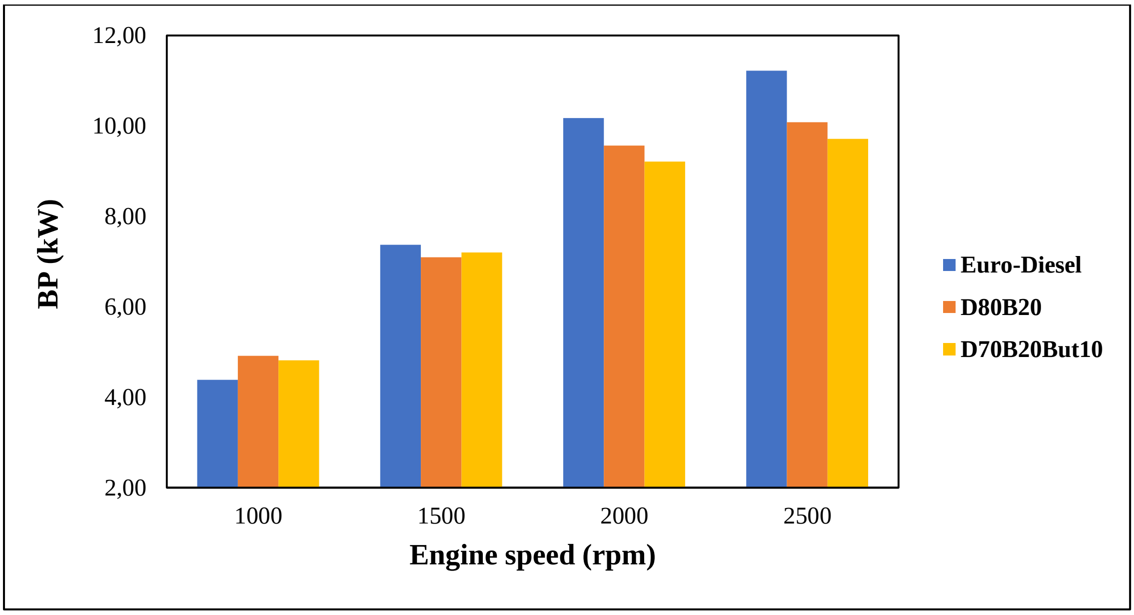


Fig. 3.3. Brake power (BP) versus engine speed at full load

3.7.2. Brake torque

The variations of brake torque at full load with respect to the tested fuels at various engine speeds are shown in Fig. 3.4.

It can be seen that the brake torque increases gradually up to a maximum value at 2000 rpm, and then falls at 2500 rpm. This can be attributed to the mechanical friction loss beside lower volumetric efficiency of the engine due to increasing speed [45, 46].

The maximum brake torque of 47.87 N.m was recorded for Euro-Diesel at 2000 rpm. The average brake torque for Euro-Diesel, D80B20 and D70B20But10 are 44.39, 42.4 and 41.5 N.m respectively. D80B20 and D70B20But10 reduced the average brake torque of 4.48% and 6.52% respectively.

It can be seen that the brake torque output values reduced with biodiesel and butanol addition. Butanol addition further reduced brake torque compared to biodiesel-diesel blends. The reduction in brake torque values is attributed to the lower calorific values and higher kinematic viscosities of both biodiesel and butanol [28, 45].

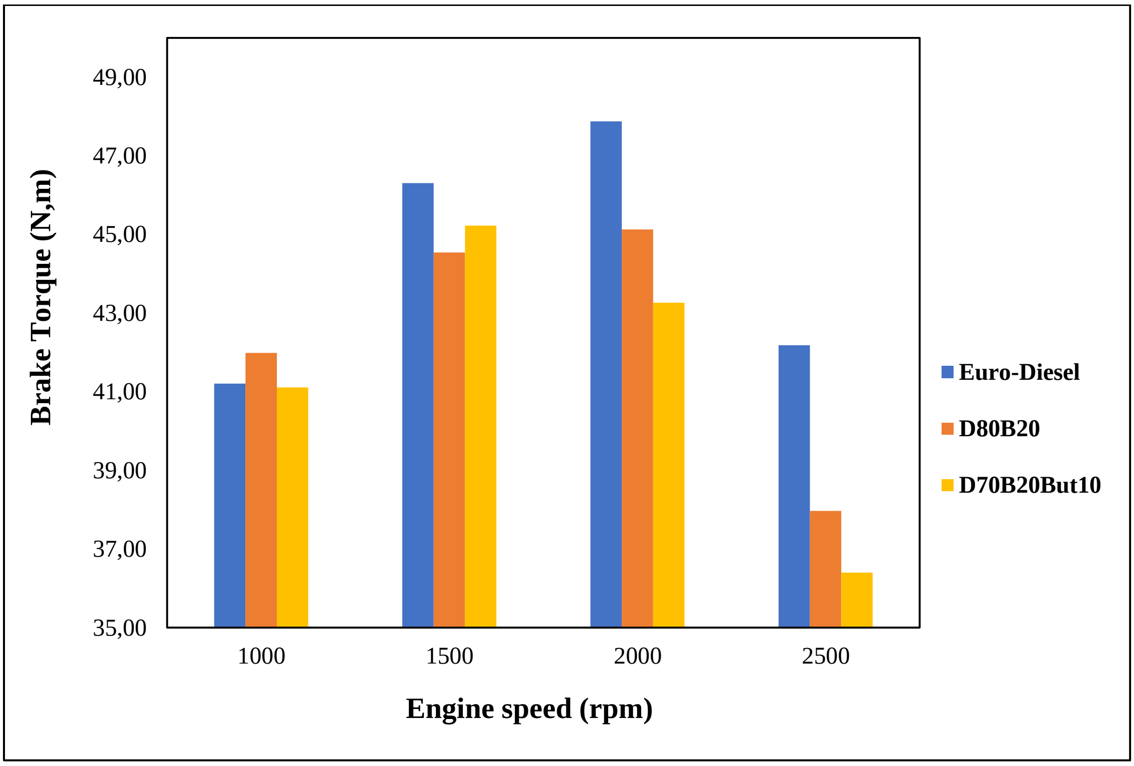


Fig. 3.4. Brake torque versus engine speed at full load

3.7.3. Brake specific fuel consumption (BSFC)

The variations of brake specific fuel consumption at full load with respect to the tested fuels at various engine speeds are shown in Fig. 3.5. The minimum brake specific fuel consumption of 255.47g/kWh was recorded for Euro-Diesel at 2000 rpm. The average brake specific fuel consumption for Euro-Diesel, D80B20 and D70B20But10 are 286.19, 287.01 and 293.18g/kWh respectively. D80B20 and D70B20But10 increased the average brake specific fuel consumption of 0.28% and 2.44% respectively.

Brake specific fuel consumption output values increased with biodiesel and butanol addition. Butanol addition further increased brake specific fuel consumption compared to biodiesel-diesel blends. The increase in brake specific fuel consumption values can be attributed to the combined effects of lower calorific, higher density and kinematic viscosity values of both biodiesel and butanol [28, 45, 46].

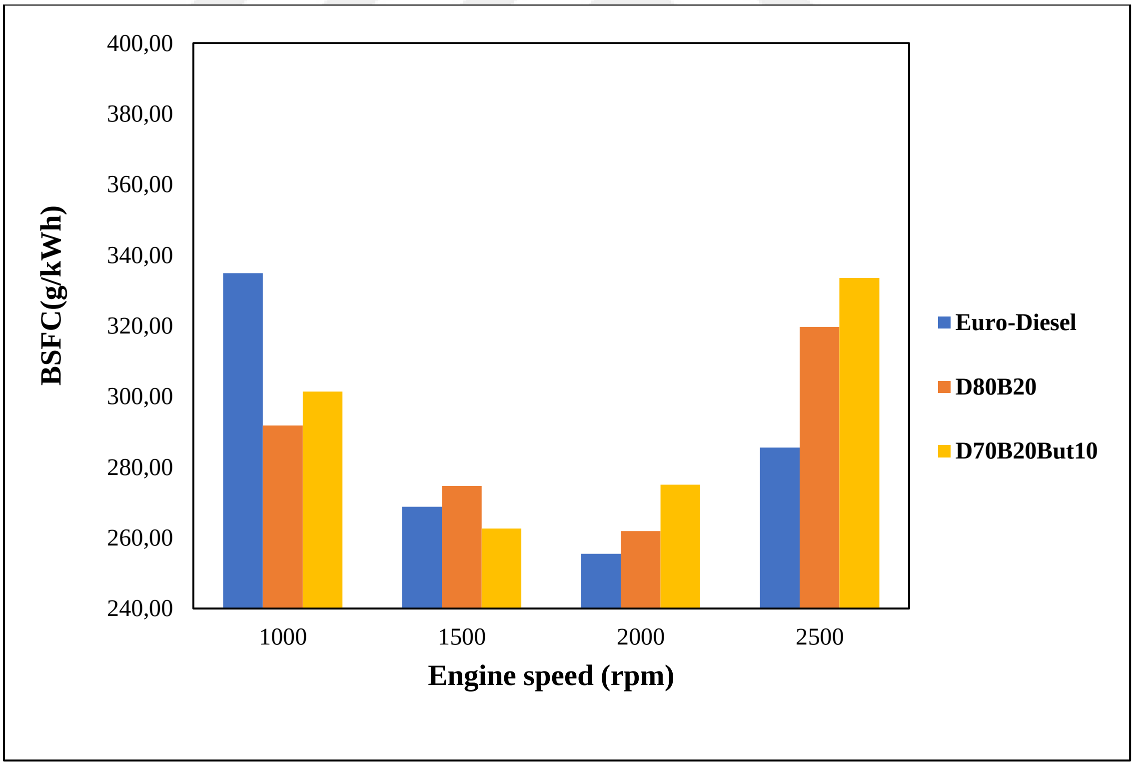


Fig. 3.5. Brake specific fuel consumption (BSFC) versus engine speed at full load

3.8. Emissions performance analysis

Emissions performance parameters of CO, HC, NO_x and exhaust gas temperature of three fuel samples namely Euro-diesel, D80B20 and D70B20but10 have been considered in this work. The following sections discuss the detailed results of these parameters.

3.8.1. CO emissions

Fig. 3.6 shows that CO emissions of both blends are lower than Euro-diesel. Biodiesel causes a reduction in CO emission when blended with diesel because of extra oxygen content of biodiesel which promotes complete combustion, and thus leads to the reduction in CO emissions. **[28, 46]**. It can be seen that the minimum CO emissions for all blends occurred at 2500 rpm. It can be also observed that CO emissions decreased with increasing speed. Compared to Euro-diesel, D80B20 and D70B20But10 reduced CO emissions of 41.61% and 33.19% respectively (On average). Biodiesel has a higher cetane number, which results in the lower possibility of formation of rich fuel zone and thus reduces CO emissions. Advance in injection of biodiesel also have an effect on CO emissions. It was reported in [14,43,47] that CO emissions reduced when the injection timing was advanced for biodiesel fuel, which leads to the advance of ignition timing. These findings are in good agreement with literature, which states that a decrease in CO emissions occurs when blending diesel with biodiesel and butanol **[28, 47-49]**. Engine load has been proven to have a significant impact on CO emissions. The literature **[50]** reported that CO emissions increased with engine load increasing. The main reason for this increase is that the air–fuel ratio decreases with increase in load, which is typical for all internal combustion engines. There is a largely unanimous conclusion about the effect of engine speed on CO emissions, that is, CO emissions for biodiesel decrease with an increase in engine speed, as the result of the better air–fuel mixing process and/or the increased fuel/air equivalence ratio with the increased engine speed **[50].**

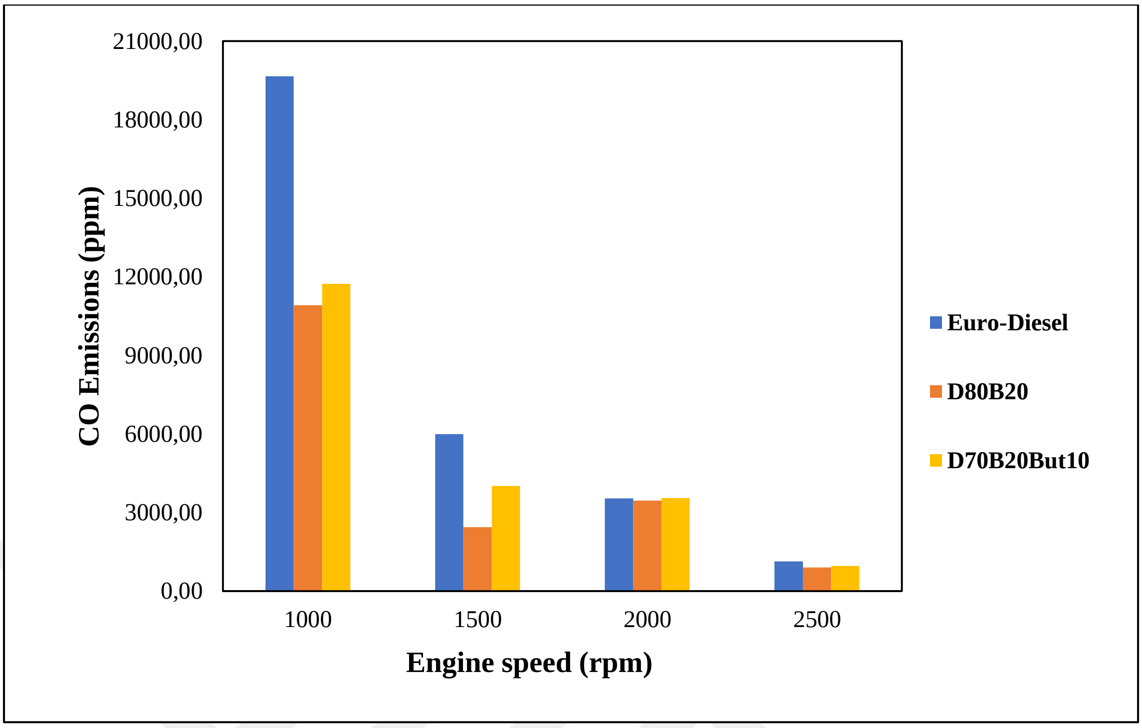


Fig. 3.6. CO emissions versus engine speed at full load

3.8.2. HC emissions

Fig. 3.7 shows that HC emissions of both blends are lower than Euro-diesel. Biodiesel causes a reduction in HC emission when blended with diesel. The high oxygen content of biodiesel resulted in a complete combustion [28, 46]. It can be seen that the minimum HC emissions for all blends occurred at 2500 rpm. It can be also observed that HC emissions decreased with increasing speed. Compared to Euro-diesel, D80B20 and D70B20But10 reduced CO emissions of 45.04% and 28.99% respectively (On average).

