T.R.
ERCIYES UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

A STUDY ON THE APPLICATION OF BIODIESEL–DIESEL–HIGHER ALCOHOL BLENDS WITH PENTANOL AND OCTANOL IN CI (DIESEL ENGINE)

Prepared by
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Supervisor
Asst. Prof. Dr. Abdulaziz MOHAMED ATABANI

MSc Thesis

Semtember 2019
KAYSERİ

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SCIENTIFIC ETHICS SUITABILITY

I declare that all information in this work was obtained in accordance with academic and ethical rules. All results and materials that not been at the essence of this work are also transferred and expressed by giving reference as required by these rules and behavior.



Sattar AL KULTHOOM

SUITABILITY FOR GUIDE

The MSc thesis entitled "**A study on the application of biodiesel-diesel-higher alcohol blends with pentanol and octanol in CI (diesel engine)**" 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 **"A study on the application of biodiesel-diesel-higher alcohol blends pentanol and octanol in CI (diesel engines)"** prepared by Sattar AL KULTHOOM under the supervision of Assist. Prof. Dr. Abdulaziz MOHAMED ATABANI was accepted by the jury as MSc. Thesis in Mechanical Engineering department.

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17/12/2019

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Director of the Institute

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Sattar AL KULTHOOM

Kayseri 2019

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MSc. Thesis, 2019
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ABSTRACT

Waste cooking oil is a mixture of animal fats and used vegetable oils. It is widely available in restaurants. During the process of frying, vegetable oil is incorporated into animal fats. In Turkey and globally, waste cooking oil can be obtained at almost no cost, only the cost of storage containers, which can be used for long period. In this work, biodiesel from waste cooking oil and its blends with Euro diesel and higher alcohols of pentanol and octanol were studied. Physicochemical properties of biodiesel and its blends were analyzed. Waste cooking oil methyl ester satisfied both EN 14214 and ASTM D 6751 standards regarding cetane number (53.9), kinematic viscosity (3.55 mm^2/s) at 40°, density (899.9 kg/m^3) at 20°, and iodine value (106.59 g iodine/100g). This was attributed to its excellent fatty acid composition profile with a degree of unsaturation of 110.58. It has been found that introducing higher alcohols to biodiesel-diesel blends improves their density and cold flow properties. Furthermore, characteristics such as DSC, FT-IR, UV-vis, TGA and NMR were adopted to evaluate the impact of pentanol and octanol addition into biodiesel-diesel blends. Finally, engine performance parameters such as BP, torque, BSFC and emissions such as CO, HC, NO_x and EGT were evaluated and presented proving the positive aspect of higher alcohols addition to the blends.

DİZEL MOTORDA, PENTANOL VE OKTANOL İLE BİYODİZEL-DİZEL YÜKSEK ALKOL KARIŞIMLARININ UYGULANMASI ÜZERİNE BİR ÇALIŞMA

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ÖZET

Atık yemeklik yağ, hayvansal yağlar ve bitkisel yağların bir karışımıdır. Yağ, restoranlarda yaygın olarak mevcuttur. Kızartma veya pişirme işlemi sırasında bitkisel yağ, hayvansal yağa katılır. Türkiye ve tüm dünyada atık yemek yağları, sadece uzun süre kullanılabilen saklama kaplarının maliyeti kadar düşük veya hiçbir maliyeti olmadan elde edilebilmektedir. Bu çalışmada, atık yemeklik yağdan elde edilen biyo-dizel, Euro dizel ile pentanol ve oktanolün yüksek alkol ile karışımları incelenmiştir. Biyodizel ve karışımlarının fiziksel ve kimyasal özellikleri ve karışımları analiz edilmiştir. Atık yemeklik yağ metil esterin, setan sayısı (53.9), 40° 'deki kinematik viskozitesi (3.55 mm^2/s), 20° 'deki yoğunluğu (899.9 kg/m^3), ve iyot değeri (106.59 gr iyot/ 100 gr) EN 14214 ve ASTM D 6751 standartları ile uyumludur. Bu sonuçlar, 110.58'lik bir doymamışlık derecesine sahip mükemmel yağ asidi bileşimi profili ile ilişkilendirildi. Biyodizel-dizel karışımlarına daha yüksek alkol ilave etmenin yoğunluğunu ve soğuk akış özelliklerini geliştirdiği bulunmuştur. Ayrıca, biyodizel-dizel karışımları içine pentanol ve butanol ilavesinin etkisini değerlendirmek için DSC, FT-IR, UV-vis, TGA ve NMR gibi özellikler kullanılmıştır. Son olarak, karışımlara yüksek alkollerin ilave edilmesinin olumlu yönlerini ispatlamak için BP, tork, BSFC gibi motor performans parametreleri ve CO, HC, NO_x ve EGT gibi emisyonlar değerlendirildi ve sunuldu.

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NOMENCLATURE

A_i	**:** Percentage of fatty acid
AFC	: Average fuel consumption
AFRL	: Alternative Fuels Research Laboratory
AMME	: *Aleurites moluccanus* oil methyl ester
B	: Biodiesel
Bp	: Brake power
BSFC	: Brake specific fuel consumption
B_{th}	: Brake thermal efficiency
CI	: Compression ignition
CAMO	: Crude *Aleurites moluccanus* oil
CHO	: Crude hemp oil
CN	: Cetane number
CO	: Carbon monoxide
CO_2	: Carbon dioxide
CSO	: Crude safflower oil
D100	: Euro diesel
DSC	: Differential scanning calorimetry
DU	: Degree of unsaturation
DI	: Direct injection
EGT	: Exhaust gas temperature
ERU	: Erciyes University
FAC	: Fatty acids composition
FAME	: Fatty acid methyl ester
FT-IR	: Fourier transform infrared spectroscopy
HC	: Hydrocarbons
HHV	: Higher heating value
HME	: Hemp methyl ester

ICE	: Internal combustion engines
IV	: Iodine value
LCSF	: Long chain saturated factor
LHV	: Lower heating value
M_i	: Molecular weight of each fatty acid
MP_n	: Melting point of each saturated fatty acid
N	: Number of double bonds of fatty acid
NMR	: Nuclear magnetic resonance
NO_x	: Nitrogen oxides
Oct	: Octanol
OS	: Oxidation stability
P	: Density
Pen	: Pentanol
PM	: Particulate matter
SME	: Safflower methyl ester
SO_2	: Sulfur dioxide
TGA	: Thermogravimetric analyses
UV-vis	: Ultraviolet–visible spectroscopy
WCOME	: Waste cooking oil methyl ester
WCO	: Waste cooking oil

INTRODUCTION

Biodiesel fuel; scientifically defined as fatty acid methyl ester (FAME) can be produced from used vegetable oils known as waste cooking oil (WCO) that are generally wasted after cooking. It can be also prepared from non-edible vegetable oils that are not suitable for human consumption and animals, fish and poultry fats. In this research, WCO collected from Erciyes University's food court was valorized and processed into waste cooking oil methyl ester (WCOME). The produced biodiesel was then blended with Euro diesel (D100) and some selected higher alcohols of pentanol (Pen) ($C_5H_{12}O$) and octanol (Oct) ($C_8H_{18}O$) at various percentages.

Characterizations of WCOME and its blends with D100, Pen and Oct were conducted at **Alternative Fuels Research Laboratory (AFRL), Erciyes University (ERU)** in accordance with ASTM D6751 and EN 14214 standards. Engine performance and exhaust emissions parameters were conducted in a single-cylinder, four stroke, naturally aspirated and direct injection diesel engine. In addition, differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible spectroscopy (UV-vis), thermogravimetric (TGA) and nuclear magnetic resonance (NMR) analyses for all blends were also examined and presented in this research.

The importance of this study is that such characteristics of DSC, FT-IR, UV-vis, TGA and NMR of different blends were fully examined and presented in order to develop renewable fuels. These analyses can be also considered for future fuel analyses as they are cheaper, faster and reliable methods rather than some other slow testing methods. The outcome of this research supports the efforts to protect our environment, promote biodiesel production in Turkey through waste valorization in addition to enhance the ongoing scientific research in the area of alternative fuels and applications of higher alcohols in compression ignition (CI) diesel engines with rewarding consequences. This research was also part of the recycling activities in ERU.

CHAPTER 1

GENERAL INFORMATION

1.1 Overview

Energy and its security is a concern of any country planning to develop. However, as it is well known, excessive burning of fossil fuels is responsible for many environmental issues such as emissions of carbon dioxide have strengthened the greenhouse effect and caused global warming [1]. Thus, examining emissions from internal combustion engines (ICE) released to the atmosphere such as soot, carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (HC), sulfur dioxide (SO_2) and carbon dioxide (CO_2) and particulate matter (PM) is much needed. Studies confirm that the fossil fuel consumption and population are in constant rapid growth, with alternatives fuels such as biofuels being under the spotlight in the last ten years. In addition to that, recycling of waste has also come in the forefront recently to produce such biofuels in a larger scale [2].

Previous, recent and on-going studies pointed out the positive impact of applying oxygenated biofuels to reduce some harmful emissions such as soot, PM and HC emissions in CI diesel engines due to achieving more complete combustion than fossil diesel [3]. Biofuels such as biodiesel has 11% oxygen by weight, while methanol, ethanol, propanol, butanol as alcohols have oxygen contents of 49.9, 34.7, 26.6 and 21.6% respectively [1, 3]. Biodiesel (methyl ester) is composed of long chain fatty acids that can be produced from edible and non-edible vegetable oils, animal fats, WCO and microalgae [1, 4, 5]. Biodiesel has been widely accepted as a potential substitute for fossil diesel because it is scalable, renewable, non-explosive, lesser emissions, ecological, has lower sulfur and aromatic content, higher lubricity, higher flash point, non-toxic, non-flammable, does not contribute to global warming, biodegradable,

excellent combustion efficiency, clean alternatives and can be produced through recycling of waste [1, 5]. Thus, many countries are putting real plans and serious efforts to use biodiesel in CI engines through blending with fossil diesel at various percentages (10-30% by volume).

On the other hand, alcohols can be produced from waste including wood, forest residues, crops and lignocellulosic components of municipal waste via different fermentation pathways [6]. Recently, the addition of lower alcohols such as methanol and ethanol and higher alcohols such as propanol, butanol, pentanol and octanol has been widely investigated with some rewarding outcome in term of engine and emissions parameters [3, 4, 7-10].

1.2 Overview of biodiesel production from WCO

Traditionally, biodiesel has been produced from edible oils such as sunflower, palm, coconut and corn oils. However, this has been proven to be expensive and leading to Fuel *vs* Energy conflict. Thus, WCO is a promising feedstock for biodiesel production globally as it is widely available, cheap and contribute to cut down the production cost [2] as 75% of biodiesel production comes from the price of the feedstock alone [1]. Availability of transportation and containers that collect waste oil is another supporting factor for this industry as many countries have achieved far progress in this regard. It is also worthy to mention that WCO causes blockages of sewage pipes if dumped directly, putting another concern on dealing with it. WCO cannot be used again as food as it is considered unhealthy. Figure 1.1 and Figure 1.2 show some photos of WCO and WCO containers.



Figure 1.1. Waste cooking oil (WCO) containers



Figure 1.2. Waste cooking oil (WCO)

1.3 Research problem

The main problem associated with the production of biofuels or alternative energy, in general, is the high cost and impact of their production on societies and economics besides their performances. Moreover, food concern is another serious issues related to this industry as still more than 75% of biofuels production comes from edible oils. On the other hand, waste generated from various sectors such as industrial, residential and commercial sectors are causing many environmental issues and add a burden to local governments seeking for more landfills. These put together the concern in recycling waste to biofuels and added-value products into real practice and many countries have already set some plans to build biorefineries.

1.4 Objectives

Given, the background and problems associated with biofuels research area, this research aim to achieve the following:

(1) Valorization of WCO into useful source of energy that may contribute to the energy sector in Turkey.

(2) Application of higher alcohols of Pen and Oct along with biodiesel-diesel blends in some selected percentages.

(3) Examining the physical and chemical properties of all blends and comparing the results with ASTM D6751 and EN 14214 standards.

(4) Characterization of all fuel blends by means of DSC, FT-IR, UV-vis, TGA and NMR analyses as they are cheaper, faster and reliable methods.

(5) Conduction of engine and emissions performance of all blends.

1.5 Organization of thesis

This thesis is broken down into four chapters as follow:

Chapter 1 Offers general information about the topic. It begins by introducing the importance of energy, climate change, global warming and alternative fuels, followed by a background that shows the importance of waste recycling to produce biofuels such as biodiesel and alcohols and the possible methods to improve the physical and

chemical properties of biofuels through blending. Research overview, problem, objectives and the existing results in literature were all included in this chapter.

Chapter 2 Clarifies in detail the research methodology and design.

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

Chapter 4 Provides a discussion and analysis of these findings besides comparing the results with existing literature and giving a summary of the key findings and puts forward some recommendations for the future work.

1.6 Literature survey

Many studies have been carried out on biofuels production and their impact on the environment as well as their application in CI diesel and gasoline engines. The effect of additives such as alcohols and nano-additives has been also examined recently.

Atabani *et al*., [1] reviewed the topic of biodiesel where various biodiesel feedstocks, oil extraction methods, biodiesel production technologies, fatty acid composition (FAC), physical and chemical properties, advantages and disadvantages of biodiesel and some problems and challenges that face biodiesel industry were comprehensively reviewed. Biodiesel can be produced by four main methods; pyrolysis, dilution with hydrocarbons blending, Micro-emulsion, and transesterification. Biodiesel properties must adhere with the international standard specifications such as the American Standards for Testing Materials (ASTM 6751) or the European Union (EN 14214). Some of the important properties include density, kinematic viscosity, cetane number, calorific value, flash point (safety concern), oxidation stability, water content and cold flow properties (cloud, pour and cold filter plugging points). It was pointed out that one of the most important factors of biodiesel industry is the cost of feedstock. This necessitates finding cheap sources such as those obtained from waste and do not compete with food crops and do not lead to land-clearing.

Kumar *et al*., [6] reviewed the topic of alcohols application in CI engines covering physical and chemical properties of methanol, ethanol and butanol, their production methods, economics and applications in CI engines. Review proved the positive impact of alcohols due to their liquid nature, high oxygen content and high latent heat of

vaporization. It was also pointed out the future of alcohols production as they can be produced from renewable biomass and waste through fermentation process. However, this is still in its infancy and more research is needed to increase both the yield and economics of the production process. Butanol, as higher alcohol, has been reported to be better than its counterpart lower alcohols (methanol and ethanol) due to better miscibility with fossil diesel, higher cetane number, density, viscosity, energy content and less corrosion effect. This has been also further supported in engine and emissions performance as butanol has superior performance than methanol and ethanol. The review also pointed out the importance of higher alcohols as next generation biofuels.

The body of literature on engine and emissions performance of binary biodiesel diesel blends is packed with many papers [11-15]. FAC has been attributed to influence the properties of biodiesel and therefore, engine and emissions performance [16]. Almost all studies confirmed the positive impact of biodiesel in reducing HC, CO, PM, soot and SO_2 when blended with fossil diesel all due to complete combustion. However, some penalties are caused as brake power (BP) reduced and brake specific fuel consumption (BSFC) increased. Moreover, most of published papers agree that NO_x emissions increase due to the effect of complete combustion that increase the adiabatic flame temperature in the combustion chapter causing nitrogen to react with oxygen and form NO_x.

Similarly, binary blends of alcohols-diesel [17-20] and alcohol-biodiesel [21, 22] and ternary blends of alcohols-diesel-biodiesel [10, 23-26] have been also extensively investigated. It was proved that alcohols addition reduce engine emissions as they have lower sulfur content and higher oxygen content than fossil diesel, while brake power and torque reduced due to their lower energy content [6]. Table 1.1 conducts a comparison between the properties of biodiesel, diesel and various alcohols types.

Table 1.1. Comparison between alcohols (methanol, ethanol, propanol, butanol, pentanol, hexanol and octanol), biodiesel and diesel properties [3, 27-29]

Properties	**Methanol**	**Ethanol**	**Propanol**	**Butanol**	**Pentanol**	**Hexanol**	**Octanol**	**Biodiesel**	**Diesel**
Molecular weight	32.04	46.07	60.1	74.12	88.15	102.18	130.23	a	142
CN	2	11	12	15	18.2-20	23	39	56	52
LHV (MJ/kg)	20	26.8	30.6	33.8	34.65	39.10	37.512	37	42.9
Latent heat of vaporization (kJ/kg)	1162	918	727.9	626	308.05	486	298	300	260
Carbon (by wt. %)	37.5	52.2	60	64.82	68.13	70.52	73.72	77.1	84-87
Hydrogen (by wt. %)	12.6	13.1	13.4	13.49	13.61	13.70	13.82	12.1	13-16
Oxygen (by wt. %)	49.9	34.7	26.6	21.59	18.15	15.70	12.29	10.8	0
Density at 15 °C (kg/m^3)	791.3	789.4	803.7	809.7	814.8	821.8	827	880-900	835
Self–ignition temperature (°C)	463	420	350	345	300	285	270	271	254-300
Flash point (°C)	11	13	22	37	49	59	81	a	74

[a] molecular weight and flash point of biodiesel varies depending on type of feedstock and fatty acids compositions

CHAPTER 2

MATERIALS AND METHODS

Research methodology is an important research element in which all materials and methods adapted to carry out the research are explained in details. In this chapter all materials such as WCO and chemicals needed to produce biodiesel besides alcohols and Euro diesel are highlighted. Moreover, the method in which biodiesel was produced was explained. This was followed by blending with Pen, Oct and D100 to form ternary blends. After which, some important characteristics such as FT-IR, UV-vis, TGA, DSC and NMR were examined. Finally, some selected engine and emissions performance parameters were also covered in this research.

2.1 Structure of research methodology

This research aims to produce biodiesel from WCO followed by blending with Pen, Oct and D100 to form binary blends. Figure 2.1 illustrates the adapted research methodology in this research.

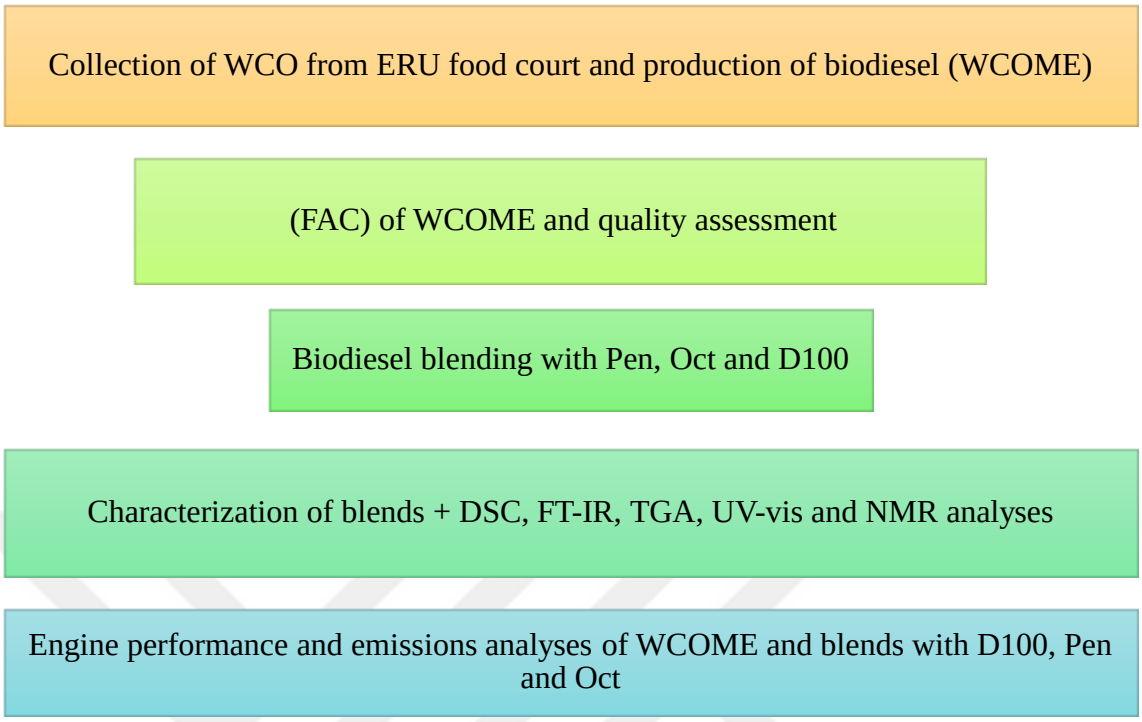


Figure 2.1. Summary of current research methodology

2.2 Collection of WCO

Crude WCO was collected from ERU food court upon permission. Crude oil was then placed in a big tank for the purpose of settling down any depositions of heavy materials and large impurities. Oil was then filtered for the purpose of removing the fine impurities. After that, it was heated at 115 °C using an oven (Kurutma Fırını Dolabı (Etüv), Mikrotest, MKD serisi, Turkey) and at 85 °C using rotary evaporator (Hahnshin Scientific Co, Hahnvapor, HS-2005V-N, South Korea) attached with water bath (Hahnshin Scientific Co, Hahnvapor, HS-3001 (PTFE coating)), vacuum pump (Rocker Scientific Co., Ltd, Chemker410, Taiwan) with vacuum pressure of 760 mmHg and refrigerated bath circulator (JS Research Inc, JSRC-13C, South Korea). All to ensure that WCO was free from water and moisture. WCO was then kept stored in jerry cans and tightened well to prevent any contact with air or sunlight to avoid degradation or oxidation. All chemicals used in this research such as pentanol ($C_5H_{12}O$), octanol ($C_8H_{18}O$), methanol (CH_3OH), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), potassium hydroxide (KOH), and filter papers were purchased from a local supplier in Kayseri, Turkey. Euro diesel was purchased from a local fuel station (OPET, Kayseri, Turkey).

2.3 Production of biodiesel from WCO

Transesterification process converts lipids to biodiesel (fatty acid methyl ester) and glycerol. In this work, one liter of WCO was reacted with 25% (v/v oil) of methanol (6:1 molar ratio) and 1% (m/m oil) of potassium hydroxide (KOH). The reaction was maintained at 60 °C in mixing device. Methyl ester was then removed from glycerol using a separation funnel. Methyl ester was washed with distilled water several times to remove the entrained impurities and glycerol and then heated to remove the excess water and methanol. Afterwards, it was further dried using sodium sulphate (Na_2SO_4). Finally, the product was filtered using qualitative filter papers. The colour of the final product was yellow.

2.4 Equipment list

Table 2.1 summarizes the equipment used in this study including their manufacturers, origin, standard method and accuracy. All equipment are existing in AFRL, ERU.

Saponification number (SN) of WCOME was predicted by the following empirical formula [2, 3, 11]:

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

Where, A_i is the percentage and MW_i is the molecular mass of each component.

Kinematic viscosity at 40 °C (KV), iodine value (IV), cetane number (CN) and oxidation stability (OS) of WCOME were predicted by the following empirical formulas **[2, 3, 16, 30]**:

$$\ln(\eta_i) = -12.503 + [2.496 \times \ln(MW_i] - (0.178 \times N) \quad (2)$$

$$IV = 1.0617(DU) - 10.805 \quad (3)$$

$$CN = -0.1268(DU) + 67.926 \quad (4)$$

$$OS = -0.0518\ (DU) + 11.121 \quad (5)$$

Where η_i represents the KV of each fatty acid at 40 °C and DU is the degree of unsaturation which is calculated from the following formula [3, 7, 16, 30]:

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

Long chain saturated factor (LCSF) was calculated from the following formula [2, 6, 10, 26]

$$LCSF = \sum \frac{(MPn * A_i)}{100} \quad (7)$$

Where, MP_n is the melting point and A_i is the percentage of each saturated fatty acid.

Higher heating value (HHV) of WCOME was predicted by the following empirical formula [7, 16]:

$$HHV = 46.19 - \left(\frac{1794}{MW_i}\right) - (0.21 \times N) \quad (8)$$

Where N represents the number of double bonds of fatty acid.

Table 2.1. Equipment list

Property	**Model**	**Manufacturer**	**Origin**	**ASTM standard**	**Accuracy**
Kinematic viscosity (KV)	TV2000-AKV	PM Tamson Instrument	Bleiswijk, Netherlands	D445	±0.1 K
Cloud point (CP)	NTE 450	Normalab	Valliquerville, France	D2500	± 0.1 °C
Pour point (PP)	NTE 450			D97	± 0.1 °C
Cold filter plugging point (CFPP)	NTL 450			D6371	
Density (ρ)	DS7800	A.Krüss Optronic GmbH	Hamburg, Germany	D1298	±0.0001 g/cm^3

2.5 Gas chromatography (GC) method of WCOME

The FAC profile of biodiesel was determined using gas chromatography (GC) (Perkin Elmer Clarus 680, USA) equipped with a flame ionization detector and a BPX70 capillary column. Analysis was made as for fat and oil derivatives standard (Fatty Acid Methyl Esters (FAME) under TS EN 14103:2011 standard for ester and linolenic acid methyl ester determination. The carrier gas was helium with column flow rate of 1.00 mL per minute. 1 μL of the sample was injected into gas chromatography. Table 2.2 shows the details of GC operating conditions.

Table 2.2. GC operating conditions

Property	**Specifications**	**Unit**
Carrier gas	Helium	
Flow rate	1.00 (column flow)	mL/min
Detector temperature	250	°C
Column head pressure	70 (flow control made)	kPa
Column dimension	BPX70	60.0 mx0.25μmx0.25 mm ID
Injector column oven	250	°C
Temperature ramp	60 (hold for 2 minutes) 10 °C/min 200 °C 5 °C/min 240 °C (hold for 7 min)	°C

2.6 NMR analysis

NMR analyses for all tested fuels were performed using Bruker AVANCE III 400 MHz spectrometer, USA equipped with suitable probes for cores of ^{1}H, ^{13}C, ^{19}F, ^{31}P in which chloroform was used as solvent and internal standard. ^{1}H and ^{13}C spectra were recorded from -2.00 ppm to 10.00 ppm at 500 MHz.

2.7 FT-IR analysis

FT-IR spectra in the mid-infrared region are used to identify corresponding functional groups in various stretching and bending vibrations in biodiesel samples. The carbonyl groups in FT-IR are sensitive to the structure of the molecule and to the effects of the substituent **[31]**. FT-IR characterization for all tested fuels was conducted using Perkin Elmer, USA in the range 4000-650 cm^{-1} and processed with a computer software program spectrum. The resolution was 4 cm^{-1} and 4 scans.

2.8 UV-vis analysis

UV-vis spectra provide information about the electronic properties of molecules. All organic compounds absorb light in the visible and ultraviolet region **[32, 33]**. UV-vis characterization to obtain UV absorption spectra for all tested fuels was conducted using Agilent Technologies Cary 60 UV-vis Spectrophotometer, USA in the wavelength range of 800–300 nm at 1 nm intervals and scanned using standard 1 cm quartz cuvettes filled with the tested fuel at room temperature.

2.9 TGA analysis

Thermogravimetric (TG) Thermograms of all tested fuels were recorded in a Shimadzu DTG 60H thermogravimetric analyzer (Japan) using a platinum pan. 10 mg of each sample was loaded into pans. Upon finishing each test, platinum pan was cleaned to make it ready for the next test. The temperature ranges from 25-600 °C with a heating rate of 10 °C/min under dry air atmosphere to determine the oxidative stability. Table 2.3 highlights the summary of TGA method. Each sample takes almost an hour. A maximum temperature of 700 °C was used as the mass remains constant until the end of analysis and all the chemical reactions have been completed at this temperature. TGA curves were used to analyze and evaluate the onset temperature of all blends.

Table 2.3. Summary of TGA method

Instrument	Shimadzu DTG 60H
Gas	Dry air
Flow rate	100 ml/min
Temperature range	25 °C to 700 °C
Heating rate	10 °C/min

2.10 DSC analysis

DSC is used to determine the crystallization onset temperature of the samples and can be plotted on the graph against heat flow. The DSC curves were obtained in a calorimeter model DSC Q20, USA with RCS90 coupled with a cooling system, both from TA Instruments. Table 2.4 highlights the summary of DSC method.

In this study, TA Q-2000 DSC analysed (WCO), (WCOME), Euro diesel (D100) and their blends with pentanol and octanol 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 2.4. Summary of DSC method

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

2.11 Engine specifications and emission device

Tecquipment TD 114 IC **(Figure 2.2)** engine instrumentation were used to test WCOME and its blends with D100, Pen and Oct. The set-up contained single cylinder CI diesel engine with air-cooling system, vertical type direct injection (DI) and coupled with a water brake dynamometer. An electronic control and measurement device was used to display performance data. The schematic diagram of the set-up is shown in **Figure 2.3**. **Table 2.5** lists the specifications of the engine and exhaust gas analyzer. All experiments were conducted at a fixed engine speed of 3000 rpm at different three loads of 1.5, 4.5 and 6 N.m respectively.

