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Ph.D. in Mechanical Engineering

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**UNIVERSITY OF GAZİANTEP
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**EXPERIMENTAL INVESTIGATION OF EFFECTS
OF THE FUELS PRODUCED FROM WASTE TIRES
ON ENGINE PERFORMANCE AND EXHAUST
EMISSIONS**

**Ph.D. THESIS
IN
MECHANICAL ENGINEERING**

**BY
ABDULKADİR AYANOĞLU
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**Experimental Investigation of Effects of The Fuels
Produced From Waste Tires on Engine Performance and
Exhaust Emissions**

**University of Gaziantep
Ph.D. Thesis
in
Mechanical Engineering**

**Supervisor
Prof. Dr. Recep YUMRUTAŞ**

**by
Abdulkadir AYANOĞLU
May 2016**

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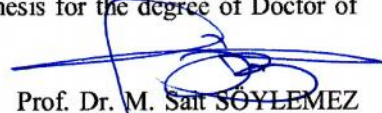
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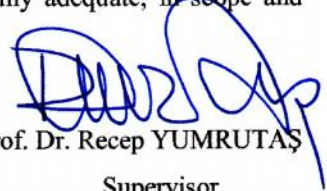
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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Abdulkadir AYANOĞLU

ABSTRACT

EXPERIMENTAL INVESTIGATION OF EFFECTS OF THE FUELS PRODUCED FROM WASTE TIRES ON ENGINE PERFORMANCE AND EXHAUST EMISSIONS

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This study focuses on the pyrolysis of waste tire by using the catalytic distillation method to obtain engine fuels by rotary kiln and batch reactors. Then each waste tire oil sample was used to pyrolyze into batch reactor. Then each waste tire oil was pyrolyzed with 2, 4, 6, 8 and 10 wt%, into batch reactor. The optimum graphic was obtained as 10 wt% CaO. Characteristics of those light and heavy fuels resembled those of gasoline (18 wt% fraction) and diesel fuel (70 wt% fraction). Characteristics of the produced fuels were named as gasoline-like fuel (GLF) and diesel-like fuel (DLF), respectively. After producing the GLF and DLF, series of tests for determining effect of the GLF and the DLF on engine performance and exhaust emission are performed using the gasoline and diesel test engines. Force, air and fuel mass flowrate to the engine, engine speed, exhaust temperature and emissions of CO, CO₂, O₂, NO, NO_x and HC for each test are measured using the fuels. It is observed that the produced GLF and DLF can be used in gasoline and diesel engines without any problem in terms of characteristics, distillation and performance tests. It is understood that the GLF and DLF increase torque, brake power, brake mean effective pressure and thermal efficiency but they decrease brake specific fuel consumption. The sulfur is decreased from 8000 to 100 ppm by oxidative desulfurization method. Costs of the GLF and DLF are obtained as US \$0.333/L and US \$0.918 /L, respectively.

Key Words:, Waste tire, waste tire oil, rotary kiln and batch reactors, pyrolysis, lime and natural zeolite additives, engine performance and exhaust emissions.

ÖZET
ATIK LASTİKLERDEN ÜRETİLEN YAKITLARIN MOTOR
PERFORMANS VE EKSOZ EMİSYONLARI ÜZERİNDEKİ ETKİLERİNİN
DENEYSEL İNCELENMESİ

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Bu çalışmada, pirolitik distilasyon yöntemi ile atık lastikten döner fırın ve kesikli reaktörlerde motor yakıtlarının üretilmesi ve üretilen bu yakıtların motor performans ve eksoz emisyonları üzerindeki etkilerinin incelenmesi amaçlanmıştır. Döner fırın ve kesikli reaktörlerden üretilen atık lastik sıvısı elde edilip Doğal Zeolit ve kireç ağ. % 2, 4, 6, 8 ve 10 kesikli reaktörde piroliz edilmiştir. Optimum distilasyon eğrisi ağ. % 10 kireç karışımıdır. Karışım distilasyon deneyine göre benzin (% 18 fraksiyon) ve dizel yakıtı (% 70 fraksiyon) karakteristikleri benzemektedir. Bu yüzden bu yakıtlar Benzin Benzeri Yakıt (BBY) ve Dizel Benzeri Yakıt (DBY) olarak adlandırılmıştır. BBY ve DBY üretildikten sonra, bu yakıtların motor performans ve emisyon testleri üzerindeki etkilerinin belirlenmesi için test motorları ile bir dizi testler gerçekleştirilmiştir. Testler sırasında motor şaftına uygulanan kuvvet, hava ve yakıt debileri, motor hızı, eksoz sıcaklığı ve emisyonlardan CO, CO₂, O₂, NO, NO_x ve HC miktarları ölçülmüştür. Yapılan karakteristik, distilasyon ve performans testlerine göre BBY ve DBY'nin motorlarda problemsiz olarak kullanılabileceği gözlenmiştir. Yapılan hesaplar sonucunda BBY ve DBY motorun torkunu, gücünü, ortalama efektif basıncını ve ısı verimini artırdığı, fakat özgül yakıt tüketimini ise düşürdüğü anlaşılmıştır. Kükürt oranı 8000 ppm'den oksidatif desulfurizasyon metoduyla 100 ppm'e düşürülmüştür. Yapılan maliyet hesaplamalarında BBY ve düşük kükürtlü DBY'nin maliyetleri sırasıyla 0.333 \$/litre ve 0.918 \$/litre olarak tespit edilmiştir.

Anahtar Kelimeler: Atık lastik, Atık lastik sıvısı, döner fırın ve kesikli reaktör, piroliz, kireç ve doğal zeolit, motor performansı ve eksoz emisyonu

To my family

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LIST OF SYMBOLS

WT	waste tire
WTO	waste tire oil
NZ	natural zeolite
CaO	lime
TG	thermogravmetric
dTG	derivative thermogravmetric
HHV	higher heating value
FT-IR	fourier transform-infrared spectroscopy
BET	brunauer-emmett-teller
GC-MS	gas chromatography–mass spectroscopy
GF	gasoline fuel
DF	diesel fuel
GLF	gasoline like fuel
DLF	diesel like fuel
HDS	hydrodesulfurization
LSDLF	low sulfur diesel like fuel
ODS	oxidative desulfurization
SI	spark ignition engine
CI	compression ignition engine
P_b	brake power
T	brake torque
Bmep	brake mean effective pressure
Bsfc	brake specific fuel consumption
V	volt
V_d	total volume of engine cylinders
m_f	fuel mass flow rate
n_r	number of crank revolutions
EGT	exhaust gas temperature

Q_{LHV}	lower heating value of the fuel
NO	nitrogen monoxide
NO_x	nitrogen oxides
CO	carbon monoxide
CO_2	carbon dioxide
O_2	oxygen
SO_2	sulfur dioxides
SO_4	sulfate
PM	particulate matter
HC	unburned hydrocarbon
HCl	hydrochloric acid
H_2O_2	hydrogen peroxide

Greek Symbols

η_{bt}	brake thermal efficiency
ω	brake angular speed

CHAPTER 1

INTRODUCTION

1.1 Introduction

Energy is a fundamental source for development of the world. Today, world's energy needs are mostly satisfied from fossil fuels such as oil, coal and natural gas. The growing consumption of fossil resources has caused to research alternative resources in the world and Turkey as well [1]. Turkey's energy necessity has increased unexpectedly and is expected to continue to grow due to immigration and urbanization. Moreover, half of the energy imports are from other countries.

Thus, a large number of research activities have been presented in the literature about alternative energy sources. Here, an important alternative is the various waste resources, which include oils, trees, plastics, tires and so on. Unfortunately, these emphasized waste energy sources cannot be directly used in engines. Before that they must be reprocessed into the international fuel standards so that their negative effects on environment and other creatures can be reduced.

A large quantity of waste resources emerges everyday around our living environment. For example, tires are significant waste energy resources. Every year, many tires are disposed into the environment. Each year approximately 242 million tires are disposed of in the United States, which corresponds to nearly one tire per US citizen per year [2]. Along the next decades, Turkey will be disposing 180,000 tons of waste tires [3]. The rate of waste tire recycling does not keep pace with the rate of new tire generation. Turkey's legislation of waste tire (26.11.2006) is similar to EU's wastes hierarchy which states that they should be prevented from waste, if not possible, wastes should be re-used, recovered and recycled, or deposited at stockpiles [4-5]. The waste tire volume comprises 80% of the total waste tires generated, which are disposed of in stockpiles. These tire stockpiles relate with many

problems such as increases in mosquito and rodent populations, long-term tire fires, and illegal tire dumping. On the other hand, these problems can be effectively reduced via proper recycling applications. As a result, the idea of generating a recycling method for the development of new products is crucial, affordable and has plentiful resources.

Waste tire is cheap to use in recycling or other industrial applications as: land filling, recoating of wheel, aggregate for buildings and especially fuel for boiler, pulp and paper mills, cement manufacturers, stoker boilers, and rotary kilns [6]. Besides, waste tire has a significant calorific value as 12,000-16,000 BTU/lb which can be used as an alternative fuel to coal, natural gas and standard petroleum fuels [7].

1.2 The scope of this study

Waste tires have to be converted to useful products for using as energy sources by thermal conversion. It has burning, gasification, pyrolysis and liquefaction methods. The most efficient and friendly method to environment is pyrolysis which will be discussed deeply at next chapters.

The objective of the study focused on producing liquid similar to standard petroleum fuels. The results from the research have been compared with literature and are very promising for future works.

The scope and outline of the Ph. D. study is organized as follows:

In Chapter 2, a literature survey is done in this chapter under four sub-titles: Introduction, recycling of waste tire, sulfur removing process, engine performance and exhaust emissions.

In Chapter 3, general information is given about fuel production system and testing procedure of waste tire and its derivatives. Rotary Kiln and Batch Pyrolysis Unit and their equipments are explained with technical properties. In this scope, control and measurement components were installed on the Batch Pyrolysis Unit which was

founded at Motor Laboratory, Mechanical Engineering Department, University of Gaziantep. Rotary Kiln Pyrolysis Unit was installed at Kudret Inkar Co., Adıyaman.

The characteristics of the waste tire and its derivatives were analyzed by density, distillation, flash point, viscosity, calorific value, moisture content, copper strip tarnish test, cold filter plugging point bath, cold filter plugging point bath, sulfur, ultimate analysis, proximate analysis, thermogravimetric analysis, infrared spectrometry analysis and gas chromatography-mass spectrometry analysis. The testing procedure of pyrolysis were investigated by the effects of catalysts, reaction time and temperature on the yields of explosion. The Instrumental Analysis was tested by linear regression and uncertainty analyses. The accuracy of test results has to be reliable and consistency. The performance and emission parameters of gasoline and diesel engine were explained deeply. The latter parameters such as brake power, brake mean effective pressure, brake specific fuel consumption, brake thermal efficiency and carbon monoxide, carbon dioxide, nitrogen monoxide, nitrogen oxides, oxygen, sulfur dioxide, unburned hydrocarbon.

In Chapter 4, products of pyrolysis are explained and also instrumental analysis is calculated for accuracy of distillation and engine tests. The pyrolysis of waste tire by using the catalytic distillation method to obtain engine fuels by rotary kiln and batch reactors. Then each waste tire oil sample was used to pyrolyze into batch reactor. At first step, waste tire is pyrolyzed in a rotary kiln reactor to obtain more gas, light liquid, heavy liquid, wax products, and less carbon black at their maximum yields as, 20%, 12%, 25%, 8% and 35% of the total weight (4 tones), respectively. Then, the heavy and light oils are reacted with additives such as natural zeolite (NZ) and lime (CaO) at different mass ratio as 2, 6 and 10 wt%, respectively, in the batch reactor to produce liquids similar to standard petroleum fuels. The heavy and light oils mixture samples are distilled to observe their optimum graphics which are similar to gasoline and diesel like fuel. Consequently, the best results are obtained from the CaO sample with 10 wt% in comparison to the ones from the gasoline and diesel fuels. At second step, the waste tire oil product that had a 40% ratio was produced with 42% char, while the remaining 18% was released into the atmosphere as a gaseous by product. The waste tire oil was mixed with two additives, namely natural zeolite and lime, at different mass ratios. Each fuel sample was exposed to pyrolytic

distillation to obtain light and heavy fuel products. Characteristics of the as-produced fuels were determined and their distillation tests were investigated. As a result of these tests, the lime mixture fuel sample at 10 wt% ratio showed the best results, acquired the optimum distillation temperatures and was close to diesel fuel. This mixture was categorized as light and heavy fuels according to its distillation test results. Characteristics of those light and heavy fuels resembled those of gasoline and diesel fuel. Fractions of the as-produced fuels were 18 wt% of waste tire oil for the light fuel, and 70 wt% for the heavy fuel. The other product was 12 wt% of residues. As a consequence of pyrolysis, results of batch reactor samples were closer than rotary kiln reactor to standard petroleum fuels. Characteristics of the produced fuels were named as gasoline-like fuel (GLF) and diesel-like fuel (DLF), respectively.

In Chapter 5, gasoline engine performance and exhaust emission tests are done for GF, GLF, GF-GLF Mixtures and GLF-Turpentine Mixtures. The engine performance and emission of spark ignition (SI) engine were tested by burning gasoline fuel (GF), gasoline-like fuel (GLF) (the 18 wt% of waste tire oil (WTO) produced from 10 wt% Lime-WTO mixture, the mixture of GF and GLF with the amounts of 10 wt%, 20 wt%, 30 wt% and the blends of GLF and Turpentine with the amounts of 10 wt%, 20 wt%, 30 wt%. During the experiments, performance parameters such as brake torque (T), power (P_b), brake mean effective pressure ($Bmep$), brake specific fuel consumption ($Bsfc$), and brake thermal efficiency (η_{bt}) were tested. Furthermore, the exhaust gas temperature (EGT) and the engine emission parameters such as, nitrogen monoxide (NO), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and unburned hydrocarbon (HC) were analyzed. The GLF added into GF has increased the P_b , T , $bmep$, and η_{bt} values, and conversely, the $bsfc$ value was decreased with the increasing amount of GLF in GF. Also, the EGT of GF was increased as well. Furthermore, the CO_2 , NO and NO_x were increased, while CO was decreased. And also, the HC and O_2 values were increased by adding GLF into GF. The increased Turpentine amount in GLF caused an increase in P_b , T , $Bmep$, η_{bt} values; however it caused a decrease in $Bsfc$ value. The EGT was increased incrementally in the engine. Besides, the CO_2 , NO and NO_x were increased, while CO was decreased. The HC and O_2 were also increased by adding more Turpentine.