These findings are in good agreement with literature that states that a decrease in HC emissions occurs when substituting diesel fuel with biodiesel and butanol [28, 47-49].

The lower heating value of the pure biodiesel implies higher fuel consumptions and therefore it could produce high local fuel to air ratios which caused an increase in HC emissions, and the high catalyst efficiency reduced the biodiesel advantage in terms of HC emissions. The sources of biodiesel also have an effect on HC emissions. Alcohol used had a significant impact on the HC emissions, because the ethyl ester showed the lower HC emissions than methyl ester in medium load conditions, and no clear trend in low load condition due to the lower volatility of ethyl esters. The properties of biodiesel are related to HC emissions. Graboski et al. [51] showed that the increase in chain length or saturation level of several biodiesels led to a higher reduction in HC emissions on an 11.1 L engine.

It is predominant viewpoint that HC emissions reduce when pure biodiesel is fueled instead of diesel. Most of researches showed that HC emissions for biodiesel reduce with the increase of biodiesel content. The feedstock of biodiesel and its properties have an effect on HC emissions, especially for the different chain length or saturation level of biodiesels. The advance in injection and combustion of biodiesel favors the lower HC emissions. There are inconsistent conclusions about effect of engine load on HC emissions for biodiesel. Although an oxidative catalytic converter has a positive impact on HC emissions for biodiesel, its function seems be weakened. Metal based additives have less efficiency to improve HC emissions for biodiesel than the others emissions. And a small proportion of ethanol and methanol added into biodiesel and its blends with diesel may be advantageous to HC emissions [50].

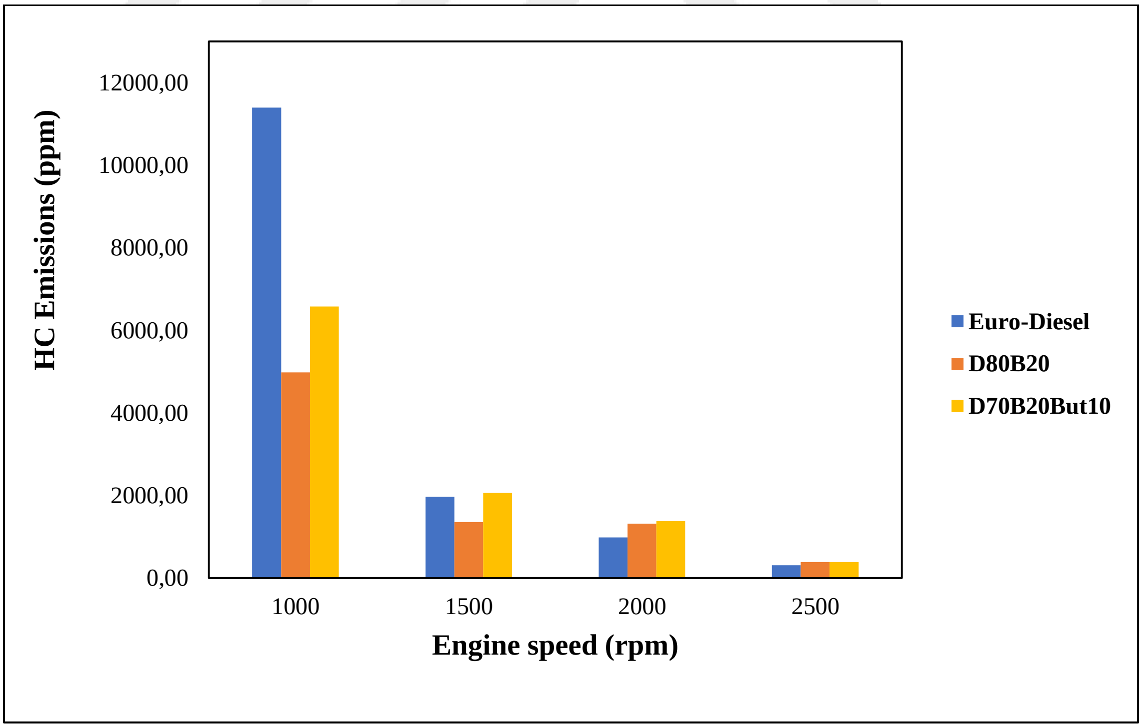


Fig. 3.7. HC emissions versus engine speed at full load

3.8.3. NO_x emissions

NO_x formation is affected by adiabatic flame temperature during combustion process [28, 46]. Any fuel with a higher heat release rate in the premix combustion phase and lower heat release rate in the late combustion phase increases NO_x emission [45]. The vast majority of literatures reported that NOx emissions will increase when using biodiesel. This increase is mainly due to higher oxygen content for biodiesel. Moreover, cetane number and different injection characteristics also have an impact on NOx emissions for biodiesel.

Fig. 3.8 shows the variation of NO_x emission values for all blends. It can be seen that the minimum NO_x emissions for all blends occurred at 2500 rpm. It can be also observed that NO_x emissions decreased with increasing speed. Compared to Euro-diesel, D80B20 reduced NO_x emissions of 3.42% while D70B20But10 increased NO_x emissions of 11.22% (On average). The content of unsaturated compounds in biodiesel could have a greater impact on NOx emissions. The larger the content of unsaturated compounds is, the more NOx emissions will reduce, which is a matter of concern[50]. The larger engine load is, the higher the level of NOx emissions for biodiesel will be, which is in line with the mechanism of NOx formation. A further study is needed to perform the effect of injection timing and injection pressure on NOx emissions of biodiesel. Metallic additives, oxide additives, emulsifier, etc. seem to be useful to improve NOx emissions of biodiesel, but the comprehensive assessments on other emissions and engine performance[51].

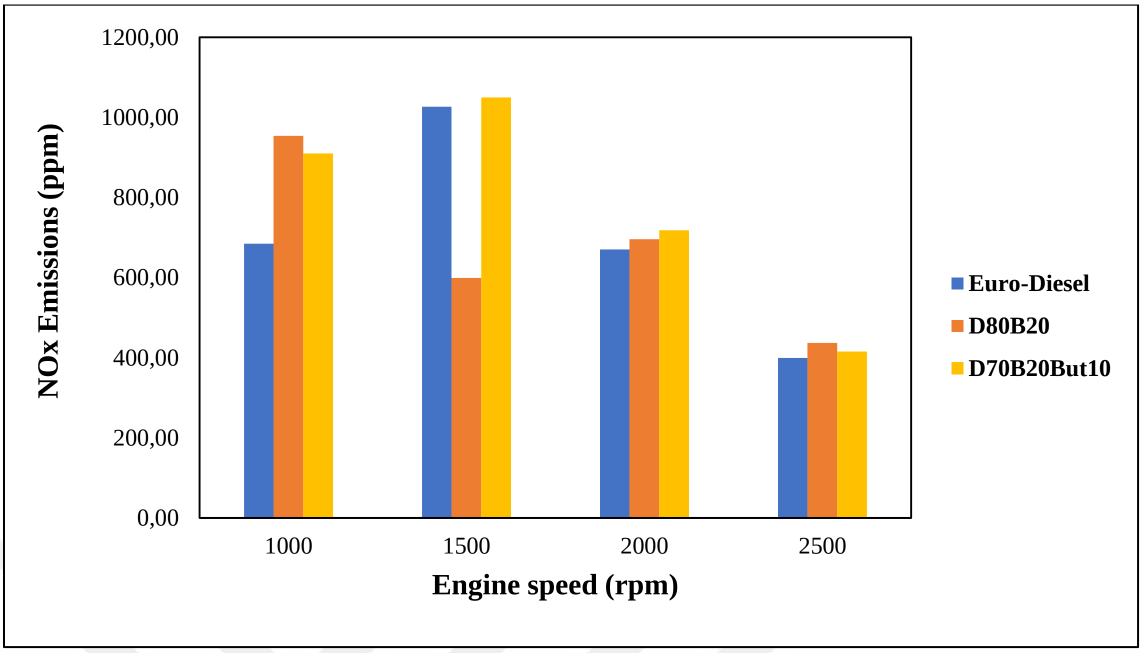


Fig. 3.8. NO_x emissions versus engine speed at full load

3.8.4. Exhaust gas temperature (EGT)

Fig. 3.9 shows that EGT of both blends are higher than Euro-diesel. Biodiesel addition causes an increase in EGT when blended with diesel. It has been observed that the maximum EGT occurred at 2500 rpm for all blends. Maximum EGT were recorded for D80B20 (589 °C). Compared to Euro-diesel, D80B20 decreased EGT for 2.37% while D70B20But10 reduced EGT for 1.49% (On average).

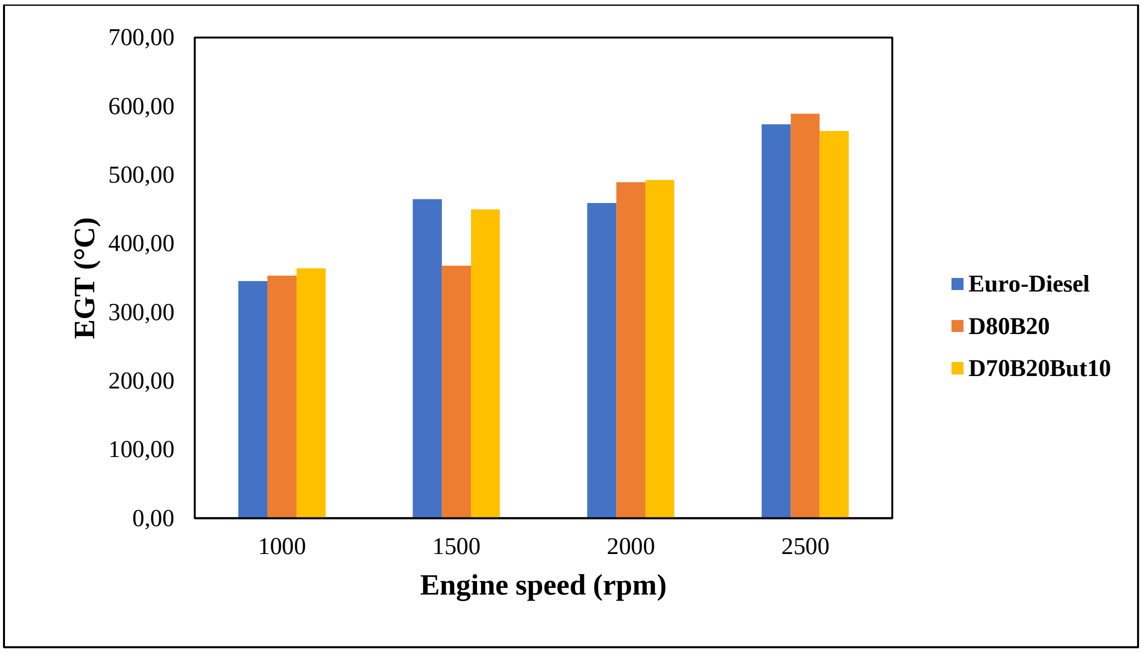


Fig. 3.9. EGT versus engine speed at full load

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

In this section discussion of the results obtained in the thesis, the future work that can be done in this area, along with some suggestions is provided.

4.1. Discussion and Conclusion

In this work, biodiesel from crude *Aleurites moluccanus* oil has been produced. It has been found that most of the properties of biodiesels agree with ASTM D6751 standards. Blending of *Aleurites moluccanus* biodiesel with Euro-diesel and butanol at different percentages has a positive impact on important physical and chemical properties such as kinematic viscosity and density while keeping acceptable range for cold flow properties. Moreover, FT-IR, TGA and DSC analyses were also considered in this thesis.

Some important engine and emissions performance parameters such as BP, brake torque, BSFC, CO, HC, NO_x and EGT were also studied. A reduction in BP, HC and CO was observed for all blends at full load compared to Euro-diesel. However, an increase in BSFC was observed. Overall, the blends appear to be good alternatives to the biodiesel-diesel blends. Thus, butanol-biodiesel-diesel blends can be considered as a potential sustainable fuel to substitute for fossil diesel.

4.2. Future Work and Suggestions

This research has been conducted using the existing facility at Alternative Fuels Research Laboratory (AFRL, Erciyes University). Besides, FT-IR, TGA and DSC analysis has been conducted at Chemistry Department, Ondokuz Mayis University. Engines and emissions performance has been conducted at Engine Laboratory, Department of Mechanical Engineering, Dicle University. All these efforts have been initiated through personal communications.

Therefore, the current study recommends further investigiation of the blends the followign aspects:

1. Running the diesel engine with higher biodiesel-butanol blending ratios.
2. The effect of injection pressure on combustion performance has to be investigated following these blends.
3. The corrosive effects of butanol in engine parts and fuel injection system in diesel engines shall be studied.
4. Studies on the lubrication properties of butanol-diesel fuel blends can be carried out.