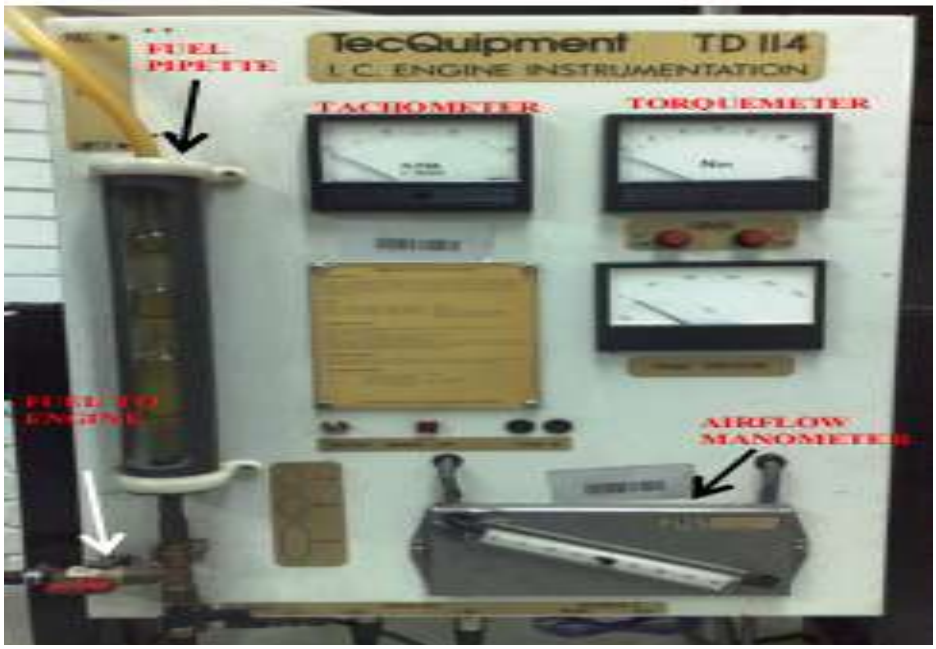
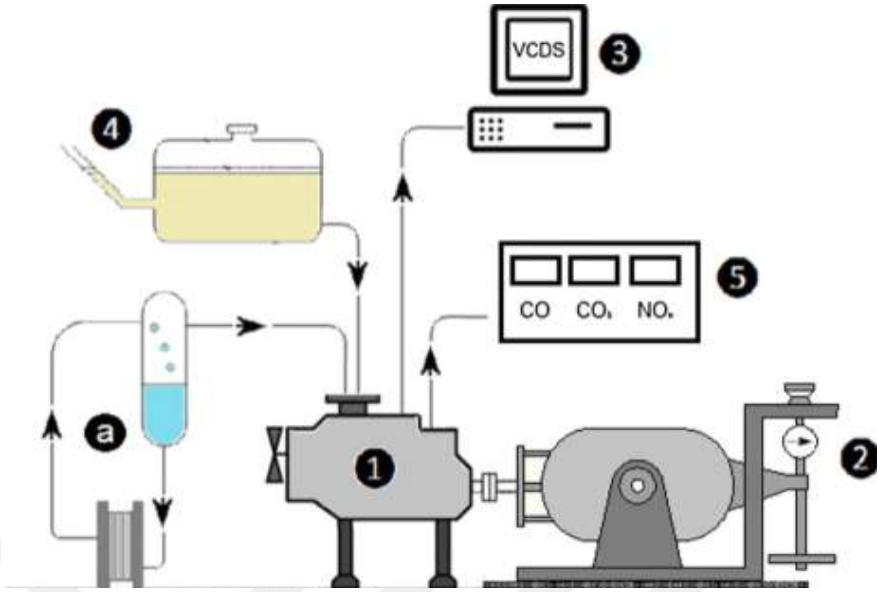


Figure 2.2. Tecquipment photo



1- Engine; 2- Dynamometer; 3- Control unit; 4-fuel tank; 5 -Exhaust gas analyzer

Figure 2.3. Schematic Diagram of the Test Engine

Table 2.5. Engine and exhaust gas analyzer specifications

Item	**Technical specification**
Model	170F
Type	Single-cylinder, vertical, 4-stroke,air-cooled, DI CI diesel engine
Bore ×stroke (mm)	70×55
Normal speed (r/min)	3000-3600 2.8 kw
Mean effective Pressure kPa (kgf/cm^2)	443.2 (4.52)
Rotary direction of Crankshaft	Clockwise from flywheel end
Mean piston speed (m/s)	5.5-6.6
Cooling type	Forced air-cooled system
Compression ratio	21/1

AIRREX GAS ANALYZER

Measurement: HC, CO, CO_2, O_2, NO_x, Lamda, AFR Measuring Method: HC, CO, CO_2: NDIR (Non-dispersive Infrared) O_2, NO_x: Electro Chemical Sensor
Gas Flow: 2~4 liter/min
Power Supply: AC 110/220V, 50/60Hz
Measure Range (Resolution) and accuracy CO: 0~9.999% (0.001%) : CO_2: 0~20.00% (0.015) HC: 1~15,000 ppm (1ppm) O_2: 0~25.00% (0.01%) NO_x: 0~5,000ppm (1ppm) Lamda:0.50~3.00 (0.01) Exhaust gas temperature (EGT): 200+1300 (±1)

CHAPTER 3

TESTS AND RESULTS

3.1. Introduction

In this chapter, Physico-chemical properties of WCO, WCOME, D100 and its blends with D100, Pen and Oct are presented and compared with some results existing in the body of literature for some other biodiesel feedstocks such as safflower, hemp and *Aleurites moluccanus*. This is followed by presenting the results of FT-IR, TGA, UV-vis, NMR and DSC analyses. Finally, engine and emissions performance analyses at different loads will be presented and analysed.

3.2 Properties of WCO, WCOME, D100 and fuel blends

Tables 3.1, 3.2 and 3.3 show the physico-chemical properties of WCO, WCOME, D100 and WCOME ternary blends with D100, Pen and Oct respectively. Properties of WCO and WCOME were also compared with the results presented in [3, 7, 30]. It can be seen that WCOME satisfies both EN 14214 and ASTM D6751 standards with excellent CN, OS, IV, KV and HHV of 53.9, 5.39 h, 106.59 g iodine/100g, 3.55 mm^2/s at 40 °C and 39.24 MJ/kg respectively. The cold flow properties of WCOME including CP, PP and CFPP were -6. -1 and -14 °C respectively indicating the relatively acceptable application of WCOME in cold flow regions.

Density is the relationship between mass and volume **[1]**. Engine performance parameters are affected by the density such as BSFC. Density is measured according to EN ISO 3675/12185 and ASTM D1298 where fuel shall be normally tested between 15 and 20 °C. Through Tables **(3.1- 3.3)**, it can be seen that density of WCO has been much improved through the transesterification process to WCOME in which density

reduced from 922.3 to 899.90 kg/m^3 at 20 °C respectively. This has been further reduced when WCOME was blended with D100 (binary blends) and D100, Pen and Oct (ternary blends) where density ranges between 834.5-847.9 kg/m^3 for all blends compared to 836.9 kg/m^3 (D100), 817.3 kg/m^3 (Pen) and 827.2 kg/m^3 (Oct). It has been found that B15Pen15D70 has the closest density to D100 (836.7 kg/m^3). These results support that blending biodiesel-diesel blends with higher alcohols remarkably improves the blend's density yielding it very close to that of D100 and thus helps improve engine and emissions performance.

Table 3.1. Physico-chemical properties of WCO

Property	**WCO**	**CHO [30]**	**CSO [3]**	**CAMO [7]**
KV at 40 °C (mm²/s)	44.61	27.28	29.79	26.91
CP (°C)	11	-11	-14	-13
PP (°C)	8	-22	-22	-17
ρ at 15 °C (kg/m^3)	925.30	927.90	925.00	924.90
ρ at 20 °C (kg/m^3)	922.30	923.10	921.00	923.00
ρ at 25 °C (kg/m^3)	919.00	-	-	-
ρ at 30 °C (kg/m^3)	915.40	-	-	-
ρ at 40 °C (kg/m^3)	908.10	-	-	-

CHO ≡ Crude hemp oil, CSO ≡ Crude safflower oil, CAMO ≡Crude *Aleurites moluccanus* oil

Table 3.2. Physico-chemical properties of WCOME

Property	**WCOME**	**HME [30]**	**SME [3]**	**AMME [7]**	**ASTM D6751**
CP (°C)	-6	3	-2	-6	-
PP (°C)	-1	-4	-7	-5	-
CFPP (°C)	-14	-10	-12	-8	-
KV at 40 °C (mm²/s)	3.55	3.87	4.017	3.85	1.9-6.0
HHV (MJ/kg)	39.24	40.41	40.60	39.38	-
CN	53.90	51.63	47.21	45.05	47 min
IV (g iodine/100g)	106.59	125.68	162.68	180.70	-
OS (h)	5.39	4.46	2.66	1.80	3 h min
SN	209.70	194.99	200.78	200.81	-
ρ at 15 °C (kg/m³)	903.20	891.50	886.50	889.60	
ρ at 20 °C (kg/m³)	899.90	-	-	885.90	
ρ at 25 °C (kg/m³)	896.20	-	-	-	860-900
ρ at 30 °C (kg/m³)	892.70	-	-	-	
ρ at 40 °C (kg/m³)	885.50	-	-	-	

HME ≡ Hemp methyl ester, SME ≡ Safflower methyl ester, AMME ≡ *Aleurites moluccanus* oil methyl ester

CP, PP and CFPP are important properties that determine the flow of any fuels at low temperature. This is more importantly at cold regions where full or partial solidification of the fuel may cause blockages of fuel lines, filters and pumps. All of which leads finally to engine damage [1]. As it has been observed from Tables 3.1-3.3, WCOME has better cold flow properties than WCO. Blending with D100, Pen and Oct further reduced and improved these properties specially for PP (-14−-33 °C for blends compared to -14 °C of WCOME) and CFPP (-13−-22 °C for blends compared to 1 °C of WCOME) indicating the positive strategy of higher alcohols effects in CI engines.

Table 3.3. D100 and blends properties

Property	**D100**	**Pen**	**Oct**	**B20D80**	**B30D70**	**B10Pen10D80**	**B15Pen15D70**	**B10Oct10D80**	**B15Oct15D70**
CP (°C)	-6			-5	-6	-5	-5	-5	-5
PP (°C)	-31			-15	-13	-22	-22	-22	-22
CFPP (°C)	-34			-14	-14	-33	-31	-33	-28
ρ at 15 °C (kg/m³)	840.4	0.1	830.6	845.4	851.4	838.3	840.3	839	841.8
ρ at 20 °C (kg/m³)	836.9	817.3	827.2	841.8	847.9	834.5	836.7	835.3	838.1
ρ at 25 °C (kg/m³)	833.3	813.3	823.6	838.2	844.4	830.8	833	831.7	834.5
ρ at 30 °C (kg/m³)	829.7	809.4	820.1	834.6	840.7	826.9	829.3	828.1	831
ρ at 40 °C (kg/m³)	822.6	801.8	813.00	827.5	833.5	819.6	822	821	823.7

3.3 FAC, DU and LCSF of WCOME

The results of FAC of WCOME were determined, compared with HME **[30]**, SME **[3]** and AMME **[7]** and presented in **Table 3.4** It can be seen that WCOME has almost a balanced FAC profile in which saturated, monounsaturated and polyunsaturated fatty acids were 31.62, 26.35 and 42.03% respectively. This has resulted in DU and LCSF of 110.58 and 21.28 in which the DU was lower than HME (128.55) **[30]**, SME (163.40) **[3]** and AMME (180.38) **[7]**. As a result, WCOME has the highest OS (5.39 h), CN (53.90) and lowest IV (106.59 g iodine/100g) among others. Linoleic acid (C18:02) was the dominant fatty acid (41.86%) followed by oleic acid (C18:01) (26.35%), myristic acid (C14:0) (20.00%), palmitic acid (C16:0) (8.03%), stearic acid (C18:0) (3.15%) and small fractions of docosanoic acid (C22:0) (0.44%) and linolenic acid (C18:03) (0.17%) achieving a FAC profile of 100% and indicated that the final product was a 100% FAME.

Table 3.4. FAC, DU and LCSF of WCOME

Fatty acid	**M_i**	**Structure**	**N**	**Chemical name**	**Formula**	**%**
Myristic	228.376	14:00	0	n-Tetradecanoic acid	$C_{14}H_{28}O_2$	20.00
Palmitic	256.43	16:00	0	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.03
Stearic	284.484	18:00	0	Cetylacetic acid	$C_{18}H_{36}O_2$	3.15
Oleic	282.468	18:01	1	Elaidoic acid	$C_{18}H_{34}O_2$	26.35
Linoleic	280.452	18:02	2	cis,cis-Linoleic acid	$C_{18}H_{32}O_2$	41.86
Linolenic	278.436	18:03	3	(9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid	$C_{18}H_{30}O_2$	0.17
Docosanoic	340.592	22:00	0	1-Docosanoic acid	$C_{22}H_{44}O_2$	0.44
Total						**100**

	WCOME	**HME [30]**	**SME [3]**	**AMME [7]**
Saturated	31.62	30.82	8.95	9.71
Monounsaturated	26.35	10.40	18.69	25.12
Polyunsaturated	42.03	58.78	72.36	65.17
Total	100	100	100	100
DU	110.58	128.55	163.40	180.38
LCSF	21.28	22.35	5.82	6.31

N ≡ Number of double bonds

3.4. NMR analyses

3.4.1. ^{13}C NMR analysis

A representative spectrum of ^{13}CNMR of WCO, WCOME, D100 and their blends with Pen and Oct are shown in **Figure 3.1** which shows the characteristic peaks of ester carbonyl (−COO−) and C−O at nearly 170 and 50 ppm, respectively. The peaks around 130 and 120 ppm indicated the unsaturation in methyl esters. Other peaks at nearly 13 ppm are due to terminal carbon of methyl groups and signals at 20–35 ppm are related to methylene carbons of long carbon chain in fatty acid methyl esters (FAMEs) **[31]**.

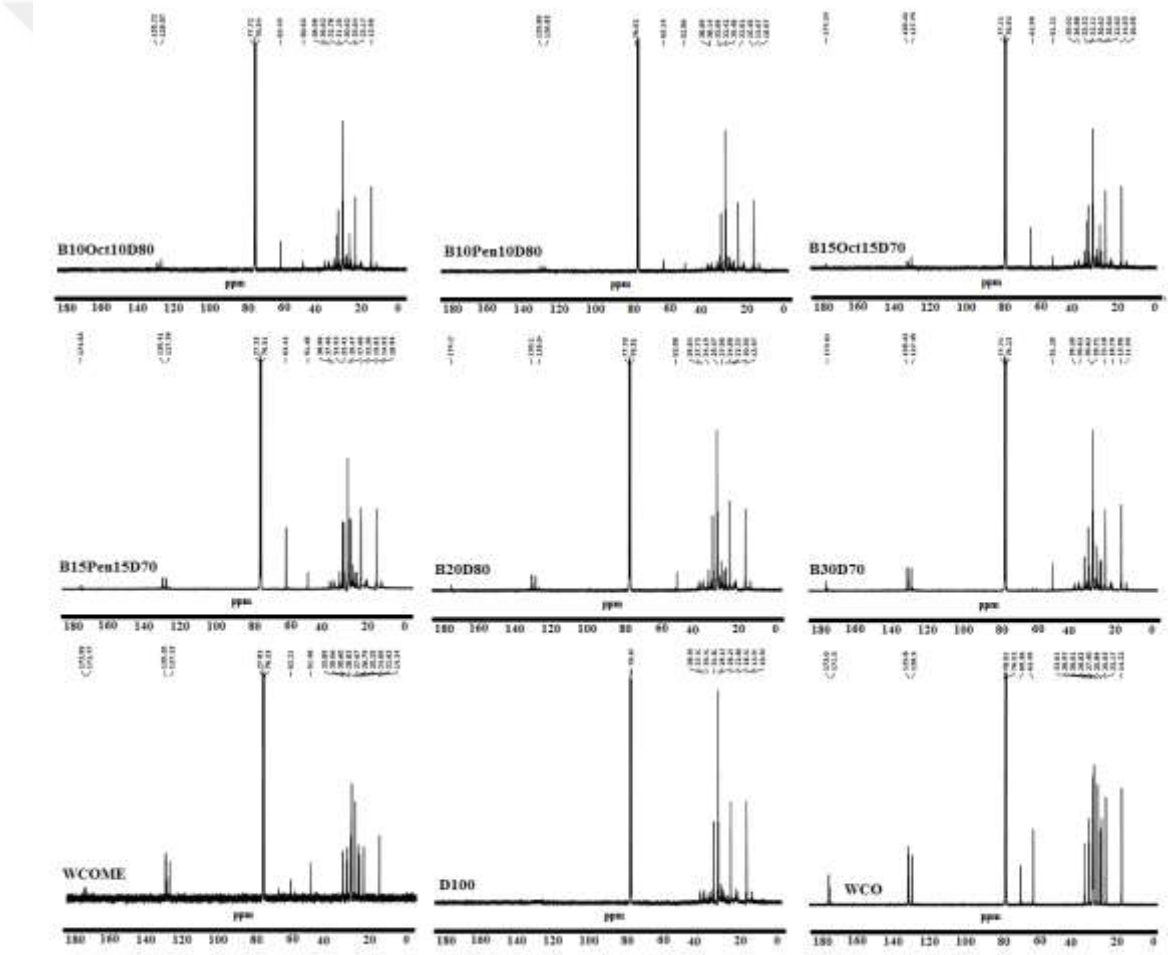


Figure 3.1. ^{13}C-NMR spectra of WCO, WCOME, D100 and their blends with Pen and Oct

3.4.2 ^{1}H NMR analysis

In this study, WCO, WCOME, D100 and their blends with Pen and Oct were characterized by ^{1}H NMR spectroscopy and its spectra are shown in Figure 3.2. The characteristic peak of methoxy protons were observed as a singlet at between 3 and 4 ppm. Triplet of α-CH_2 protons at around 2 and 2.5 ppm. These peaks indicate the presence of methyl esters in biodiesel. Other observed peaks were between 0.7 and 0.9 ppm of terminal methyl protons [31].

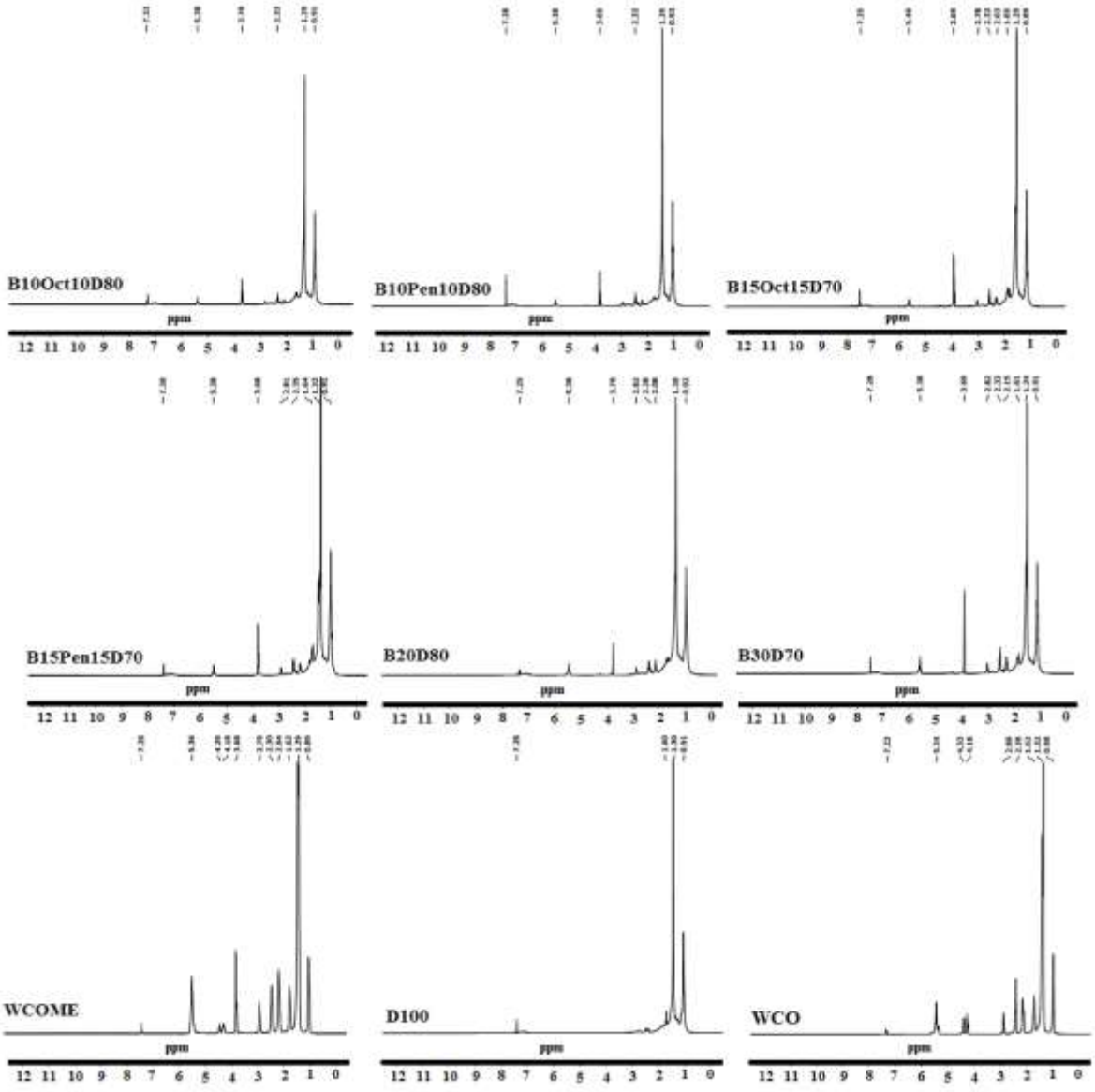


Figure 3.2. ^{1}H-NMR spectra of WCO, WCOME, D100 and their blends with Pen and Oct

3.5 DSC analysis

The crystallization onset temperatures of WCO, WCOME, D100 and their blends with Pen and Oct under N_2 atmosphere were studied using DSC and presented in Table 3.5 The onset temperatures for WCOME, WCO and D100 are -4.66, -5.46 and -5.81 °C respectively and hence biodiesel crystallizes faster than diesel. The crystallization onset temperatures of B10Oct10D80, B10Pen10D80, B15Oct15D70, B15Pen15D80, B20D80 and B30D70 are -5.99, -5.64, -5.90, -6.17, -5.81 and -5.90 °C respectively, below WCOME which signifies that the addition of diesel and alcohols lowers the crystallization temperature of biodiesel. Addition of diesel and alcohols reduces the crystallization of biodiesel [34].

Table 3.5. Crystallizations onset temperature (°C) of WCO, WCOME, D100 and their blends with Pen and Oct

Sample	**Crystallizations onset temperature (°C)**
B10Oct10D80	-5.99
B10Pen10D80	-5.64
B15Oct15D70	-5.90
B15Pen15D70	-6.17
B20D80	-5.81
B30D70	-5.90
WCOME	-4.66
WCO	-5.46
D100	-5.81

3.6 FT-IR analysis

Figure 3.3 and Table 3.6 displays the infrared spectra of WCO, WCOME, D100 and binary biodiesel-diesel blends and ternary biodiesel-diesel-pentanol/octanol blends (B20D80, B30D70, B10Pen10D80, B15Pen15D70, B10Oct10D80, B15Oct15D70). 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 ~ 1743.4 cm^{-1} to monitor the progress of the reaction. It can be observed peaks that can be attributed to the stretching of C=O. The stretching of O-CH_3, represented by the absorbance at 1200 cm^{-1}, is typical

of biodiesel. The esteric –COC vibration at 1155.6 cm^{-1} reveals medium intensity bands, and the presence of the $(CH_2)_n$ group vibration band is seen at nearly 721.8 cm^{-1}. The peak at nearly 1361 cm^{-1} correspond to the asymmetric stretching of $–CH_3$. 3339.6 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 pentanol and octanol. The results for the blends show that the intensities of the stretches at 1745.84 cm^{-1} increase with the concentration of the biodiesel in the blends Figure 3.4. All results confirm the existence and purity of WCOME, D100 and their blends with Pen and Oct [35, 36].

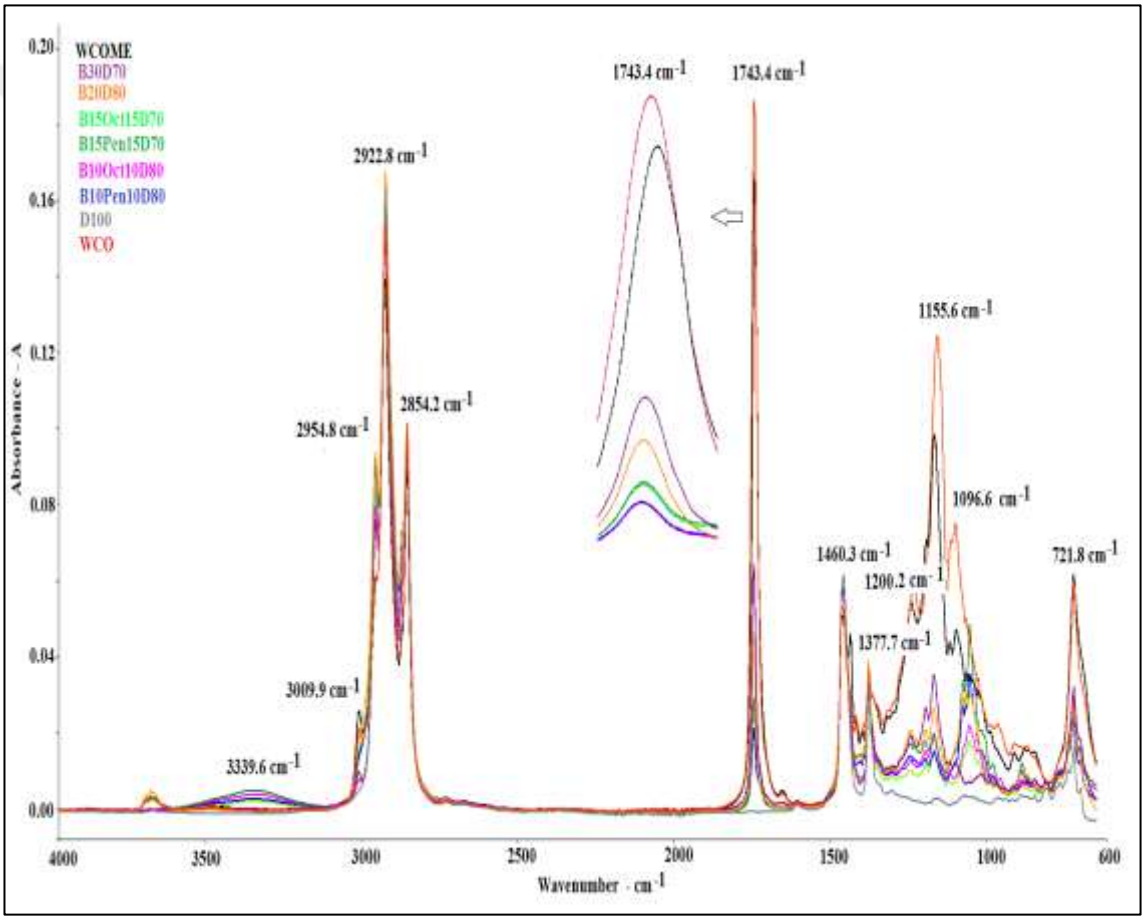


Figure 3.3. Infrared spectra of WCO, WCOME, D100 and their blends with pentanol and octanol

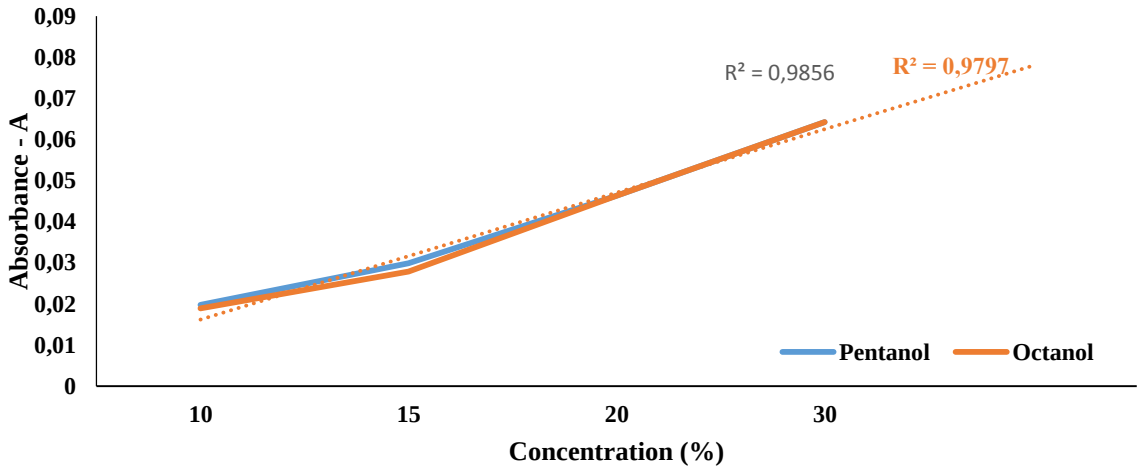


Figure 3.4. Fitting between absorbance and % concentrations of blends

Table 3.6. Functional group frequencies of WCO, WCOME, D100 and their blends with Pen and Oct [36]

Absorption bands (cm^{-1})	**Functional group**
3339.6	O-H Stretching vibration (alcohols)
3009.0	=C-H Asymmetrical stretching (alkenes)
2954.8-2922.8	C-H Asymmetrical stretching (alkanes)
2854.2	C-H Symmetrical stretching (methylene)
1743.4	C=O Stretching (ester carbonyl)
1460.3-1377.7	C-H Bending and rocking (methyl or - CH_3)
1200.2	C-O Stretching (alkoxy esters, ethers or C-O-C)
1155.6	C-O-C Symmetric stretching vibration
721.8	=C-H and Bending of alkenes (methylene)

3.7. UV-vis analysis

Figure 3.5 shows a typical family of absorbance curves for diluted WCOME in the range of 800 to 400 nm. The absorbance for WCOME also produced very similar absorbance, with no statistically significant differences. Therefore, biodiesel does not affect the absorbance in this band, as biodiesel blends do not have chemical components that contribute to significant absorption in this range. According to the UV-vis spectroscopy data, it is noteworthy that this technique can provide useful information

about the quality of biodiesel [32]. This UV-vis spectroscopy determination constitutes a different approach from the measure of primary and secondary oxidation products, for example, peroxides, ketones, acid, aldehydes and others. Figure 3.5 showed that the samples presented absorption at between 400–500 nm. This behaviour occurs due to the oxidation of polyunsaturated fatty acids, is accompanied of the displacement of isolated double bonds for conjugated double bonds [37].