In Chapter 6, diesel engine performance and exhaust emission tests are done for DF, DLF and LSDLF. Diesel-like fuel (DLF) produced from waste tire oil (WTO) is used in the Diesel engine to obtain effect of the DLF on the engine performance and its emissions. The performance characteristics such as engine torque, engine power, brake specific fuel consumption (Bsfc), exhaust temperature and the emission parameters such as oxides of nitrogen (NO_x), sulfur dioxides (SO_2), carbon monoxides (CO) and total unburned hydrocarbon (HC) are tested. The DLF is obtained by using pyrolytic distilling unit that consists of a reactor, condenser, filters, collector, thermocouple and an electronic panel. Characteristics of the DLF such as viscosity, density, heating value, flash point, sulfur and distillation are also tested. Many of the physical and chemical properties and distillation curves for the DLF are seen to be similar to diesel fuel. The performance results which are engine torque, engine power, and Bsfc are also quite close to those of Diesel fuel. Brake thermal efficiency decreases while Bsfc increases for the DLF. It can be concluded that the DLF can be used in a diesel engine as a fuel without any problem.

After producing the DLF, oxidative desulfurization (ODS) method was used to obtain lowest sulfur amount. Different parameters were optimized such as acid types, acid-hydrogen peroxide molar ratios, temperature, time, ratio of water and acetonitril washing and duration time of extraction. The sulfur was decreased from 8000 to 100 ppm after the treatment of ODS. Characteristics of the low sulfur diesel-like fuel (LSDLF) such as viscosity, density, heating value, flash point, sulfur and distillation are also tested. The physico-chemical properties and distillation curves for the LSDLF are seen to be similar to diesel fuel. The performance results which are engine torque, engine power, and Bsfc are also quite close to those of diesel fuel. thermal efficiency decreases while Bsfc increases for the LSDLF. As a consequence, the LSDLF and a diesel fuel were burned in a diesel engine to investigate their effects on engine performance and emission parameters. Performance and emission of the fuels were tested for each sample without any problem.

In Chapter 7, the GLF, DLF and LSDLF costs were calculated by using such parameters as fuel production process, raw materials and chemicals costs with energy consumption.

In Chapter 8, conclusions and recommendations are pointed out for future studies. Less energy and reaction duration were needed to decrease cost of GLF and LSDLF. Instead of electricity, natural gas or coal was need to use. A new desulfurization methods was need to used for decreasing DLF cost. Unit production costs of GLF and DLF can be decreased via using different energy sources.

CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

Used polymer products are increasing every year and vehicle tires compose most of them in the world. Namely, approximately 17 million tons of used tires are produced each year [4]. A tire contains more than 100 heterogeneous components. The main components are vulcanized rubber, rubber filler, rubberized fabric, steel cord, fillers like carbon black or silica gel, sulfur, zinc oxide, processing oil, fabric belts, steel wire-reinforced rubber beads, and etc. A typical major tire composition is shown at Table 2.1 [8].

Table 2.1. The distribution of tire components [8].

Tire components	wt%
Natural rubber	15-19
Carbon black	24-28
Synthetic rubber	25-29
Steel cords	9-13
Textile cords	5-6
Chemical additives	14-15

Tires have been designed to the demands of consumers. A typical tire cross-section is shown at Figure 2.1 [8].

The fundamental compositions of tires are similar to each other. However, rubber structure compounds can change according to formulas of carbon and hydrogen as hydrocarbons. Single-double monomers of carbon-hydrogen bonds have been repeated from 1,000 to 20,000 for high molecular structure of polymer.

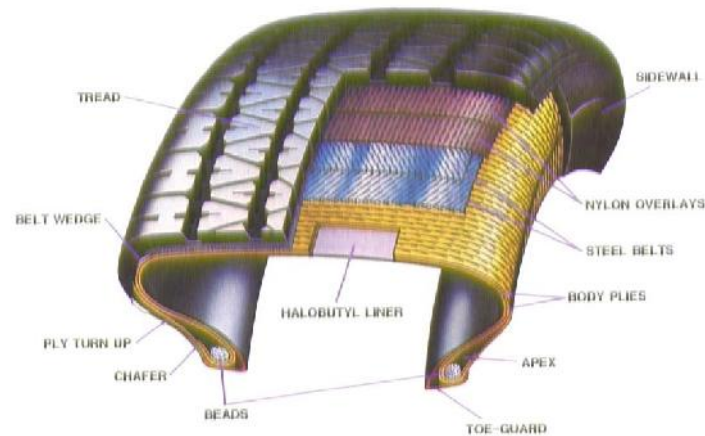


Figure 2.1. A typical tire cross-section [8].

2.2 Recycling of Waste Tire

Waste tire require to convert high energy products such as gas, liquid and solid by thermal decomposition, shown at Figure 2.2 [9].

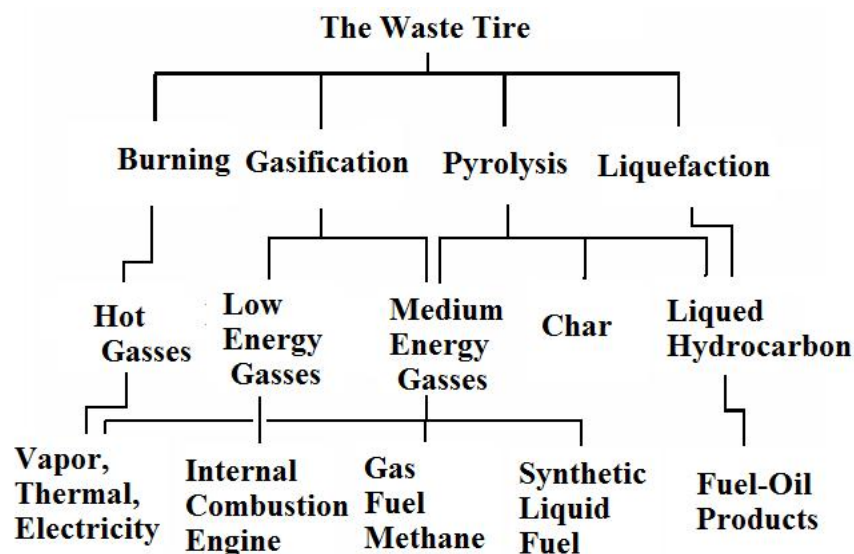


Figure 2.2. Thermal conversion of waste tire [9].

Waste tire is converted in three types of thermal conversion: burning, gasification and pyrolysis. The difference between these processes is related with condition of methods and finalproducts. The burning process generates heat for system for all of the components. The gasification process aims to produce high yield, and mainly low-molecular-weight gas at high temperature with air, oxygen, or steam from char and tars [10].

The pyrolysis process goals to convert waste to useful and upgraded, higher value fuel, chemicals, and other parts. Pyrolysis is a kind of thermal decomposition method process by means of high temperature, in an oxygen-free condition. The process is the total of many parallel and subsequent reactions. The reactions have been completed up to equilibrium. The organics transform into volatile material and solid residue under thermal cracking, and some of the volatile fractions can be condensed as liquid. The gas fraction contains hydrogen, methane and carbon oxides, liquid fraction contains water, tar and oils (organic compounds), and char contains fixed carbon and ashes (metals, oxides and inert matter) [11–13].

In the last decade, pyrolysis of waste tires has received a renewed attention since the process may be optimized to produce some high quality fuels and products. Waste tire has five products: oil, released gas, char, residual steel products, and others. All these products have the potential to be reused. The released gas has adequate calorific value [14-15].

The yield and compositions of products (gas, liquid and solid) have been affected from such parameters as Reactors (fixed bed, screw kiln, rotary kiln, vacuum and conical reactors etc.), Pyrolysis (slow, fast, catalytic and co-pyrolysis etc.) and other values (temperature, heating rate, pressure, residence time, particle size, carrier gas flow rate, and type etc.) [16].

There are pyrolysis technologies available for high yield products. The type of reactor influences the heat transfer process, product distribution, and processing capacity. All these characteristics have a remarkable effect on the pyrolysis process. For example, a higher heating rate breaks bonds to increase liquid yields, even residence time increases the char yield [16].

The slow pyrolysis gives an idea for decomposition of polymer under low temperatures with long residence time for more product yield such as coke, tar and other products. The fast pyrolysis is contrary to slow pyrolysis which decomposed into short time at rapid higher heating rates. The catalytic pyrolysis is given to any pyrolytic reaction by using catalytics (Y-type and ZSM-5) to increase single ring aromatic compounds as benzene, toluene and the m-, p- and o-xylenes [16].

The waste tire pyrolysis related with various technologies and process conditions will be shown in following literature studies:

Shredded tires (mixtures from trucks, tractors, and cars) have a 5 mm average size, a mass flow rate of 3.5, 6 and 8 kg/h, are pyrolyzed at auger reactor at 600, 700 and 800°C, by nitrogen gas flow (11.4, 68.4 and 144 LN/h), respectively. The reaction time was changed from 1.5 to 5 min. As a result of 600 and 800 °C pyrolysis temperature; solid, liquid and gas fractions were of 40.6 wt%, 39.0 wt%, and 41.0 wt%, and also 41.0 wt%, 27.5 wt%, and 31.5 wt%. The temperature and mass flow rate influence the pyrolysis process due to volatile residence time at the reactor [17].

Different types of waste tire pieces (25x30 mm²) were treated at fixed bed reactor at 500 °C, 10 °C/min heating rate for 1 hour. Consequently, the average fraction yields of solid, liquid and gas were 37.9, 60.1, 2.4 wt%, respectively. Thus, the gas composition and aromatic compounds of liquid fraction is verified due to tire types [18].

2–3 cm wide waste tire was exposed at fixed bed reactor under nitrogen gas at a flow rate of 1 L/min at a temperature of 300 °C and 700 °C. The best result was observed at 500 °C as liquid, gas and solid fractions were 38.0, 17.2 and 44.8 wt%, respectively. At high temperature of pyrolysis, liquid characteristics did not change extremely [19].

The waste tires with sizes of 2, 4, 8 and 12 cm³ were pyrolyzed at fixed bed reactor under 8 L/min nitrogen gas, at a temperature range from 375 °C to 575 °C. The best result was obtained at 475 °C, for 4 cm³ size feedstock for which the liquid yield was 49 wt%. Besides, the gas yield increased from 8 to 18 wt% and also the char yield decreased as temperature was increased. The physical properties were similar to the properties of diesel fuel. However, the higher sulfur amount and lower flashpoint were a problem [20].

The waste tires with two particle sizes of 0.32 mm and 0.8 mm were pyrolyzed at circulating fluidized bed reactor, under a slight vacuum of 103 °C/s and the reaction time was around 1–5 s. The best results were observed at 450 °C. As the vaporization

residence time increased from 1 to 5 s, the liquid and char decreased while the gas increased slightly [21].

Shredded automobile tire diameters were changed from 0.2 to 1.6 mm² which pyrolyzed in a fixed bed reactor under the nitrogen gas at a 75 cm/min flow rate. The pyrolysis temperature was at 350 °C and 700 °C with a heating rate of 5 and 20 °C/min for 30 min. By increasing temperature, char yield decreased and gas yield increased but liquid fraction yields stayed approximately constant [22].

Shredded scrap tires with sizes of 13–15 mm were pyrolyzed continuously at rotary kiln reactor that the system feed at a range of 12 and 15 kg/h. The pyrolysis temperature ranged from 450 °C to 650 °C and pressure was between (negative) -10 and -20 Pa. As a result, by increasing temperature, the char remained constant around 40 wt%. However, liquid yield increased at a maximum level of 45.1 wt% at 500 °C [23].

Chinese car tires with a size range of 20–60 mesh were pyrolyzed at a fixed bed reactor by adding NaOH catalytic. During the process, the volatile gas vacuum was at 3.5–10.0 kPa range and the temperature verified between 450 and 600 °C. By increasing temperature, liquid fraction decreased by the effect of NaOH. The maximum liquid fraction yield was 49.7 wt% at 480 °C, later this fraction decreased with increasing pyrolysis temperature [24].

Tire powder (200 and 400 µm) was pyrolyzed at a fixed bed reactor under a nitrogen gas with a flow rate of 0.56 m/s with a temperature range from 400 °C to 600 °C by a heating rate of 300 °C/min for 15 min reaction time. As a consequence, liquid and solid yields were around 43 and 38 wt% at 500 °C. The pyrolysis was not affected from the reaction time and heating rate on the total conversion [25].

Particle size was about 2 mm, which pyrolysis temperature verified from 375 °C to 500 °C at a fixed bed reactor with 10 °C/min heating rate under nitrogen gas with a flow rate of 100 mL/min for 1 h. The highest liquid yield (60 wt%) was obtained at 425 °C. Solid yield decreased up to 26 wt% at 450 °C and then remained almost

constant. The liquid fraction was observed 79.77 wt%. The liquids were similar to standard fuel [26].

Powder tires with 600 μm particle size were pyrolyzed under CO_2 gas at flow rates of 50 and 150 mL/min in a fixed bed reactor where the temperature changed between 800 °C and 900 °C. Furthermore, duration time was adjusted to 60, 90, 120, 150 and 180 min, respectively. The best result was found at 900 °C, 150 mL/min of CO_2 and 180 min of duration time, where the liquid, gas and solid fractions were 48.5, 26.0 and 25.6 wt%, respectively [27].

A tire with a size of 420 mm was pyrolyzed at 200 mL/min, the gas for 1 h at temperatures of 350, 450 and 550 °C in a quartz tube reactor. At 350, 450 and 550 °C, solid, liquid and gas fractions were 50, 30 and 20 wt%; 40, 33 and 27 wt%; and 33, 38 and 29 wt% respectively. Therefore, by increasing temperature solid yield decreased but liquid and gas fractions increased [28].