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APPENDIX (A)

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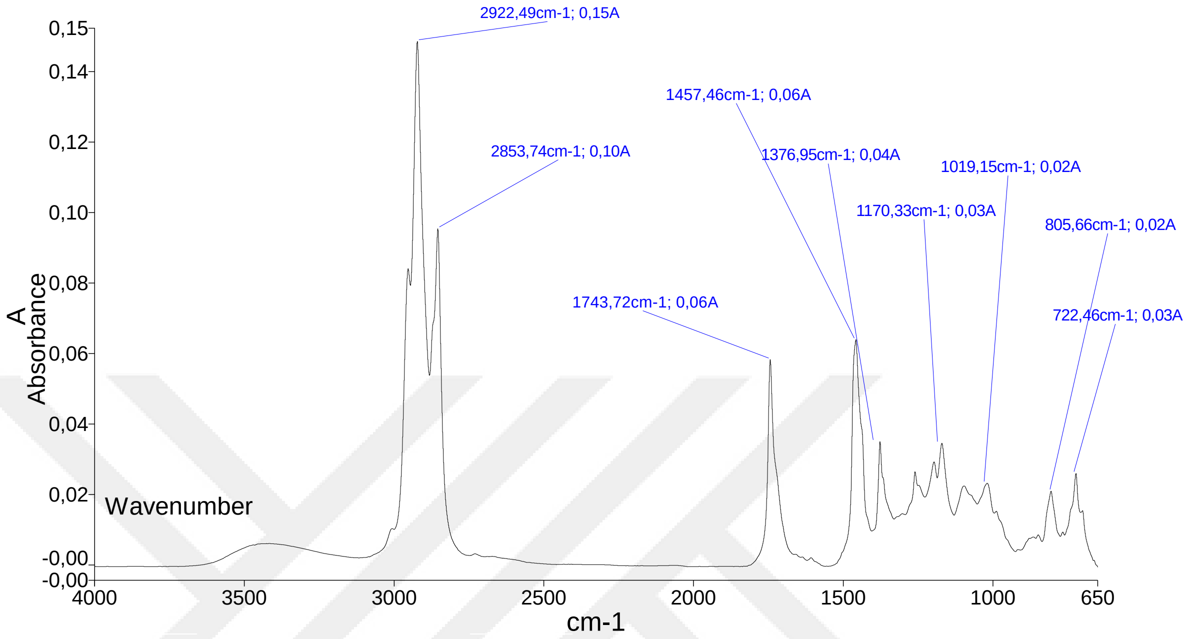

Absorption bands (cm^{-1})	**Functional group**	**Absorption intensity**
2922,49	C-H Vibration	Strong
2853,74	CH_2 Asymmetric and symmetric vibration	Strong
1743,72	C=O Stretching vibration (Ester)	Strong
1457,46	CH_2 Scissoring vibration	Middling
1376,95	CH_2 and CH_3 deformation	Middling
1170,33	C-O-C symmetric stretching vibration	Middling
1019,15	C-O-C anti-symmetric stretching vibration	Weak
805,66	Epoxy ring vibration	Middling
722,46	CH_2 rocking vibration	Weak

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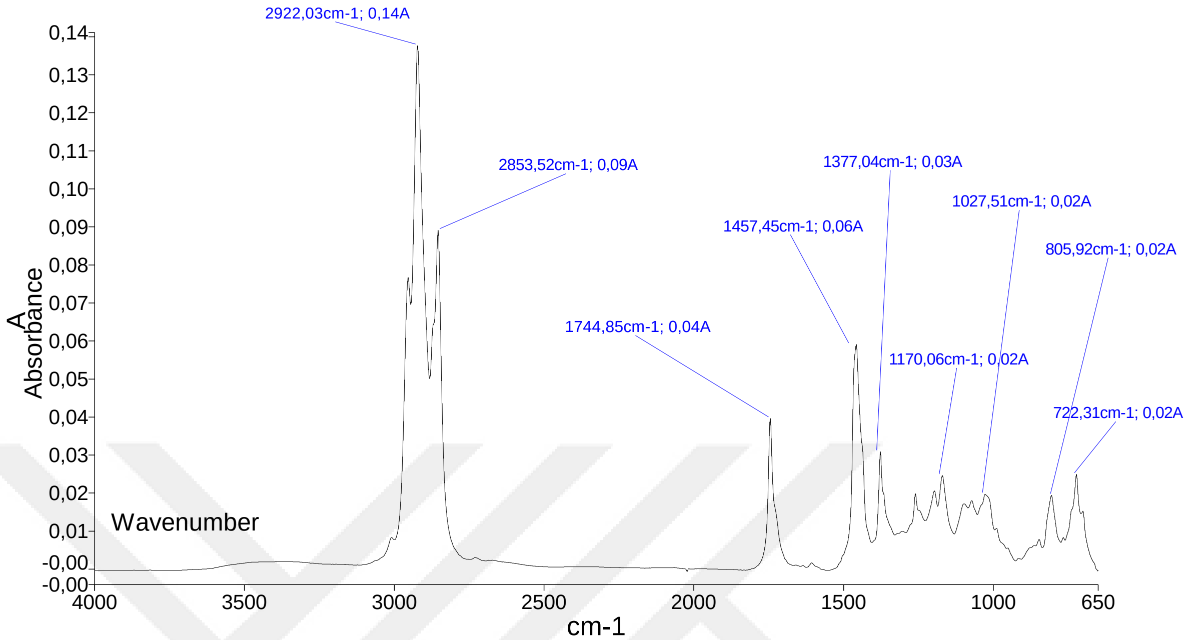
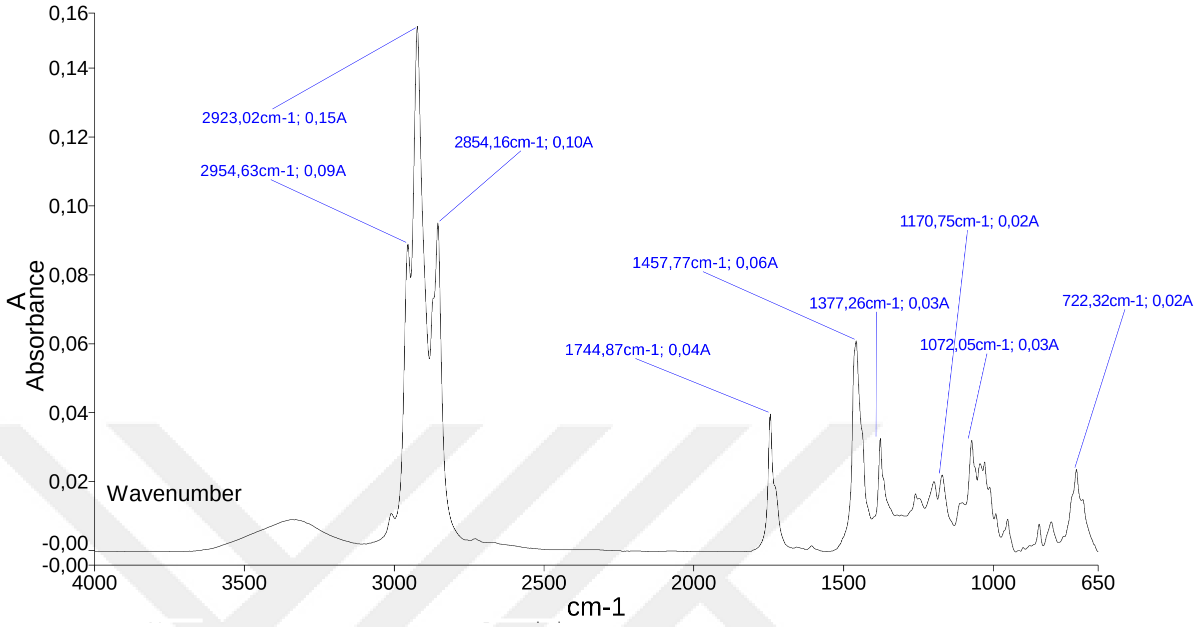


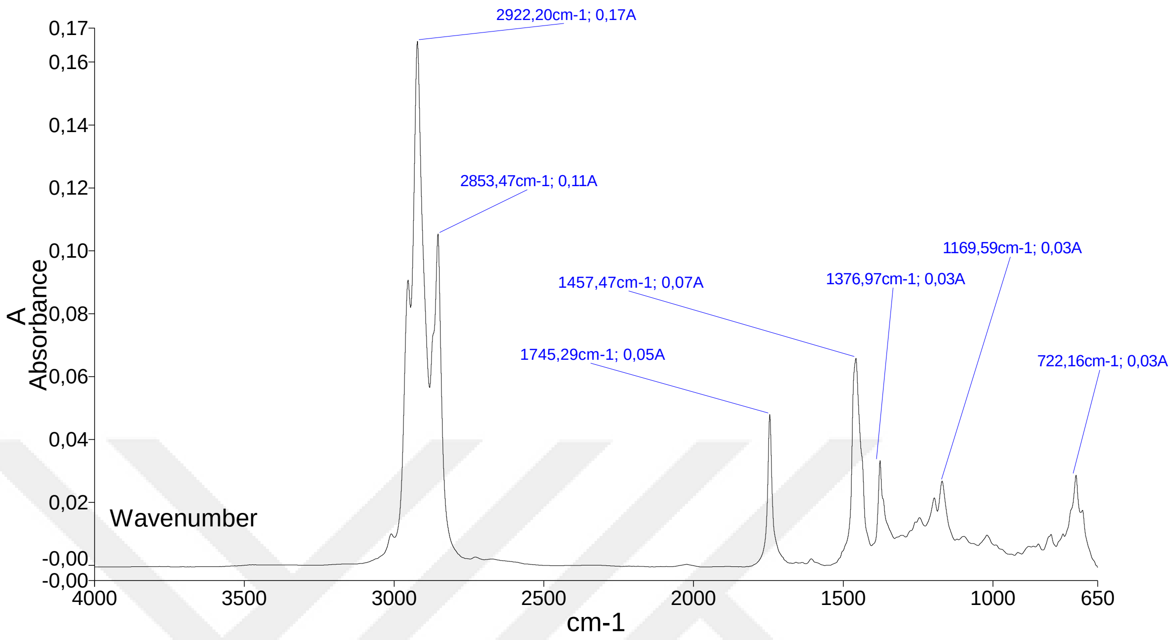
Absorption bands (cm^{-1})	**Functional group**	**Absorption intensity**
2922,03	C-H Vibration	Strong
2853,52	CH_2 Asymmetric and symmetric vibration	Strong
1744,85	C=O Stretching vibration (Ester)	Strong
1457,45	CH_2 Scissoring vibration	Middling
1377,04	CH_2 and CH_3 deformation	Middling
1170,06	C-O-C symmetric stretching vibration	Middling
1027,51	C-O-C anti-symmetric stretching vibration	Weak
805,92	Epoxy ring vibration	Middling
722,31	CH_2 rocking vibration	Weak

B20BUT20D60



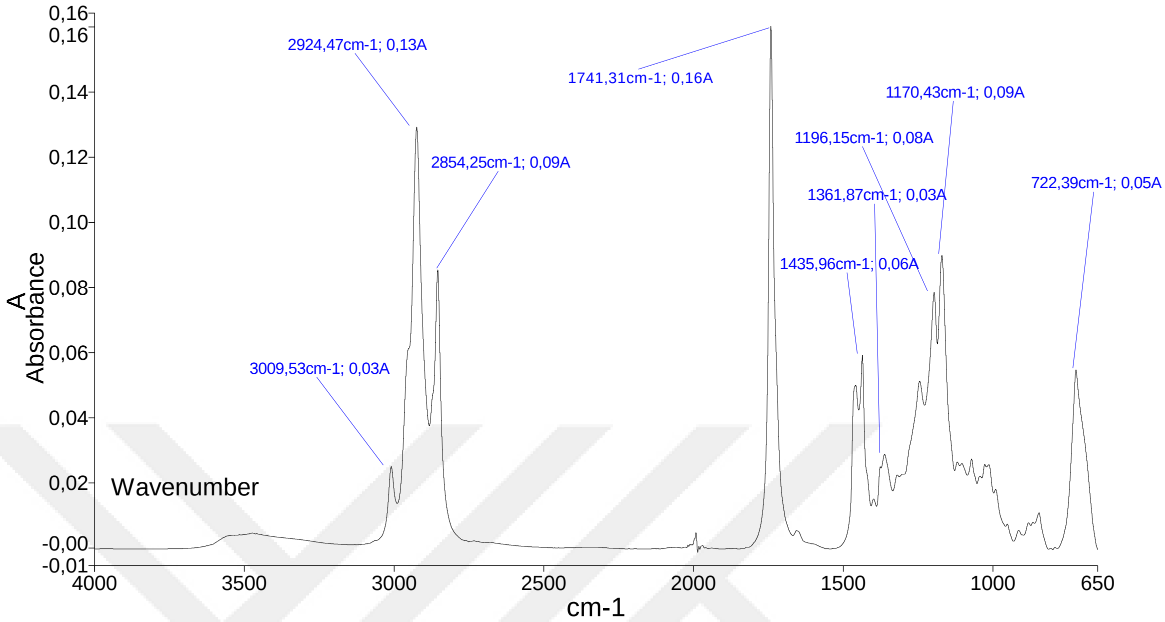
Absorption bands (cm-1)	Functional group	Absorption intensity
2954,63	CH_3 asymmetric and symmetric stretching vibration	Strong
2923,02	C-H Vibration	Strong
2854,16	CH_2 Asymmetric and symmetric vibration	Strong
1744,87	C=O Stretching vibration (Ester)	Strong
1457,77	CH_2 Scissoring vibration	Middling
1377,26	CH_2 and CH_3 deformation	Middling
1170,75	C-O-C symmetric stretching vibration	Middling
1072,05	C-O-C anti-symmetric stretching vibration	Weak
722,32	CH_2 rocking vibration	Weak