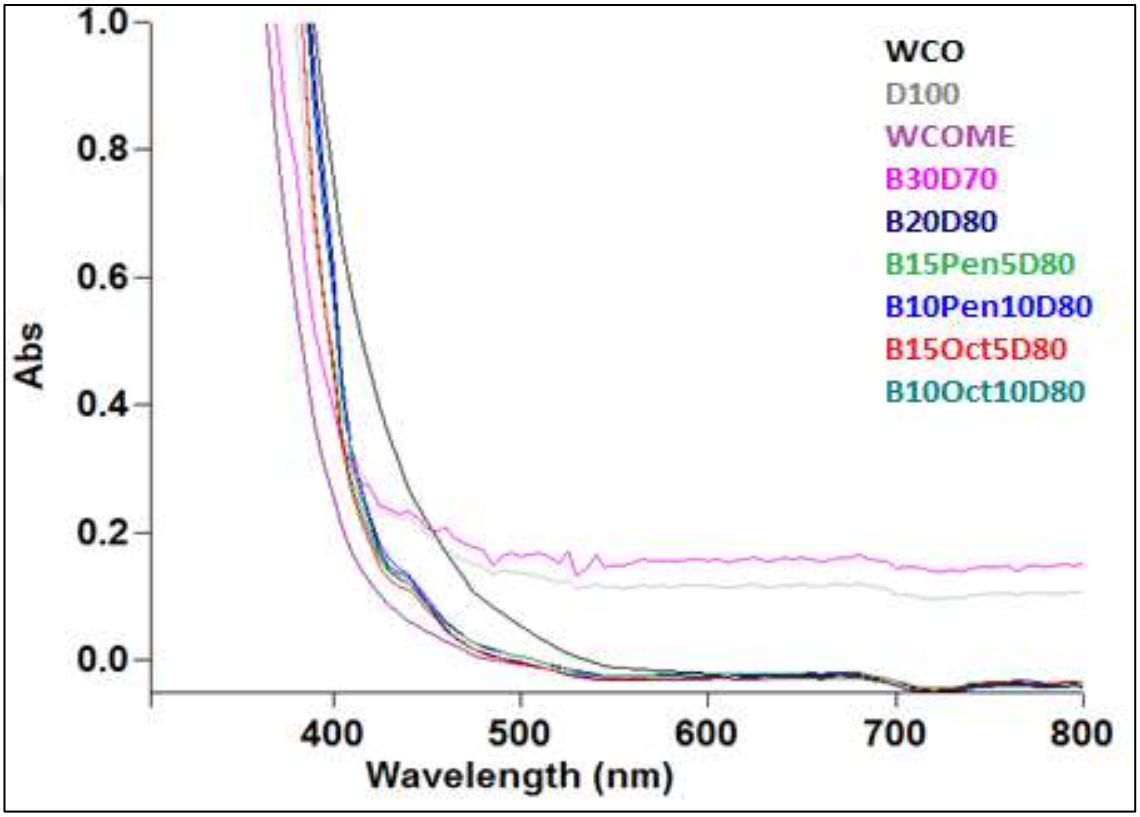


Figure 3.5. UV absorbance spectra of WCO, WCOME, D100 and their blends with Pen and Oct

3.8. TGA

Thermal stability of WCO, WCOME, D100 and their blends with Pen and Oct were quantified by TGA. The thermal stability is a quality indicator parameter for esters. 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 thermal degradation occurred in a single continuous step in the temperature range 50-380 °C for WCOME, D100 and their blends with Pen and Oct in Figure 3.6 and Figure 3.7 respectively. In these temperature ranges, the mass losses occur at levels of 95.5-98.8% for WCOME, D100 and their blends with Pen and Oct. The thermal onset temperatures were represented in Table 3.7.

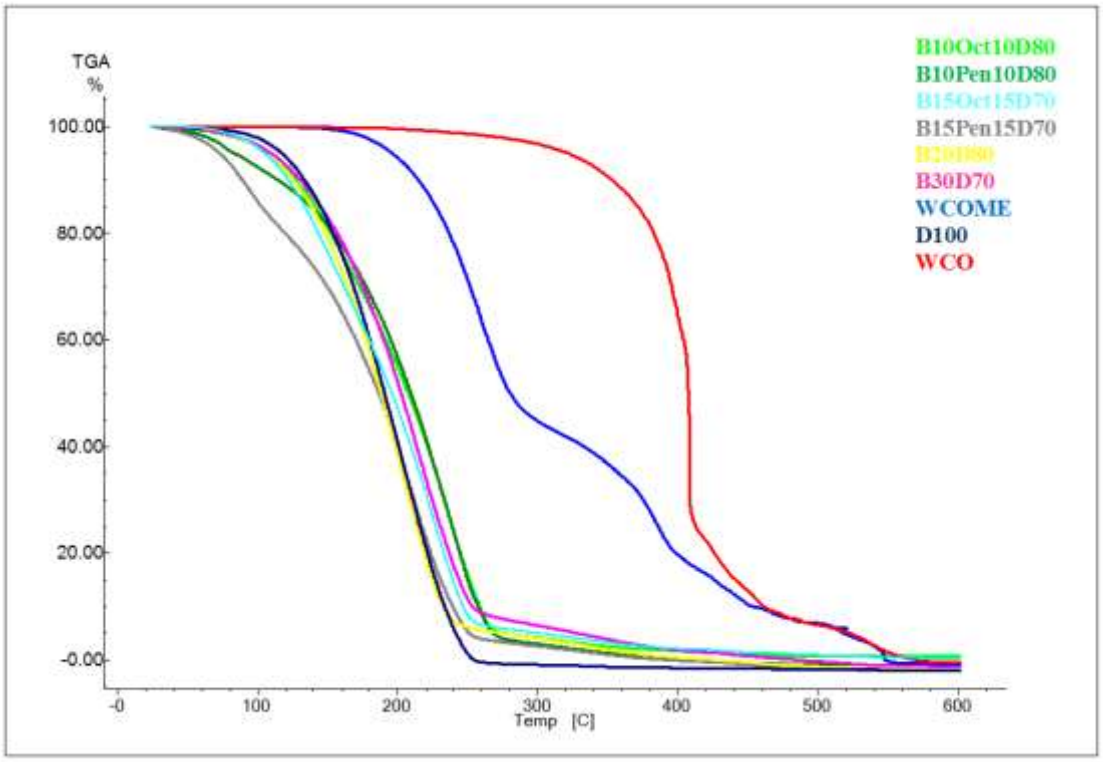


Figure 3.6. TGA of WCO, WCOME, D100 and their blends with Pen and Oct for thermal stability

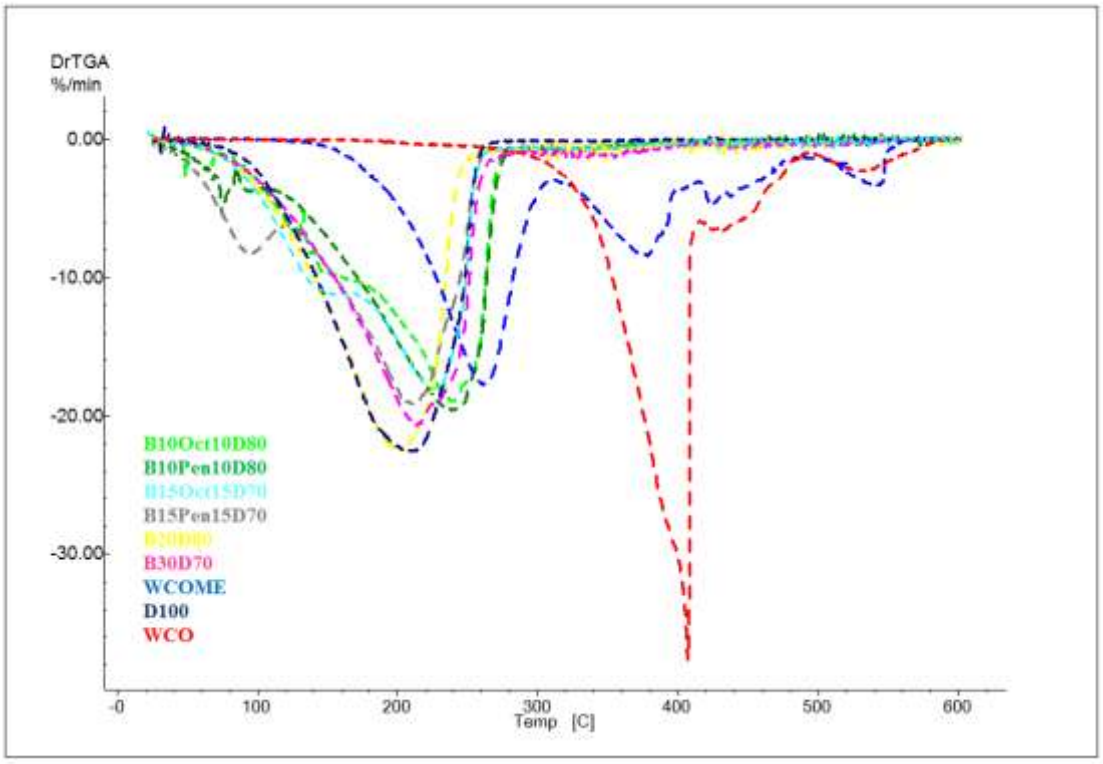


Figure 3.7. Derivative Thermogravimetric analyses (DTGA) of WCO, WCOME, D100 and their blends with Pen and Oct for thermal stability

Table 3.7. TGA Analysis of WCO, WCOME, D100 and their blends with Pen and Oct for thermal stability

Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B10Oct10D80	10	45-340	113.3	97.3
B10Pen10D80	10	50-350	95.7	97.3
B15Oct15D70	10	80-350	92.1	95.5
B15Pen15D70	10	50-340	72.5	95.9
B20D80	10	70-370	89.8	97.6
B30D70	10	96-380	117.1	95.6
WCOME	10	175-550	191.9	98.8
D100	10	110-380	121.4	98.8
WCO	10	210-580	333.5	98.8

3.9. Engine performance analyses

3.9.1. BSFC

Figure 3.8 illustrates the results of BSFC of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. It can be seen that BSFC decreases with increasing load for almost all tested fuels at the same speed. The average BSFC for all tested fuels in this study were D100 (494.8kg/kwh), B20D80 (572.69 kg/kwh), B30D70 (588.75 kg/kwh), B10Oct10B80 (512.40 kg/kwh), B15Oct15D70 (606.86 kg/kwh), B10Pen10D80 (474.12 kg/kwh) and B15Pen15D70 (552.45 kg/kwh). Therefore, compared to D100, the average increase/decrease in BSFC for B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were 15.74, 18.99, 3.56, 22.65, -4.18 and 11. 65% respectively. These results can be attributed to the combined effect of density, calorific value, cetane number and kinematic viscosity of fuel blends [38]. The lowest recorded BSFC was observed for B10Oct10D80 at 4.5 N.m load with 307.61 kg/kWh while the highest recorded BSFC was observed for B15Oct15D70 at 1.5 N.m load with 999.33 kg/kWh.

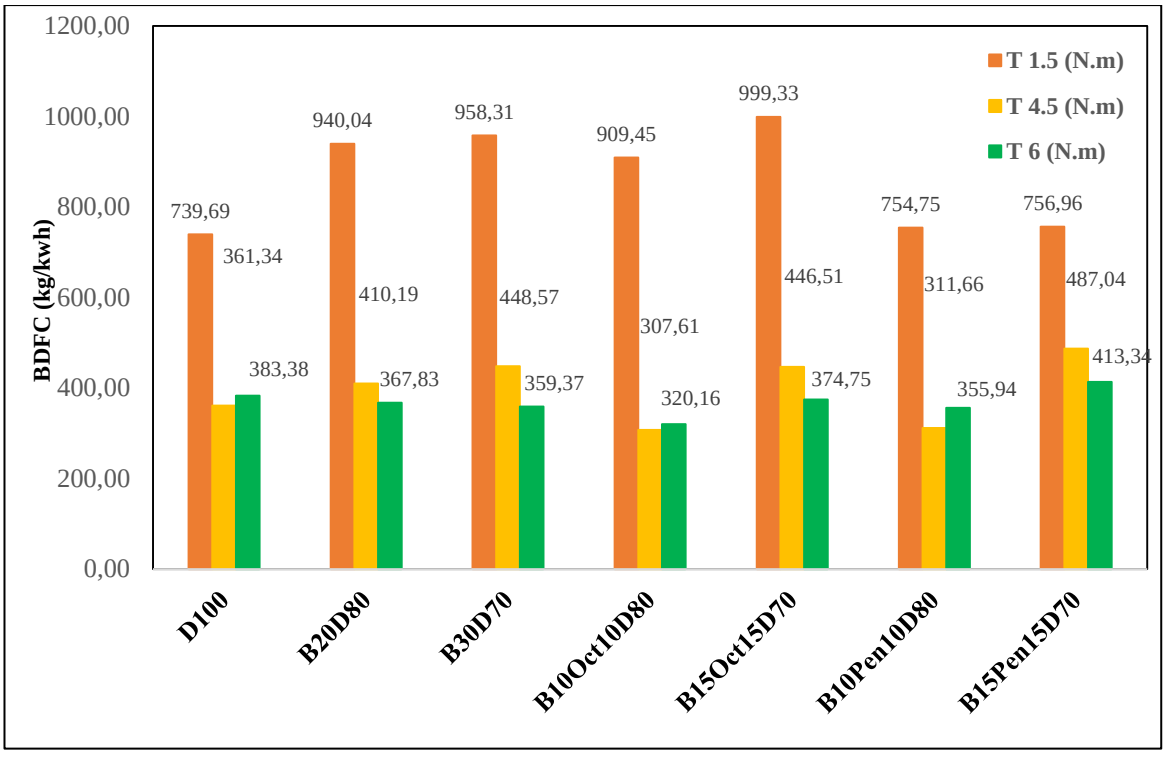


Figure 3.8. BSFC of all fuel samples at constant speed of 3000 rpm and different loads

3.9.2. Average fuel consumption (AFC)

Figure 3.9 illustrates the results of AFC of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. It can be seen that AFC increase with increasing load for almost all tested fuels at the same speed. The average AFC for all tested fuels in this study were D100 (0.15 kg/s), B20D80 (0.16 kg/s), B30D70 (0.16 kg/s), B10Oct10B80 (0.12 kg/s), B15Oct15D70 (0.17 kg/s), B10Pen10D80 (0.14kg/s) and B15Pen15D70 (0.17kg/s). Therefore, compared to D100, the average increase/decrease in AFC for B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were 8.26, 11.22, -15.07, 14.08, -7.45 and 15.08% respectively. The lowest recorded AFC was observed for B10Oct10D80 at 1.5 N.m load with 0.09 kg/s while the highest recorded AFC was observed for B15Pen15D70 at 6 N.m load with 0.22 kg/s

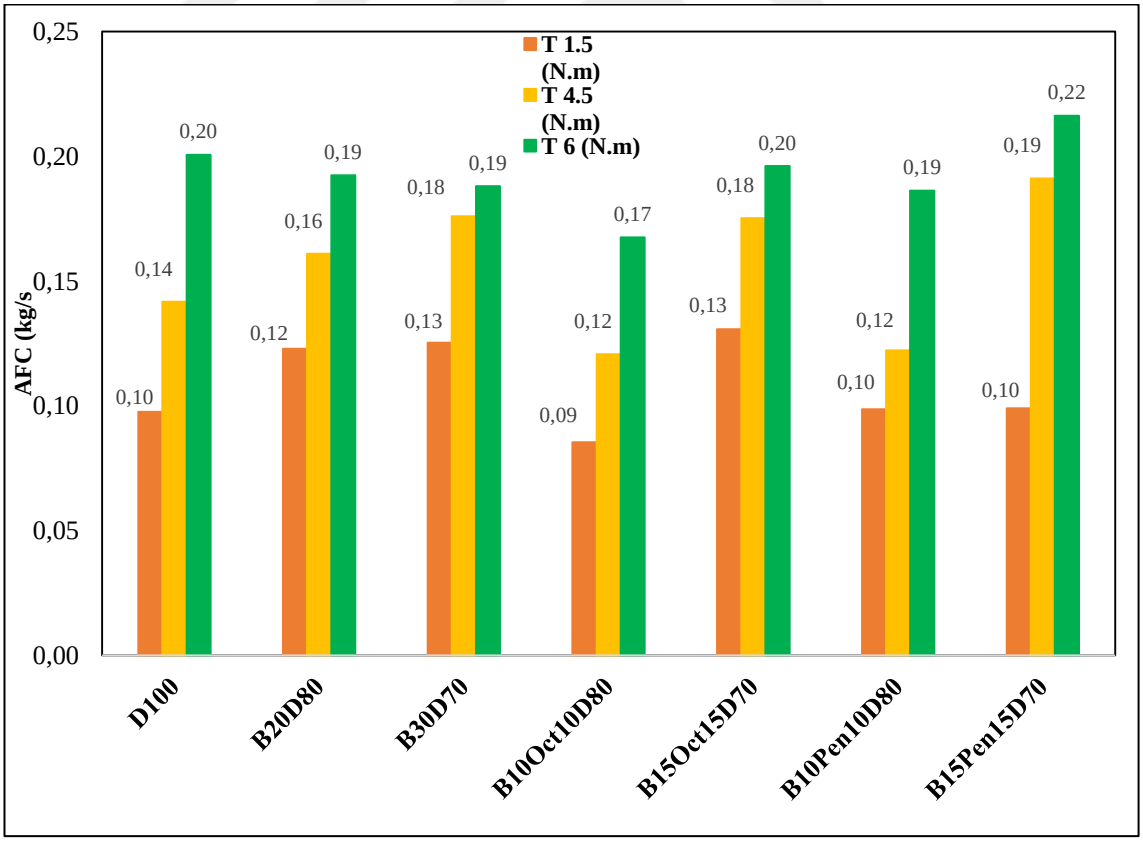


Figure 3.9. AFC for all fuel samples at constant speed of 3000 rpm and different loads

3.9.3. Break thermal efficiency (η_{bth})

Figure 3.10 illustrates the results of brake thermal efficiency (η_{bth}) of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. It can be seen (η_{bth}) increase when the load increased from 1.5 N.m to 4.5 N.m and then reduced again when the load increased to 6 N.m. The average η_{bth} for all tested fuels in this study were D100 (0.19%), B20D80 (0.19%), B30D70 (0.18%), B10Oct10B80 (0.21%), B15Oct15D70 (0.18%), B10Pen10D80 (0.22%) and B15Pen15D70 (0.18%). Therefore, compared to D100, the average increase/decrease in η_{bth} for B20D80, B30D70, B10Oct10, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were 0%, -4.59%, 11.99%, -6.53%, 14.64 and -6.53% respectively. The lowest recorded η_{bth} was observed for B15Oct15D70 and B30D70 at 1.5 N.m load with 0.09% while the highest recorded η_{bth} was observed for B10Oct10D80 at 4.5 N.m load with 0.28%.

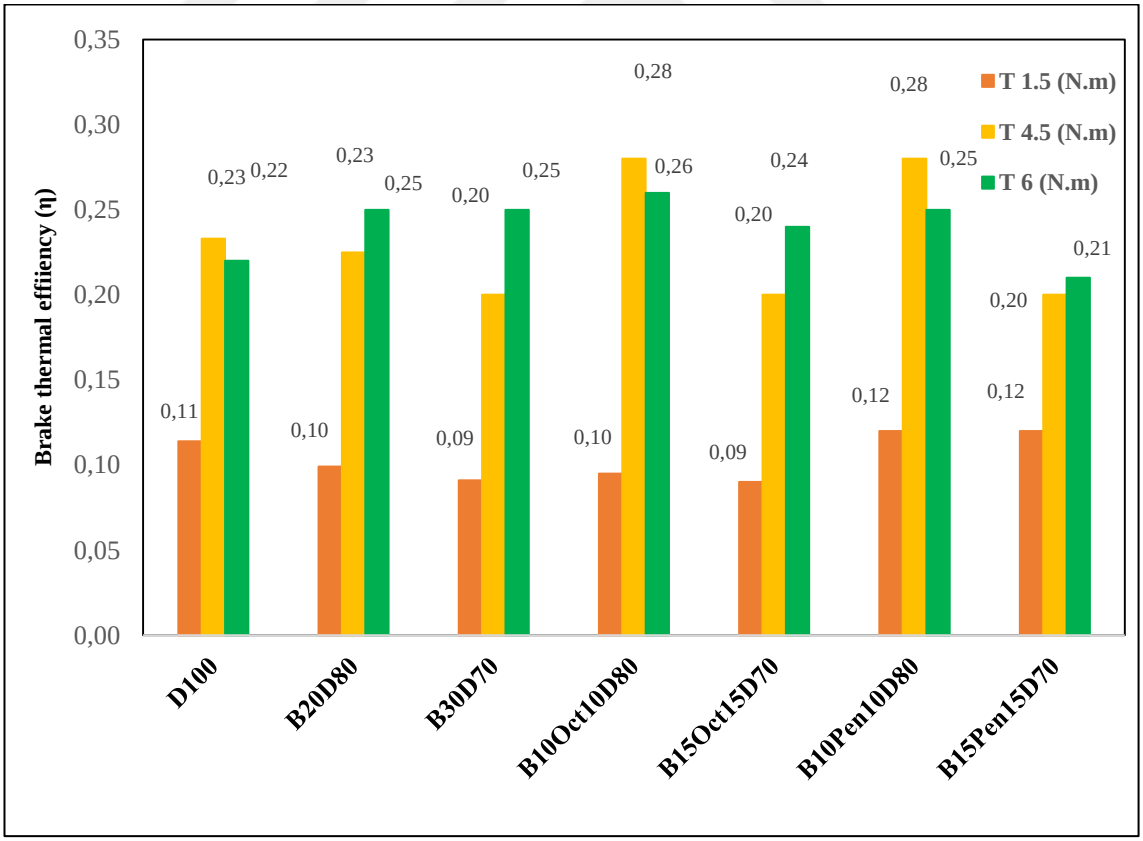


Figure 3.10. B_{th} (η) for all fuel samples at constant speed of 3000 rpm and different loads

3.9.4 Exhaust gas temperature (EGT)

Figure 3.11 illustrates the results of EGT of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. It can be seen that EGT increase with the increasing load for almost all tested fuels at the same speed. The average EGT for all tested fuels in this study were D100 (175 °C), B20D80 (130 °C), B30D70 (152 °C), B10Oct10B80 (122 °C), B15Oct15D70 (135 °C), B10Pen10D80 (118 °C) and B15Pen15D70 (133 °C). Therefore, compared to D100, the average decrease in EGT for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were -2.71, -13.33, -30.48, -22.86, -32.38 and -23.81% respectively. The effect of blending WCOME, Pen and Oct with D100 in reducing the EGT is obvious in this study. Apart from that, the lowest recorded EGT was observed for B15Oct15D70 at 1.5 N.m load with 95 °C while the highest recorded EGT was observed for D100 at 6 load with 195 °C.

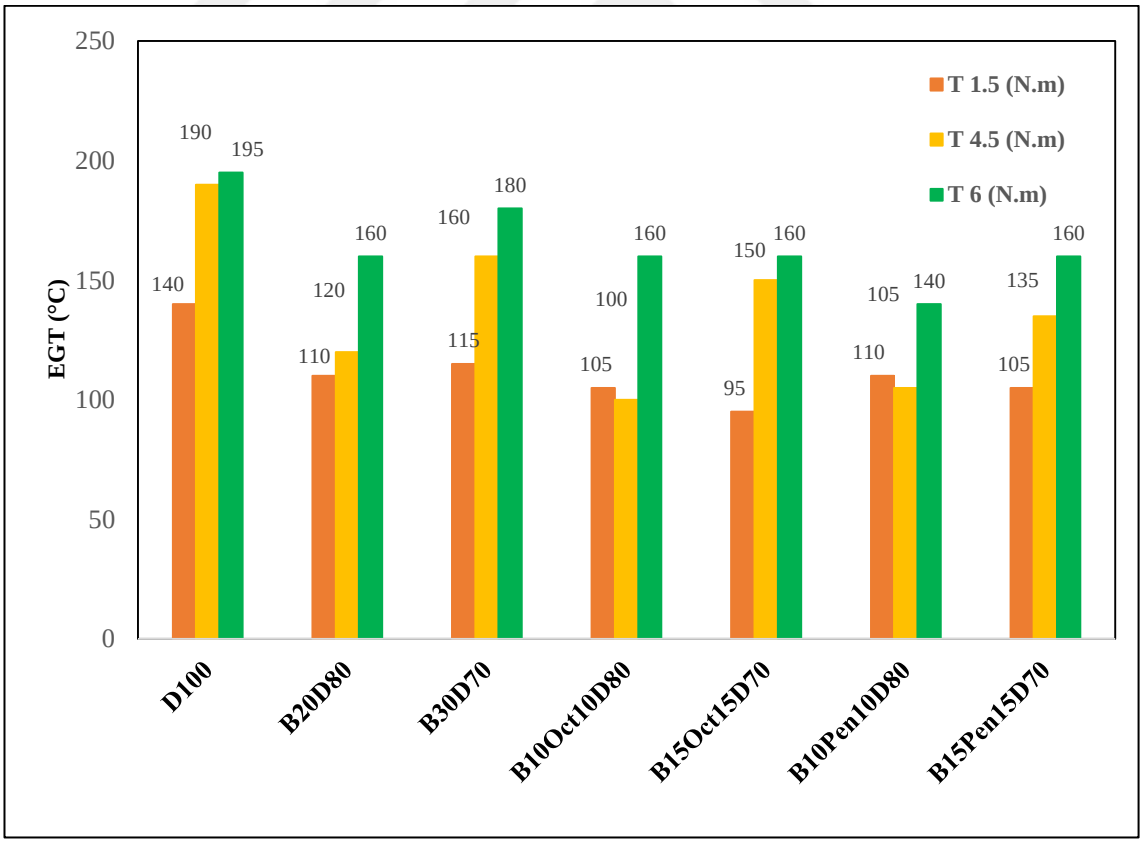


Figure 3.11. EGT for all fuel samples at constant speed of 3000 rpm and different loads

3.10 Emissions analyses

3.10.1 CO

Figure 3.12 illustrates the variation of CO emissions results of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. The average CO emissions for all tested fuels in this study were D100 (0.131 %vol), B20D80 (0.121 %vol), B30D70 (0.153 %vol), B10Oct10B80 (0.045 %vol), B15Oct15D70 (0.062 %vol), B10Pen10D80 (0.077 %vol) and B15Pen15D70 (0.081 %vol). Therefore, compared to D100, the average increase/decrease in CO emissions for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were -7.40, 17.35, -65.31, -52.30, -40.82 and -38.01% respectively. The effect of blending Pen and Oct with biodiesel-diesel in reducing CO emissions is obvious in this study. Apart from that, the lowest recorded CO emissions was observed for B10Oct10D80 at 6 N.m load with 0.026 %vol while the highest recorded CO emissions was observed for B30D70 at 6 N.m load with 0.178 %vol.