A shredded truck tire was fed by 33 kg/h in a semi-continuous pilot plant at 500 °C, 12 kPa. The maximum liquid, gas and char yields were 53.7, 7.0 and 39.3 wt%, respectively. The naphtha and *dl*-limonene were around 23.7 and 3.6 wt%, respectively. The *dl*-limonene yield increased by decreasing pressure [29].

Shredded tires (6.35-12.70 mm) were pyrolyzed at a bench scale reactor that was operated on a semi-continuous feedstock at 13 kg/h. The highest liquid, carbon black and gas yields were 55.6 wt%, 25.6 wt% and 6 wt%, respectively. The steel and fiber amount was 9.5 wt% at 415 °C with 2 kPa [30].

Scrap tires (less than 2 cm) were pyrolyzed at a pilot scale rotary kiln reactor, as the feeding rate was fixed at 4.8 kg/h and nitrogen gas flow rate was 1.4 m³/h with 3 rpm rotation. The maximum products were obtained at 550 °C and the char, liquid and gas yields were 49.09 wt%, 38.12 wt% and 2.39 wt%. The temperature did not affect volatilization reaction and products yield [11].

A waste tire (1 cm diameter and 3 mm thickness) was exposed at 550 °C in a fixed bed reactor by nitrogen flow gas as 0.2 L/min, for 15 min. The product yields of

liquid, gas, and char were 12 wt%, 53 wt% and 35 wt%. The hydrogen and methane fractions were increased by temperature asdehydrogenation [31].

A scrap tire (20 mm x 20 mm) was exposed at 450 °C in a fixed bed reactor by nitrogen flow gas as 0.4 L/min, for 4 h with 12 °C/min heating rate. The highest product yields rangewere determined for solid, liquid, and gas as 64–51 wt%, 30–43 wt% and 2.4–4.4 wt%. The gas fraction depends on temperature which the high temperature cause to crack heaviest compounds [32].

A waste tire (lower than 1 mm size) was exposed at 450 °C in a conical spouted bed reactor. The highest product yields rangewere determined for solid, liquid, tar and gas as 33.9–35.8 wt%, 44.5–55.0 wt%, 9.2–11.5 wt%, 1.8–6.8 wt%. The products yields were compared with batch pyrolysis. The light aromatic compounds which were higher than batch reactor, alsothe heavy liquid fraction was higher than the batch reacor [33].

A waste tire (between 1 and 5 cm diameter) was exposed at 500-600 °C in a rotary kiln reactor for 30 min. The highest product yieldswere determined for solid, liquid and gas as 33-34 wt%, 67–66 wt%, 9.2–11.5 wt%, 1.8–6.8 wt% respectively. Gas and solid amounts were increased by reaction time and heating ratio which cause to decrease liquid amount [34].

Two types of powder had 200 and 600 µm average size which exposed at Radio-frequency (RF) plasma reactor at 600 and 2000 W with 3000 and 8000 Pa under nitrogen gas as flow rate of 0.2–0.5 g/min. By increasing power; solid conversion increased from 40 to 76.8 wt%, and the H₂ increased from 38.6 to 44.4 vol%. The same result was found by increasing pressure. The highest compound of gasses were H₂, CO, CH₄ and CO₂ [12].

Banar et. al. [13] has produced a tire derived fuel (TDF) at a temperature range between 350 °C and 600 °C, with 5 °C/min and 35 °C/min heating rates by raising 50°C for each experiment at a batch reactor. The optimum oil yield was found to be 38.8 % wt. at 400 °C with 5 °C/min. The chemical and physical property results of TDF were analyzed and found to be similar to the ones of diesel fuel.

Paradela et. al. [35] aimed to recover three waste types (biomass, plastics and used tires) by pyrolysis process. The yield and composition of products were changed by reaction conditions. The pyrolysis temperature varied between 350 °C and 450 °C. The explosion duration was changed between 5 min and 30 min at 5.5 °C/min heating rate. The amount of alkenes in gas and liquid fractions were increased by extending the process duration. Furthermore, by increasing the reaction temperature, the liquid yield was decreased and the solid and gas yields were increased.

Quek et. al. [36] pyrolyzed three different brands of automobile tires under nitrogen atmosphere at five heating rates within a constant time. Particularly, they developed a new algorithm to produce more liquid products. A significant result was observed that heating rates, which affect pyrolysis reactions, was more available between temperatures of 450 K -1000 K. The scrap tire was depolymerized at heating rates varying between wide ranges of 10–50 K min⁻¹. The best results were obtained at high heating rates (>30K min⁻¹) for the desired characteristic products.

At a fixed bed reactor, scrap tires were pyrolyzed with three types of zeolites at 10 °C/min⁻¹ heating rate, up to 500 °C and kept for 1 hour or more. The oil and gas yields were influenced and increased by the catalyst [37].

The waste tire decomposed as gas, liquid and solid fractions at Figure 2.2. The pyrolysis method can be explained by average of the elemental analysis for waste tire and its' products. The waste tire liquid can be used in engine; however, a high sulfur content is needed to decrease standard sulfur content [11].

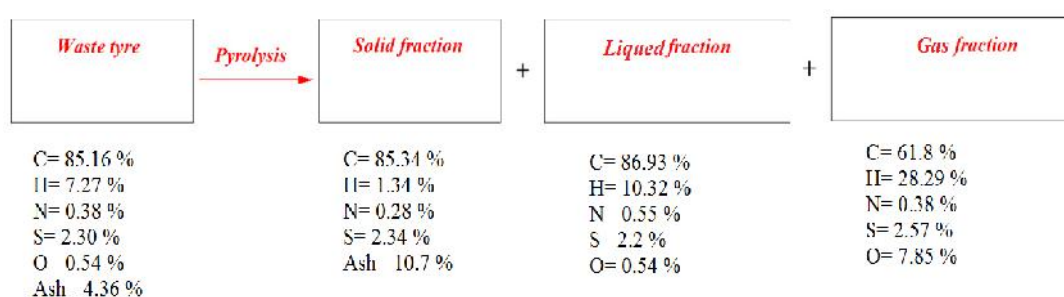


Figure 2.3. Products of pyrolysis with elemental analysis [11,38].

2.3 Sulfur Removing Process

The high amount of sulfur compounds in fossil fuels caused SO_x emission which contributes to air pollution, health and environmental hazards from acid rains. The main aims to decrease high sulfur level to low level. The EU and the USA have brought down the sulfur level for diesel transport fuel from 500 ppm to 50 ppm and it reduced to 10 ppm by the year 2010 which shown at Figure 2.3 [7,39].

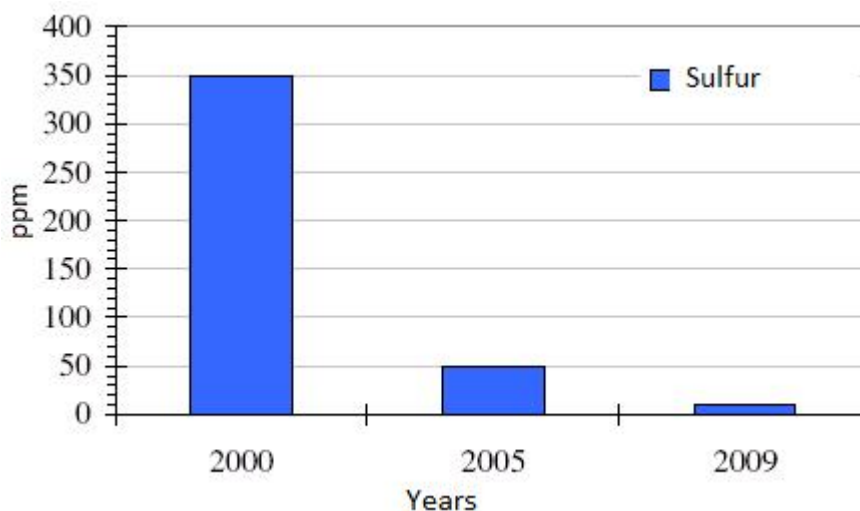


Figure 2.4. Sulfur amount in fuel [7,39].

The char and derived oil produced from used tire to decrease sulfur amount. The heating rate and end temperature were compared to realize sulfur removing from waste tire. The desulfurization was decreased by increasing temperature from 400°C to 1000°C . However, the heating rates variance ($1\text{--}10^\circ\text{C}/\text{min}$) did not any affect on desulfurization [40].

The truck tires were desulfurized at 350°C under 7 MPa hydrogen pressure with carbon black supported catalysts of Co-Ni, Co-Mo and Ni-Mo which could decrease the sulfur amount. The best reducement was done by Ni-Mo from 0.77 % to 0.57 % [41].

The pyrolytic tire oil was treated at five stages to decrease sulfur amount as: H_2SO_4 , activated Bentonite-CaO, vacuum distillation, oxidative desulfurization and washing drying. Firstly, oil was mixed with 8 wt% of H_2SO_4 for 4 h at 50°C , then residual was removed and Activated Bentonite-CaO was added for 4 h at 70°C . Next, oil was filtered and vacuum distilled, then treated with formic acid and H_2O_2 for 2 h at 60°C .

°C. Finally, oil was filtered and washed with distilled water and dried at 110 °C for 30 min. The sulfur decreased from 1.13 % to 0.43 % [42].

The naphtha fraction that was produced from waste tire, it was desulfurized by adding H₂O₂ and tire char individually, which maximum sulfur removing ratio were 41.5 % and 47.6 %, respectively. When both of them were used (H₂O₂ and tire char) together, the reduction become as 57.8 %. The highest desulfurization was 75.2 %, which occurred at HNO₃-treated chars in aqueous medium of pH 4, adjusted using formic acid [43].

The ultrasound method was used to remove sulfur from tire oil. Oil was mixed with tetraoctylammonium bromine, H₂O₂, and phosphotungstic acid, and then oxidized by irradiating with 20 kHz ultrasound for 20 min at 88 °C. The oil was extracted by acetonitrile. 43.6 % sulfur was removed from oil. Finally, the method was repeated with alumina oxide absorption which removed 68.2 % of sulfur amount [44].

The waste was condensed by pyrolysis to oil which contain a high amount of sulfur compounds (1.15 wt%). Thus, the hydrodesulfurization (HDS) catalyzed by molybdenum (Mo), nickel–Mo (NiMo) or cobalt–Mo supported on alumina were used to remove sulfur. The highest sulfur removal (87.8 %) was reacted at 250 °C for 30 min with a 2 wt% NiMo/catalyst under 20 bar of hydrogen pressure [45].

The tire oil was mixed with zeolite to decrease sulfur amount. Then, sulfur of tire oil (1.22 wt%) reduced by copper-loaded catalysts (HBETA, HY, HMOR) were 0.764, 0.800, and 0.842 wt% in oil for Cu/HBETA, Cu/HY and Cu/HMOR cases [46].

In this first method, 100 mL of tire oil, 14 mL of 85 % wt formic acid and 6 mL of 50 wt% hydrogen peroxide were mixed in a three necked round bottomed flask with reflux condenser, and heated in the ultrasound bath filled with silicone oil at 70, 80 or 90 °C, during the specified time, and stirred at 400 rpm in the ultrasound bath and left decanting for 0.5–1 h. The lower aqueous layer was removed and the upper hydrocarbon layer was extracted with 100 mL of methanol with vigorous manual stirring for 2 min. The tire oil reacted at 70 °C, for 30 min with stirring at 400 rpm

and ultrasound irradiation, followed by extractions with methanol (1:1 v/v WTPF-methanol). The achieved desulfurization rate was only 53.0 % [47].

2.4 Engine Performance and Exhaust Emissions

Due to standard petroleum fuel price increase, a new alternative fuel needs to be used in engine. A good and alternative fuel to fossil fuel is tire oil which has many advantages for environment and atmosphere, besides decreases green house effect. The physico-chemical properties of tire oil resemble to diesel fuel except it has a lower flash point and higher sulfur amount.

The tire-derived fuel (TDF) mixed with diesel fuel as TDF10 (contains 10 % tire derived fuel and 90 % diesel fuel in volume basis), TDF30, TDF50, TDF70, TDF90 and diesel fuel, were tested in a diesel engine (DI) at four engine speeds (1400 rpm, 2000 rpm, 2600 rpm, and 3200 rpm). The smoke opacity, HC, and, CO reduced while NO increased with the increasing TDF. Furthermore, TDF did not have an important effect on T, P, Bsf_c and, η_{th} as compared with diesel fuel. Besides, TDF can be burned in engine without any performance loss in engine up to TDF70, which affect smoke opacity, CO, and HC emissions [42].

The tire pyrolysis oil (TPO) derived from waste automobile tires were analyzed to burn in diesel engine. However, the crude TPO has a higher viscosity and sulfur content. The TPO was distilled by vacuum distillation to DTPO (Distilled Tire Pyrolysis Oil). The DTPO-diesel fuel (DF) blends were burned in engine. The 100 % DTPO cannot be burned purely in engine. However, by mixing DTPO with diesel, it can be burned in engine. The smoke capacity, HC and CO amounts of blends were more than DF. Besides, heat release (except initial stages) and pressure rate of DTPO-DF blends observed an increasing more than DF [48].

The waste tire was pyrolyzed to produce tire pyrolysis oil (TPO). Then, TPO sulfur was removed by vacuum method. Besides that, desulphurized tire pyrolysis oil (DTPO) and diesel fuel (DF) were mixed at lower and higher concentrations which were used in diesel engine without any engine adjustment. The 100 % DTPO was run

at a diesel engine but the engine was failed. Thus, the 90 % DTPO and 10 % DF (DTPO 90) were blended to be burned in a diesel engine [49].

The tire pyrolysis oil (TPO), obtained from waste automobile tires by vacuum pyrolysis method, was run on engine as TPO 20 (20 % vol.) up to TPO70 blend with reference diesel (RF). The smoke capacities, HC and CO were higher than diesel, inversely η_{th} was lower compared to diesel. The Bsf_c was higher for all TPO–RF blends compared to RF [50].