B20D80



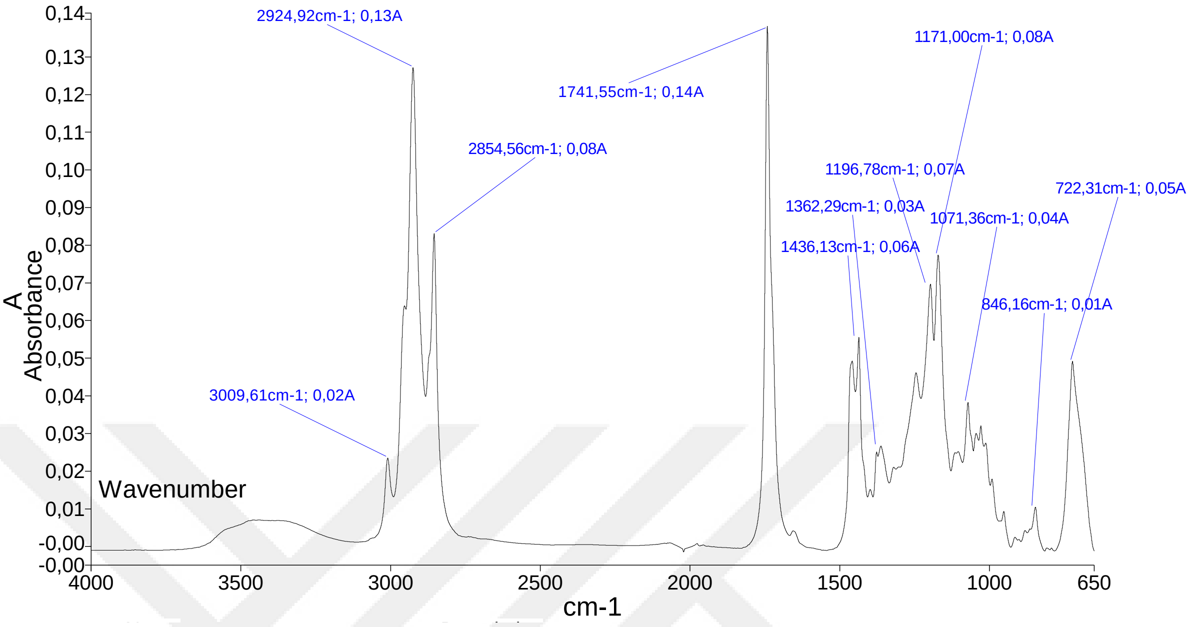
Absorption bands (cm^{-1})	**Functional group**	**Absorption intensity**
2922,20	C-H Stretching vibration	Strong
2853,47	CH_2 Asymmetric and symmetric vibration	Strong
1745,29	C=O Stretching vibration (Ester)	Strong
1457,47	CH_2 Scissoring vibration	Middling
1376,97	CH_2 and CH_3 deformation	Middling
1169,59	C-O-C symmetric stretching vibration	Middling
722,16	CH_2 rocking vibration	Weak

B80BUT20



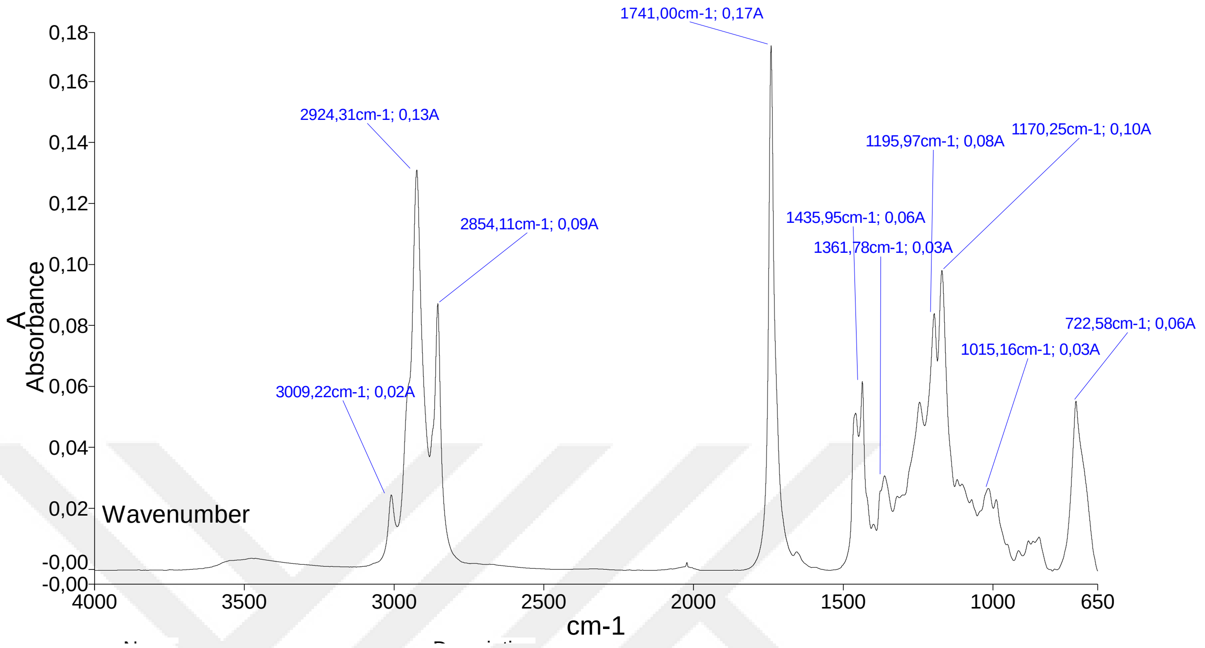
Absorption bands (cm^{-1})	Functional group	Absorption intensity
3009,53 – 2924,47	C-H Stretching vibration	Strong
2854,25	CH_2 Asymmetric and symmetric vibration	Strong
1741,31	C=O Stretching vibration (Ester)	Strong
1435,96	CH_2 Scissoring vibration	Middling
1361,87	CH_2 and CH_3 deformation	Middling
1196,15 – 1170,43	C-O-C Symmetric stretching vibration	Middling
722,39	CH_2 rocking vibration	Weak

B90BUT10



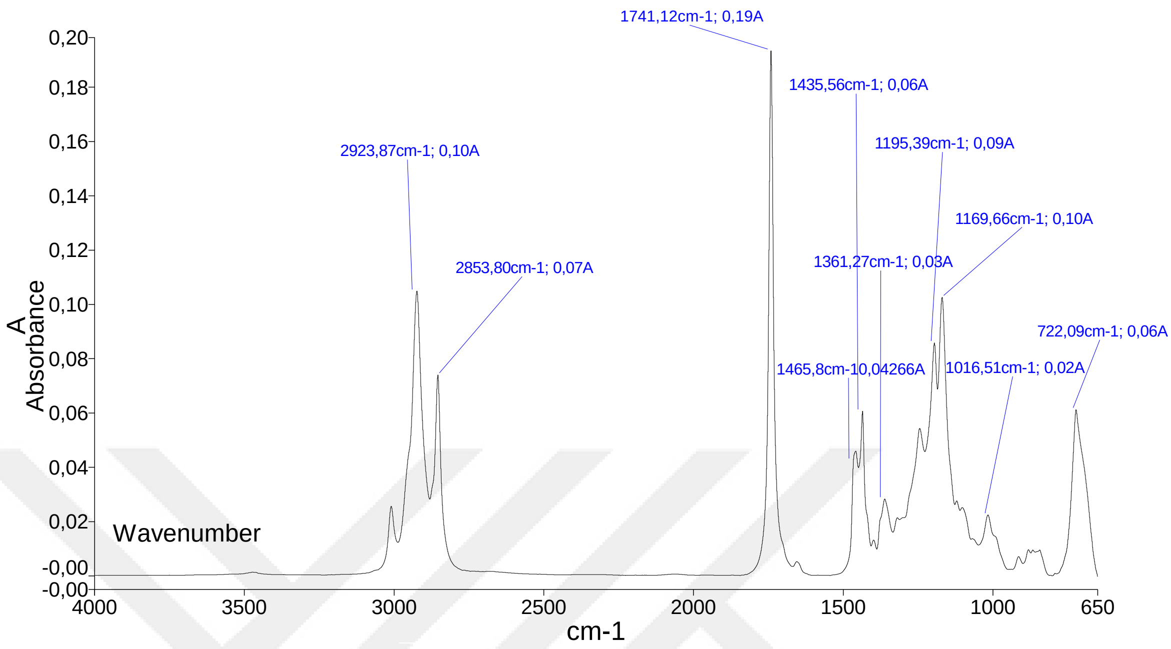
Absorption bands (cm^{-1})	**Functional group**	**Absorption intensity**
3009,61 – 2924,92	C-H Stretching vibration	Strong
2854,56	CH_2 Asymmetric and symmetric vibration	Strong
1741,55	C=O Stretching vibration (Ester)	Strong
1436,13	CH_2 Scissoring vibration	Middling
1362,29	CH_2 and CH_3 deformation	Middling
1196,78- 1171.00	C-O-C Symmetric stretching vibration	Middiling
1071,36	C-O-C Anti-symmetric stretching vibration	Weak
846,16	Epoxy ring vibration	Middling
722,31	CH_2 rocking vibration	Weak

B95BUT5



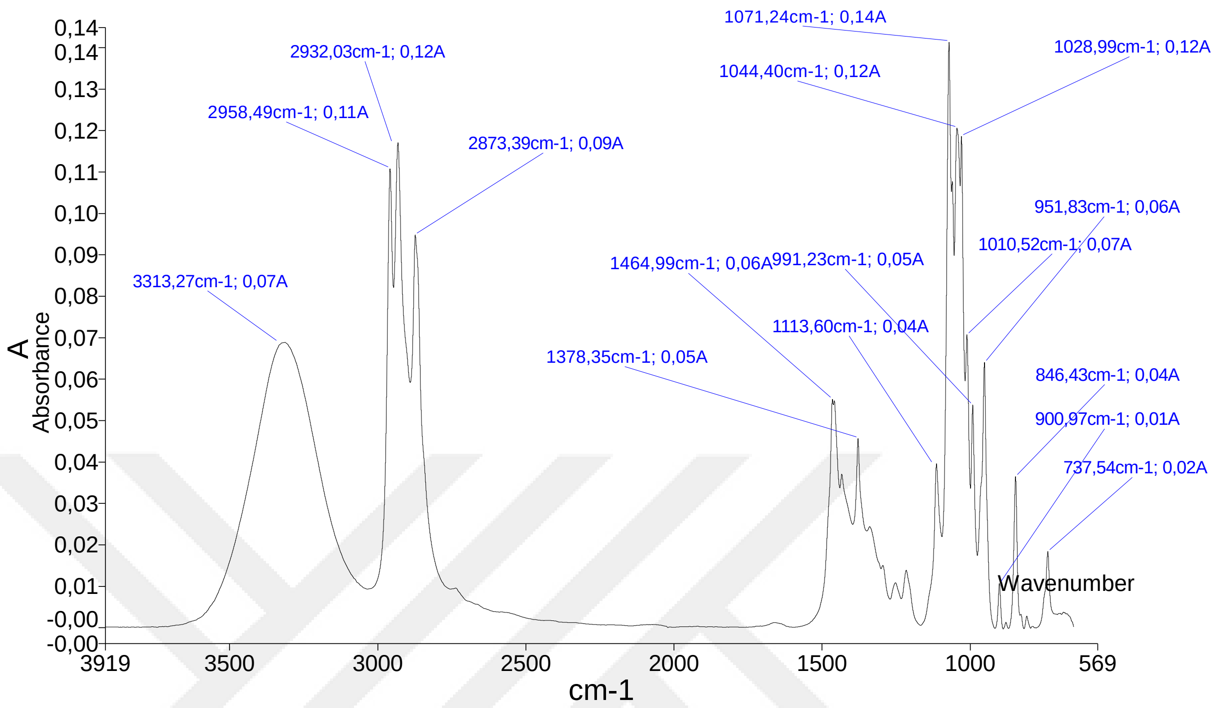
Absorption bands (cm^{-1})	Functional group	Absorption intensity
3009,22 – 2924,31	C-H Stretching vibration	Strong
2854,11	CH_2 Asymmetric and symmetric vibration	Strong
1741,00	C=O Stretching vibration (Ester)	Strong
1435,95	CH_2 Scissoring vibration	Middling
1361,78	CH_2 and CH_3 deformation	Middling
1195,97 – 1170,25	C-O-C Symmetric stretching vibration	Middiling
1015,16	C-O-C Anti-symmetric stretching vibration	Weak
722,58	CH2 rocking vibration	Weak

B100



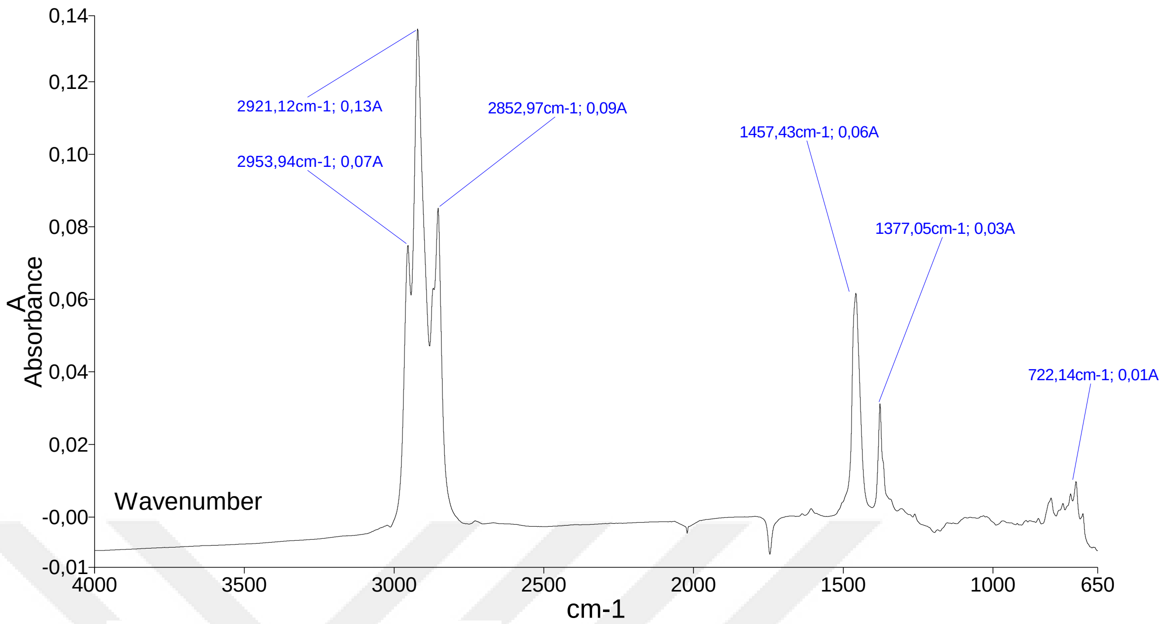
Absorption bands (cm^{-1})	Functional group	Absorption intensity
3009,59 – 2923,59	C-H Stretching vibration	Strong
2853,8	CH_2 Asymmetric and symmetric vibration	Strong
1741,12	C=O Stretching vibration (Ester)	Strong
1435,56	CH_2 Scissoring vibration	Middling
1361,27	CH_2 and CH_3 deformation	Middling
1195,39 – 1169,66	C-O-C Symmetric stretching vibration	Middiling
1016,51	C-O-C Anti-symmetric stretching vibration	Weak
722,09	CH_2 rocking vibration	Weak