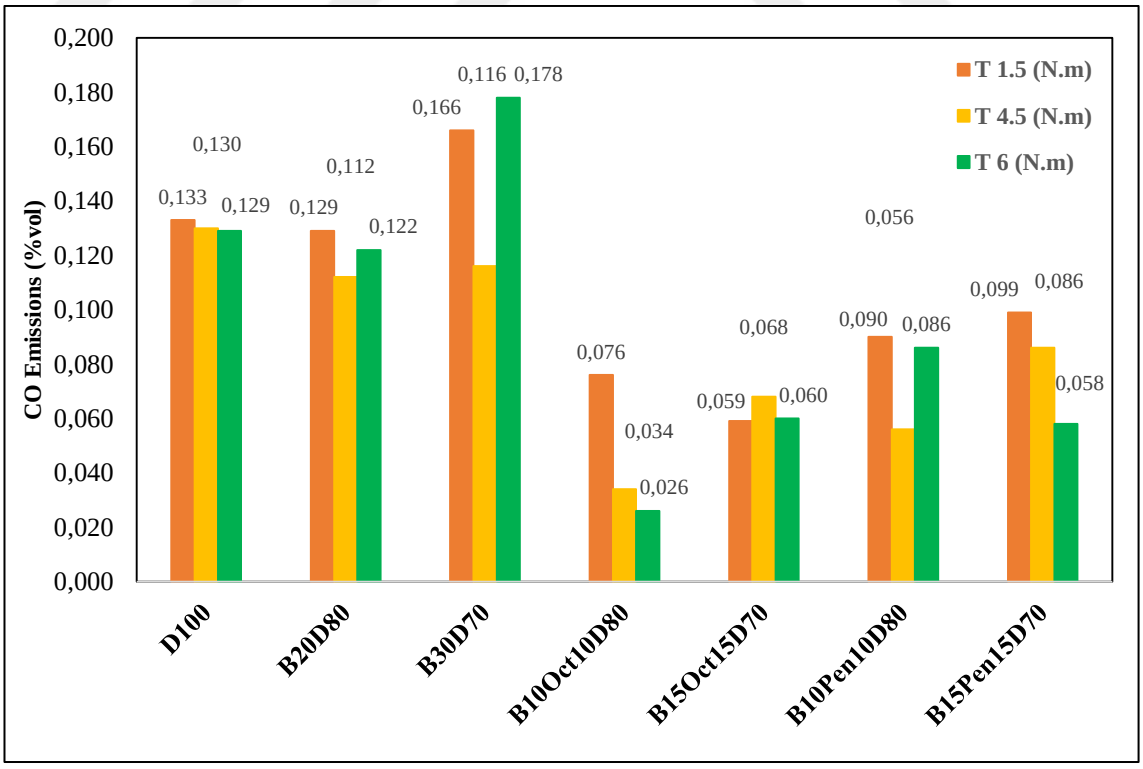


Figure 3.12. CO emissions for all fuel samples at constant speed of 3000 rpm and different loads

3.10.2 CO_2

Figure 3.13 illustrates the variation of CO_2 emissions results of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. The average CO_2 emissions for all tested fuels in this study were D100 (4.92 %vol), B20D80 (5.62 %vol), B30D70 (5.88 %vol), B10Oct10B80 (4.88 %vol), B15Oct15D70 (4.82 %vol), B10Pen10D80 (4.7 %vol) and B15Pen15D70 (5.56 %vol). Therefore, compared to D100, the average increase/decrease in CO_2 emissions for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were 14.15, 19.43, -0.95, -2.10, -4.6 and -12.93% respectively. The effect of blending Pen and Oct with biodiesel-diesel in reducing CO_2 emissions is obvious in this study. Apart from that, the lowest recorded CO_2 emissions was observed for B10Pen10D80 at 4.5 N.m load with 3.11 %vol while the highest recorded CO_2 emissions was observed for B15Pen15D70 at 1.5 N.m load with 6.48 %vol.

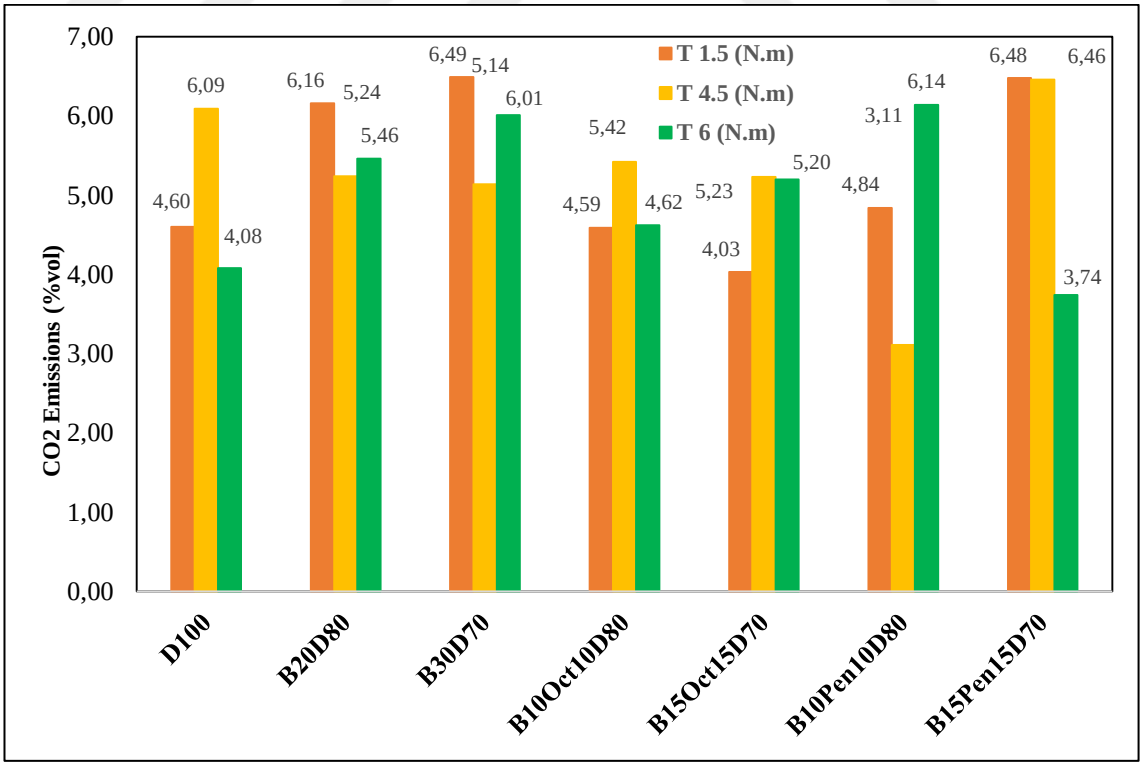


Figure 3.13. CO_2 emissions for all fuel samples at constant speed of 3000 rpm and different loads

3.10.3 O_2

Figure 3.14 illustrates the variation of O_2 emissions results of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. The average O_2 emissions for all tested fuels in this study were D100 (14.93 %vol), B20D80 (17.51 %vol), B30D70 (17.07 %vol), B10Oct10B80 (17.07 %vol), B15Oct15D70 (17.47 %vol), B10Pen10D80 (18.12 %vol) and B15Pen15D70 (17.15 %vol). Therefore, compared to D100, the average increase in O_2 emissions for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were 17.33, 14.34, 14.34, 17.02, 21.42 and 14.90% respectively. The effect of blending WCOME, Pen and Oct with diesel in increasing O_2 emissions is obvious in this study. Apart from that, the lowest recorded O_2 emissions was observed for D100 at 1.5 N.m load with 12.20 %vol while the highest recorded O_2 emissions was observed for B10Pen10D70 at 4.5 N.m load with 18.21 %vol.

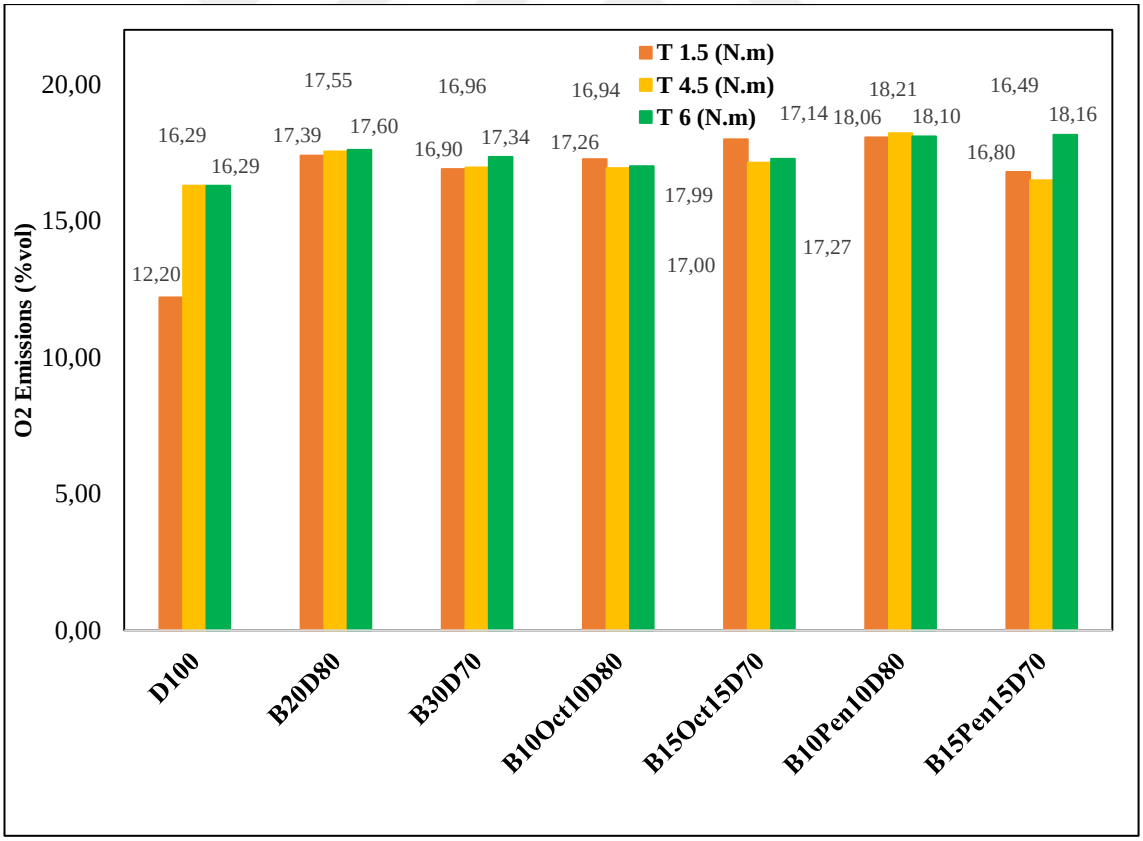


Figure 3.14. O_2 emissions for all fuel samples at constant speed of 3000 rpm and different loads

3.10.4 HC emissions

Figure 3.15 illustrates the variation of HC emissions results of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. The average HC emissions for all tested fuels in this study were D100 (43 ppm), B20D80 (44 ppm), B30D70 (51 ppm), B10Oct10B80 (14 ppm), B15Oct15D70 (15 ppm), B10Pen10D80 (14 ppm) and B15Pen15D70 (18 ppm). Therefore, compared to D100, the average increase/decrease in HC emissions for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were -2.31, 18.46, -68.46, -65.38, -66.92 and -59.23% respectively. The effect of blending Pen and Oct with biodiesel-diesel in reducing HC emissions is obvious in this study. Apart from that, the lowest recorded HC emissions was observed for B10Oct10D80 at 6 N.m load with 0ppm while the highest recorded HC emissions was observed for B30D70 at 6 N.m load with 60ppm.

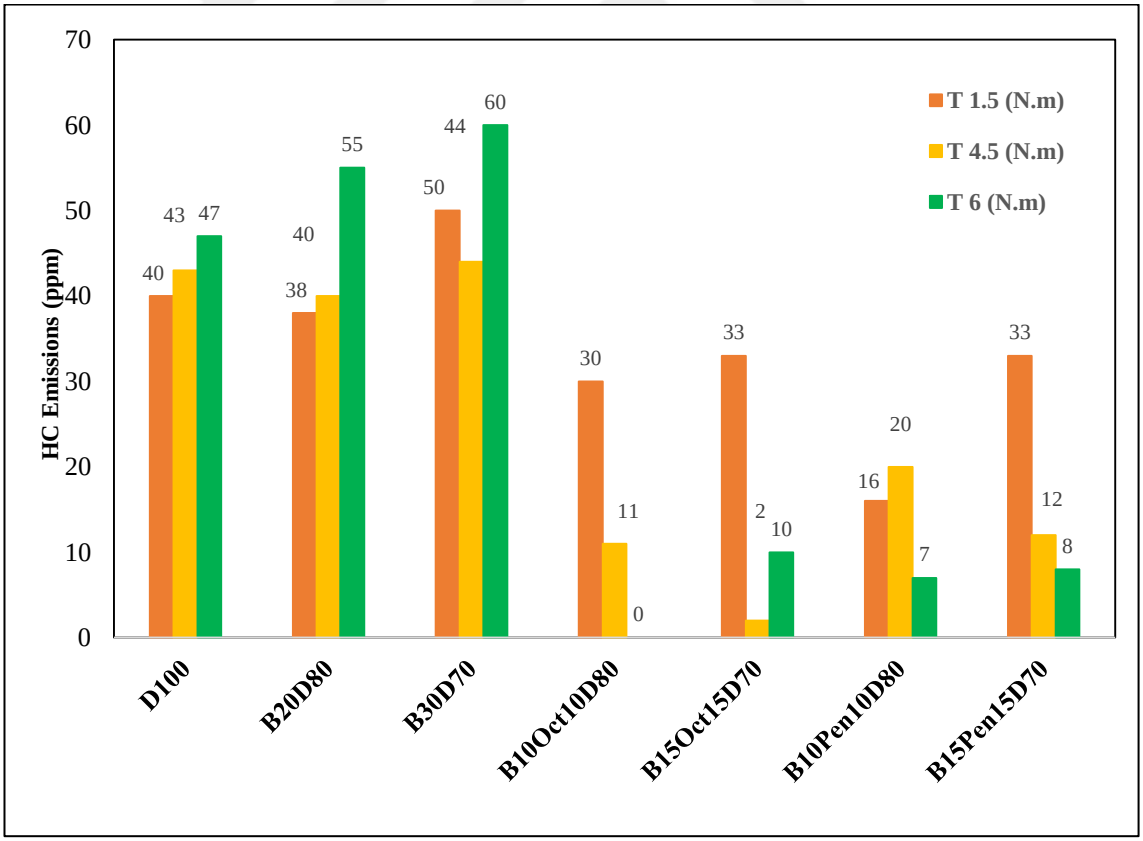


Figure 3.15. HC emissions for all fuel samples at constant speed of 3000 rpm and different loads

3.10.5 NO_x emissions

Figure 3.16 illustrates the results of NO_x emissions of D100, B20D80, B30D70, B10Oct10D80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 respectively at different loads and constant engine speed of 3000 rpm. The average NO_x emissions for all tested fuels in this study were D100 (50 ppm), B20D80 (47 ppm), B30D70 (57 ppm), B10Oct10B80 (43 ppm), B15Oct15D70 (35 ppm), B10Pen10D80 (39 ppm) and B15Pen15D70 (38 ppm). Therefore, compared to D100, the average decrease in NO_x emissions for B20D80, B30D70, B10Oct10B80, B15Oct15D70, B10Pen10D80 and B15Pen15D70 were -6.04, -14.09, -12.75, -30.20, -22.15 and -23.49% respectively. The effect of blending WCOME, Pen and Oct with D100 in reducing NO_x emissions is obvious in this study. Apart from that, the lowest recorded NO_x emissions was observed for B15Oct15D70 at 1.5 N.m load with 23 ppm while the highest recorded NO_x emissions was observed for B30D70 at 6 N.m load with 60 ppm.

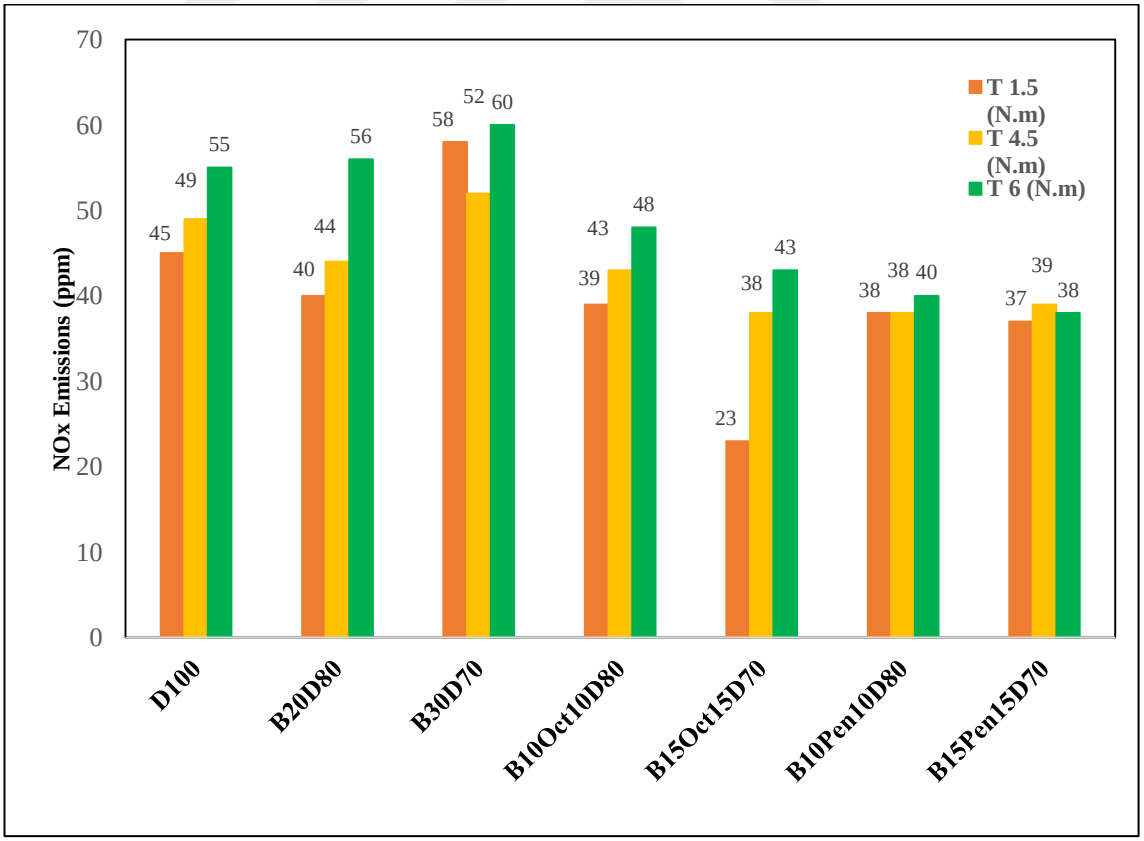


Figure 3.16. NO_x emissions for all fuel samples at constant speed of 3000 rpm and different loads

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, conclusion of the current study and some future directions were provided.

4.1. Discussion and conclusion

This work has been conducted at Alternative Fuels Research Laboratory (AFRL), Erciyes Üniversitesi (ERÜ), Kayseri, Turkey as well as the chemical laboratories of Ondokuz Mayıs Üniversitesi (OMÜ), Samsun, Turkey and engine laboratory of Al-Technalogya University, Baghdad, Iraq. The aims of this research were to recycle WCO into biodiesel. Properties of WCOME has been found to be better than some other feedstocks. This was due to its excellent DU (110.58). With these finding; OS, CN, IV and KV of biodiesel were 5.39 h, 53.9, 106.6 g iodine/100g and 3.55 mm^2/s respectively, all of which satisfying ASTM D 6751 standards. Blending WCOME with D100 and higher alcohols of Pen and Oct was the second aim of this research in which the qualities of all binary (biodiesel-diesel) and ternary (biodiesel-diesel-alcohols) blends were assessed by FT-IR, TGA, NMR, DSC and UV-vis characteristics. All of which confirmed the existence of WCOME, D100, Pen and Oct in the prepared fuel samples and proved the effectiveness of these techniques as cheap, fast and reliable methods that can replace some expensive equipment that measure the properties of fuels such as cold flow properties, thermal degradation and oxidation stability.

Apart from that, some engines and emissions performance parameters such as BSFC, B_{th} (η), AFC, EGT, CO, CO_2, NO_x and HC were also studied. An increase in BSFC coupled with a decrease in EGT were observed for all binary and ternary blends compared to D100. Variation in AFC, B_{th}, CO, CO_2, HC and NO_x were observed in this

study with some marginal increase/decrease compared to D100. All of which proved that addition of Pen and Oct to the binary biodiesel-diesel blends is acceptable for application in DICI engines due to their higher cetane numbers, flash point and calorific value compared to lower alcohols and closer density and kinematic viscosity to D100.

4.2. Future work and suggestions

This study conducted in-depth analyses/characterization of ternary (biodiesel-diesel-alcohols) blends, besides testing their effect in a single cylinder DI CI diesel engine at constant speed of 3000 rpm and three different loads of 1.5, 4.5 and 6 N.m respectively. Therefore, things can be targeted in future studies for the ternary (biodiesel-diesel-alcohols) blends can be suggested as follow:

1. Run the engine with different injection timings and pressures.
2. Run the engine at different speeds and constant load.
3. Test the effect of some other higher alcohols such as hexanol ($C_6H_{14}O$) and decanol ($C_{10}H_{22}O$) and compare that with Pen and Oct.
4. Engine operation at different fuel flow rates and temperatures.

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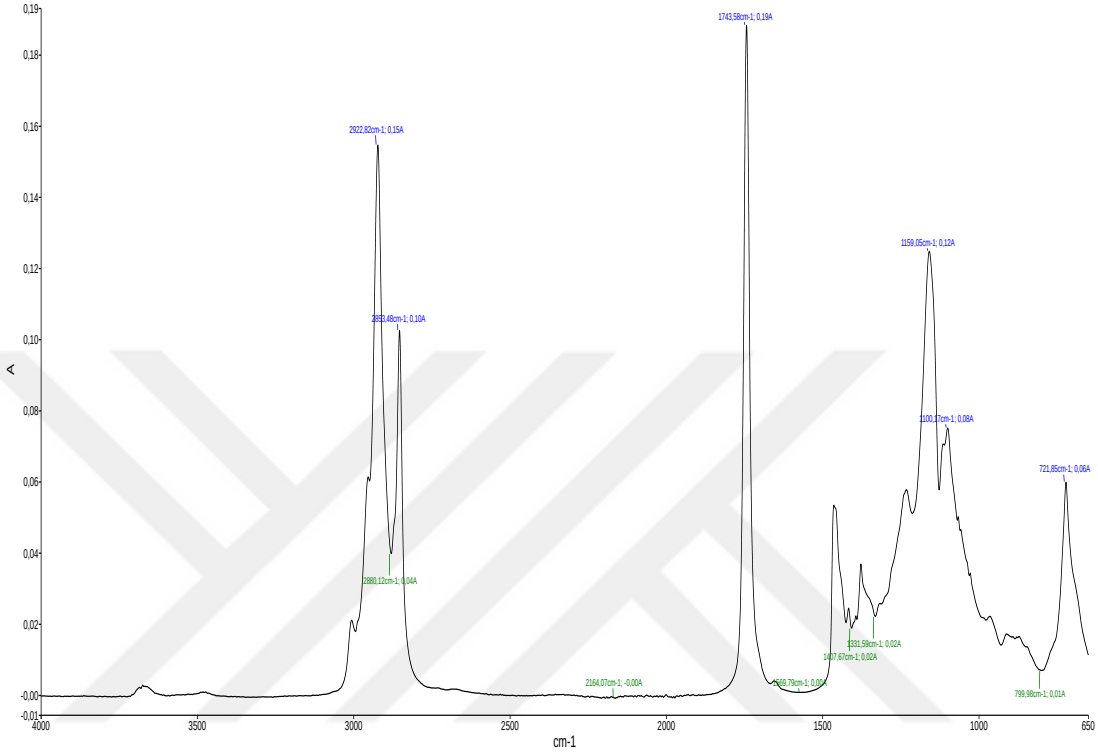
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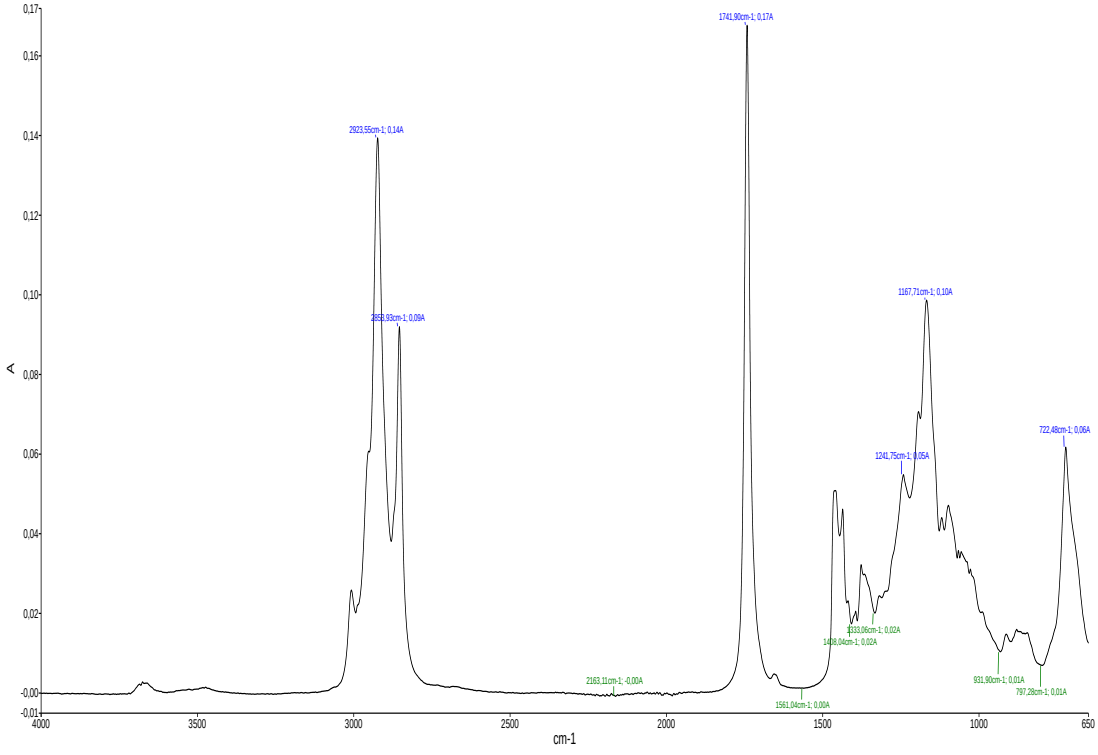
APPENDIXS

APPENDIX (A)