The 10 %, 30 %, and, 50 % of tire pyrolysis oil (TPO) was mixed with diesel fuel (DF). The η_{th} increased with increasing TPO in DF concentration. The ignition delays of TPO-DF were longer than DF and the TPO-DF blends had higher PAH that they caused high emissions of NO, HC, CO, and smoke. The increased amount of TPO in DF, the peak and rate of pressure were increased by comparing with DF. As a results of aromatic contents and viscosity, TPO can burn in engine by mixing with DF [51].

The pyrolytic tire oil was analyzed with standard methods, showing density, viscosity, calorific value, and flash point comparable to Diesel fuel (DF) with the exception of two important properties; higher sulfur content and a lower cetane number. The tire pyrolysis oil (TPO) and diesel fuel (DF) were blended a volume basis of TPO 40-DF 60. The different engine speed of TPO20 did not cause any significant difference for T, P, Bsf_c, and exhaust emissions of DF, while TPO40 found to be worse in combustion characteristics. Besides, the sulfur amount caused environmental problems [52].

The tire pyrolysis liquid (TPL) fuel (5 vol%) and an animal-fat biodiesel (50 vol%) were mixed with two diesel fuels. The two diesel blends with the animal-fat biodiesel were tested in a diesel automotive engine (model M1D) with common-rail injection system and diesel oxidation catalyst (DOC). As a result of adding TPL in biodiesel, carbonyl emissions also increased [53].

A tire pyrolysis liquid (TPL) was produced in a continuous auger reactor, and mixed with 5 vol% (5TPL) with commercial diesel fuel (100DF) which burned in Nissan

diesel automotive engine (model M1D) with common-rail injection system. The Bsf_c and η_{th} were low at low load, then the load increased which cause the Bsf_c and η_{th} become equal to DF. However, Total hydrocarbon (THC) was lower at low load but similarly increasing at higher load. And also, the NO emissions were higher for higher load. From the results, low volume amount of TPL can be mixed with DF [54].

The 80 % biodiesel was mixed 20 % tire oil which was burned at optimum injection timing and nozzle opening pressure (NOP) to compare with diesel compression ratio. The compression ratios (CR) were 16.5, 17.5 and 18.5. Higher CR at full load caused shorter ignition delay, maximum cylinder pressure, and higher heat release rate and also increased η_{th} as compared with diesel combustion. The smoke capacity, CO, and HC were reduced by about 10.5 %, 32 % and 17.4 %. Finally, those of compression ratio applied at full load to observe change. Only, NO was greater than other condition [55].

CHAPTER 3

FUEL PRODUCTION SYSTEMS AND TESTING PROCEDURE

3.1 Introduction

Pyrolysis is one of the most favorable and effective disposing method, which is environmental friendly and efficient. It is the thermal degradation of solid wastes at high temperatures in the absence of air to produce char, pyrolytic oil or syngas [42]. The waste tire expose in pyrolysis unit to produce gasoline and diesel like fuel. The test results of tire products compared with standard petroleum fuels, besides theoretical validation analyses were done for accuracy of sample results and equipments. The pyrolysis unit was designed and each of its parts was explained in the following sections. Then, physicochemical properties were analyzed with explanation of the procedure. Finally, the instrumental analyses were done for distillation and engine test.

3.2 Batch Pyrolysis Unit

The pyrolysis and distillation system founded at Internal Combustion Engine Laboratory, Department of Mechanical Engineering, University of Gaziantep, was used to pyrolyze and separate liquid oil and solid fuel from each other. For this purpose, some control and measurement elements were installed on the system. Schematic and picture representation of the system is shown in Figures 3.1 and 3.2. The system has several components which are reactor, control panel, fuel storage tank, blender, and heat exchanger or condenser. Main functions of the components will be given below shortly.

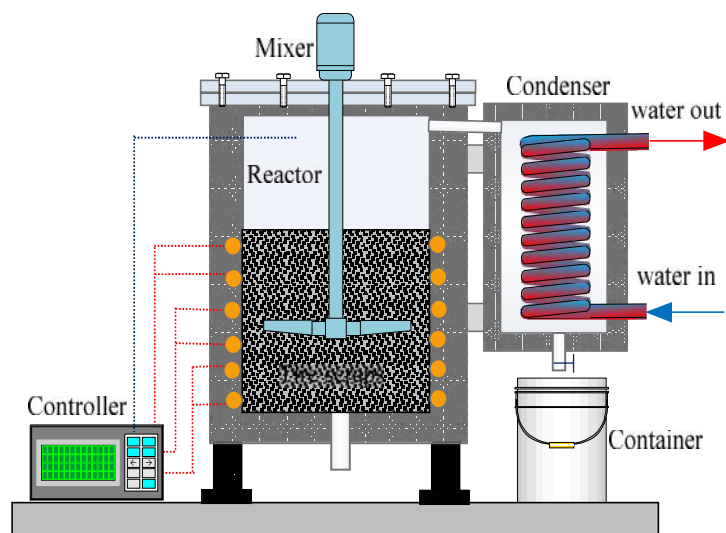


Figure 3.1. Schematic of the batch reactor pyrolysis system.



Figure 3.2. Picture of the batch reactor pyrolysis system.

The reactor is the most important part of the system, shown at Figure 3.3. It is used for heating and melting of waste tire scraps. Basically, the reactor has cylindrical shape with inner diameter and overall effective chamber length of about 30 and 40 cm, respectively. Its capacity is enough for producing a volume of approximately 10 liters of tire oil. The capacity is sufficient for testing all characteristics of the produced fuel. The reactor includes an electrical heating unit which has a heating capacity of 5 kW. It can be used to heat the waste tire scraps up to a temperature of 600 °C. The electrical heater has resistance heaters, and a voltage control which is used to adjust the heating rate. Temperature measurements were done via thermocouples placed in the middle of the reactor.



Figure 3.3. The reactor of the batch reactor pyrolysis system.

The condenser unit cooled the gas by water which exist from reactor, shown at Figure 3.4. The gas cooled from 140 °C to 430 °C. It works between It has 5 mm of diameter with 0.2 thickness, length 16 m of copper, inserted as spiral. The cooling water flow rate is 2 L/min.



Figure 3.4. The condenser of the batch reactor pyrolysis system.

The reactor components were Pt100 platinum resistance thermometer and electronic thermostat Enda ETC 942 which shown at Figure 3.5. PT100, a temperature range - 200 °C~+850 °C which measure 0°C at 100 Ohm and 100 °C at 138.4 Ohm. In a

measurement, 0.4 °C happens at 50 °C, if it generalized, there is a linear correlation between Ohm and temperature [7].



Figure 3.5. Thermocouple (PT100).

ETC 942 (programmable digital thermostat), which shown at Figure 3.6, used a microprocessor with a selectable relay or SSR control output for On/Off, P, PI, PD, PID or soft start/self-tuning. NO or NC relay show 4 various types of output by alarm by the input of Pt100 and thermocouples (J, K, T, S, R). Optional RS485 module is connected with Modbus RTU protocol. The digit display views on a 2x4 [7].



Figure 3.6. Control Panel (ETC 942).

The electrical heating power was selected as 8 kW. During the reaction, mixer at 150 rpm, has 200 W, satisfied uniform temperature distribution. The stainless steel reactor has 5 mm thickness and insulated with 100 mm stone wool layer. The general properties of reactor are shown at Figures 3.7-3.11 [7].

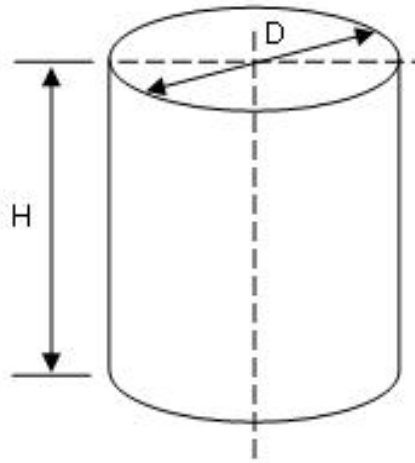


Figure 3.7. The reactor dimension.

The electrical unit can heat mixture to up to 350 °C. It was aimed 15 kg sample of fuel obtained for each experiment. Hence the inner volume of reactor can be determined.

$$m = V\rho \quad (3.1)$$

$$V = \frac{m}{\rho} = \frac{15}{890} \cong 0.022m^3$$

The height (H) and diameter (D) of reactor were 0.25 m and 0.35 m.

The maximum temperature and outside temperature were 400°C and 25°C with 20 kg:

$$Q = 20 \times 1.9 \times (400 - 25) \text{ kj}$$

$$Q = 14,250 \text{ (kj)}$$

The optimum reaction time was 300 min.:

$$\dot{Q} = \frac{Q}{\Delta t} = \frac{14,250}{5 \times 60} = 4.75 \cong 5 \text{ kW}$$

The reactor is insulated which does not exceed 35 °C when the ambient temperature is $T_o = 25$ °C. Outside heat transfer coefficient is assumed as $h_o = 25 \text{ W/m}^2 \text{ } ^\circ\text{C}$.

The inside reactor surface and outside temperatures were predicted as 400 °C and 25 °C. Other assumptions are determined as follow:

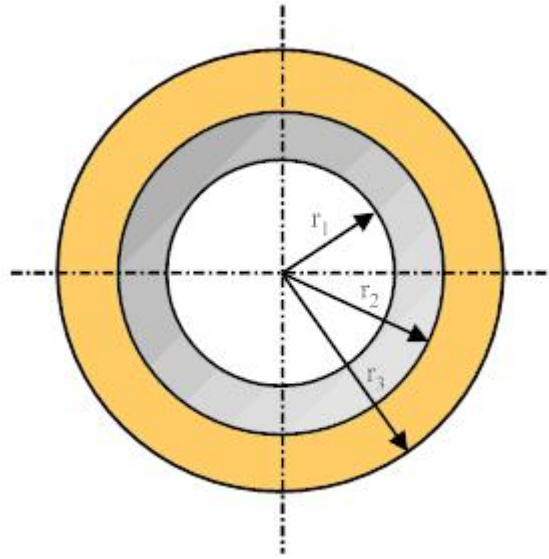


Figure 3.8. Reactor covered with stone wool.

- Heat transfer is steady
- Thermal conductivities are constant
- The thermal contact resistances are negligible

The dimensions of reactor are $r_1 = 150$ mm and $r_2 = 155$ mm.

$$R_1 = R_{\text{reactor}} = \frac{\ln \left[\frac{r_2}{r_1} \right]}{2\pi k_1 L} \quad (3.2)$$

$$R_2 = R_{\text{insulation}} = \frac{\ln \left[\frac{r_3}{r_2} \right]}{2\pi k_2 L} \quad (3.3)$$

$$R_o = R_{\text{convection}} = \frac{1}{h_o A_3} \quad (3.4)$$

Total resistance is calculated by series resistances:

$$R_{\text{total}} = R_1 + R_2 + R_o \quad (3.5)$$

$$Q = \frac{T_i - T_o}{R_{total}} = \frac{T_i - T_o}{\frac{\ln\left[\frac{r_2}{r_1}\right]}{2\pi k_1 L} + \frac{\ln\left[\frac{r_3}{r_2}\right]}{2\pi k_2 L} + \frac{1}{h_o A_3}} \quad (3.6)$$

The heat loss rate calculated as:

$$Q = \frac{T_3 - T_o}{\frac{1}{h_o A_3}} \quad (3.7)$$

Eq. (3.5) is equal to Eq. (3.6).

$$\frac{T_i - T_o}{\frac{\ln\left[\frac{r_2}{r_1}\right]}{2\pi k_1 L} + \frac{\ln\left[\frac{r_3}{r_2}\right]}{2\pi k_2 L} + \frac{1}{h_o A_3}} = \frac{T_3 - T_o}{\frac{1}{h_o A_3}} \quad (3.8)$$

Eq. (3.7) for r_3 by using EES (Engineering equation solver) software was given $r_3 = 0.2417$ m stone wool insulation thickness determined as: $t = 0.08669$ m = 8.67 cm.

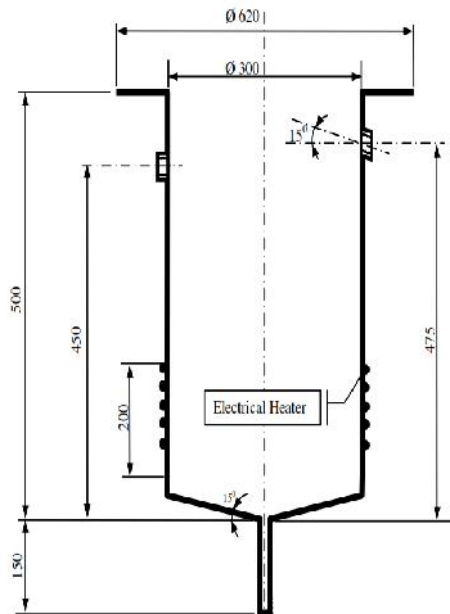


Figure 3.9. The inner reservoir of reactor.

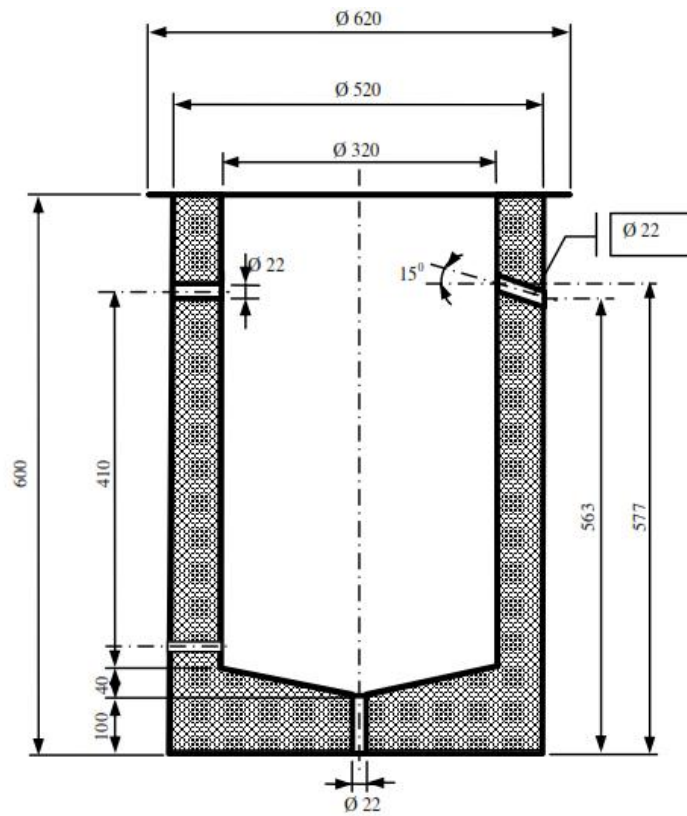


Figure 3.10. The outer structure of reactor.