BUT100



Absorption bands (cm^{-1})	Functional group	Absorption intensity
3313,27	O-H Stretching vibration	Strong
2958,49 – 2932,39	C-H Stretching vibration	Strong
2873,39	CH_2 Asymmetric and symmetric vibration	Strong
1464,99	CH_2 Scissoring vibration	Middling
1378,35	O-H Bending in plane vibration	Middling
1113,6 – 1071,24 - 1044,40	C-O Symetric stretching vibration	Strong
1028,99 – 1010,52 - 991,23	C-O Anti-symmetric stretching vibration	Strong
951,83 - 900,97 – 846,43	CH_2 rocking vibration	Weak
737,54	O-H Bending vibration	Various

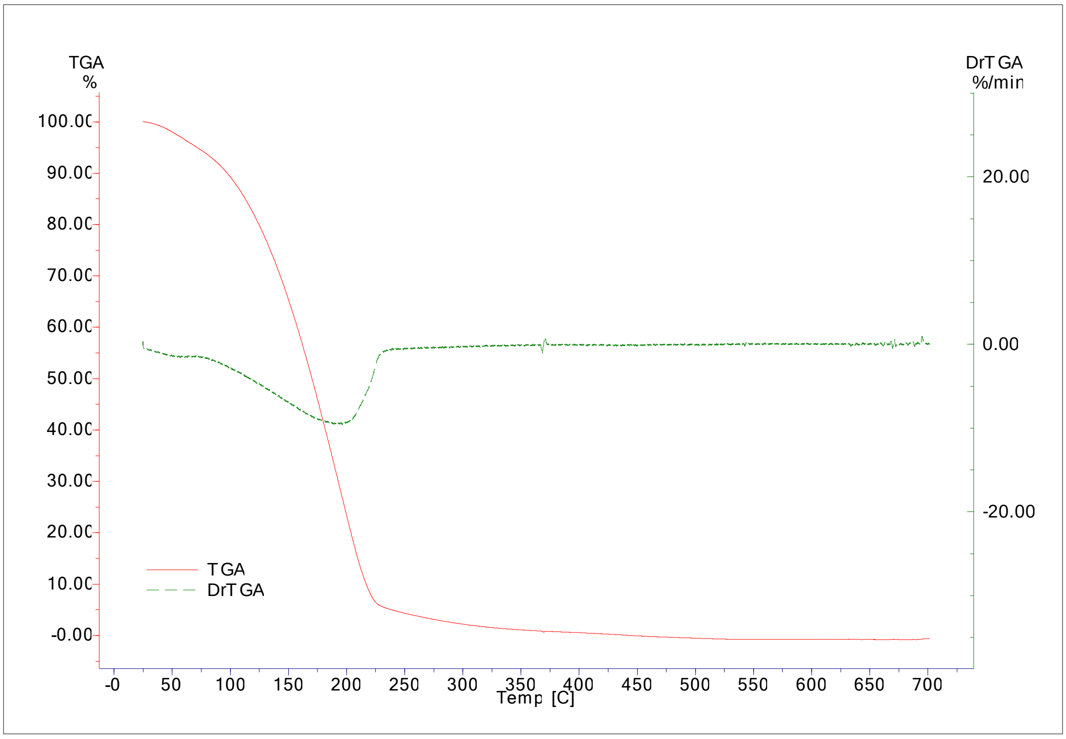
D100



Absorption bands (cm^{-1})	**Functional group**	**Absorption intensity**
2953.94	C-H Stretching vibration	Strong
2921.12	C-H Stretching vibration	Strong
2852.97	CH_2 Asymmetric and symmetric vibration	Strong
1457.43	CH_2 Scissoring vibration	Middling
1377.05	CH_2 and CH_3 deformation	Middling
722.14	CH_2 rocking vibration	Weak

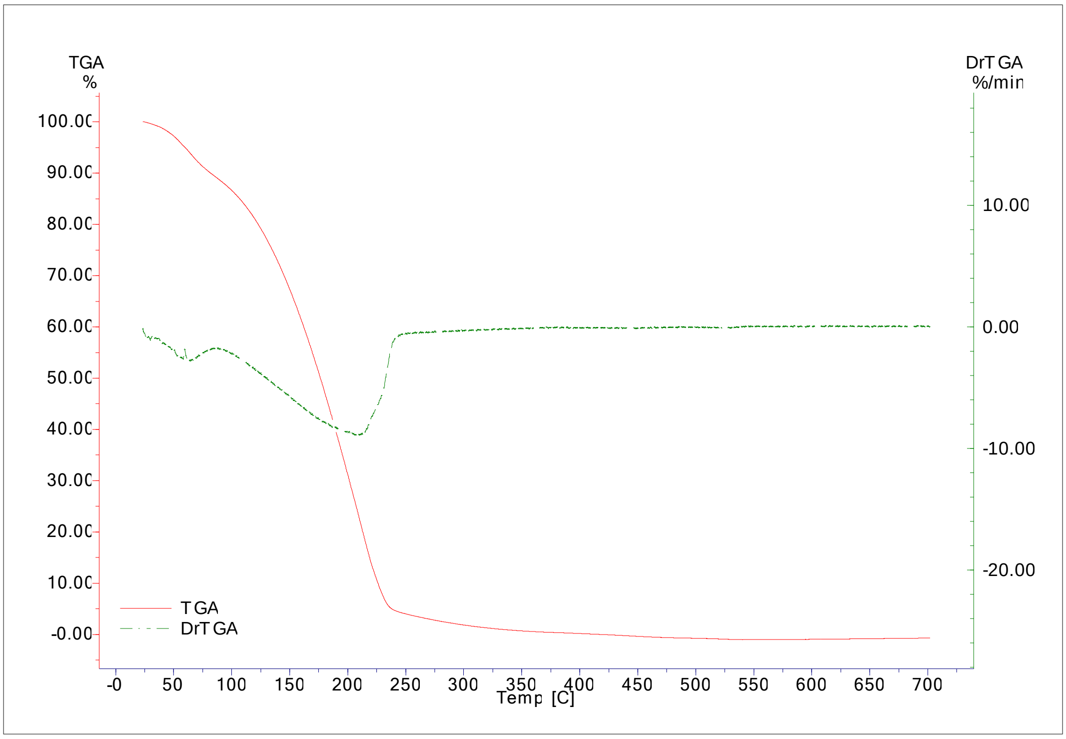
APPENDIX (B)

B20BUT5D75



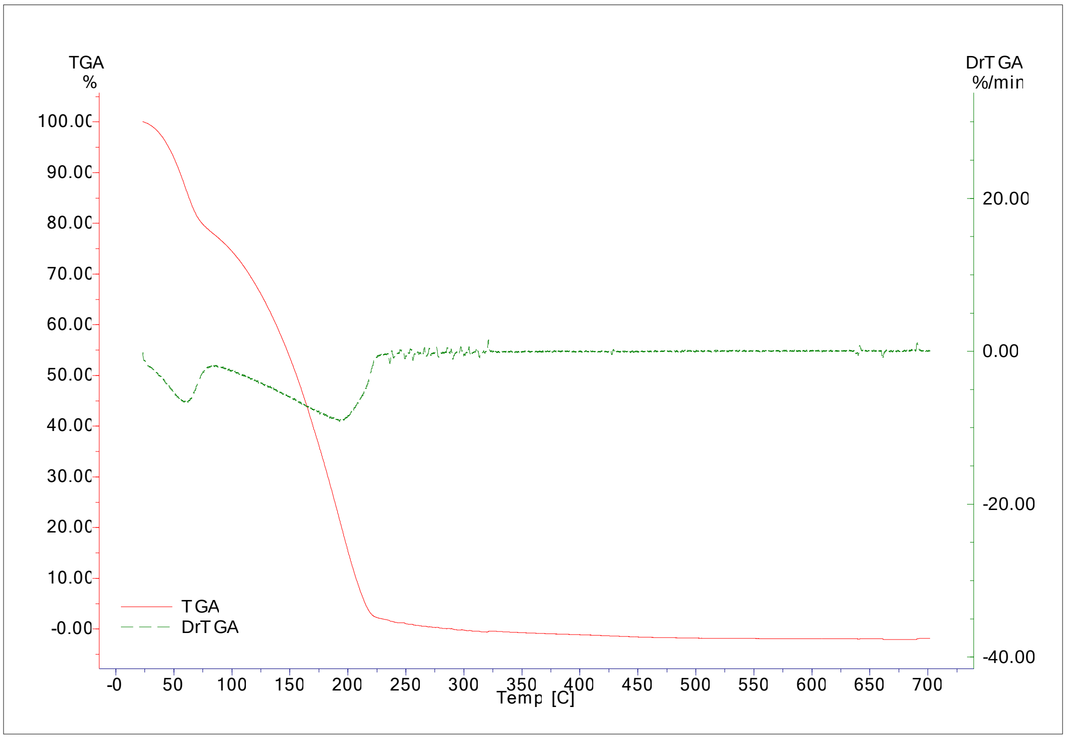
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20BUT5D75	10	30-200	144.7	96.0

B20BUT10D70



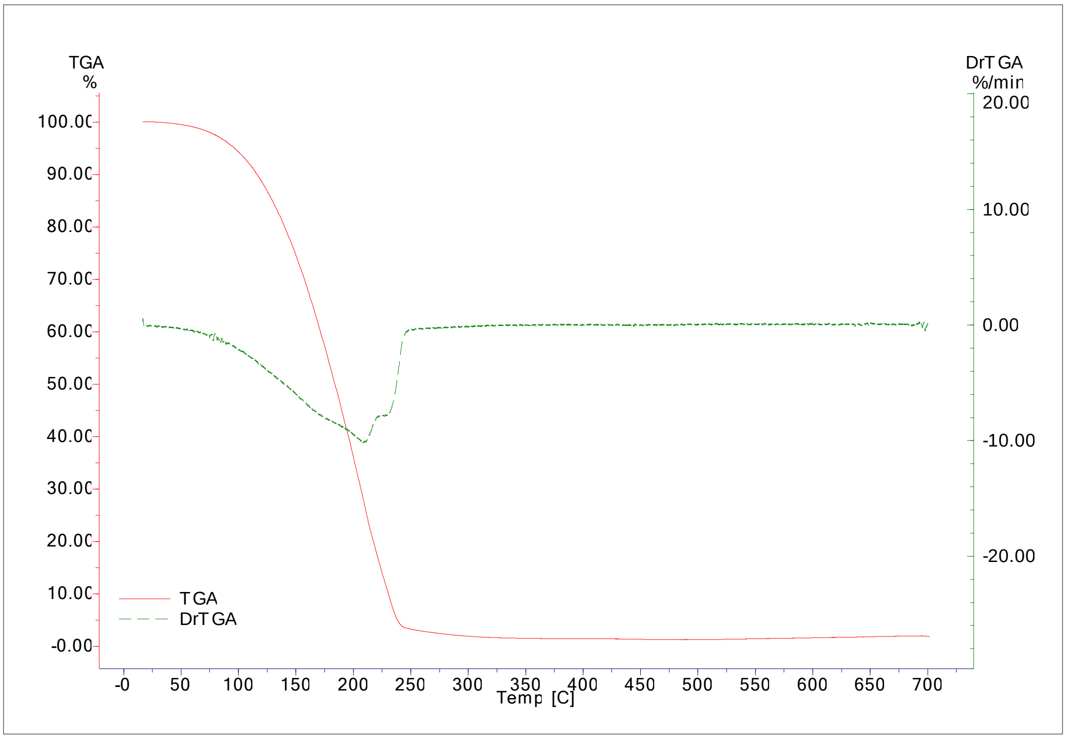
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20BUT10D70	10	30-275	130.7	96.7