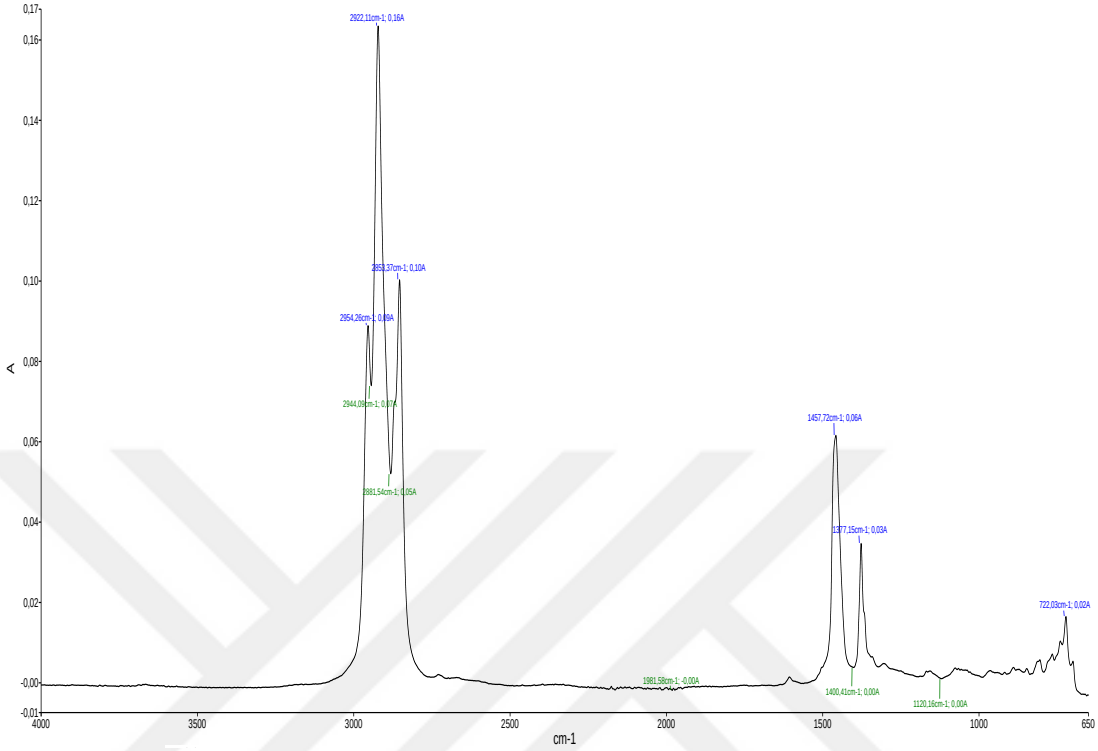
WCO



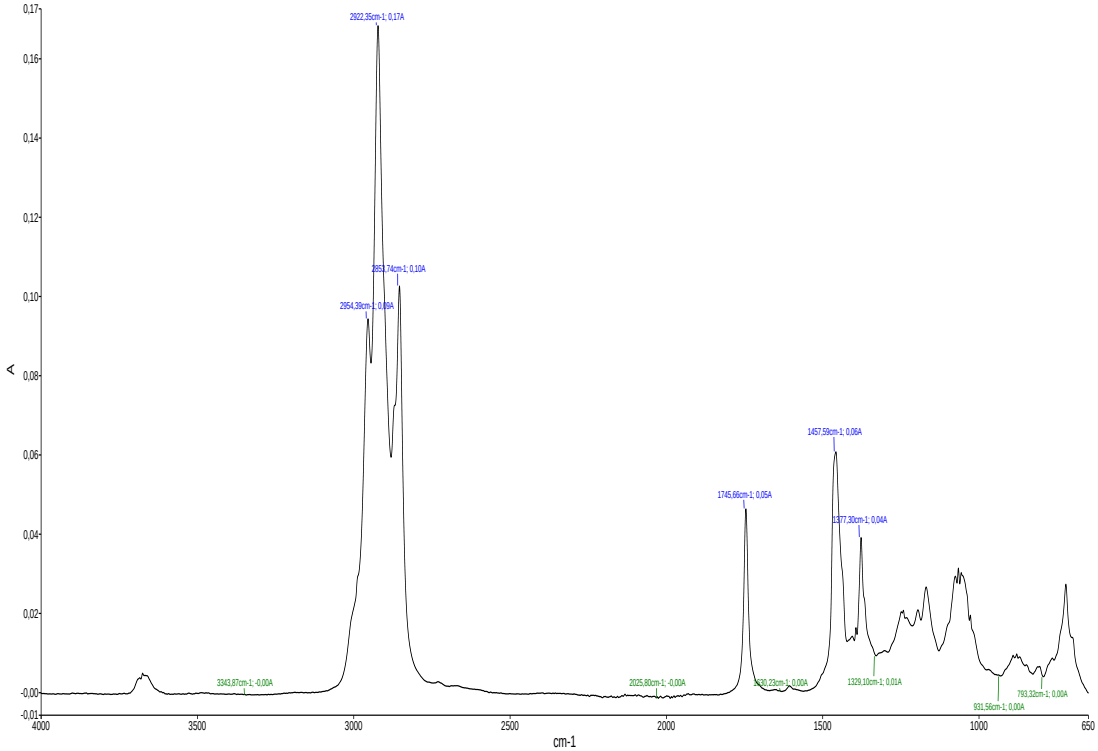
WCOME



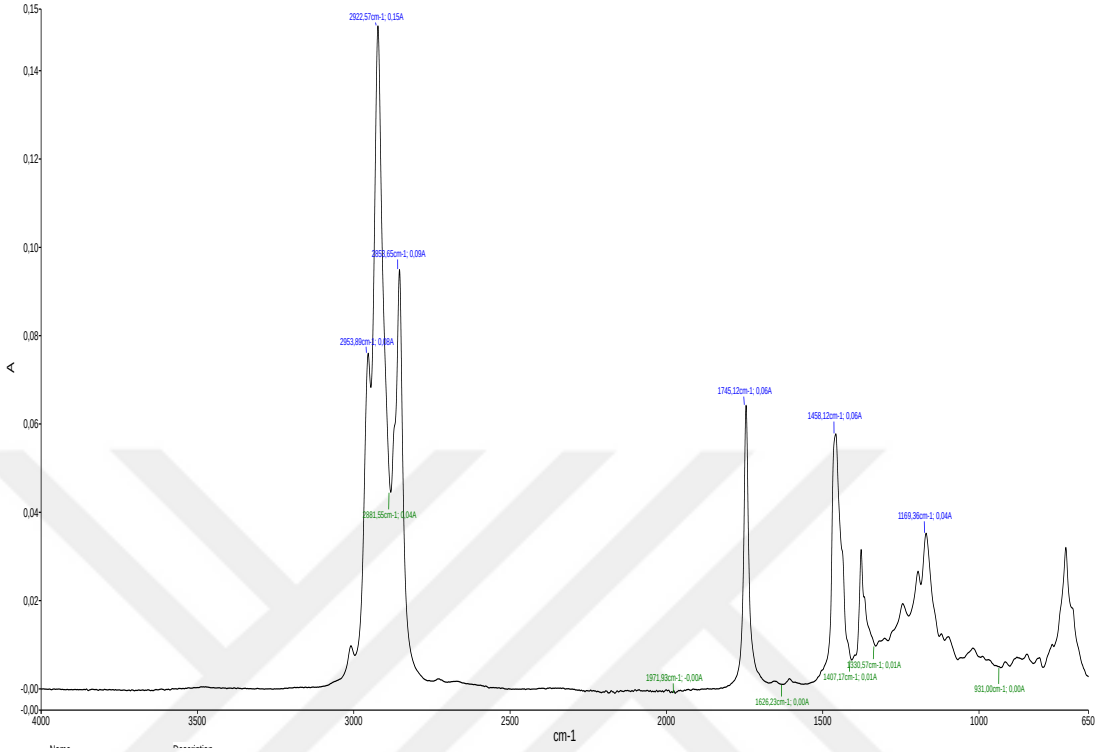
D100


2922.11cm-1; 0,16A
2853,37cm-1; 0,10A
2954,26cm-1; 0,09A
2944,09cm-1; 0,07A
2881,54cm-1; 0,05A
1457,72cm-1; 0,06A
1377,15cm-1; 0,03A
722,03cm-1; 0,02A
1981,58cm-1; -0,00A
1400,41cm-1; 0,00A
1120,16cm-1; 0,00A
A
cm-1

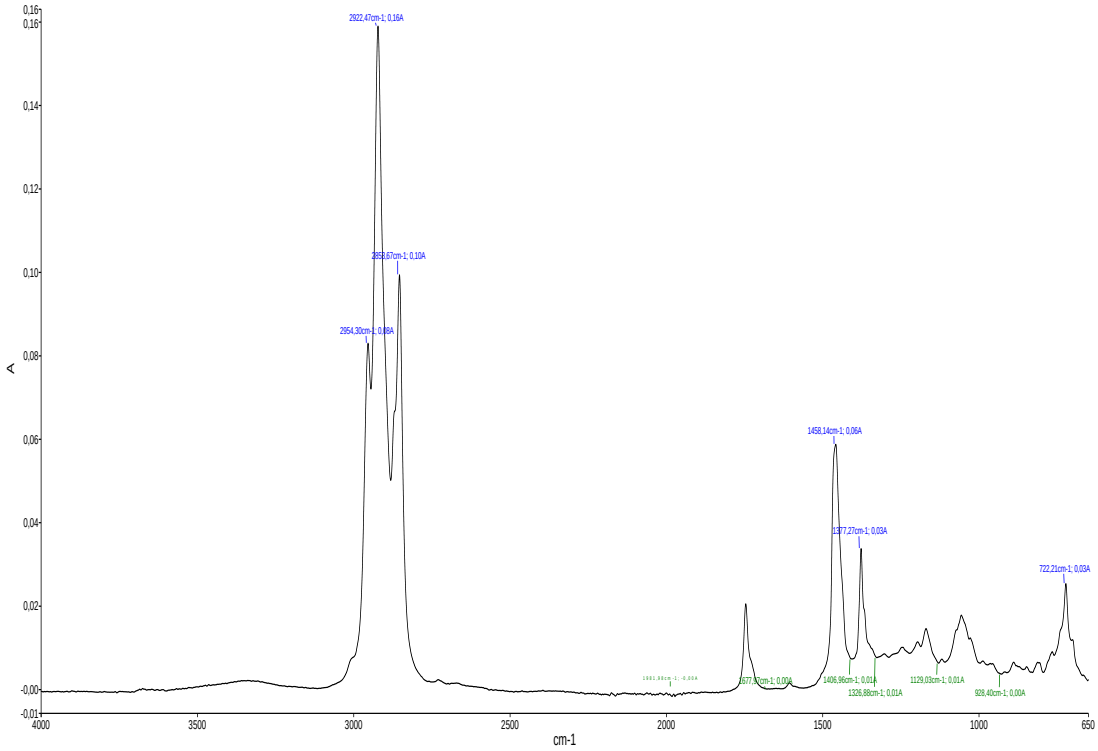
B20D80


2922,35cm-1; 0,17A
2853,74cm-1; 0,10A
2954,38cm-1; 0,09A
1745,66cm-1; 0,05A
1457,59cm-1; 0,06A
1377,30cm-1; 0,04A
3343,87cm-1; -0,00A
2025,80cm-1; -0,00A
1329,10cm-1; 0,01A
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A
cm-1

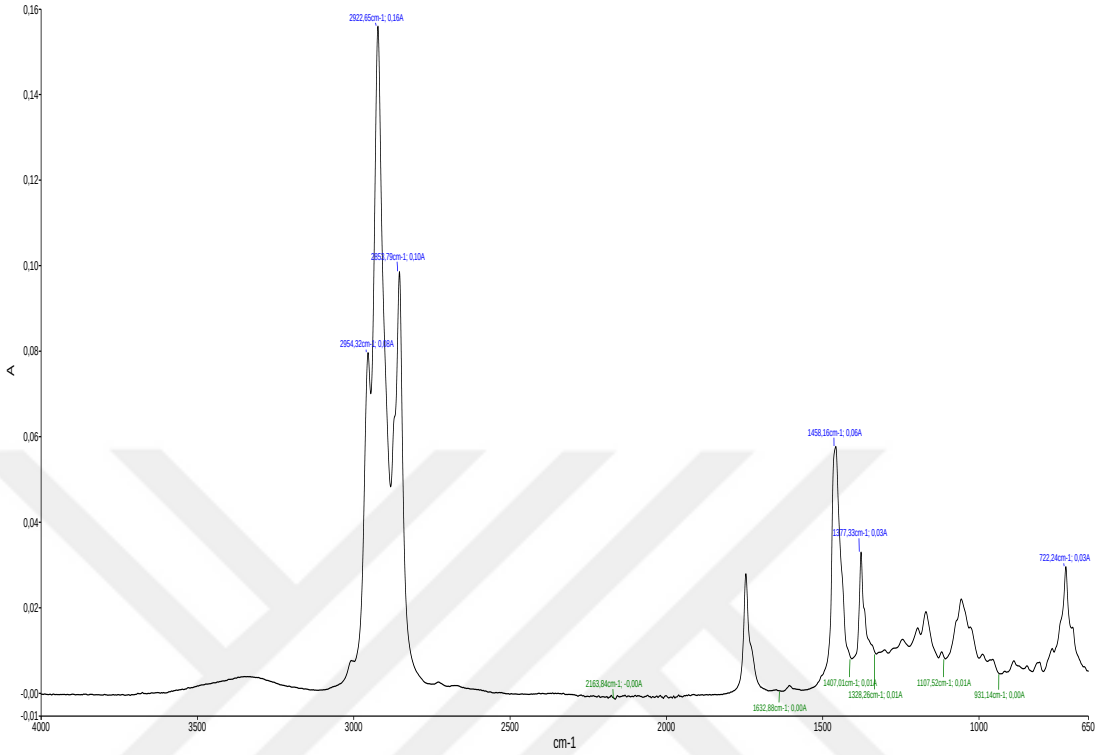
B30D70



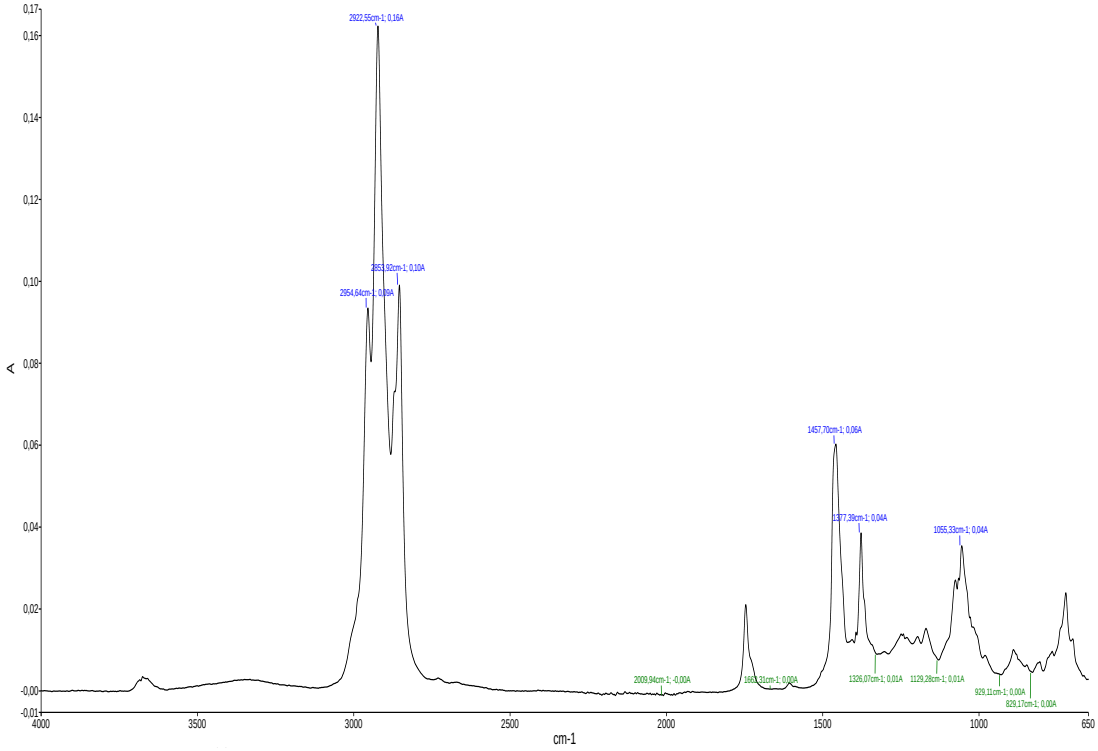
B10Oct10D80



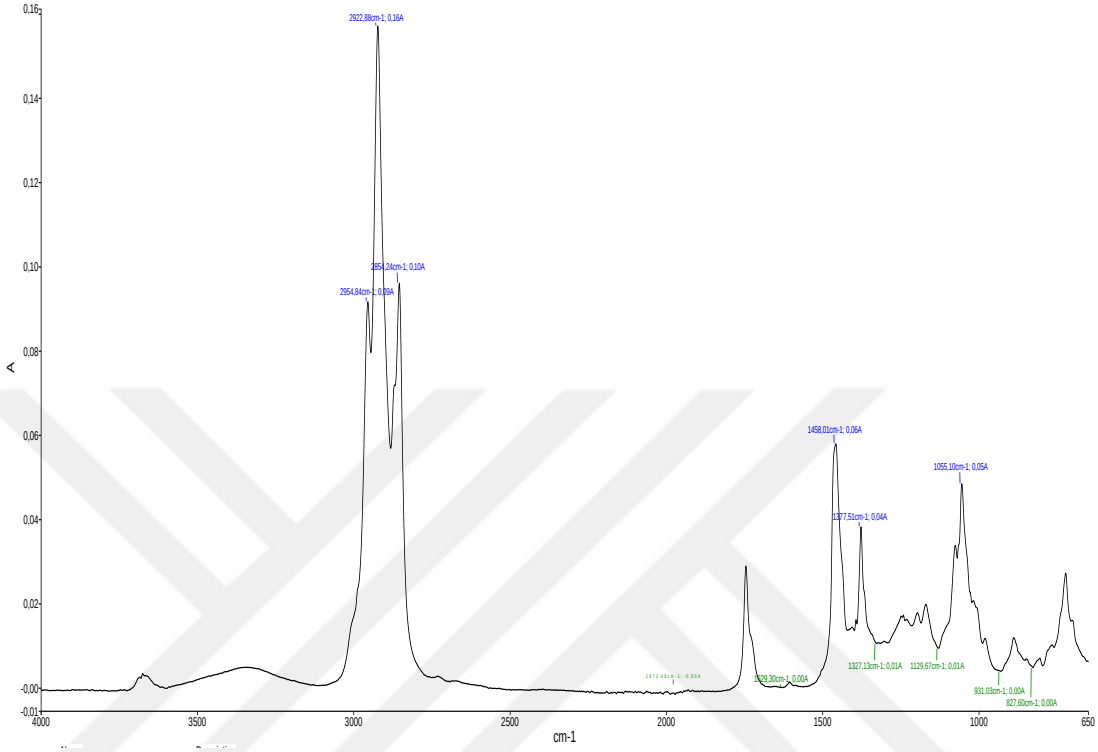
B15Oct15D70



B10Pen10D80

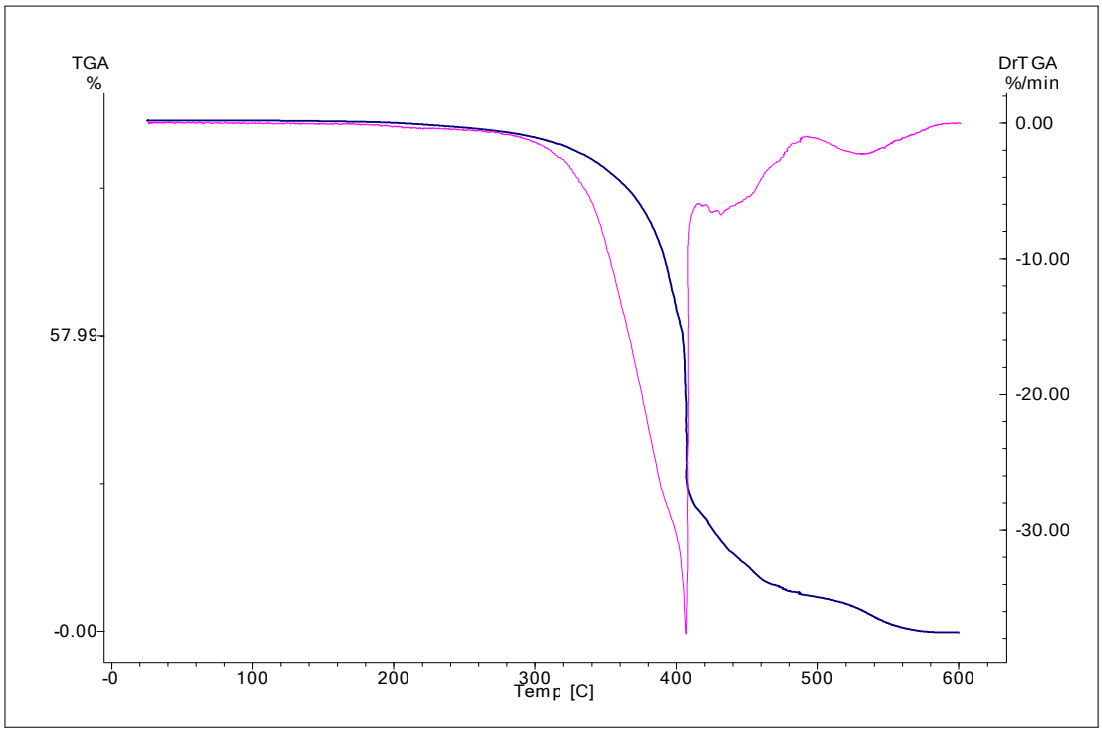


B15Pen15D70



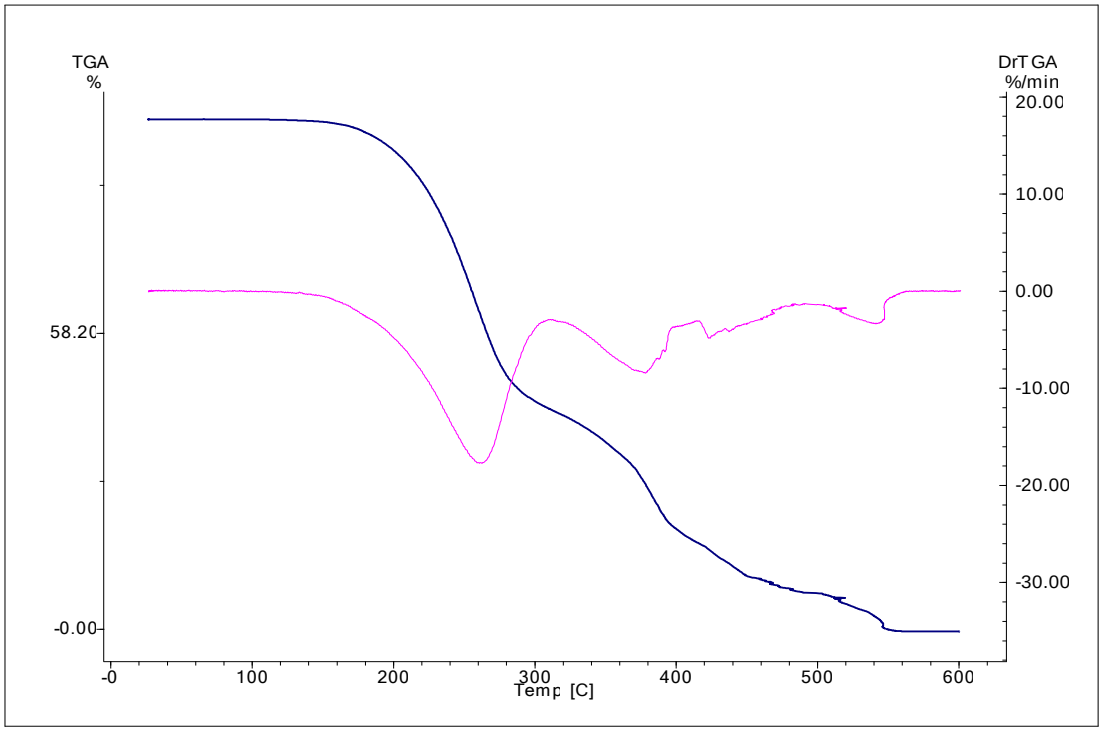
APPENDIX (B)

WCO



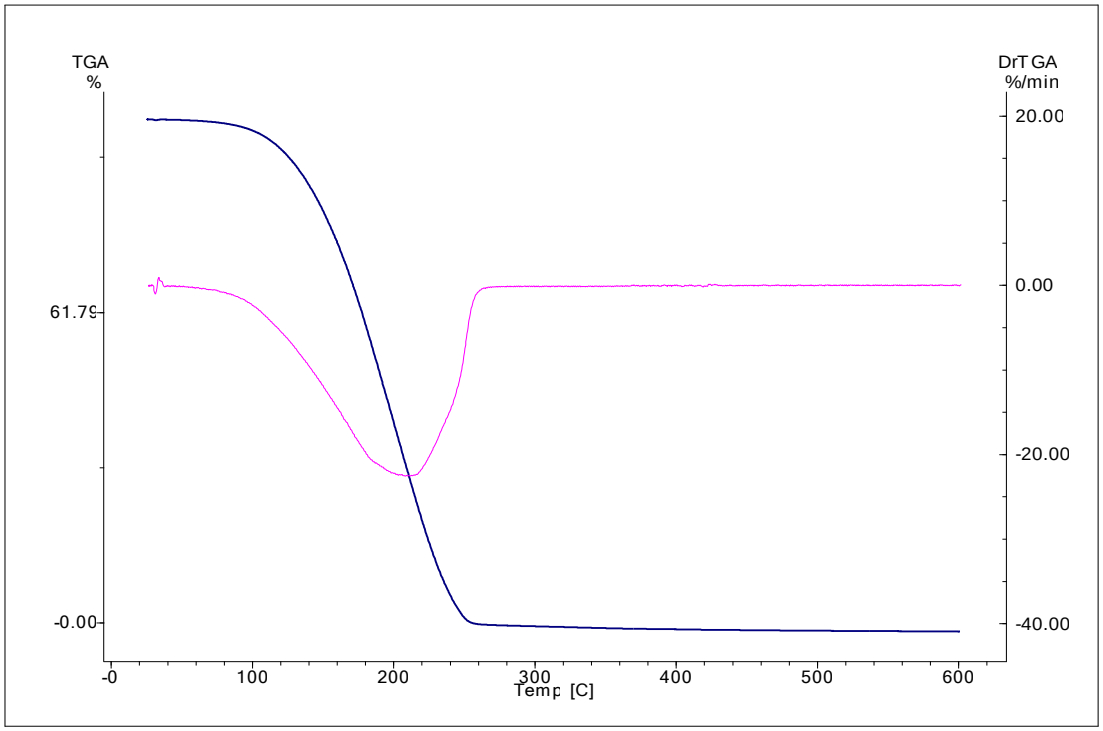
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
WCO	10	335.4	210-580	98.8

WCOME



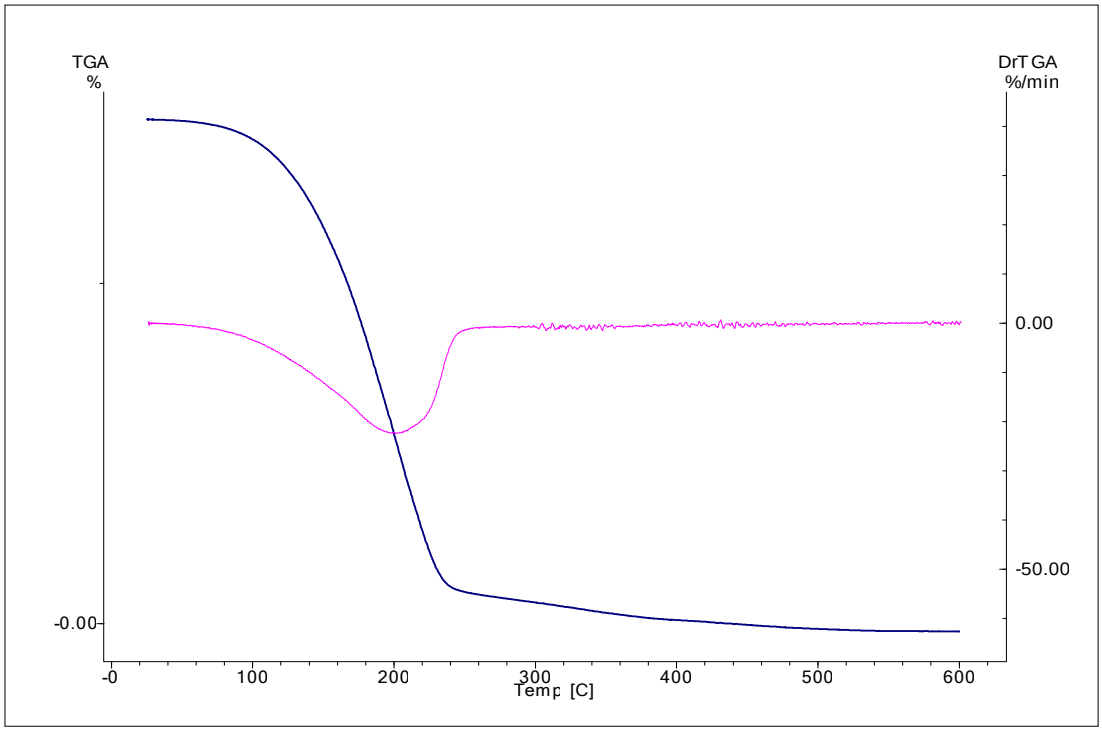
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
WCOME	10	191.9	175-550	98.8