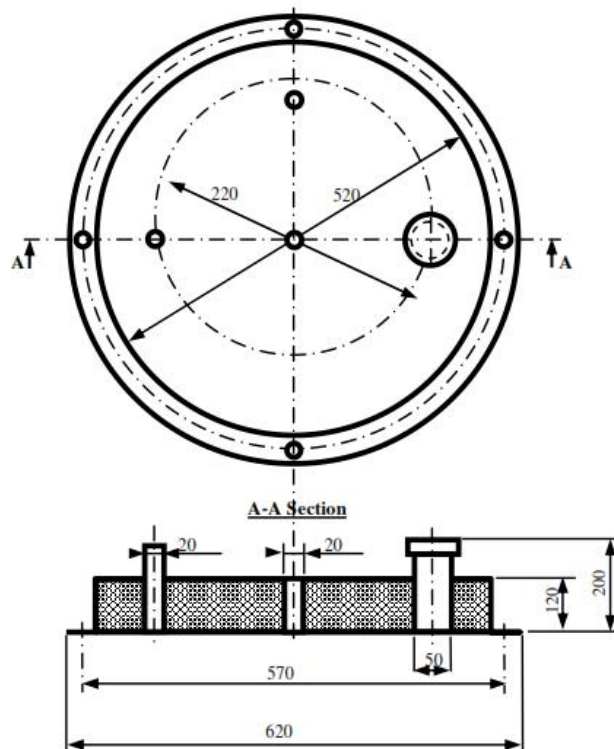


Figure 3.11. The top cover of reactor.

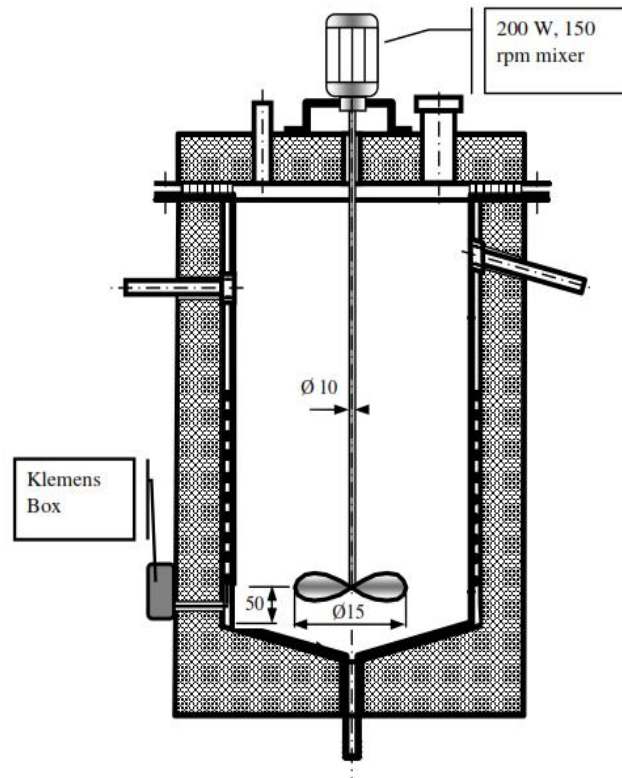


Figure 3.12. The constructed reactor.

3.3 Rotary Kiln Pyrolysis

The rotary kiln pyrolysis of a waste tire was founded at Adıyaman region, known as Kudret Inkar Waste Tire Recycle Co., Turkey. In this system, the waste tire is pyrolyzed and then, condensated by a heat exchange system containing three heat exchangers such as high, medium and low, in order to separate the sample into three types of liquid. For this purpose, the rotary kiln reactor, electric and electronic control panel and its other parts are installed on the system. The system is shown in Figure 3.13. The system has several components, namely the rotary kiln reactor, heating furnace, feed hopper, control panels, carbon black tank, high-medium-low heat exchangers, wax-heavy oil-light oil tanks, aqueous phase pool, water tank, separator and the non-condensable gas tank. The basic components functions will be shortly declared below.

Reactor is the main component of the system. The waste tire scraps are heated and molten at the rotary kiln reactor. It has either cylindrical or spherical shape with an internal diameter of 2.2 m and a length of 6.6 m and has one tone of volume. There is a heating furnace unit under the reactor, which burns coal to run the system and after a while a certain non-condensable gas is burned in the furnace instead of coal usage. The rotation speed can be varied between 0.5 min^{-1} and 3 min^{-1} and the optimum temperature is 400°C .

The rotary kiln has consumed 10 kW electricity per hour. The electric devices have a motor (7.5 kW), reduction machine (500 W), a middle voltage blower (3 kW), two oil pumps (500 W), 5 fans (250 W), 2 water pumps (2.2 kW), a controller, and an air lock valve for charcoal drain.

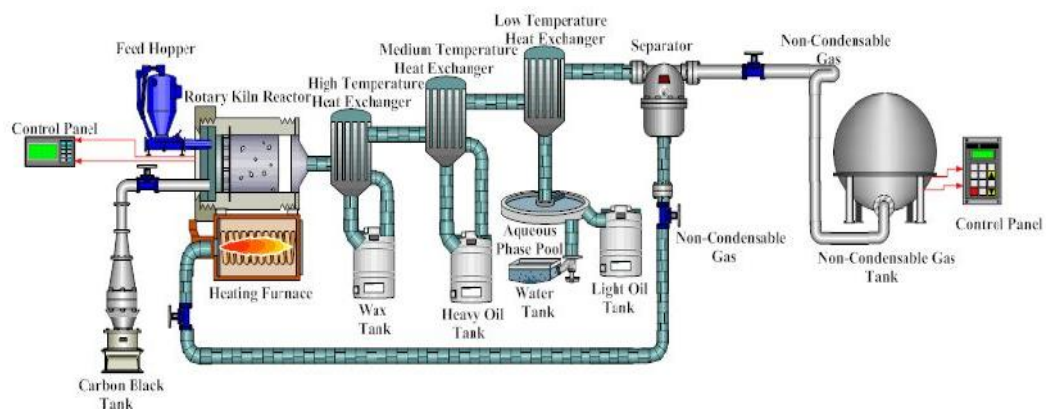


Figure 3.13. Schematic of the rotary kiln reactor pyrolysis system.

The feed hopper can feed by waste tire, shown in Figure 3.14.



Figure 3.14. The picture of feed hopper.

Rotary kiln reactor has a size of 2.2 m x 6.6 m, and 14 mm thickness (such thickness is for the safety consideration), which prevent heat loss in the reactor, and has a horizontal rotary with control panel and alarm system, shown in Figure 3.15. Burning system (heating system) has two phases; at the first phase, coal (about 300 kg) or wood (about 50 kg) or of oil/gas (about 600 L) was used at burner. Then, the rotary kiln starts to work and non-condensable gas produce during the pyrolysis, which can be used instead of previous fuels (coal, wood, oil/gas) at the second phase.



Figure 3.15. The rotary kiln reactor.

Gas separator system separates the heavy oil and the pyrolysis gas by control panel to adjust pressure switch and gauge, and flame proof blower shown in Figure 3.16.



Figure 3.16. Gas separator system.

The cooling system has 3 set condensers (with a diameter: 50 cm and a length: 3 m) with spray cooling 16 pieces pipes with a diameter of 133 mm and a length of 1 m, shown in Figure 3.17.



Figure 3.17. Condensers and spray cooling pipes.

The two water seals release the pressure when the non-condensable gas rises, shown in Figure 3.18.



Figure 3.18. Water seal.

The discharge system collects the carbon black from the reactor and bagging. The total capacity 10,000 kg per day shown in Figure 3.19.



Figure 3.19. Carbon black discharge system.

3.4 Testing Equipments

The physicochemical properties of fuel were tested at Fuel Test Laboratory, Mechanical Engineering Department, Gaziantep University and Central Research Laboratory, Bilecik Seyh Edebali University. The test equipments are explained shortly below. All of the equipments are marked as CE and also confirm with ASTM, Dyne, EN and TSE.

3.4.1 Distillation

The distillation test, by using a K45000 apparatus, was performed under standard conditions. Likewise, the liquid has evaporated and condensed under standard conditions between 25°C and 400°C. It confirms with ASTM D86 and EN133 shown in Figure 3.20.



Figure 3.20. Distillation device.

3.4.2 Density

The density characterizes the physical property quality of sample, and was tested between 15 °C and 35 °C. It confirms with ASTM D-1513 shown in Figure 3.21.



Figure 3.21. Density device.

3.4.3 Flash point

The flash point sample was tested by using a K16200 Pensky-Martens Closed Cup Flash Tester model. The device works through closed cup techniques with two options, namely, speed stirring and smooth slides shutter mechanism. Here, the flame gets into the cup to burn the liquid with the turn of a knob. The flash point was determined between 10 °C and 40 °C. It confirms with ASTM D93 shown in Figure 3.22.



Figure 3.22. Closed-cup flash device.

3.4.4 Kinematic viscosity

The kinematic viscosity was tested by a Kohler brand K21410 model apparatus at 40°C. The amount of the fuel sample was 60 mL, and flowed through a calibrated

orifice within time measured by Saybolt Universal Seconds (SUS) standards. It confirms with ASTM D88, D244 and EN102 shown in Figure 3.23.



Figure 3.23. Kinematic viscosity device.

3.4.5 Heating value

The HHV was tested in a sample, which typically weighs 1-2 g. It was pressurized under excess O_2 and then, it was submerged under 2000 mL water. Finally, the electricity ignited the sample. It confirms with ASTM D-5865 shown in Figure 3.24.

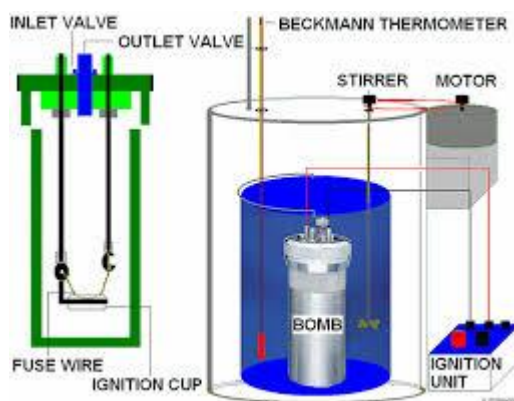


Figure 3.24. Bomb calorimeter device.

3.4.6 Moisture content

The extraction solvent was put into the titration cell. First, titration moisture in the solvent with Karl Fisher reached to equilibrium and then sample was added. Next,

the sample was titrated to determine a known factor (mg H₂O/mL) until the end point was found. Finally, the moisture concentration of the unknown sample could be calculated [7]. It confirms with ASTM D-1619 shown in Figure 3.25.



Figure 3.25. Moisture content device.

3.4.7 Copper strip tarnish test device

The Copper Strip Tarnish Test relates with degree of corrosivity of any fuel sample as shown at Fig. 3.24. A polished copper strip was immersed in 30 mL of sample at 50 °C [56]. After three hours of test, the strip corrosivity was checked by ASTM D130, D6074 and D6158 standards. Diesel fuel was slight tarnish and tire oil was moderate tarnish [57]. However, DLF was between slight and moderate tarnish because of 10 wt% CaO treatment shown in Figure 3.26.



Figure 3.26. Copper strip tarnish device.

3.4.8 Cold filter plugging point (CFPP) and cloud point (CP)

Cold Filter Plugging Point (CFPP) was done to determine fuel sample flow characteristics at low temperature which flows through a wire mesh filter under

standard test conditions. The test conforms to ASTM D6371, IP 309 and DIN 51428. The system contained Filter Plugging Point Apparatus, Vacuum System and Cooling Bath. The sample was refrigerated by using cascade hermetic cooling to reach temperatures as low as -90°F (-68°C) [58]. The sample which included paraffin compound started to form cloudy wax. This reduced the flow of fuel quickly and starved the engine. The CFPP of DLF was 44°C which is close to fuel temperature [56] shown in Figure 3.27.

The cloud point (CP) is the temperature at which wax crystals begin to form in a petroleum product as it is cooled. A change in temperature at which clouding starts to occur is therefore expected upon addition of any additive. The difference between the cloud point values for the two samples is not abnormal and is not significant. Cloud point is measured at intervals of 2.5°C .



Figure 3.27. Cold filter plugging point (CFPP) and cloud point (CP) bath device.

3.4.9 Sulfur

The Eltra CS580 sulfur analyzer was used to determine the sulfur content in the samples under pure oxygen at temperatures between 600°C and 1450°C . It confirms with ASTM D-1619 shown in Figure 3.28.



Figure 3.28. Sulfur analyzer.

3.4.10 Ultimate analysis

The ultimate composition was tested by Eltra CS580. The device calculates the percentages of C, H and N present in the sample under high temperature (1000 °C-1100 °C). The electrical conductivity difference between helium reference (ultra-high purity, 99.999 %) and the reaction gas was measured, and then, their O₂ percentages were evaluated. The Eltra CS580 sulfur analyzer was used to determine the sulfur content in the samples under pure oxygen at temperatures 600 °C and 1450°C. It confirms by ASTM D-1619 shown in Figure 3.29.



Figure 3.29. Ultimate analysis device.

3.4.11 Proximate analysis

A gram sample (250 mesh) put in crucible and heat up to 110 °C in the furnace for 1 hour to determine moisture amount. It confirms by ASTM D-3173. The crucible was

removed from the furnace and put into desiccators for cooling shown in Figure 3.30. After cooling, the desiccators was weighed for moisture amount calculation as:

$$\text{Moisture amount, \%} = [(A-B) / A] \times 100 \quad (3.9)$$

A: sample weigh, g.