B20BUT20D60



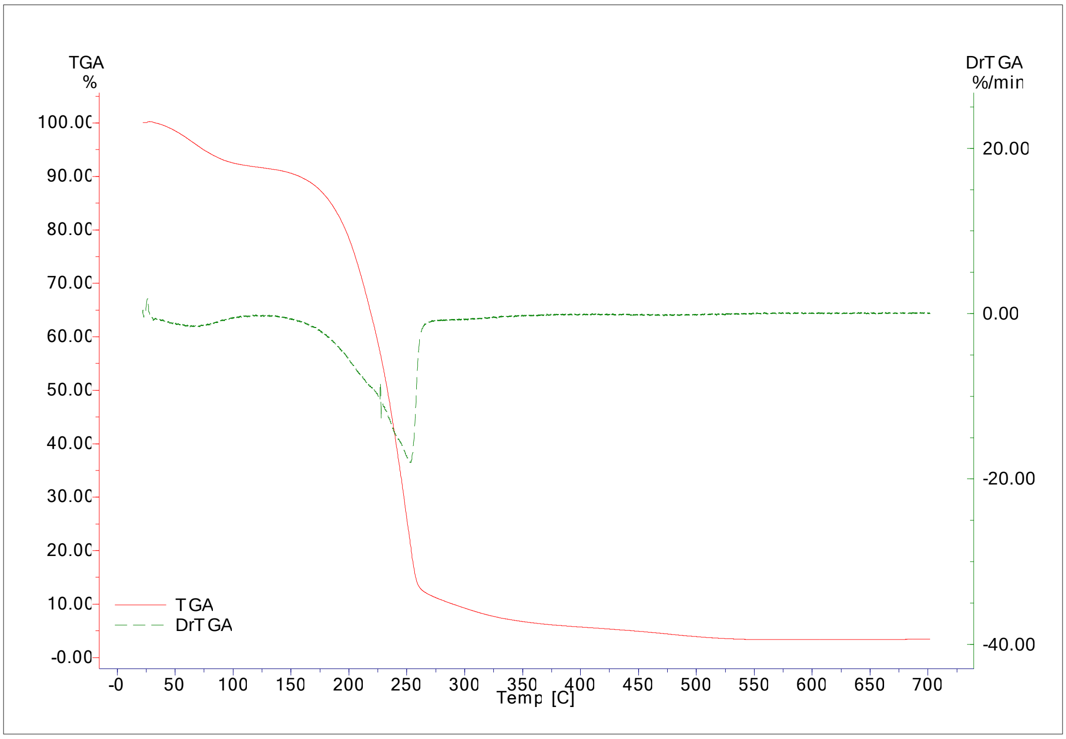
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20BUT20D60	10	30-240	134.3	97.1

B20D80



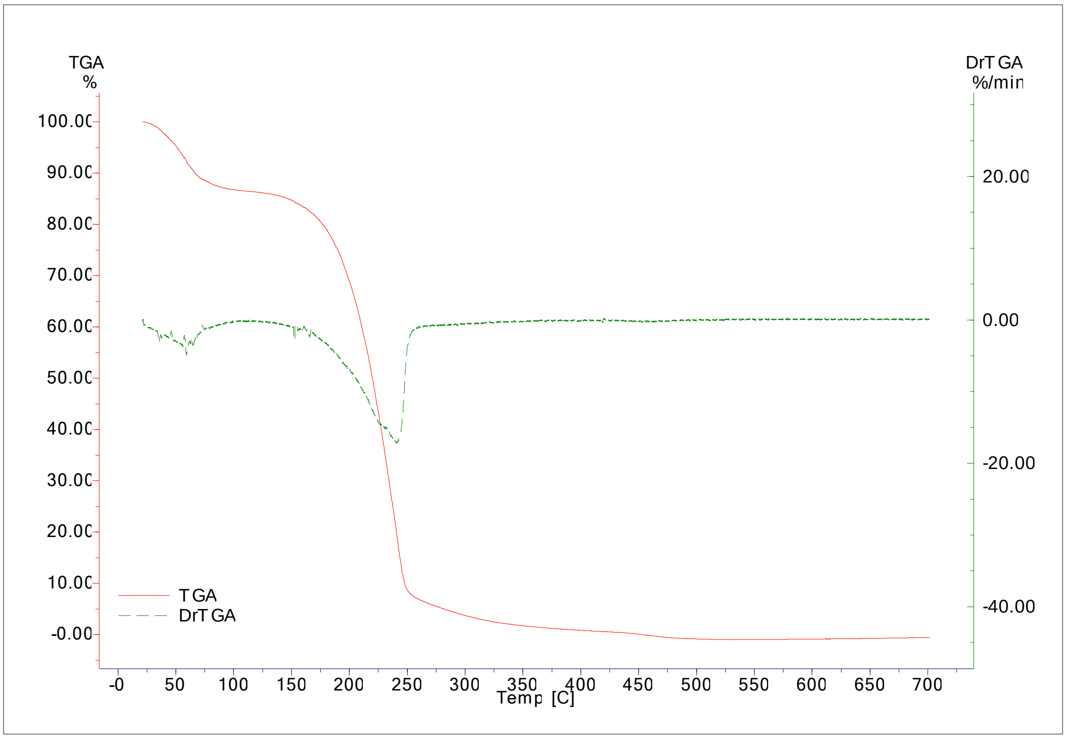
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20D80	10	30-255	151.0	96.8

B80BUT20



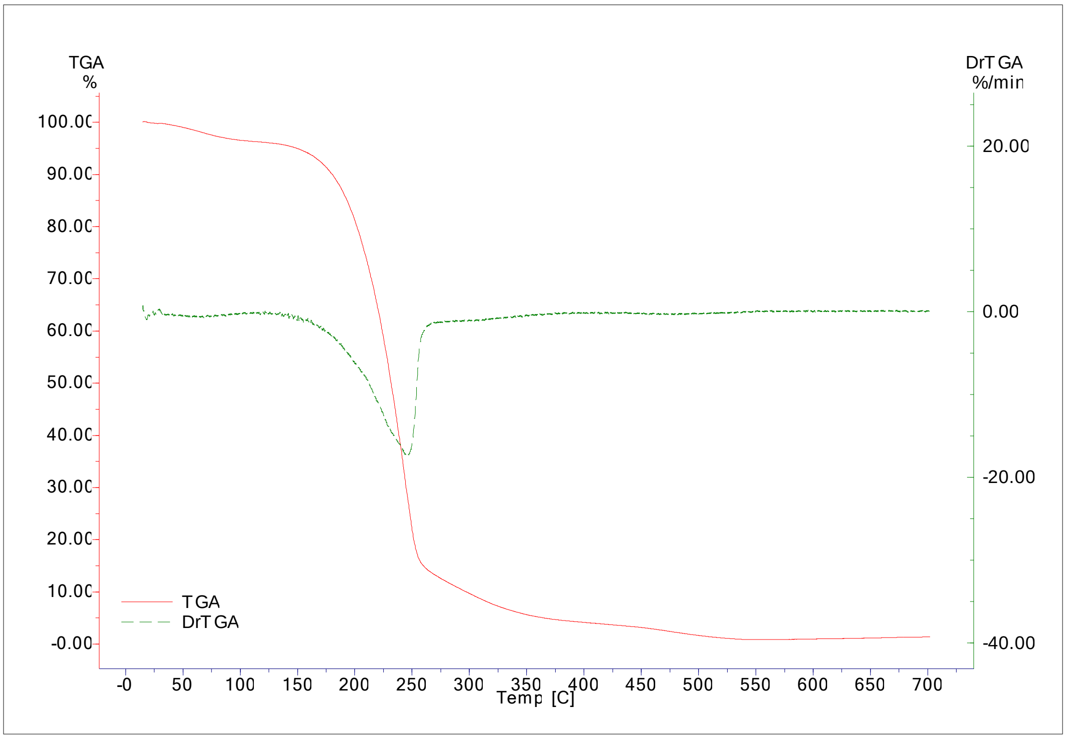
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B80BUT20	10	30-350	212.9	95.9

B90BUT10



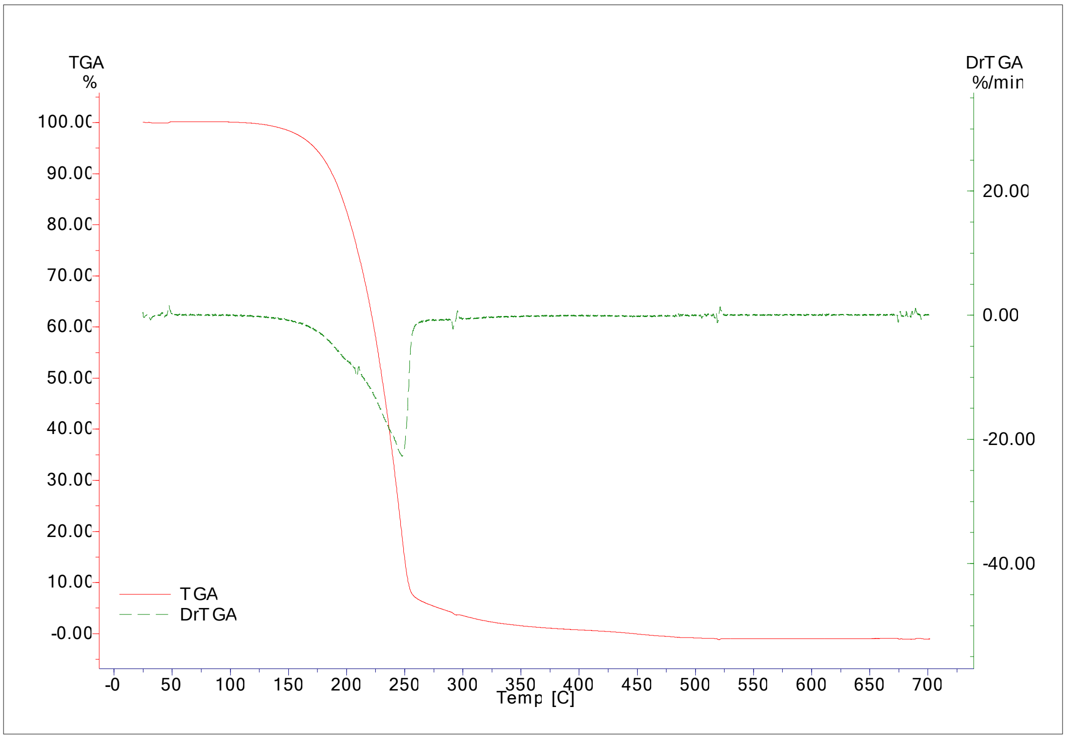
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B90BUT10	10	30-345	206.5	97.7

B95BUT5



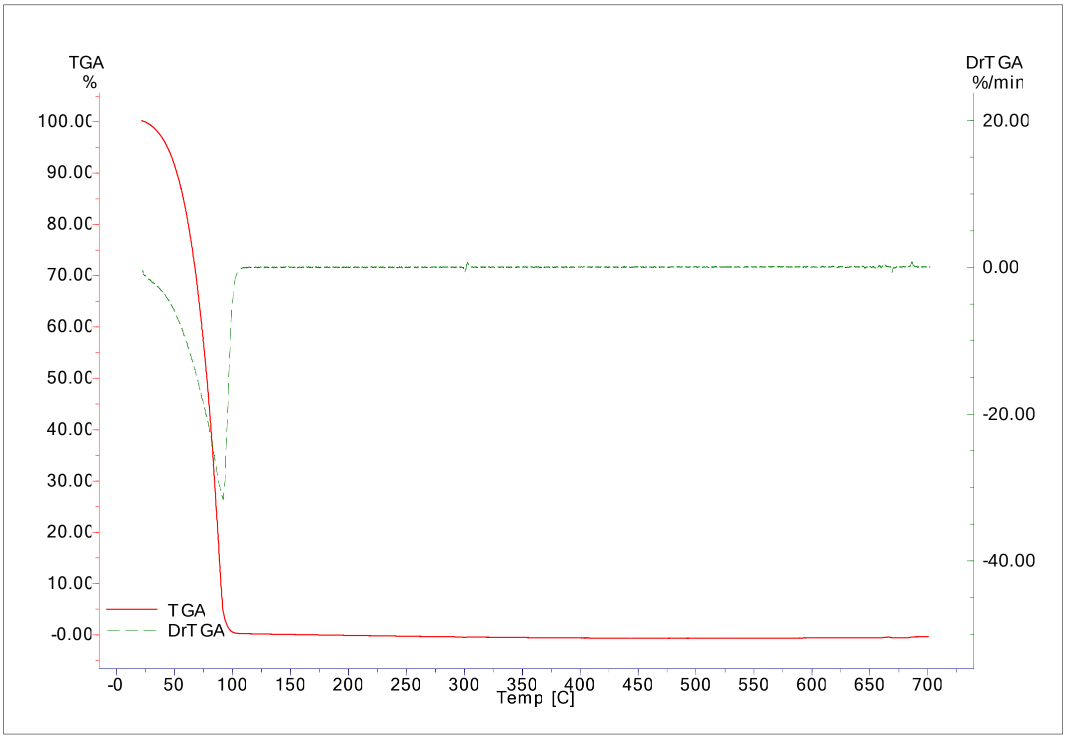
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B95BUT5	10	30-375	207.2	95.1

B100



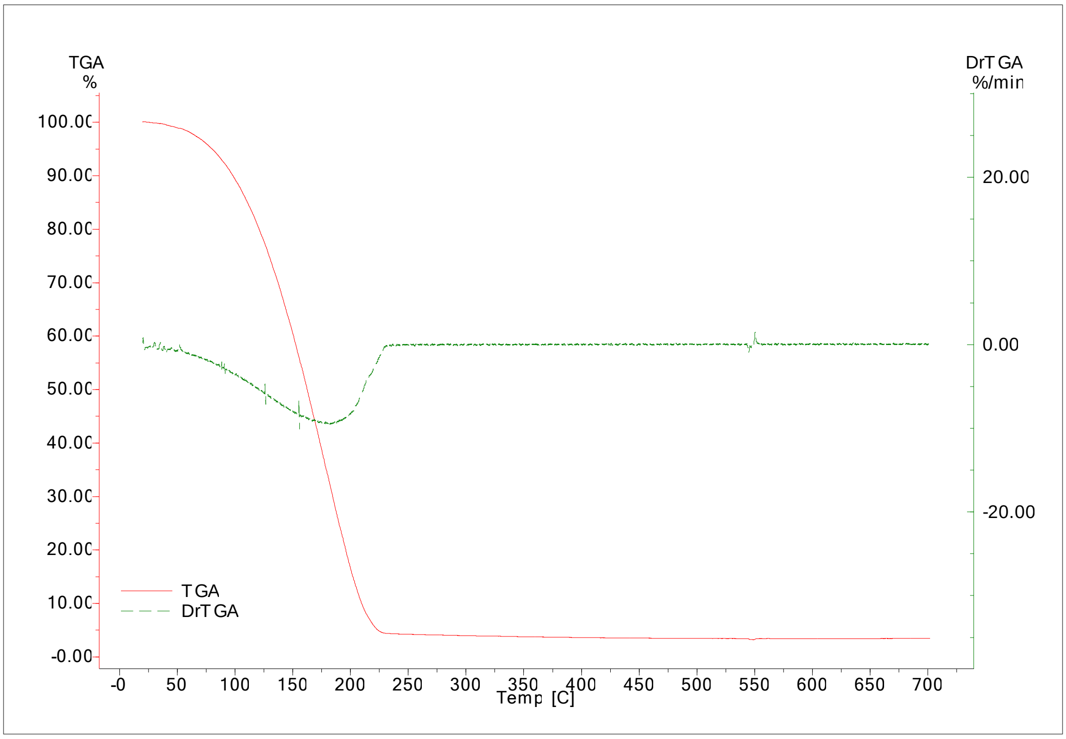
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B100	10	30-350	219.8	98.5