D100



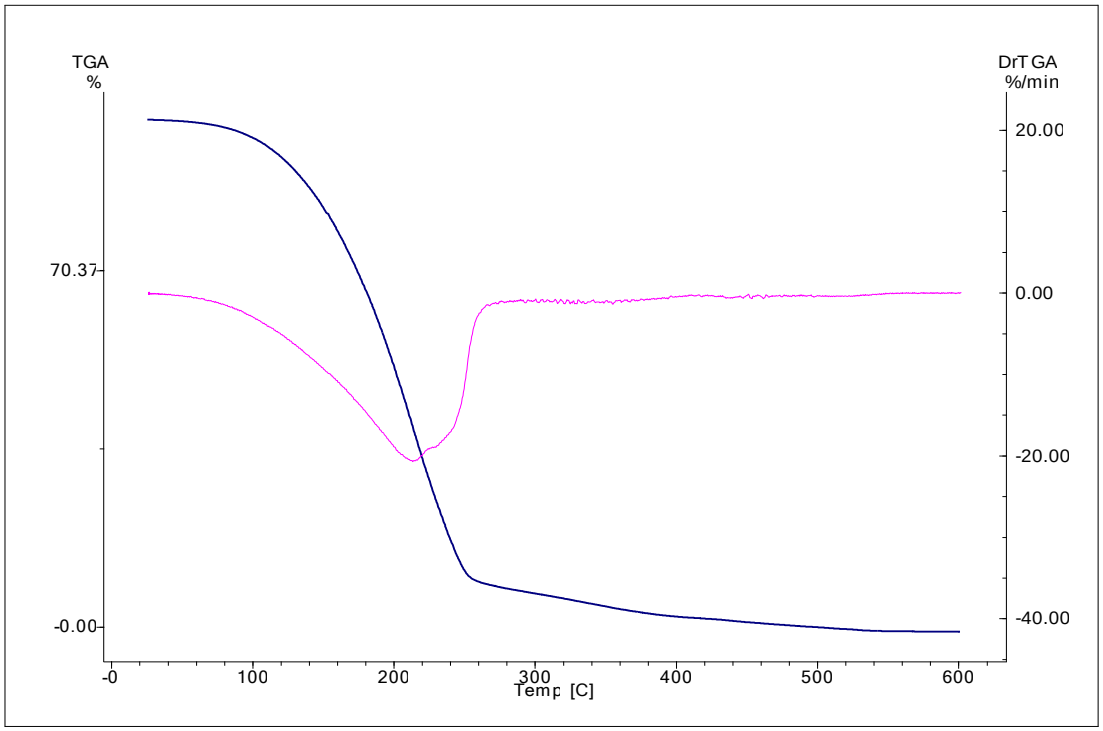
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
D100	10	121.4	110-380	98.8

B20D80



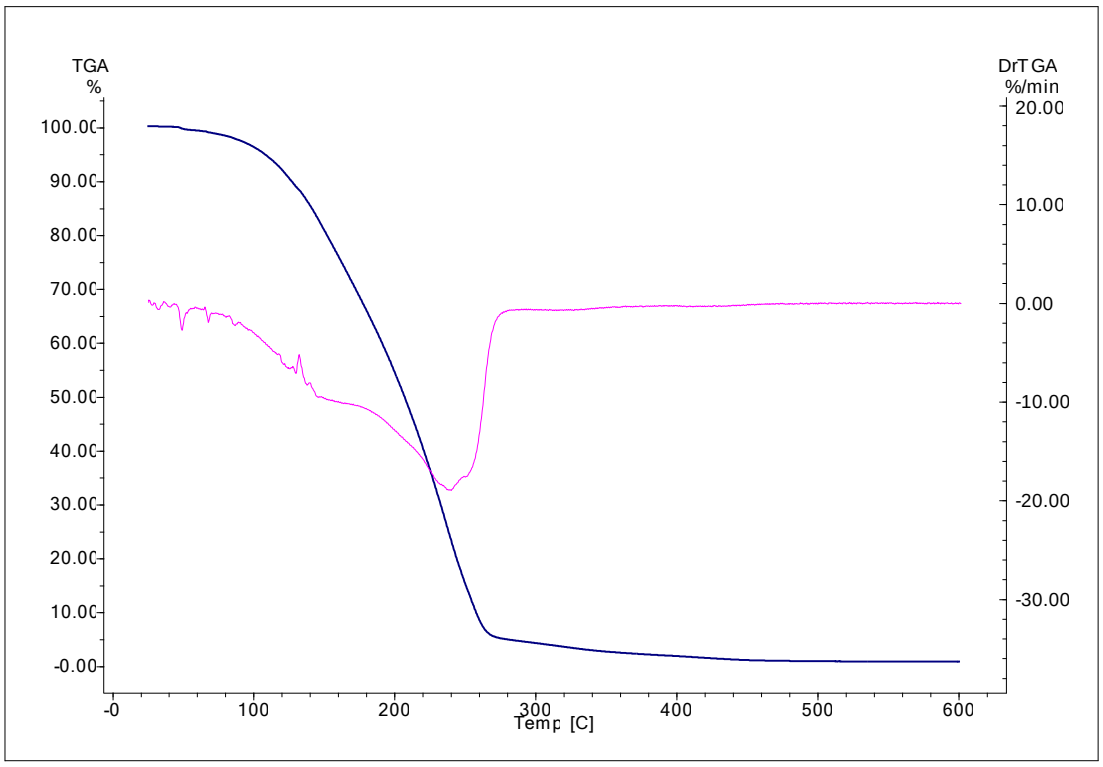
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B20D80	10	89.8	70-370	97.6

B30D70



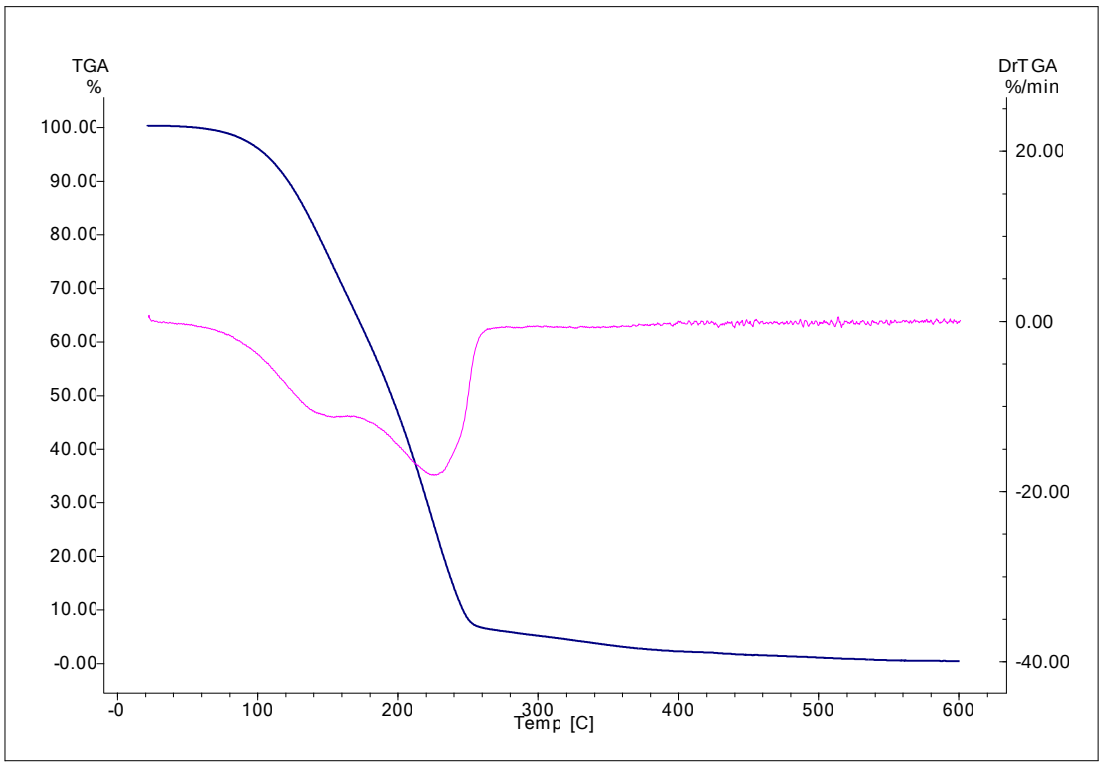
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B30D70	10	117.1	96-380	95.6

B10Oct10D80



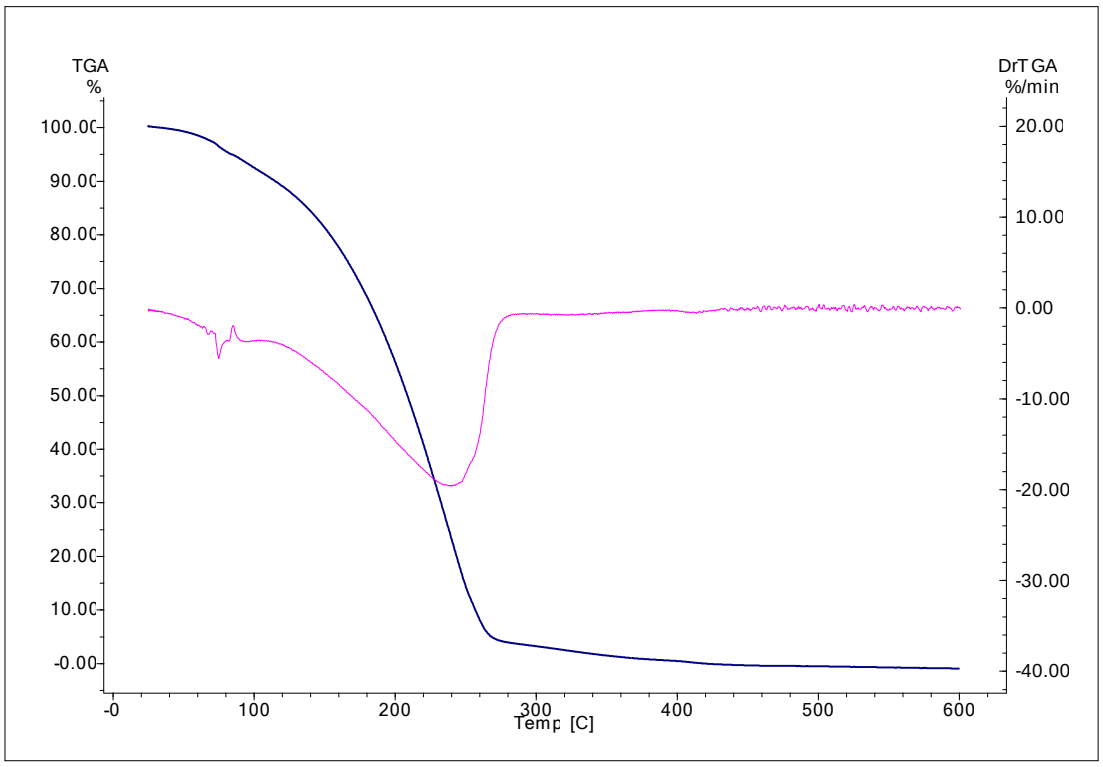
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B10Oct10D80	10	45-340	113.3	97.3

B15Oct15D70



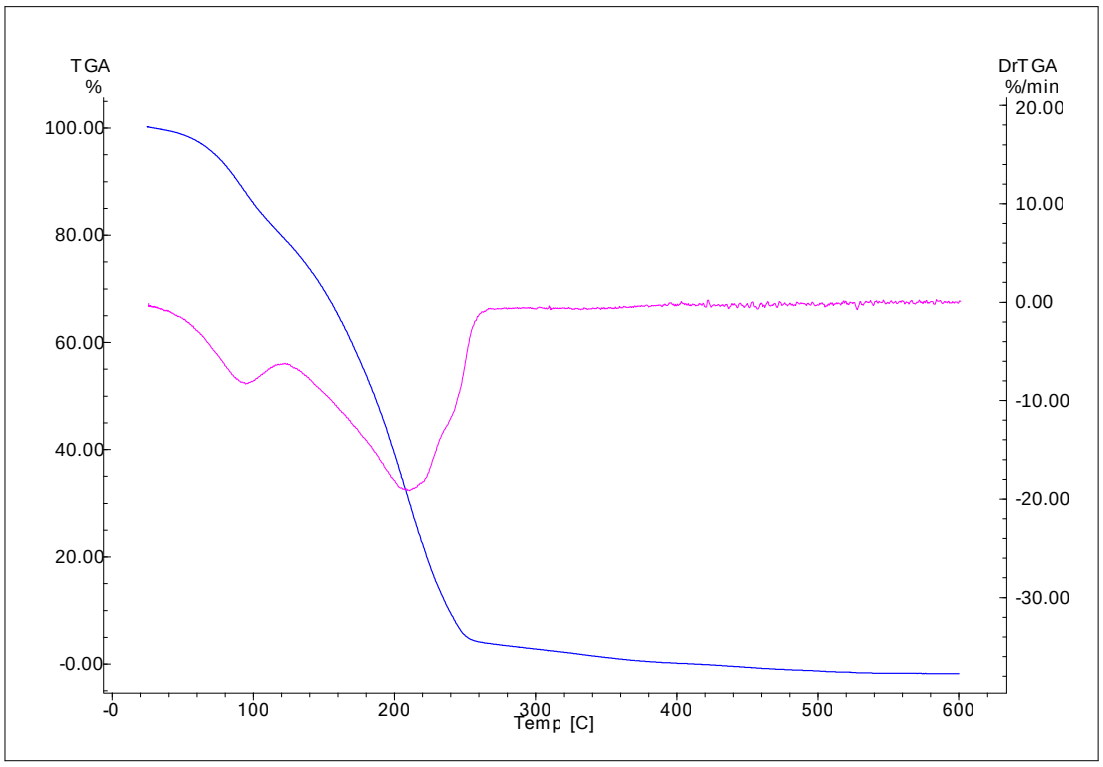
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B15Oct15D70	10	80-350	92.1	95.5

B10Pen10D80



Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B10Pen10D80	10	50-350	95.7	97.3

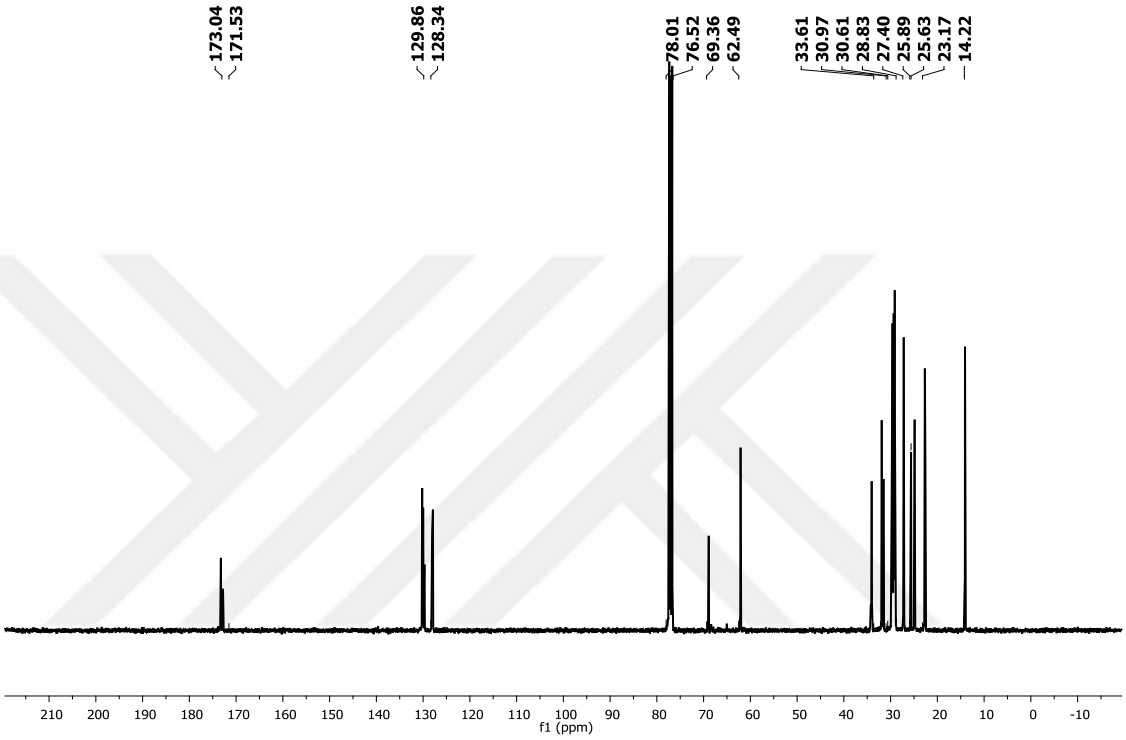
B15Pen15D70



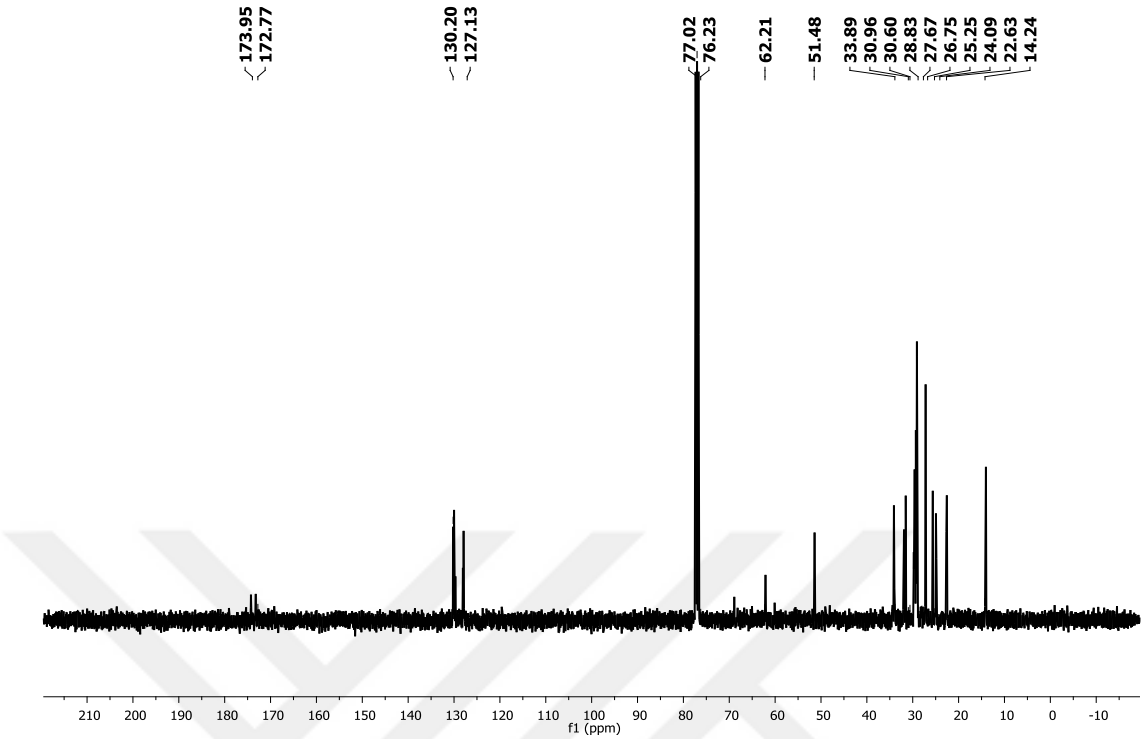
Sample name	Heating rate (°C/min)	Temperature Ranges (°C)	Onset temperature for thermal degradation (°C)	Mass loss under dry air (%)
B15Pen15D70	10	72.5	50-340	95.9

APPENDIX (C) NMR

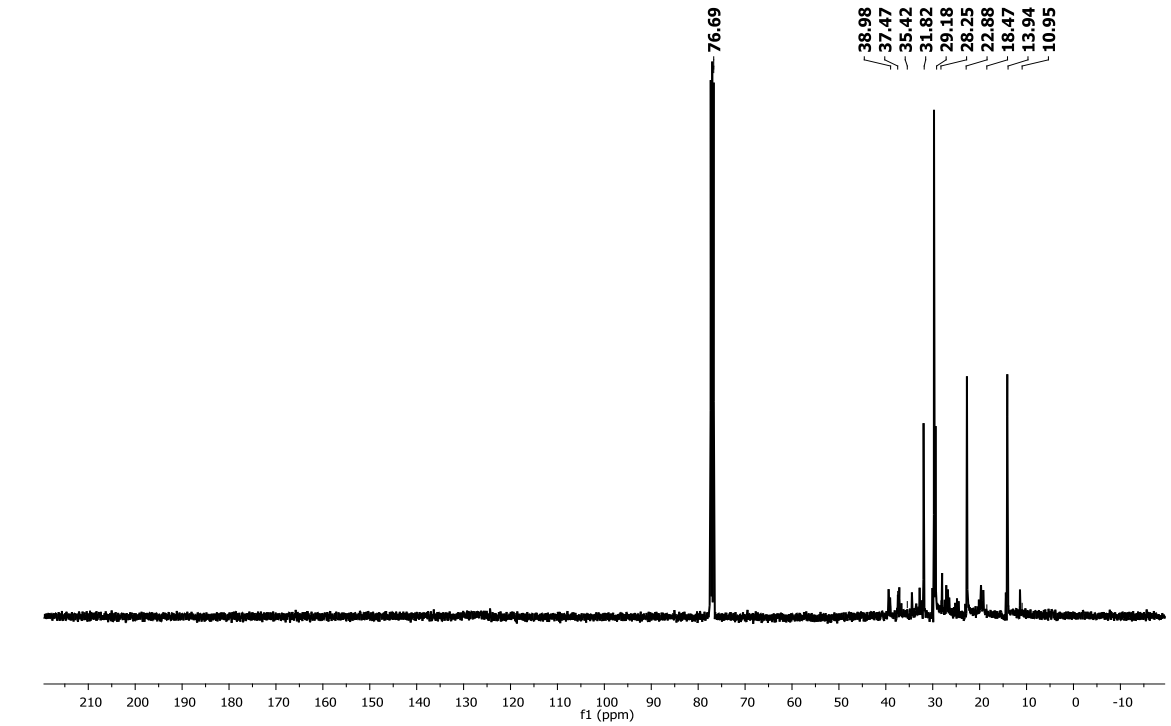
WCO



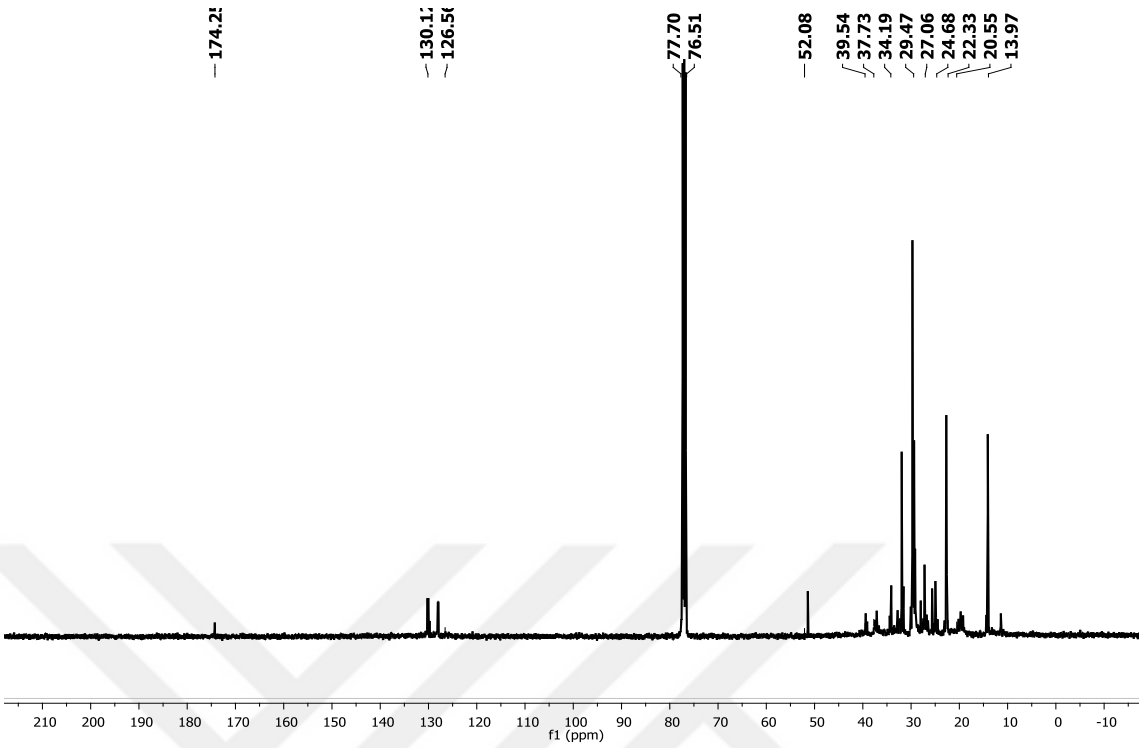
WCOME


173.95
172.77
130.20
127.13
77.02
76.23
62.21
51.48
33.89
30.96
30.60
28.83
27.67
26.75
25.25
24.09
22.63
14.24
f1 (ppm)

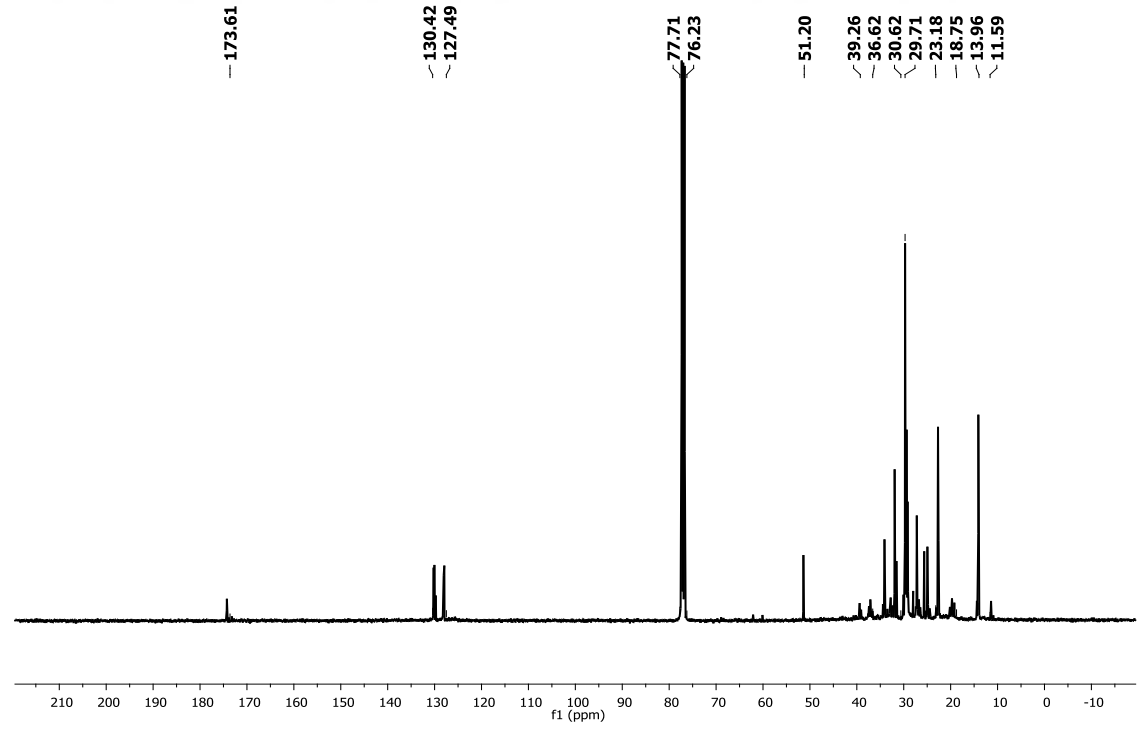
D100


76.69
38.98
37.47
35.42
31.82
29.18
28.25
22.88
18.47
13.94
10.95
f1 (ppm)