B: sample weigh after treating at furnace, g.

The ash amount confirms with ASTM D-3174. The moisture amount in the sample was used for ash test. The crucible was put into the furnace to heat incrementally up to 450-500 °C for 1 hour, then heat up to 700-750 °C for 1 hour, and then wait for 2 hours at 750 °C. The crucible was removed from the furnace and it was put into the desiccators for cooling. After cooling, the desiccators were weighed for moisture amount calculation as:

$$\text{Ash amount, \%} = [(A-B) / C] \times 100 \quad (3.10)$$

A: The sample taken from furnace (crucible + ash weight), g.

B: Empty crucible weight, g.

C: Sample weight, g.

A gram sample (250 mesh) put in crucible and heat up to 950 °C in the furnace for 7 min. to determine volatile material amount. It confirms by ASTM D-3175. The crucible was removed from the furnace and it was put into the desiccators for cooling. After cooling, the desiccators were weighed for moisture amount calculation as:

$$C, \% = [(A-B) / A] \times 100 \quad (3.11)$$

A: Sample weight, g.

B: The sample taken from furnace, g.

C: Weight Loss, %.

D: Moisture amount, %.

$$\text{volatile material, \%} = C - D \quad (3.12)$$

The ASTM D-3172 confirms for fixed carbon amount is calculated as:

$$\text{Fixed carbon, \%} = 100 - (\text{Moisture, \%} + \text{ash, \%} + \text{volatile material, \%}) \quad (3.13)$$



Figure 3.30. Furnace and desiccators.

3.4.12 Thermogravimetric Analysis

Thermogravimetric analysis is done by a Setaram Labsys Evolution analyzer under pure O₂ gas at 100 mL/min flow rate. The sample weighs approximately 15 mg and is heated from 25 °C up to 1250 °C with heating rate of 10 °C/min. The proximate analyses are also done by Setaram Labsys Evolution TGA [59]. It confirms by ASTM D-1619 shown in Figure 3.31.



Figure 3.31. Setaram labsys evolution analyzer.

3.4.13 Infrared Spectrometry (FT-IR) Analysis

The Perkin Elmer FT-IR Spectrum 100 detects the IR-spectra of the liquids. Here, the functional groups in sample compounds are investigated. The 4300 cm⁻¹–225 cm⁻¹ wave length range and 0.4 cm⁻¹ resolution is utilized for the experiment [59-60]. It confirms by ASTM D-1619 shown in Figure 3.32.



Figure 3.32. Perkin elmer FT-IR spectrum 100.

3.4.14 Surface Area (BET)

The surface area, pore volume and size distribution values are examined by nitrogen adsorption–desorption isotherms method performed by Micromeritics ASAP 2020 device. The Hg porosimetry technique is used to determine macropores. The device can take measurements between $0.005 \text{ m}^2/\text{g}$ and $5000 \text{ m}^2/\text{g}$ and the diameter range from 3.5 to 5000 (Å). The samples are ground into 150-200 mm size particles to be used for the experiment. The sample is outgassed overnight at 373 °K and followed by nitrogen sorption at 77 °K. The total surface area and micropore volumes are calculated by BET- and t-plot equations, respectively. The mesopore volume is taken as the difference between the total and micropore volume [59]. It confirms by ASTM D-1619 shown in Figure 3.33.



Figure 3.33. Micromeritics ASAP 2020 device.

3.4.15 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The fuel's chemical composition is tested by using GC-MS Perkin Elmer Clarus 600 device. The sample is tested in a Perkin Elmer elite 5-MS capillary column (30 m x 0.25 mm i.d.; 0.25 μ m film thickness). Helium (He) flows at 1 ml/min as the carrier gas. The GC oven temperature is hold at 40 °C for 1 min, and then set to 100 °C, 160 °C and 280 °C at heating rates of 4 °C/min, 4 °C/min and 5°C/min, respectively, and then, kept at 280 °C. The injector temperature is 220 °C and 1 μ l. The MS spectrum is determined at EI ion source of 70 eV. Split ratio is 10:1 [59,61]. It confirms by ASTM D-1619 shown in Figure 3.34.



Figure 3.34. GC-MS perkin elmer clarus 600 device.

3.5 Testing Procedure

The WTO has a high amount of sulfur, black carbon particles, and other impurities. The main aim was to decrease the sulfur amount while pyrolyzed the WTO. The restructure of WTO exposed to resemble standard fuels. Thus, some additives were added under high temperatures in pyrolysis system. The testing procedure can be summarized as follows.

The WTO was purified from a filter, and then put into the reactor by mixing with two types of additives; natural zeolite (NZ) and Lime (CaO) with mass basis of 2 %, 4 %, 6 %, 8 % and 10 %. Each sample was distilled and collected in a container. Besides, physicochemical properties were analyzed to compare with standard fuels in

the following section. The best result among the samples was selected to burn in standard engines.

3.6 Instrumental analysis

Any experimental study needs a statistical method for modeling and investigating the relationship between variables. The regression analysis correlates test parameters and prediction parameters for a best fit function [62]. The equipment selection, test condition, device calibration, test environment, observation by expert, reading and test planning can cause errors and uncertainties in the experiment. Thus, error and uncertainty analyses are used for measurements of physical quantities [62].

3.6.1 Linear regression analysis

The regression analysis is a statistical method for reproducing dependent and independent variables' association [63]. The total variability degree was computed by the independent variables and the coefficient of determination ($R^2(\text{adj.})$). The best simulation relevant is described by a regression line having a slope of 1.0, an intercept of 0, and an R^2 of 1.00, and is essentially overlaps with “the line of perfect fit”. Analysis of variance (ANOVA) is to determine whether several groups are equal or not. Thus, t -test is applied to more than two groups for statistical significance. The t -statistic is a deviation ratio for estimating the notional value and the standard error [64]. The analysis was performed by using SPSS, ver. 22.0.

The largest connection variable would be with R^2 , which affects the straight line strength relationship, and is defined as:

$$R^2 = \frac{SSY - SSE}{SSY} \quad (3.14)$$

where, SSY = Total sum of squares

$$= \sum (y_i - y_{\text{mean}})^2 \quad (3.15)$$

SSE = Error sum of squares

$$= \sum (y_i - y_{\text{predicted}})^2 \quad (3.16)$$

The straight line regression equation variables would be:

$$y = \beta_0 + \beta_1 X_1 + E_n \quad (3.17)$$

y=Distillated Volume (V), β_0 =Constant, β_1 =Coefficient, X_1 =Temperature (T)

This can be modified as:

$$V = \beta_0 + \beta_1 \times T \quad (3.18)$$

3.6.2 Uncertainty Analysis

Any test result contains some uncertainty level which causes gaps of accuracy measurement and approximations in data reduction relations. Additionally, individual inaccuracies transfer into uncertainty results [62].

The uncertainty in calculated results is related to primary uncertainty for each independent variable. This is based on the method of Kline and McClintock (1953) which state:

$$R = f(x_1, x_2, \dots, x_n) \quad (3.19)$$

Eq. 3.19 is the common form of R calculation which is a function of n variables $x_1, x_2, \dots, x_n$. The uncertainty is calculated by individual variables as:

e_R is uncertainty estimation total results of R,

x_i is uncertainty estimation,

$\partial R / \partial x_i$ is sensitivity coefficient.

The confidence level of equation is 95 % for each e_{x_i} value and also for e_R . Holman [65] have determined uncertainty analysis Eq. 3.20 as:

$$e_R = \left[\left(\frac{\partial R}{\partial x_1} e_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} e_2 \right)^2 + \dots + \left(\frac{\partial R}{\partial x_n} e_n \right)^2 \right]^{1/2} \quad (3.20)$$

3.7 Engine test parameters

The engine performance and exhaust emission were tested for sample produced from WT to determine whether it burned efficiently in a standard engine as gasoline and diesel. Furthermore, measurements and experimental set up which were used for performance and exhaust emission parameters are declared deeply.

The Fiat 131 SI test engine set-up was installed at Internal Combustion Engine Laboratory, Mechanical Engineering Department, University of Gaziantep. Schematic drawing and picture of the SI test engine are represented at Figures 3.35 and 3.36. The SI test engine specifications are four-stroke and four cylinders, water cooled cooling system, fueled with carburetor and naturally aspirated. Each cylinder has 76 mm bore and 71.5 mm stroke. The highest engine power output was 52.2 kW at 5500 rpm. The engine specifications are declared at Table 3.1 [66]. All of the experimental procedure and equipments will be explained through section.

The engine test parts are weighing device, inclined manometer, dynamometer, tachometer, transducer, data logger, a personal computer (PC) and exhaust gas analyzer. The test parts were adjusted and data logger systems were transferred data into the PC. The SI engine runs 30 minutes to get ready for experiments. The engine worked without any problem. The data logger functions and computer, measuring elements, and techniques of experimental are discussed as follows.

The sensitivity of weighing machine is 0.1 g which was used to measure fuel consumption. Orifice meter coupled to an inclined manometer was used for measuring intake air mass flow rate. A large air tank connected to the engine carburetor with a plastic pipe was used for damping out the pulsations produced by the engine to form a steady flow of the intake air. Air flow was realized by pressure difference which formed by a pipe bowl at the entrance of the air tank, was measured by a pressure transducer with analog output. Another analog/digital converter was used to change and transfer the digital signal to the PC for a time interval [66].

The hydraulic dynamometer with a range of 0–100 Nm was used to measure torque. The engine speed mechanism was conducted with spark plug and a microprocessor

which counts the ignition number by 1 rpm of engine speed. A step motor controls throttle valve for engine speed which has 1.8° sensitivity by using this software. Consequently, the small time intervals were realized at different engine speed kinds [66].

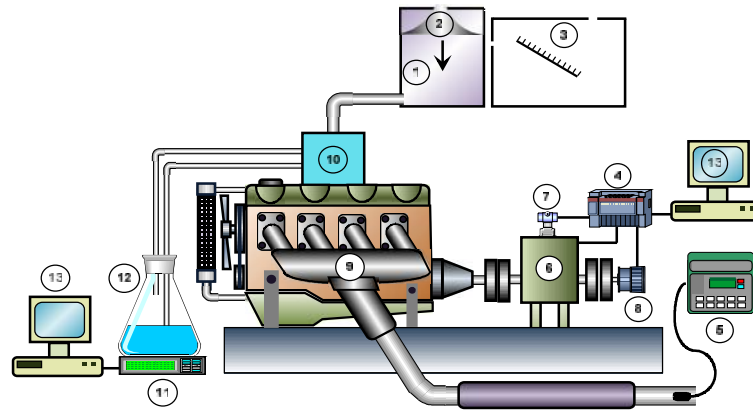


Figure 3.35. Schematic drawing of the SI test engine.

[1) air tank, 2) orifice, 3) inclined manometer, 4) data logger, 5) exhaust gas analyzer, 6) dynamometer, 7) transducer, 8) tachometer, 9) exhaust manifold, 10) carburetor, 11) weighing device, 12) fuel container, 13) computer.]



Figure 3.36. Picture of the SI test engine.

Table 3.1. Test engine specifications

Type	Fiat
Engine type	Four-stroke
Fuel type	Gasoline
Swept volume	1297 cm ³
Cylinder bore	76 mm
Cylinder stroke	71.5 mm
Compression ratio	7.8:1
Number of cylinders	4
Cooling type	Water cooled in closed circuit
Fuel supply system	Naturally aspirated carburetor
Maximum torque	12.5 kg.m at 3000 rpm
Maximum power	52.2/70 kW/ HP at 5500 rpm
Engine position	Vertical

The engine torque is measured by using water brake dynamometer. It converts the rotating torque to stable torque. By increasing water amount in the dynamometer, the load or resistance is also increased in engine which causes to increase speed of engine. The engine produced power and absorbed by the dynamometer, then adsorbed energy was converted into heat energy in the dynamometer absorption unit. Finally, the dynamometer absorption unit transferred heat energy into flowing tap water. The water generally enters approximately at 15 °C and exists at 50 °C.

Figure 3.37 shows power absorption unit components. The rotors are fastened to the main shaft and stators are housed when it rotates, within a trunnion bearing and restricted by the hydraulic load cells.

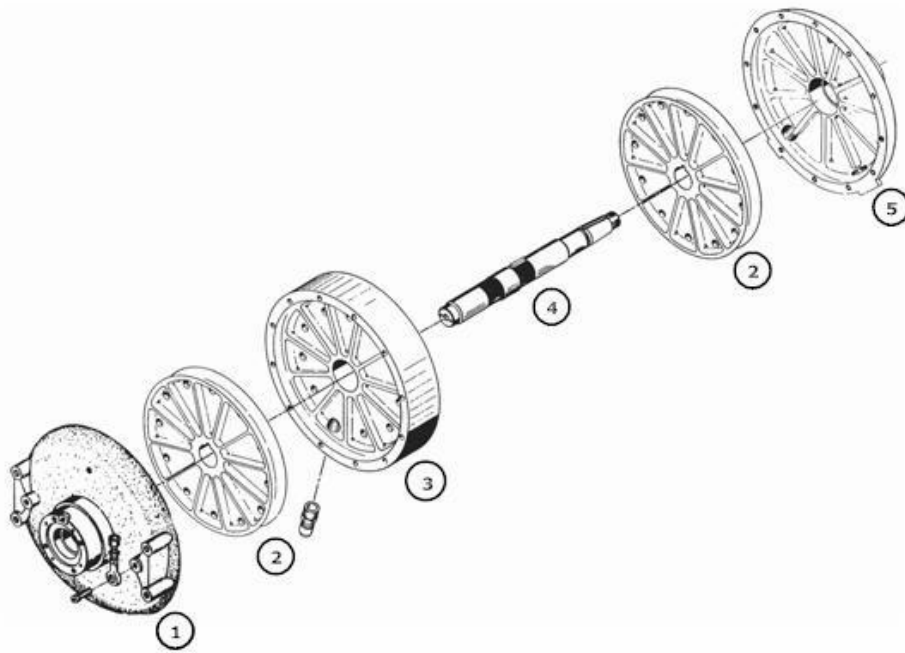


Figure 3.37. The parts of Go Power DA 516 model water brake dynamometer. [1) front cover (stator), 2) rotors, 3) body of absorption unit, 4) main shaft, 5) backcover (stator).]