BUT100



Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
BUT100	10	30-120	75.3	99.3

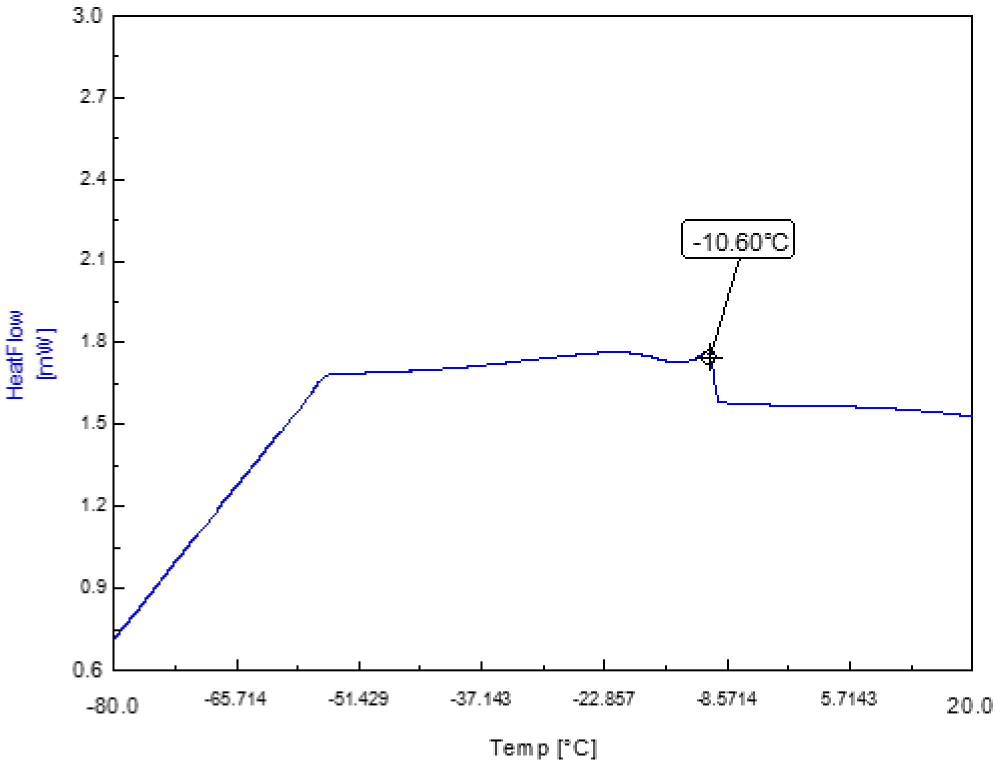
D100



Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
D100	10	30-320	117.7	96.0

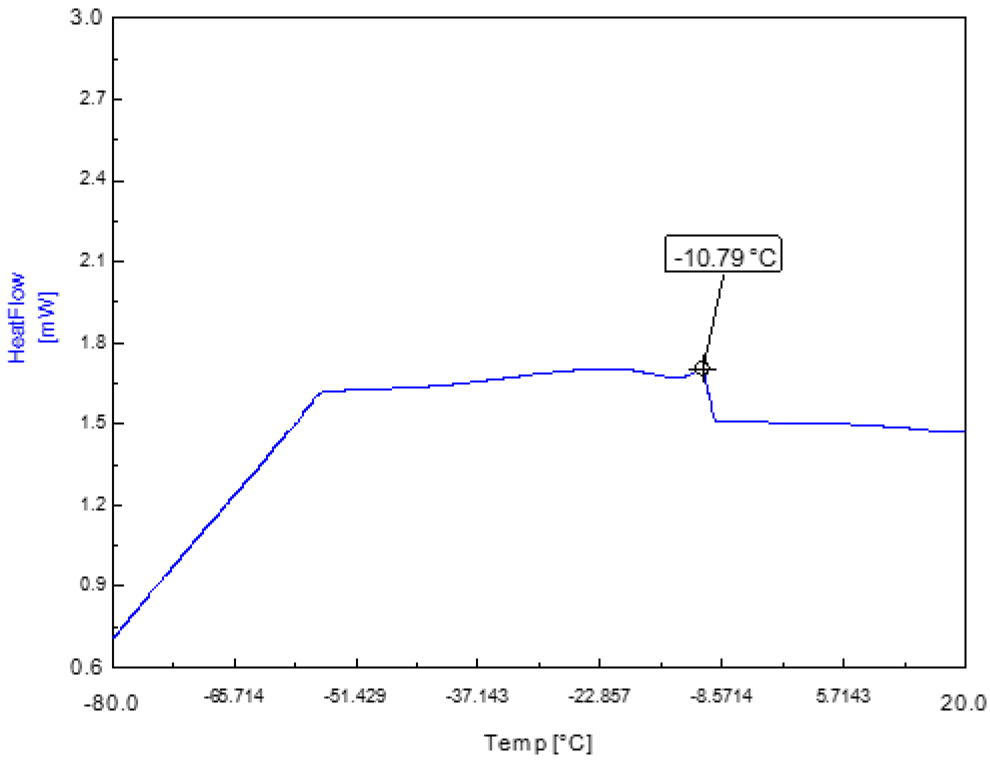
APPENDIX (C)

B20BUT5D75



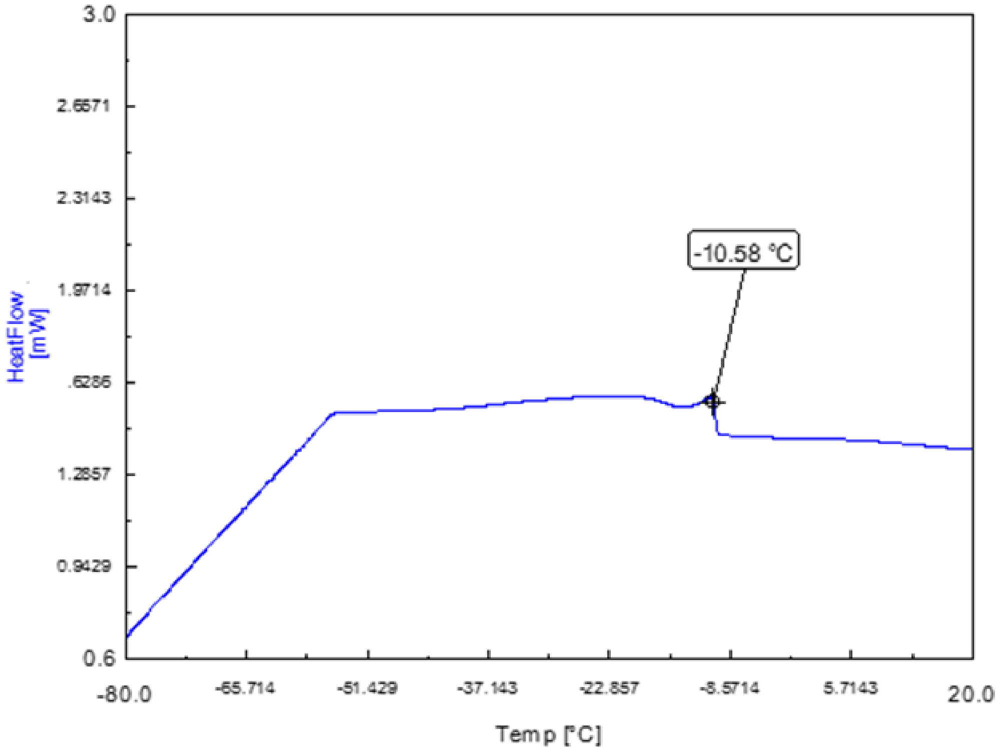
Sample	Crystallizations onset temperature (°C)
B20BUT5D75	-10.60

B20BUT10D70



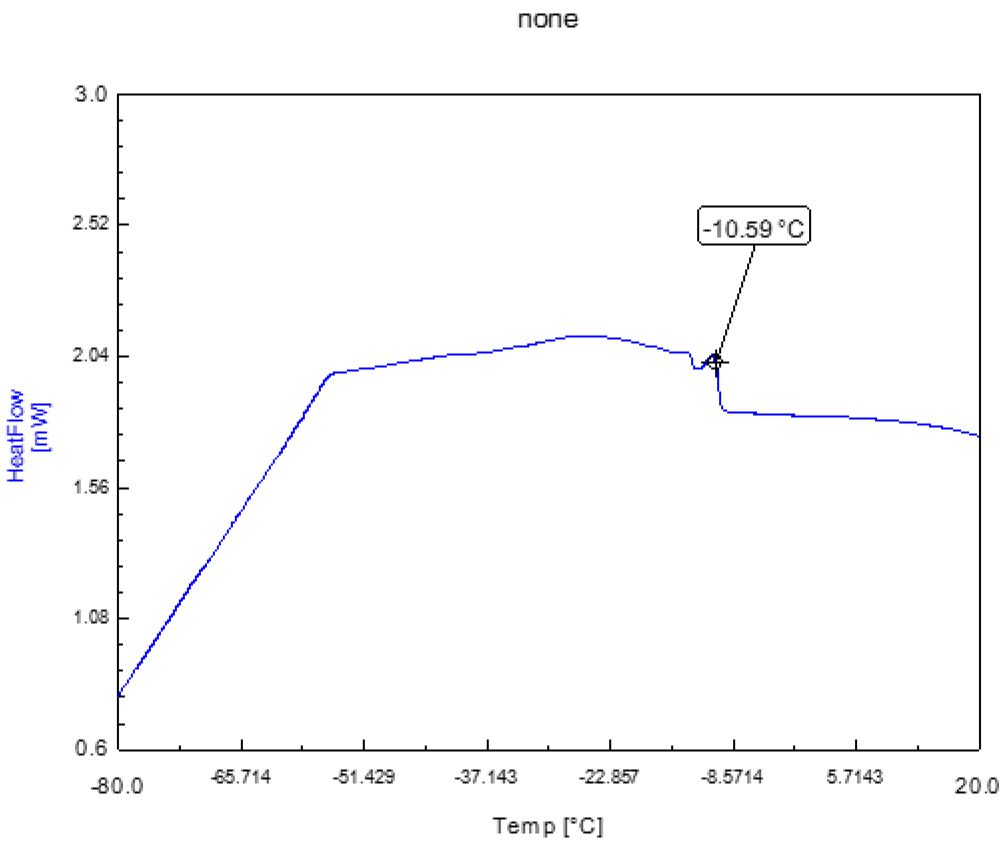
Sample	Crystallizations onset temperature (°C)
B20BUT10D70	-10.79

B20BUT20D60



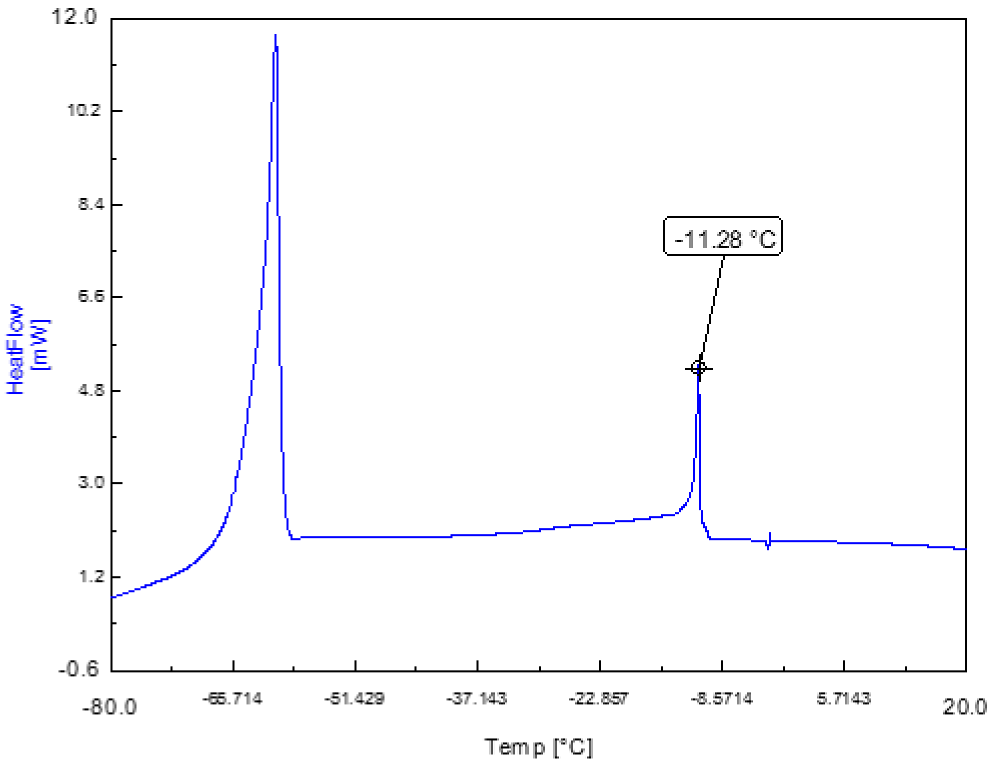
Sample	Crystallizations onset temperature (°C)
B20BUT20D60	-10.89