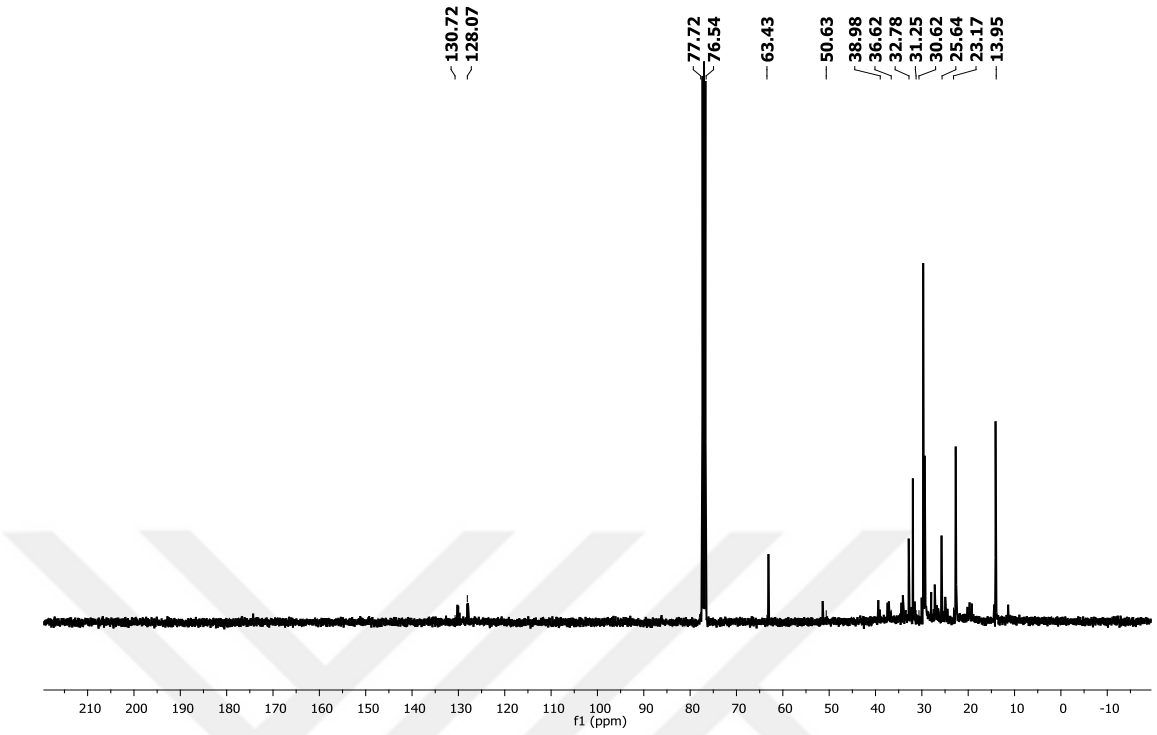
B20D80



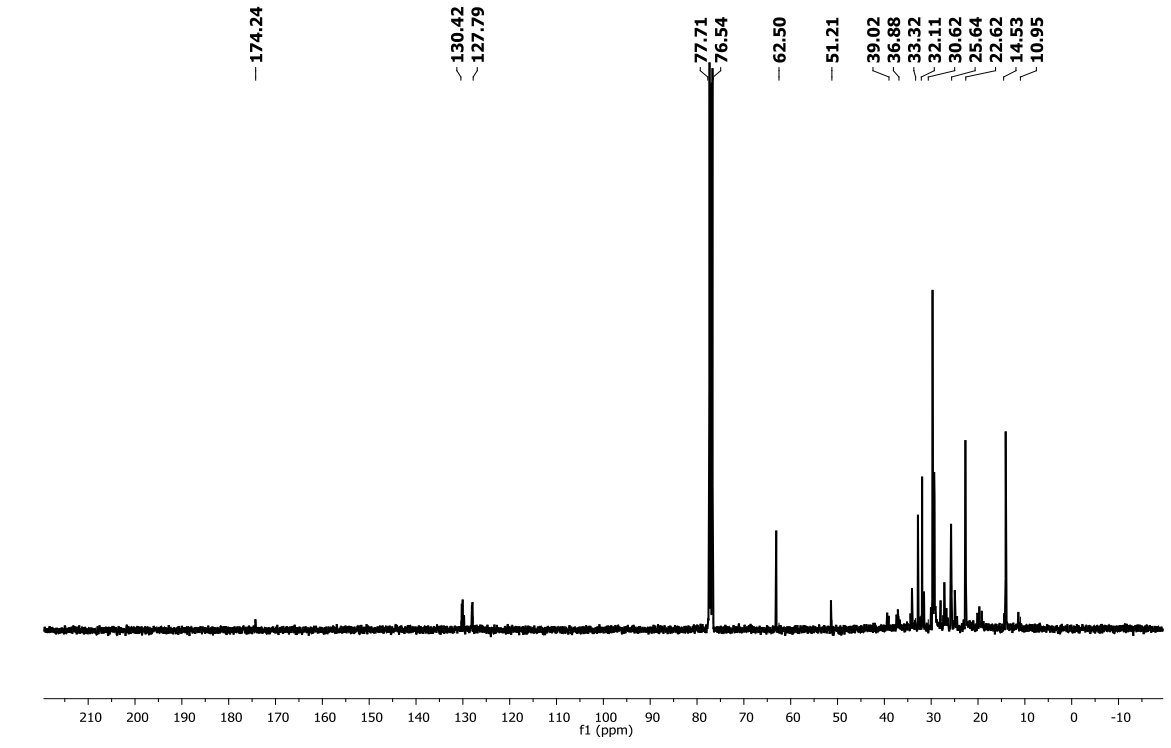
B30D70



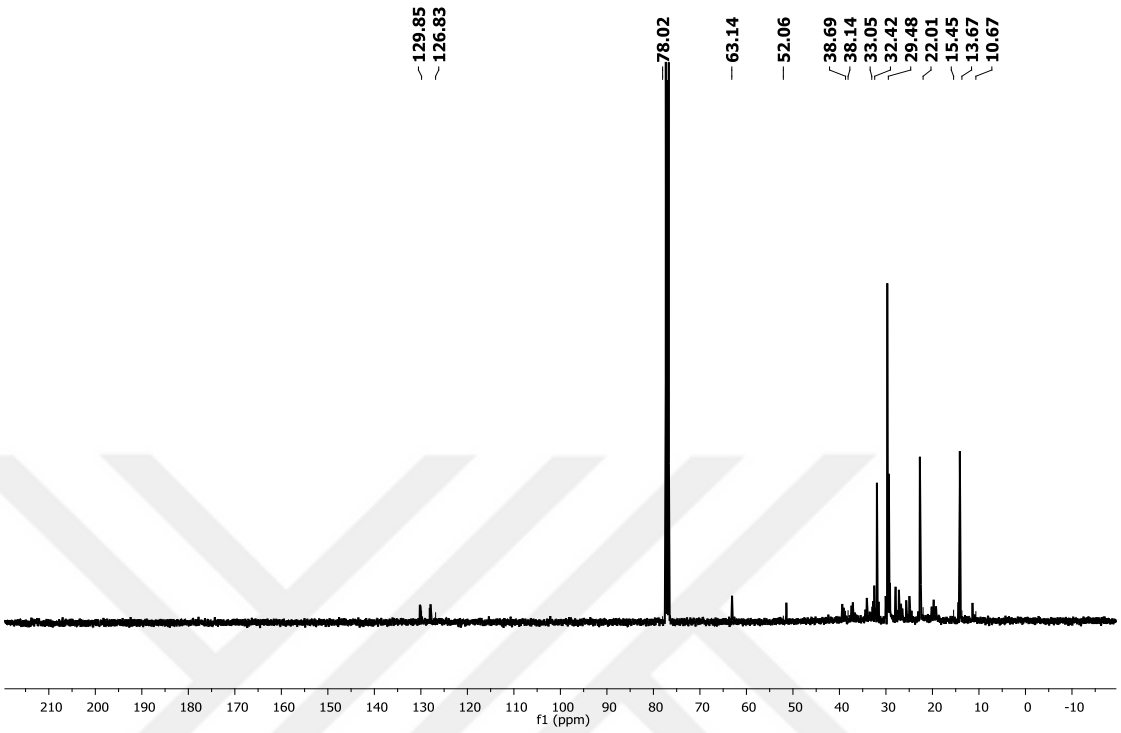
B10OCT10D80



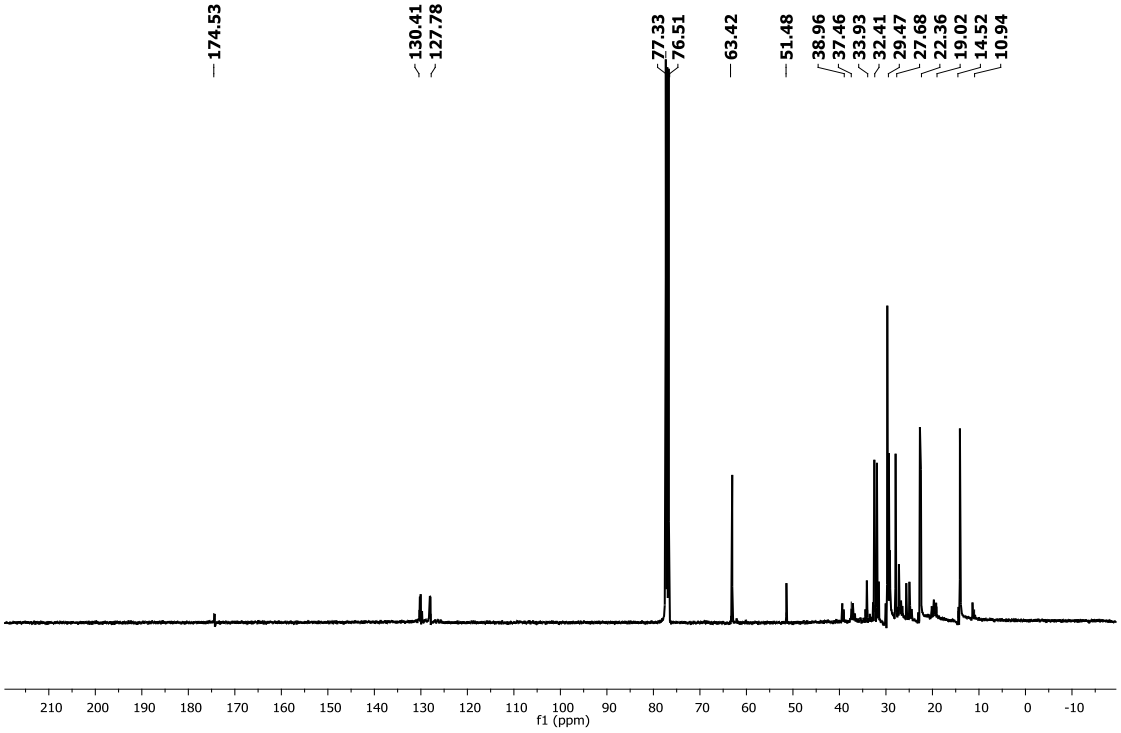
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B10Pen10D80

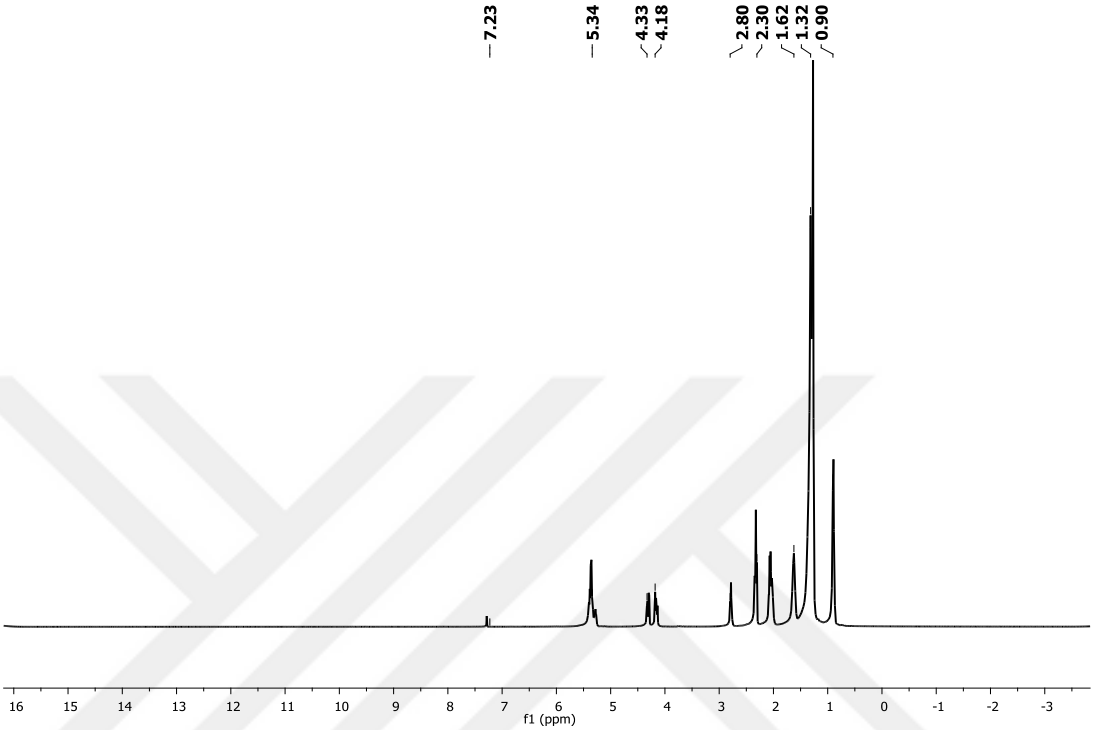


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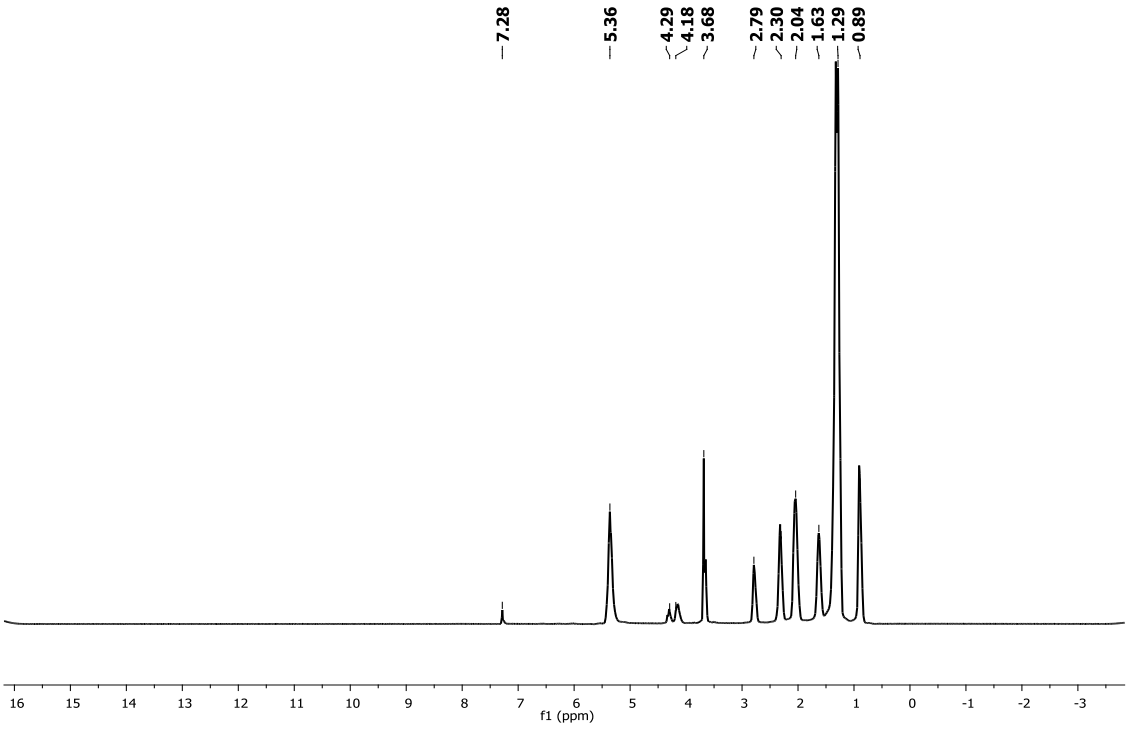


APPENDIX (D) H NMR

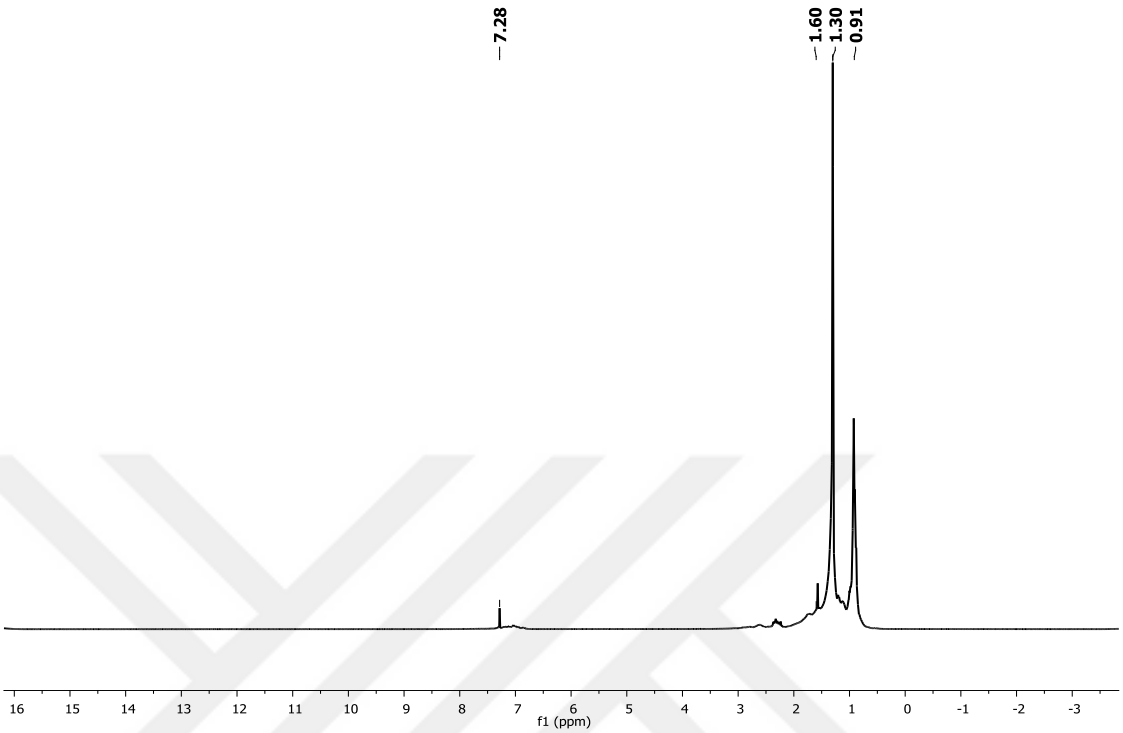
WCO



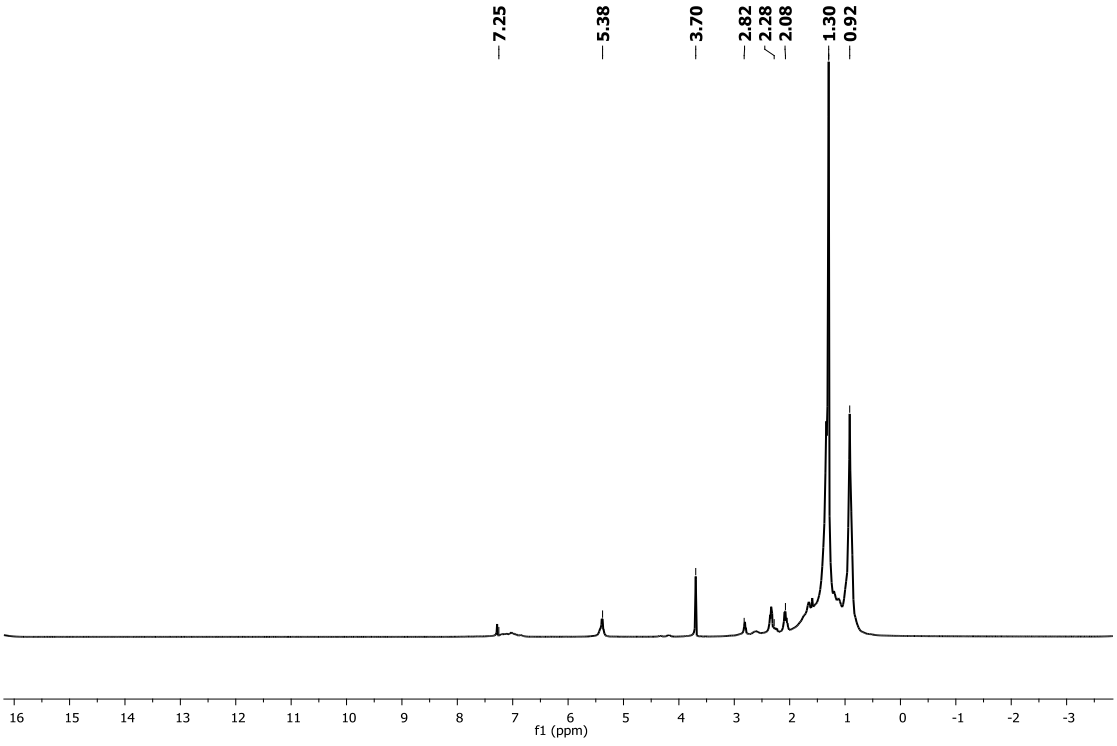
WCOME



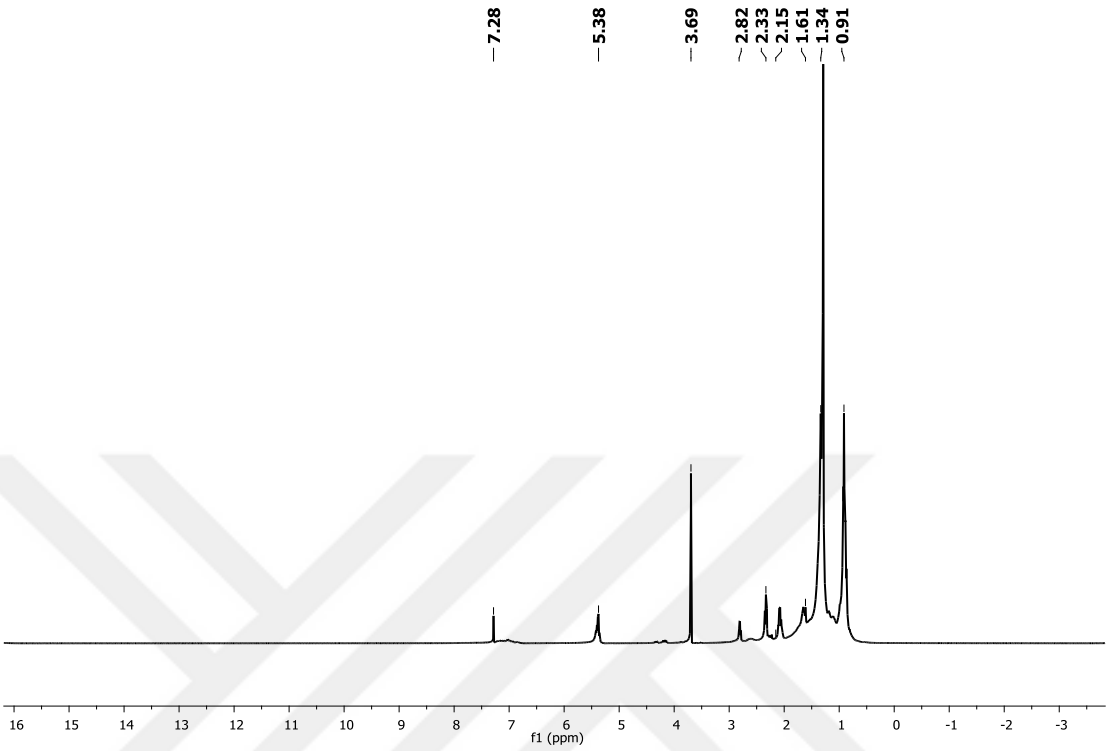
D100


7.28
1.60
1.30
0.91
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

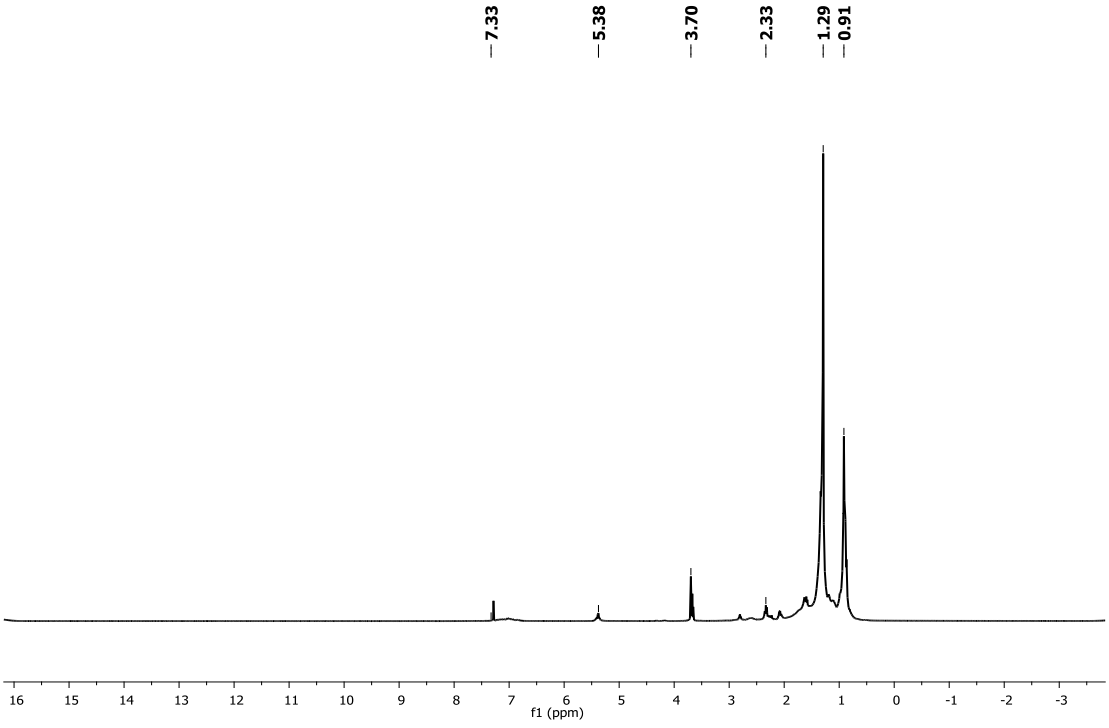
B20D80


7.25
5.38
3.70
2.82
2.28
2.08
1.30
0.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