When the force was applied to the hydraulic load cell piston the pressure induced in the load cell is transferred to pressure transducer. The dynamometer properties listed at Table 3.2 and picture shown at Figures 3.38 and 3.39 respectively. By applying force a pressure happens at dynamometer which can be measured by voltmeter.

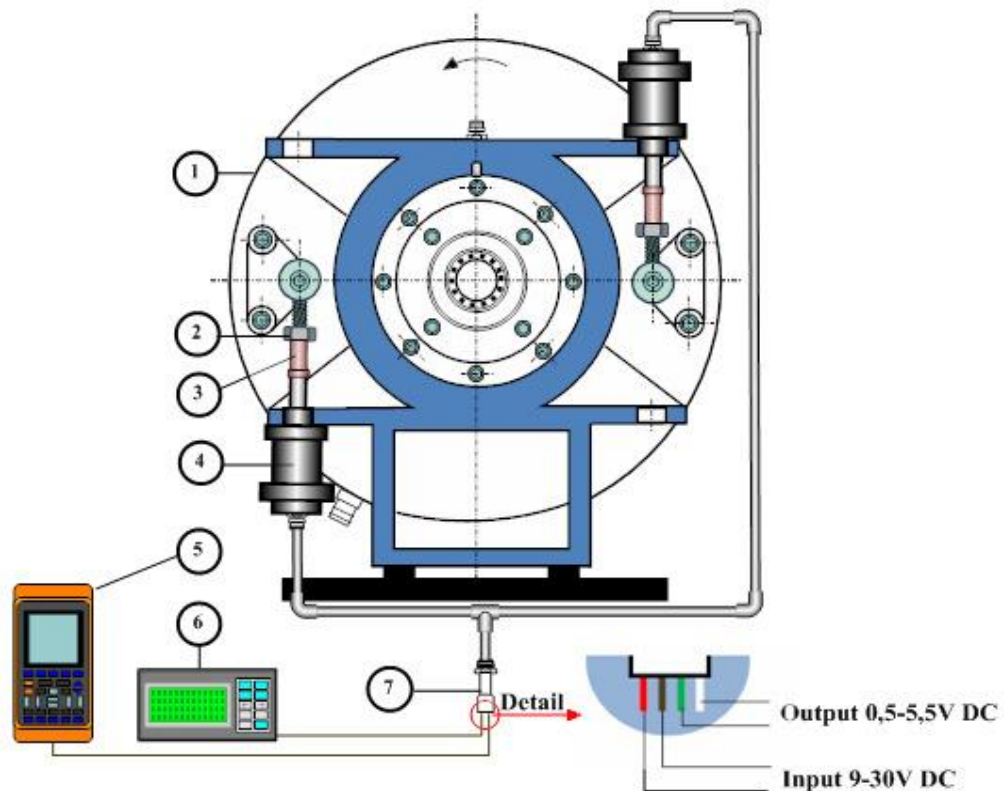


Figure 3.38. Schematic representations of water brake dynamometer and measurement devices.

[1) dynamometer body, 2) jam nut, 3) end push rod, 4) hydraulic load cell, 5) digital voltmeter, 6) electrical power supply, 7) transducer.]



Figure 3.39. Go power system DA 516 model water brake dynamometer.

Table 3.2. Specifications of used dynamometer.

Type of absorption	Water brake
Construction	High strength aluminum alloy
Operating range (rpm)	5000 continuous, 10,000 intermittent
Torque transducer	Hydraulic load cell
Rotation direction	Clockwise or counter clockwise
Inlet water flow rate (l/s)	2.2
Inlet water pressure (kPa)	240
Water outlet	Gravity drain to atmosphere
Max. torque capacity (Nm)	1017
Max. power capacity (kW)	596
Weight (kg)	43

Firstly, dynamometer is calibrated by removing air from hydraulic system. Then engine is run without load as idle. During the engine runs, jam nuts are loosened for controlling pressure in hydraulic cylinders for reading 0.5 volt at digital voltmeter and then nuts were fastened. Transducer gives 0.5-5.5 volt in 0-250 psi linear pressure value.

The voltage converted into torque by Eq.3.21.

$$T = V \cdot \frac{250}{5} \text{ (ft.lb)} \quad (3.21)$$

Cole Parmer C-68075-50 type pressure transducer was used to torque measurement. The properties were given in Table 3.3. The accuracy is $\pm 0.25\%$ full-scale, which shown in Figure 3.40.

Table 3.3. Properties cole parmer C-68075-50 transducer.

Output	0.5 to 5.5 V
Accuracy	$\pm 0.25\%$ full-scale
Process connection	1/4" NPT(M)
Power	9 to 30 VDC
Electrical connections	2-ft cable
Dimensions	2 3/4"L x 1 1/2" dia
Wetted parts	17-4 PH stainless steel
Range	0 to 250 psig



Figure 3.40. Cole parmer C-68075-50 transducer.

The diesel engine was used for fuel sample test at Dicle University's Mechanical Engineering Department shown at Figures 3.41 and 3.42. Performance and emission parameters were adjusted by the control panel and the exhaust analyzer. The engine and a hydraulic dynamometer were connected each other to measure performance and emission parameters. The engine model was 4 LD 820. It has a single-cylinder; four-stroke, air cooled, and naturally aspirated direct injection. The cylinder bore was 102 mm with a stroke of 100 mm. The maximum power output was 15 Hp at 2600 rpm. The engine specifications are declared at Table 3.4 [66]. All of the experimental procedure and equipments will be explained.

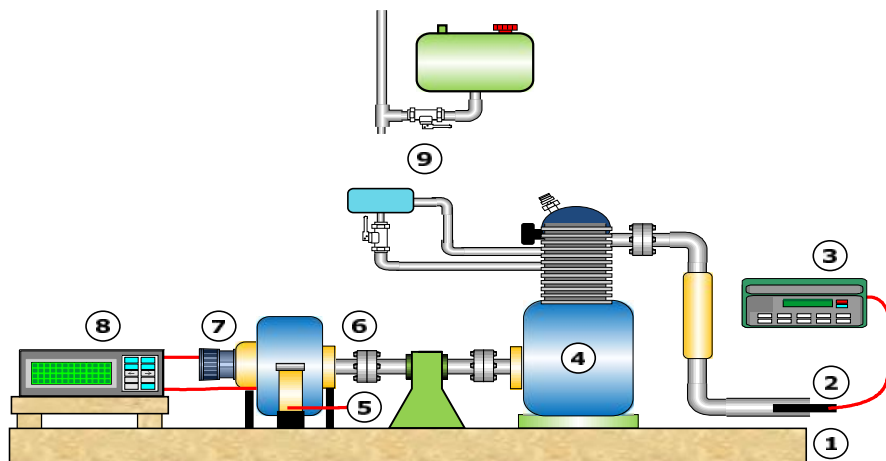


Figure 3.41. Schematic diagram of the test engine and exhaust analyzer. [1) engine chassis, 2) exhaust gas analyzing probe, 3) exhaust gas analyzer, 4) single cylinder diesel engine, 5) load cell, 6) dynamometer, 7) tachometer, 8) control unit, 9) fuel burette, 10) fuel container.]



Figure 3.42. Picture of the diesel test engine and its dynamometer.

Table 3.4. Main specifications of the test engine.

Engine model	4 LD 820
Engine Type	Four stroke
Fuel type	Diesel
Bore	80 mm
Stroke	70 mm
Swept volume	406 cm ³
Compression ratio	18:1
Injection pressure	20 MPa
Cooling type	Air cooled
Maximum torque	40 Nm at 2000 rpm
Maximum power	10 kW at 2000 rpm
Engine position	Vertical

The engine performance parameters are vital and should be specified. These parameters are brake torque (T), brake power (P_b), brake mean effective pressure ($Bmep$), brake specific fuel consumption ($Bsfc$) and the brake thermal efficiency. In addition to these, engine parameters were computed by fuel and air expending, HHV_{fuel} , torque and speed.

3.7.1 Brake power (P_b)

Brake power was figured out by torque. The torque carried out in the cradled housing was calculated by the moment arm multiplied by weight [67]:

$$T = F \cdot d \quad (3.22)$$

where T is the brake torque in Nm, F is the applied load in N, and d is the distance from the center of rotor in m. Each speed could be computed by using the torque value and the angular speed. The brake power was turned over by the engine and was absorbed by the dynamometer [67], whose formula is given in the equation below.

$$P_b = \frac{2\pi \cdot \omega \cdot T}{1000} \quad (3.23)$$

where P_b is a brake power in kW, ω is an angular speed in rev/sec.

3.7.2. Brake mean effective pressure (Bmep)

Mean effective pressure is a distinct parameter for engines. It is characterized by the average gas pressure. It compresses piston(s) through one engine cycle completion. It shows engine development degree [67]. So, the brake power was used in the equation, therefore the average gas pressure could be called as the brake mean effective pressure [67]. That application was calculated as:

$$Bmep = \frac{P_b \cdot n_r \cdot 1000}{V_d \cdot \omega} \quad (3.24)$$

where n_r is the number of crank revolutions within one complete cycle, which is 2 for a four-stroke engine, and V_d is the total volume of the engine cylinders in dm^3 .

3.7.3. Brake specific fuel consumption (Bsfc)

The other parameter for the engine is the brake specific fuel consumption (Bsfc) which is determined through volumetric fuel consumption [68]. It is calculated by [69]:

$$\text{Bsfc} = \frac{\dot{m}_f}{P_b} \cdot 10^3 \quad (3.25)$$

where Bsfc is the brake specific fuel consumption in g/kW.h, and $\dot{m}_f$ is the fuel mass flow rate in kg/h.

3.7.4. Brake thermal efficiency (η_{th})

The brake thermal efficiency is concerned to the effective power, fuel mass flow rate and lower heating value (Q_{LHV}) of the fuel [69].

$$\eta_{bt} = \frac{P_b \cdot 3600}{\dot{m}_f \cdot Q_{LHV}} \quad (3.26)$$

where Q_{LHV} is the lower heating value of fuel in kJ/kg.

3.8 Exhaust Emission Parameters

The fuel characteristics, atomization rate, combustion chamber shape, engine speed, and air-fuel ratio are the most important parameters that significantly affect emissions [70-71]. The exhaust emission should be measured by a sensitive device. The Testo 350 model gas analysis device was used to measure the exhaust emissions. This device could detect carbon monoxide (CO), sulfur dioxide (SO₂), and nitrogen dioxide (NO_x) emissions, and also oxygen (O₂), and carbon dioxide (CO₂) emissions. After the engine reached the measurement conditions, the analyzer probe was placed in the exhaust pipe. The emission results and performance parameters results will be explained and discussed in the following section. The specifications of Testo 350 gas analyzer device was listed at Table 3.5 and was shown at Figure 3.43.



Figure 3.43. Picture of testo 350 gas analyser.

Table 3.5. Specifications of testo 350 gas analyser.

Specifications	Sensor Type	Range	Max. Perception time (s)	Accuracy
O ₂	Electrochemical	0-25%	20	±0.1%vol
CO	Electrochemical	0-8000ppm	50	<300=±10ppm
CO ₂	Electrochemical	0-99%	-	-
NO	Calculated	0-4000ppm	40	<100ppm=±5ppm
NO _x	Electrochemical	0-4000ppm	-	0.1
C _x H _y	NDIR	0-5%	20	±5%
Tgas	Thermocouple K	0-1000°C	-	±(3% rdg+0.3)

3.8.1 Carbon Monoxide (CO)

Carbon monoxide (CO) is a colorless, odorless, tasteless, and highly toxic gas. One carbon atom and one oxygen atom are bonded by a covalent double and a dative covalent. CO₂ is produced from oxygen-carbon compounds reaction. However, decrease of oxygen causes to produce CO, which is produced due to combustion fuel at incomplete combustion which was caused by low air-fuel ratio. CO reacts with hemoglobin in the blood to produce carboxyhemoglobin (HbCO), which is ineffective for delivering oxygen to the body tissues (a condition known as anoxemia). CO concentrations as low as 667 ppm can cause up to 50% of the body's

hemoglobin to convert to HbCO. Besides, CO is an atmospheric pollutant. At low speeds, the CO amount is high in emission [72].

3.8.2 Carbon Dioxide (CO₂)

Carbon Dioxide is a colorless, odorless gas. A carbon atom is covalently double bonded to two oxygen atoms. CO₂ is one of the several greenhouse gases causing global warming. CO₂ also affects oceans, seas and rivers by dissolving in water to form carbonic acid. When the air/fuel ratio is richer, the maximum level of CO₂ emissions is obtained [73].

3.8.3 Nitrogen Monoxide (NO) and Nitrogen Oxides (NO_x)

Nitrogen monoxide and dioxides have harmful effect on environment and climate change, especially on ozone layer and human health. They react with moisture in the lungs by forming nitric acid, and lead to respiratory diseases [72]. The motor design and technology, particularly spraying time, flame temperature, heat transfer distribution, and ignition delay affect NO_x emissions. The rich air/fuel mixture and high temperature lower oxides of nitrogen [70, 71].

3.8.4 Oxygen (O₂)

Oxygen is a colorless and odorless diatomic gas (constitutes 20.8% of the earth's atmosphere). Two atoms of the element bind to form deoxygenate (O₂). It is highly reactive element and easily oxidizes with other elements during the combustion. The high amount of oxygen (O₂) improves burning and satisfies rich combustion [72].

3.8.5 Sulfur Dioxide (SO₂)

Sulfur Dioxide is a toxic gas with a pungent, irritating, and rotten smell. SO₂ is bent molecule with C_{2v} symmetry point group. It is described as two resonance bonding structure by considering s and p orbital. The sulfur reacts with oxygen to produce

SO₂ which has a significant impact on environment and human health. The SO₂ emissions cause acid rains and harm people, animals and natural life [70-71].