B20D80



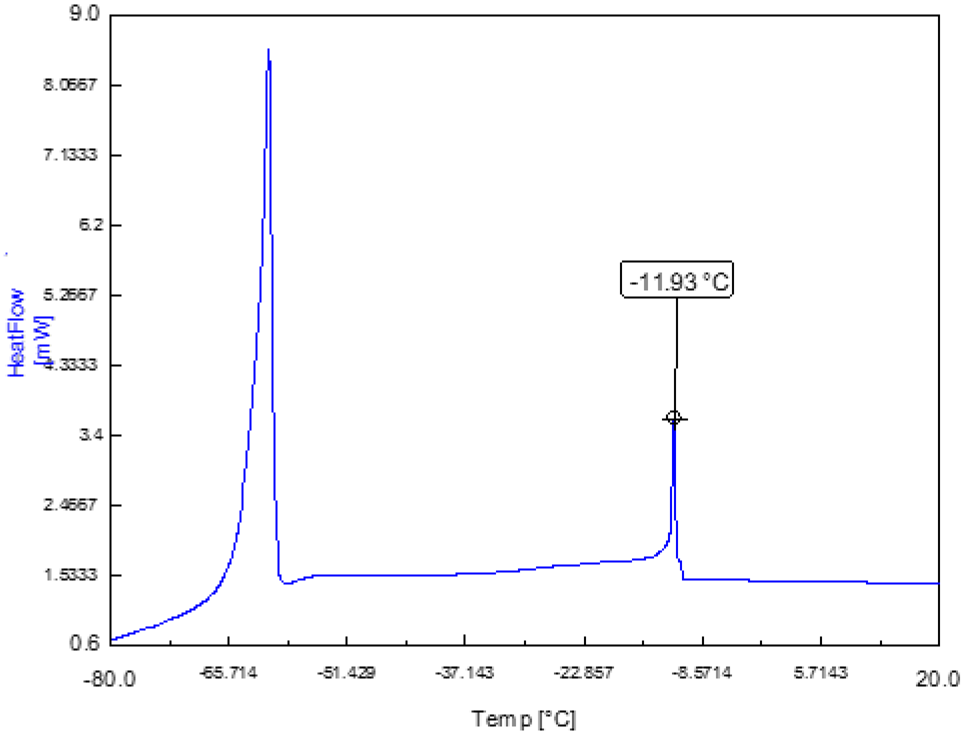
Sample	Crystallizations onset temperature (°C)
B20D80	-10.59

B80BUT20



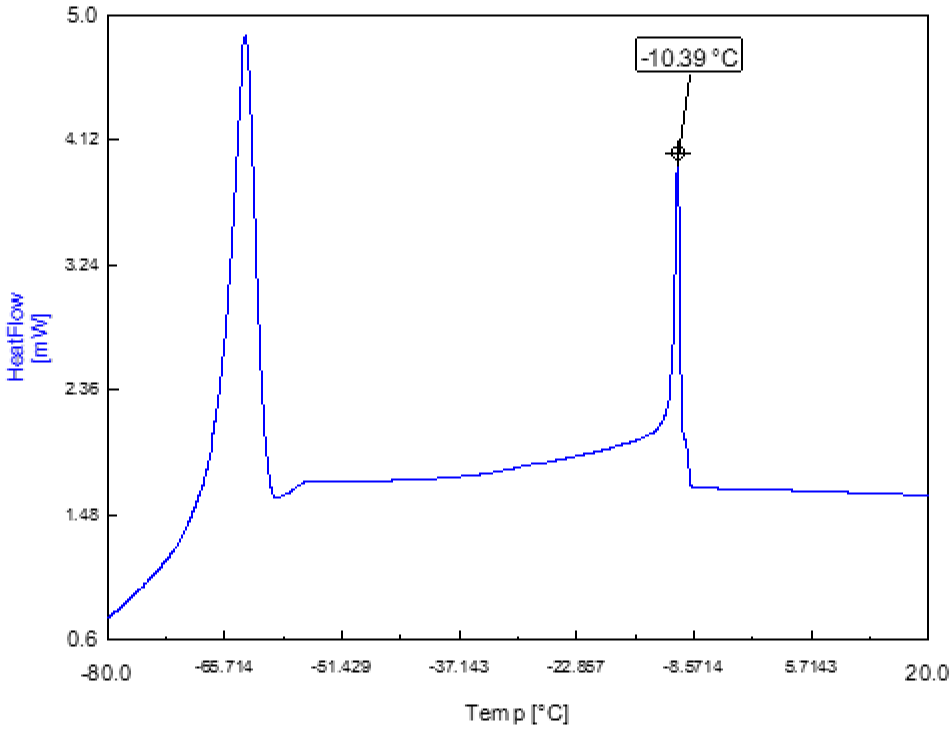
Sample	Crystallizations onset temperature (°C)
B80BUT20	-11.28

B90BUT10



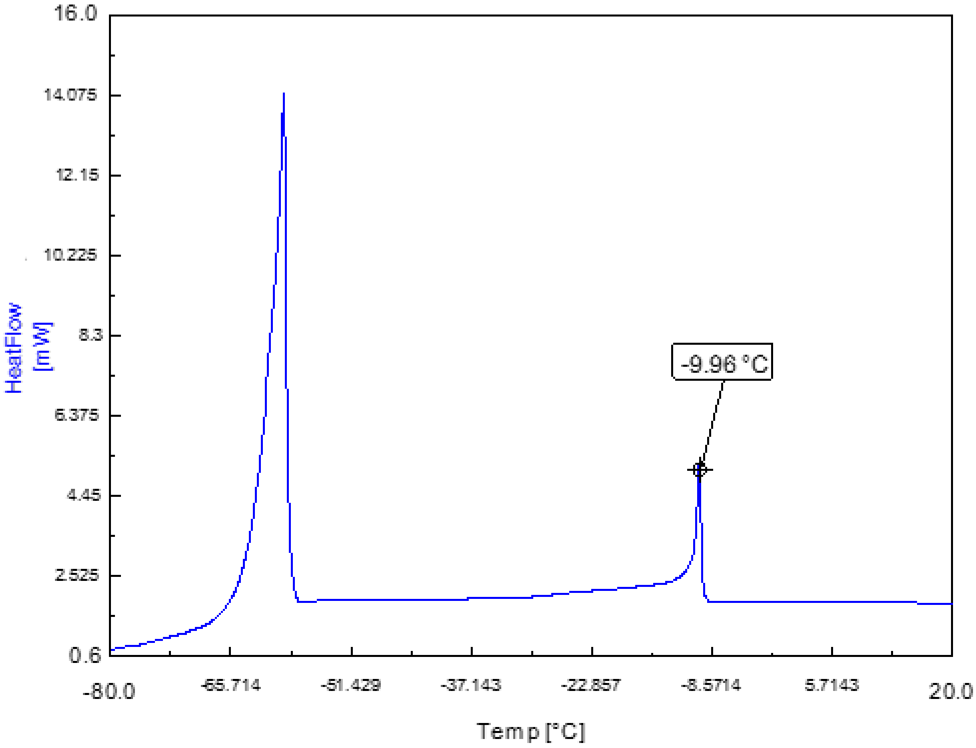
Sample	Crystallizations onset temperature (°C)
B90BUT10	-11.93

B95BUT5



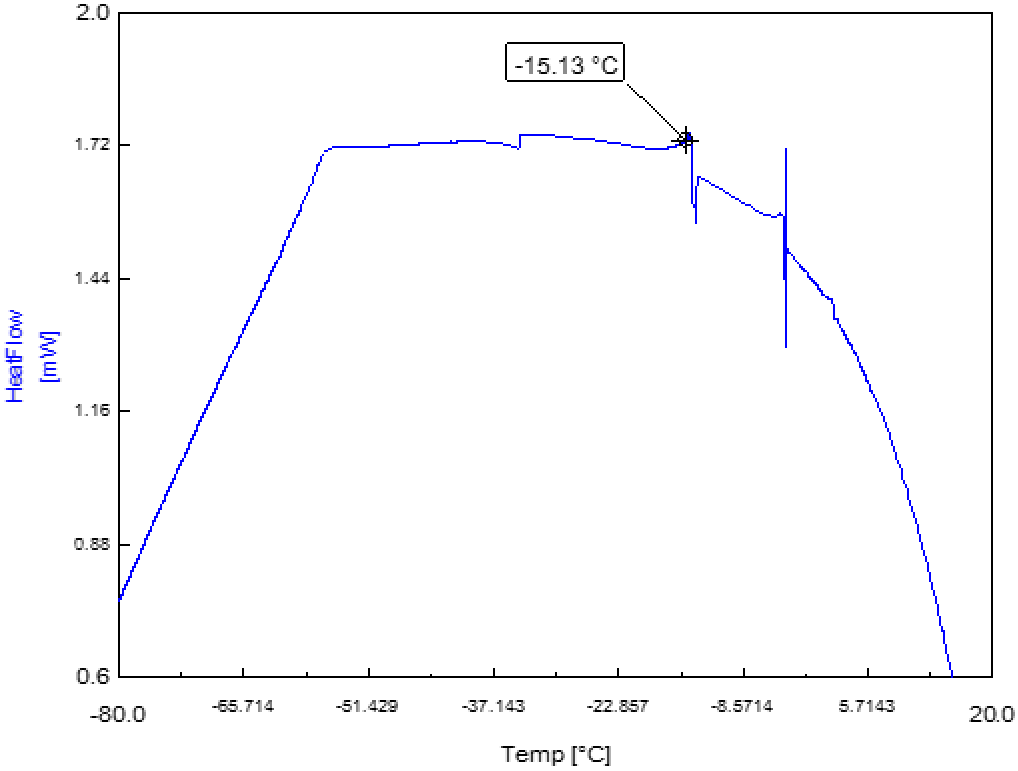
Sample	Crystallizations onset temperature (°C)
B95BUT5	-10.39

B100



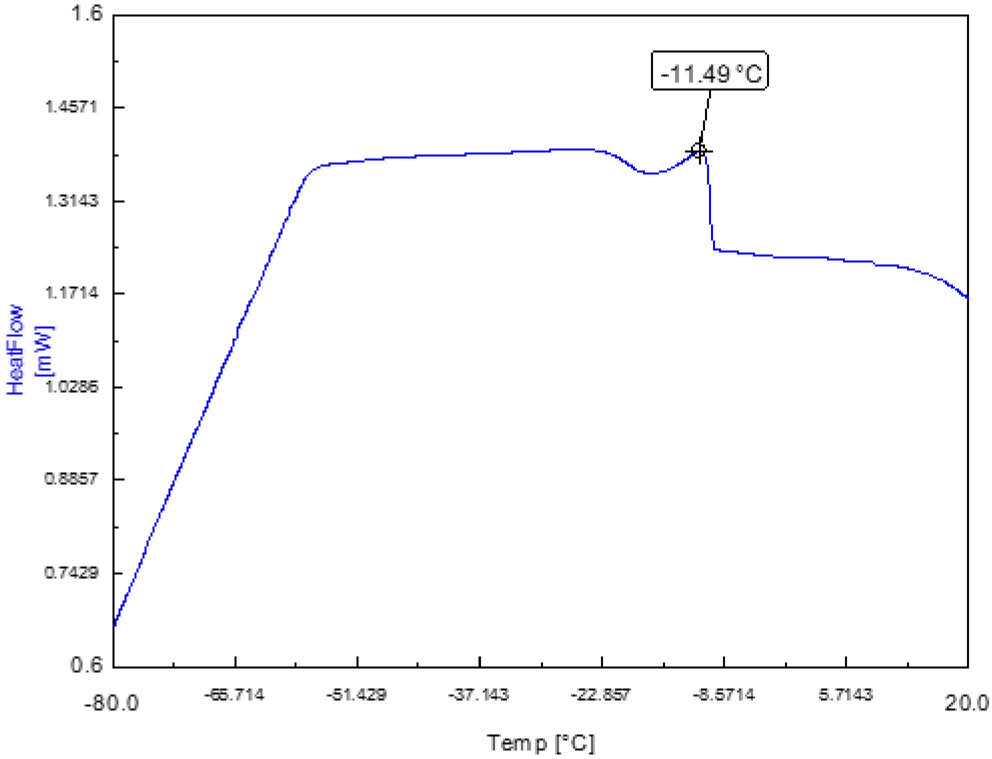
Sample	Crystallizations onset temperature (°C)
B100	-9.96

BUT100



Sample	Crystallizations onset temperature (°C)
BUT100	-15.13

D100



Sample	Crystallizations onset temperature (°C)
D100	-11.49

CURRICULUM VITAE

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EDUCATION

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MSc	Erciyes University, Graduate School of Natural and Applied Sciences	2017
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High School	Med Laid El-Khalifa, Batna	2010

PROFESSIONAL EXPERIENCE

Year	Institute	Mission
2016/2017	Alternative Fuel Research Laboratory (AFRL)	MSc Researcher
2015/2016	Kardel Furniture	Export Sales Marketing Responsable
2011/2013	El Bahdja meubles	Sales Manager

LANGUAGES

Arabic, English, Turkish, French and Tamazight

PUBLICATIONS

Evaluation, characterization and engine performance of complementary fuel blends of butanol-biodiesel-diesel blends from Aleurites moluccanus as potential alternative fuels for ci engines. This paper has been submitted to the 2nd International Conference on Alternative Fuels and Challenges (ICAFE 2017) to be presented during 23-25th October 2017 in Daegu, South Korea.

The paper is also intended to be submitted to an International Journal.