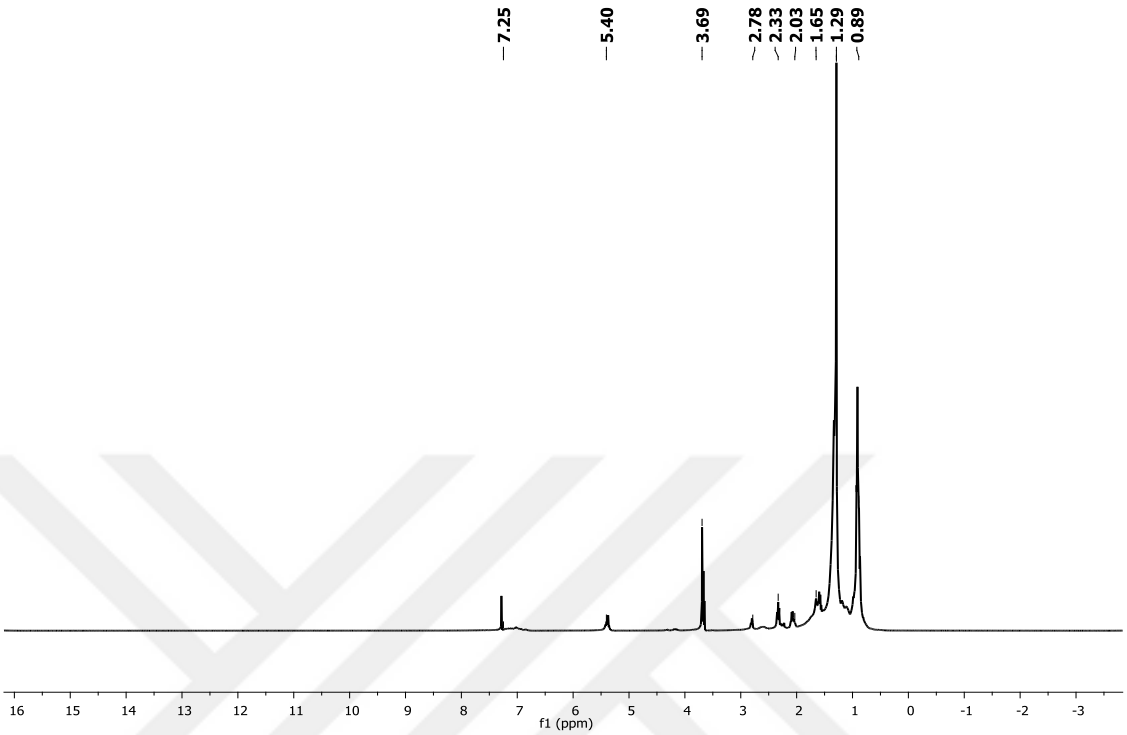
B30D70



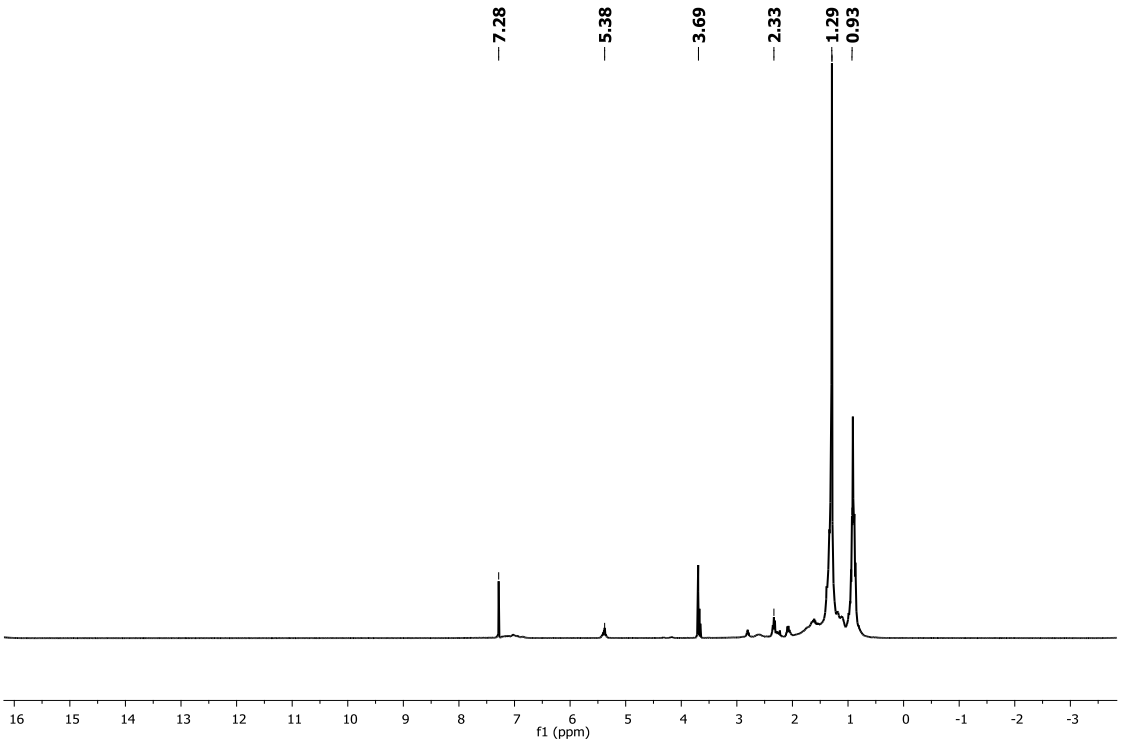
B10Oct10D80



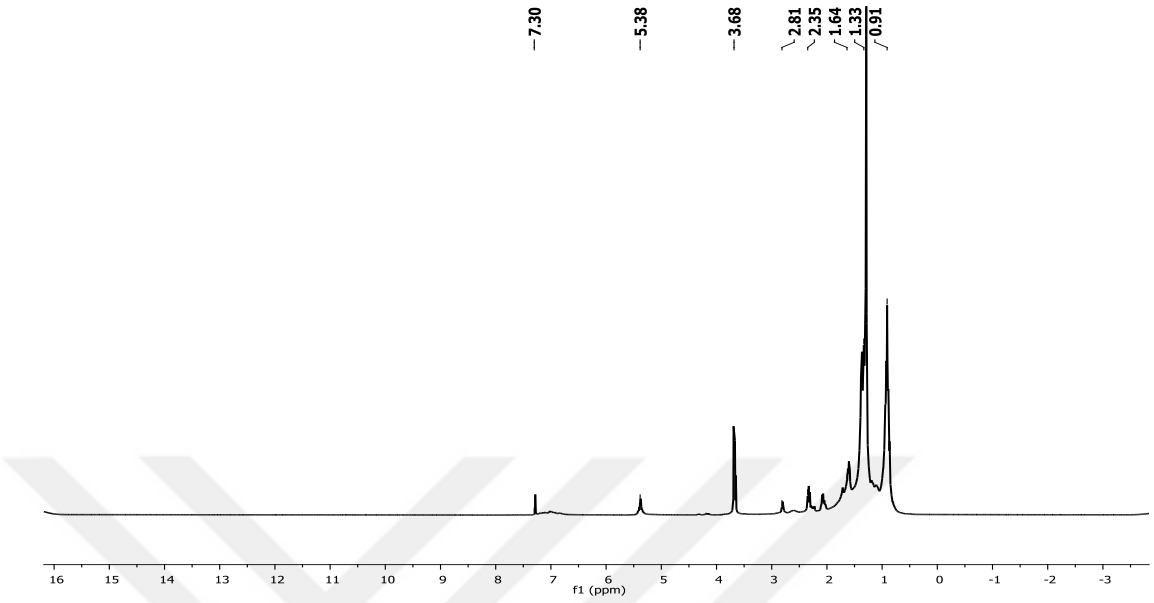
B15Oct15D70



B10Pen10D80

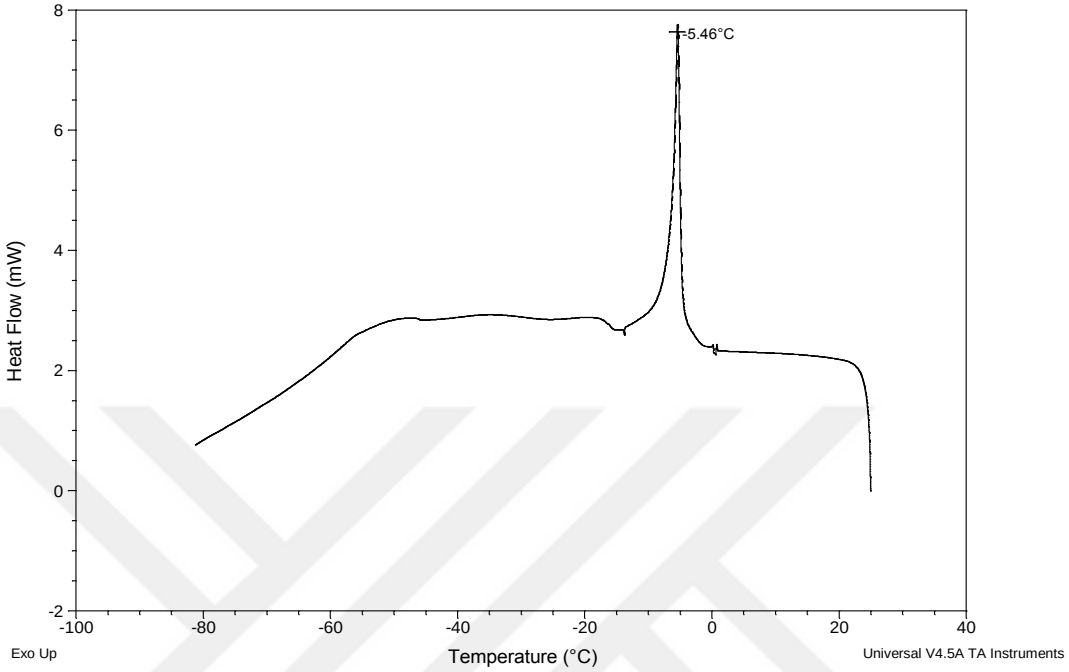


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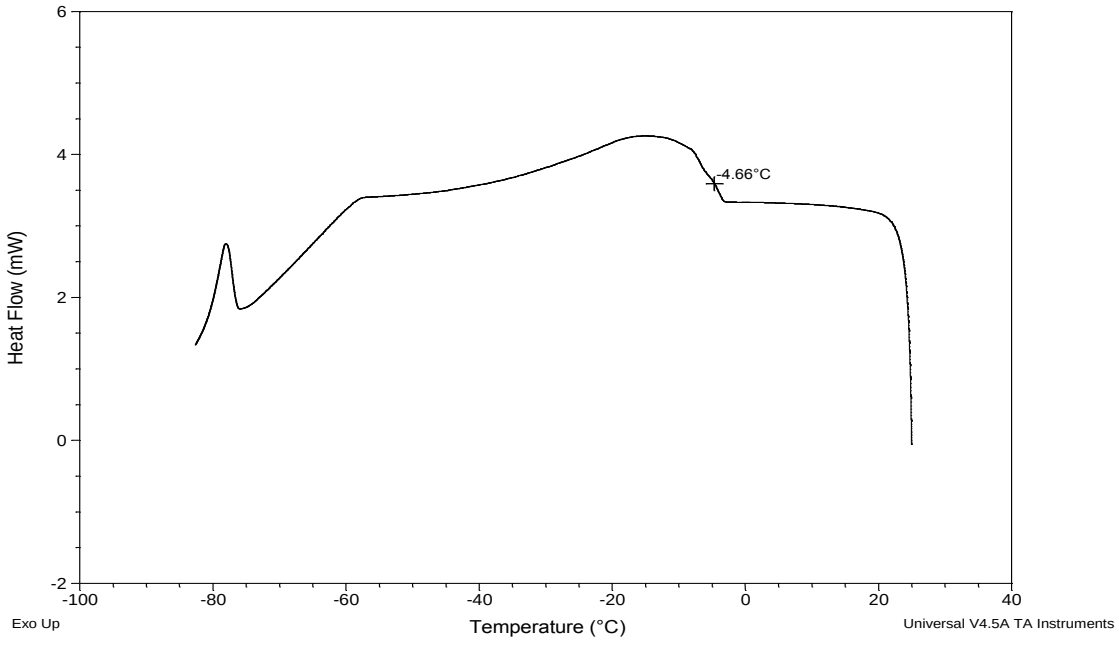
APPENDIX (E) DSC

WCO



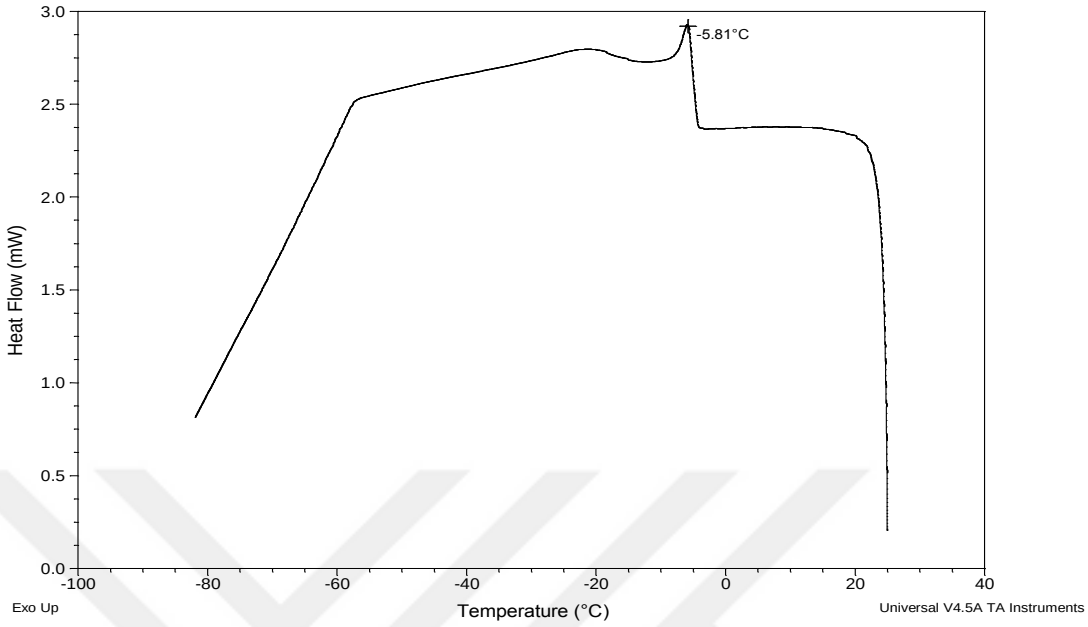
Sample	Crystallizations onset temperature (°C)
WCO	-5.46

WCOME



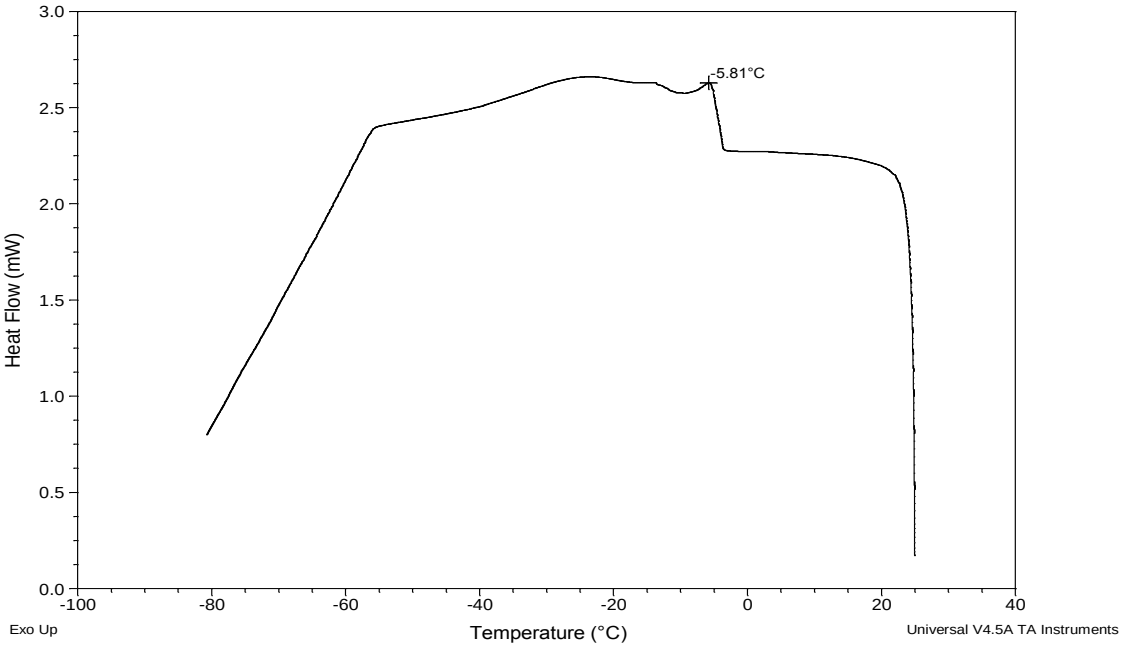
Sample	Crystallizations onset temperature (°C)
WCOME	-4.66

D100



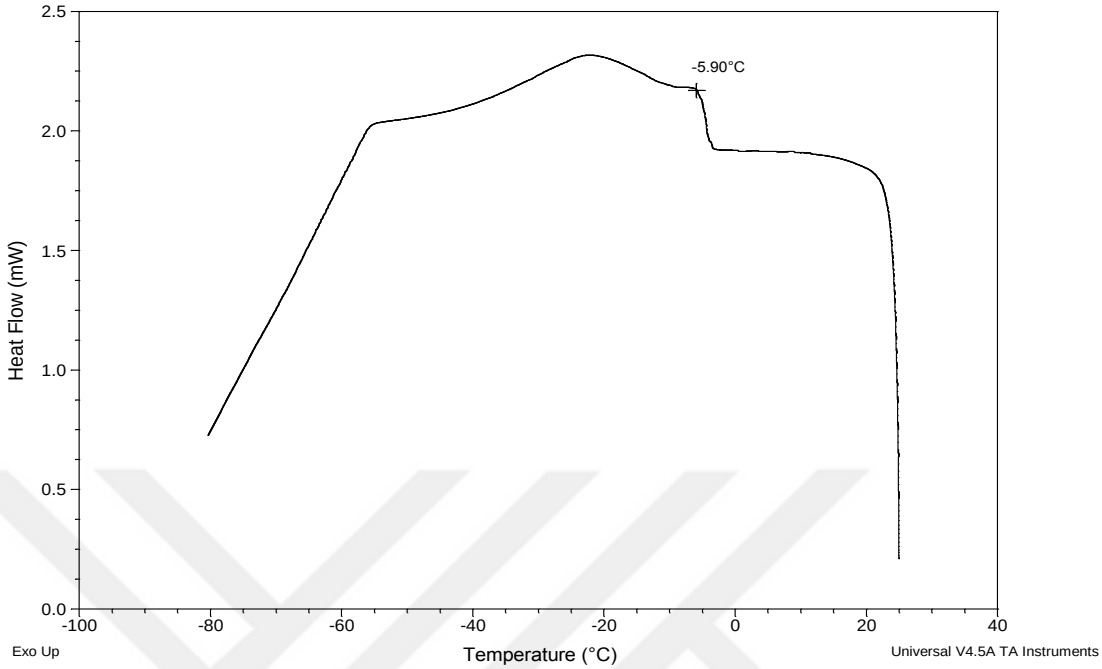
Sample	Crystallizations onset temperature (°C)
D100	-5.81

B20D80



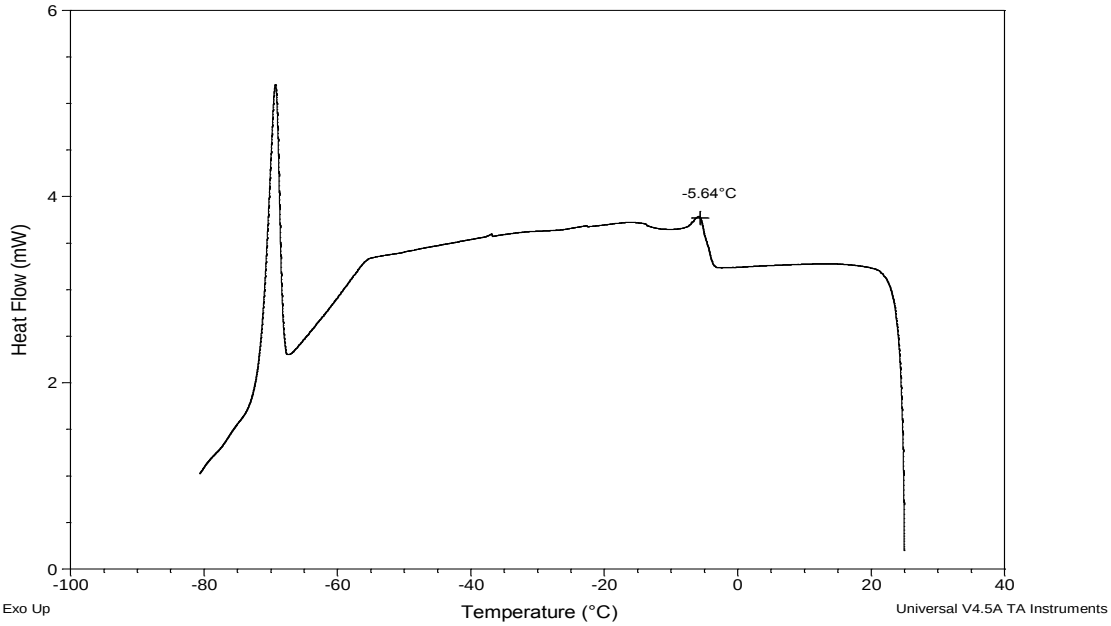
Sample	Crystallizations onset temperature (°C)
B20D80	-5.81

B30D70



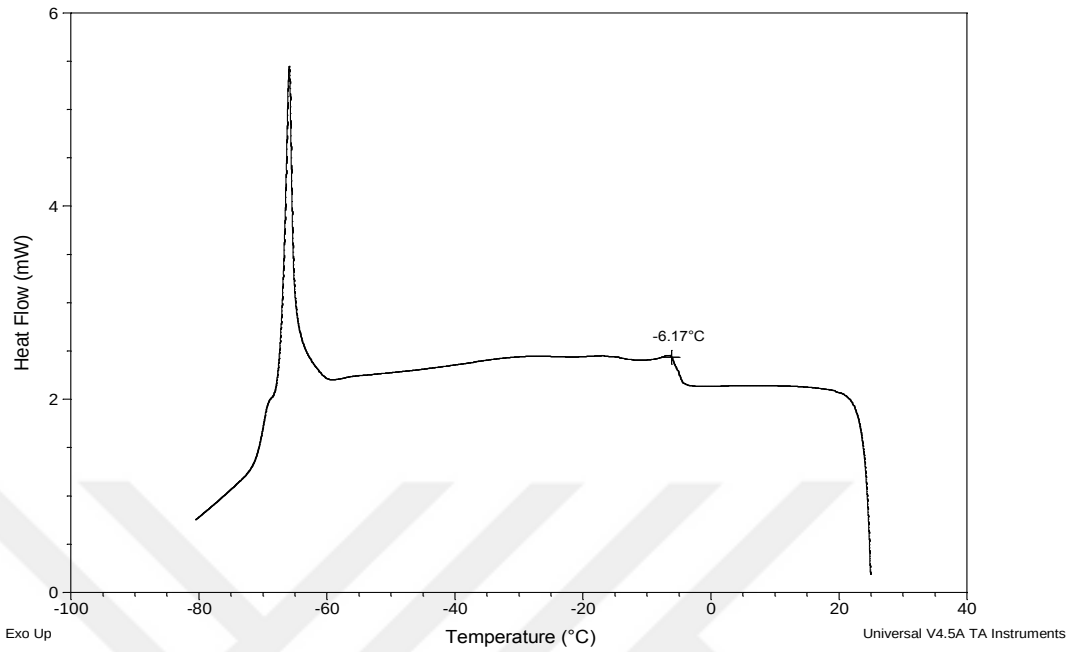
Sample	Crystallizations onset temperature (°C)
B20D80	-5.90

B10Oct10D80



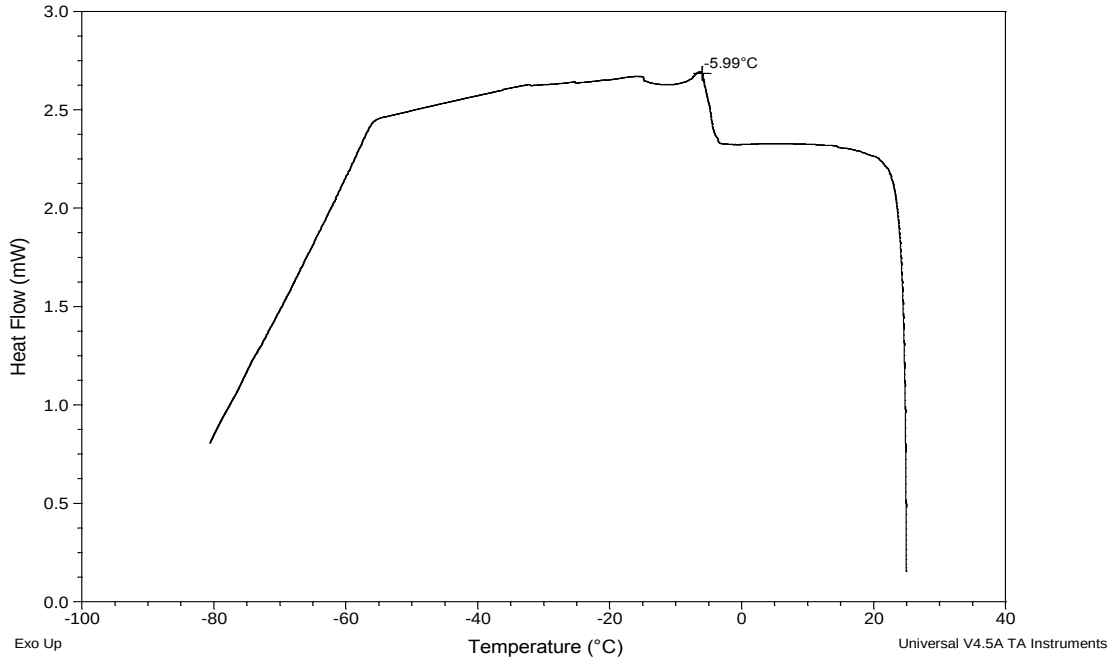
Sample	Crystallizations onset temperature (°C)
B10Oct10D80	-5.64

B15Oct15D70



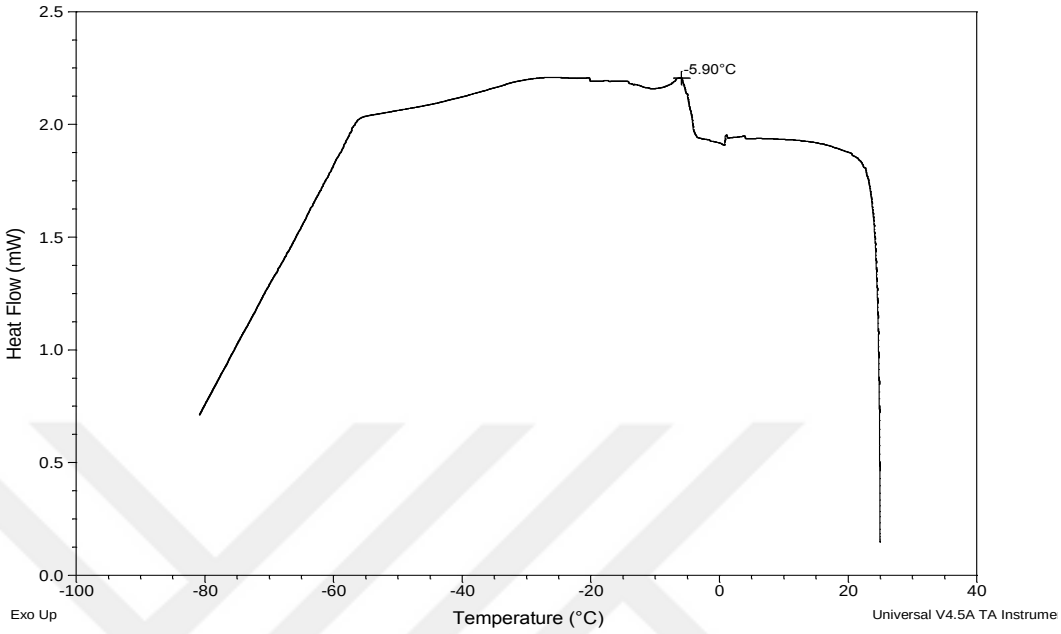
Sample	Crystallizations onset temperature (°C)
B15Oct15D70	-6.17

B10Pen10D80



Sample	Crystallizations onset temperature (°C)
B10Pen10D80	-5.99

B15Pen15D70



Sample	Crystallizations onset temperature (°C)
B15Pen15D70	-5.90

CURRICULUM VITAE

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EDUCATION

Degree	Institution	Date of Graduation
MSc	Erciyes University	2019
Undergraduate	Al-Mustansirya University	2001
High school	Bagdat High School	1995

Languages

Arabic, English, Turkish