3.8.6 Unburned Hydrocarbon (HC)

The unburned HC (hydrocarbon) emission occurs at incomplete combustion which is semi-oxidation or not oxidation of the fuel when the temperature cannot reach ignition temperature or there is lack of oxygen in the environment [74]. HC is related with the injection geometry system and the combustion chamber. The HC emissions are reduced by increasing air revolution movements (turbulence) [75].

CHAPTER 4

PRODUCTION OF GASOLINE AND DIESEL LIKE FUEL FROM ROTARY KILN AND BATCH PYROLYSIS

4.1 Introduction

Pyrolysis is an interesting method and, also, gets attention as a non-conventional technique in tire recycling research. In this process, the heat breaks down chemical bonds and decomposes the compound structure under non-oxygen atmosphere at high temperatures. Thereby, the high molecular weight polymers in tire rubber are reduced to low ones in forms of gas, solid and liquid that can be used as chemical energy resources. The inorganic residues such as steel and carbon black still remain solid at the end of this process [76]. Thermal and pyrolytic distillations are applied to waste tire for its conversion into petroleum fuel. Furthermore, many tests are used to determine whether the products of waste tire can be used as standard fuel.

4.2 The waste tire

There are many tire types that have been produced in Turkey. The basic composition of a tire is known as rubber and fillers including non-homogenous distributions of carbon black, steel, sulfur, zinc oxide, processing oil and vulcanization accelerators. Table 4.1 declares the proximate, ultimate analysis and HHV results. The ash content shows various inorganic materials (zinc, clay, and silica) that are dependent on the formulation and manufacturing of the tire [77]. Thus, the waste tires are separated into various sized particles. The cross-section particles are cut to remove the steel cords and textile fabrics from rubber. The rubber is then powderized to pass through a 20-40 mm sieve.

Table 4.1. The ultimate, proximate and HHV analysis of waste tire.

Ultimate Analysis (wt%)		Proximate Analysis (wt%)		HHV (MJ/kg)
C	80.46	MC	1.62	36.34
H	8.14	VM	63.41	
N	0.82	FC	21.86	
S	3.68	Ash	13.21	
O ^a	6.9			

^aBy difference, MC: Moisture Content, VM: Volatile Material, FC: Fixed Carbon

The proximate, ultimate, HHV and TG/dTG analyses are applied to explain the waste tire properties. As a result of these analyses, the waste tire is determined to be beneficial to pyrolyze. The ultimate analysis gives an idea about the chemical composition of the sample in wt% of carbon, hydrogen, oxygen, sulphur and nitrogen after the organic compounds combustion is completed. Therefore, the elemental composition analysis is available for the waste tire. The proximate analysis shows the wt% of organic and inorganic materials in the sample, such as moisture, volatile matter, fixed carbon, and ash contents. The ash content shows various inorganic materials (zinc, clay, and silica) that are dependent on the formulation and manufacturing of the tire [77]. According to the literature, the proximate, ultimate analysis and HHV values are found to be similar to the ones from previous research [20,78].

The thermogravimetric analysis provides the pre-information for the study that gives a good idea about the thermal decomposition characteristics of the tire material [32] and is majorly related with the type of rubber's chemical compound [20]. Generally, rubbers include natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). Thermogravimetric (TG) and its derivative (dTG) curves of waste tire are shown in Fig. 4.1. As it can be observed from the TG curve in Figure 4.1, the thermal decomposition of tire material begins around at 200 °C and makes a sharp slope up approximately between the temperatures of 375 °C and 450 °C. The decomposition reaction happens between 200 °C and 450 °C. These results are compatible with the related literature [32,79]. On the other hand, the dTG curve has a dominant slightly round peak around the temperatures between 400 °C and 500 °C and indicating the presence of a large amount of SBR in the waste tire. This result proves that SBR is in good agreement with the relevant research [20,80].

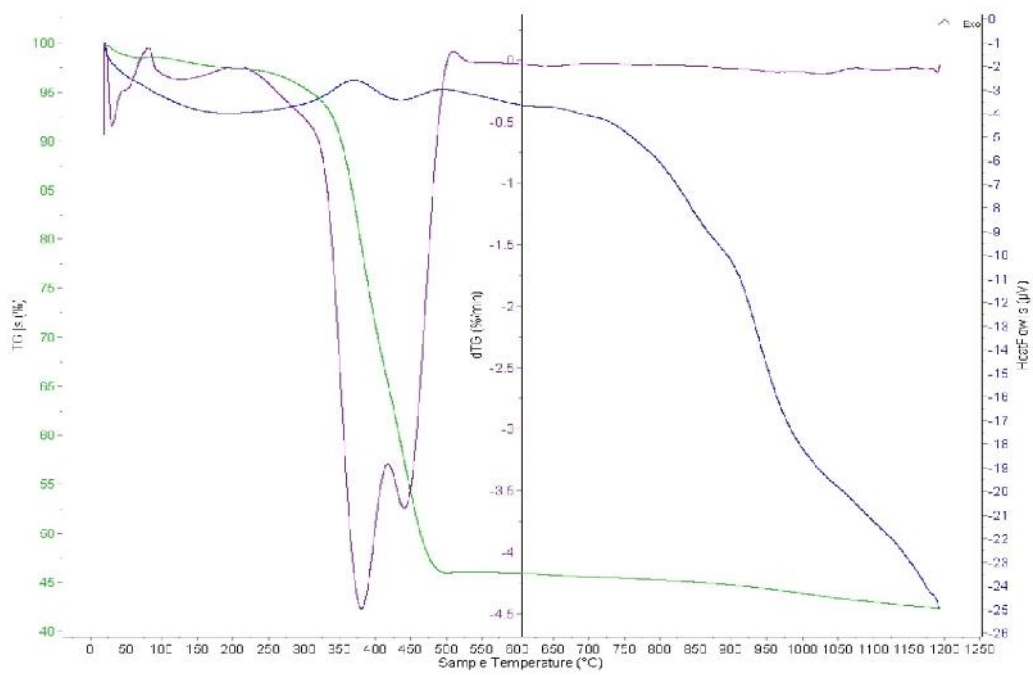


Figure 4.1. TG/dTG of waste tire.

The pyrolysis kinetic analysis process has been applied to thermal decomposition by many researchers. The obtained data from this process gives some idea about any kind of materials' pyrolysis kinetics. Moreover, it is essentially correlated with the material's decomposition mechanism. The kinetic mechanisms are calculated by using equations for thermal decomposition [81,83]. In this study, pyrolysis kinetics of waste tire was analyzed by both thermogravimetry (TG), and differential thermogravimetry (DTG). The analysis results are given as;

The solid decomposition at a non-isothermal mode can be explained as [84]:



The general formula for solids' decomposition is given as the following:

$$\frac{dx}{dT} = k(T) f(x) \quad (29)$$

And, the decomposed sample can be calculated as:

$$x = \frac{w_i - w_t}{w_i - w_f} \quad (30)$$

where; x is conversion rate, w_i is the initial sample mass, w_t is the actual mass and w_f is the mass after pyrolysis.

The normalized weight loss data form (x) and the reaction constant rate $k(T)$ is calculated by the Arthenius Equation [82] as defined with temperature dependence as:

$$k(T) = Ae^{\frac{-E_a}{RT}} \quad (31)$$

where; E_a is the activation energy (kJ mol^{-1}), T is the absolute temperature (K), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and A is the pre-exponential factor (min^{-1}).

The function, $f(x)$, and its derivative are used to determine the solid-state amount for the first reaction; thus many researchers restricted the mathematical function $f(x)$ to the following expression [85-86].

$$f(x) = (1-x)^n \quad (32)$$

For a constant heat rate, $\frac{dT}{dt}$,

$$\frac{dx}{dT} = \frac{A}{RT} e^{\frac{-E_a}{RT}} (1-x)^n \quad (33)$$

The following Equation is obtained from Eq. (6) by making it linear with arrangements as:

$$\ln\left(\frac{dx}{dT}\right) - n \ln(1-x) = \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT} \quad (34)$$

The plot of $\ln\left(\frac{dx}{dT}\right) - n \ln(1-x)$ versus $(1/T)$ should give a straight line for the correct value of the reaction order, n . The activation energy and the pre-exponential

factors are calculated from the slope of $(-\frac{E_a}{RT})$, and are intercepted with the function of $\ln\left(\frac{A}{\beta}\right)$ [82].

The $T_i = 260\text{ }^{\circ}\text{C}$, $T_f = 563^{\circ}\text{C}$ and $T_{\max} = 380^{\circ}\text{C}$ were obtained from Figure 4.1, under $4^{\circ}\text{C}/\text{min}$ heating rate and also 42.36 wt% residue was calculated as a result. The kinetic parameters were calculated by the Arrhenius method and declared as; $E_a = 60.12\text{ kJ mol}^{-1}$ (activation energy), $\log A = 3.81\text{ min}^{-1}$ (pre-exponential factor) and $R^2 = 0.959$.

A tire consists of over a hundred different materials, including rubber and fillers, i.e. carbon black or silica gel, steel, sulfur, zinc oxide, etc. The natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR) and their blends are common rubbers that are used to make tires. The rubber and its other components are degraded at different temperature ranges and their thermal decomposition gives information about the rubber type inside them and their ingredients as well [80,87]. The tire rubber (SBR, NR and BR) and its components' devolatilization, which was conducted under 5 K min^{-1} and 80 K min^{-1} heating rates, was studied by Williams and Besler [88]. The waste tire, containing three main components such as NR, SBR and BR, generated a sharp peak at around 643 K, a round peak in the 673–733 K range and another sharp peak at around 733 K in its DTG curve [83].

From the TG-DTG curve of waste tire shown in Figure 4.1, it can be observed that the first and second step weight losses amount were about 8 wt% and 18 wt%, respectively, which were taken place between $20\text{ }^{\circ}\text{C}$ – $40\text{ }^{\circ}\text{C}$. Thereby it can be understood from the DTG curve that the moisture in waste tire was vaporized. Based on the TG graphic, it can be determined that the thermal decomposition was started approximately at $25\text{ }^{\circ}\text{C}$ and was followed by both a minor and major weight losses while the reaction was going on. Finally, the decomposition was completed at $550\text{ }^{\circ}\text{C}$ and no significant weight loss was observed after this temperature. The degradation curve indicates that the waste tire mostly consisted of SBR and NR.

4.3 Batch Pyrolysis

4.3.1 Introduction

The waste tire was firstly cut into small pieces, and the steel wires and fabric fibers were removed from the tire pieces. The pieces were then washed and dried. The as-cleaned tire pieces were weighed and then filled into the reactor. The waste tire were heated up (450 °C) and then exposed to thermal and pyrolytic treatments in order to convert them into liquid. The as-obtained samples were named as WTO. The characterization, distillation, heating capacity and chemical analysis tests of the as-produced WTOs were examined to compare with diesel. As a result of tests, the WTO was similar to diesel. But it needs to react with some catalytic to get more similar to diesel. Thus, the WTO samples were mixed with calcium oxide (CaO) and natural zeolite (NZ) additives at different ratios of 2 %, 4 %, 6 %, 8 % and 10 %, respectively. In relevant literature, there is no example study about the liquid products being separated into two fractions that are resembling diesel and gasoline fuels. Thus, in this paper, the authors represent a detailed characterization of the 10% CaO/WTO mixture, which was separated into two fractions as light and heavy fuels. The elemental analysis, gross calorific values, density, flash point, viscosity, sulfur content, and distillation tests were performed for these fuels. Then, each test result was compared with petroleum-derived fractions' distillation data, and also the other properties were compared with those of gasoline and diesel fuels. Since, the first fraction or light fuel resembles to gasoline, it is called as gasoline-like fuel (GLF). The second one or the heavy fuel, which resembles diesel fuel, was named as diesel-like fuel (DLF). Finally, the GLF and DLF were both analyzed in details to determine whether they are useful for engines or not.

The lime (CaO) or calcium carbonate is used as additives in this study. The addition of CaO both reduces the sulfur emissions and upgrades the oil quality. Furthermore, the CaO can be used as an absorber to increase the aliphatic amounts and aromatic hydrocarbons [89,90]. The additives are used in different pyrolysis studies by categorizing a feedstock of materials. Especially, zeolite types are used in many researches as ZSM-5, Y-Zeolite etc. The zeolite additive is used to obtain more chemical feedstock. On the other hand, decreasing the heating rate and increasing the process duration are the other important parameters for the pyrolysis [91]. Besides,

the aromatic ring compounds' concentration is increased in a certain manner by using the zeolite catalysts. Similar researches have been published in the literature [92,93]. Table 4.2 shows NZ compositions. The physical properties of NZ are determined at Table 4.3. The catalysts have been reacted in tire pyrolysis process to increase the aromatic compounds' yield [37]. Since its specific density and specific surface values are high, the NZ-1 is used for this reaction. Here, the zeolite pores and the number of cations number placed around them enable great product quality control degree and product structure modification possibility, as well. The CaO can also improve the product quality, increase the gas yield and decrease the tar yield. Here, the H₂, CH₄ and C₂–C₅ hydrocarbon yields are increased while CO yield is decreased. As a result, the alkanes with long chains are broken into shorter chain hydrocarbons by adding CaO in the reaction medium [94]. NZ-1 is inserted in water to adjust the temperature (24.85°C–74.85°C). 1 N HCl solution is mixed to remove CO₂ and then, the mixture is cleaned by de-ionized water to release gas. The method is continuously applied to zeolite until no chlorine is precipitated with 0.01 N AgNO₃. The SO₂ is absorbed by NZ-1 until it vanishes [95].

Table 4.2. Natural zeolite (NZ) samples compositions (wt%).

Constituents	NZ-1	NZ-2	NZ-3
SiO ₂	64.3	62.2	63.5
Al ₂ O ₃	13.5	11.9	12.4
Fe ₂ O ₃	2.7	1.5	1.4
CaO	2.0	2.2	2.1
MgO	0.9	0.6	0.7
Na ₂ O	2.9	0.8	1.6
K ₂ O	1.6	3.7	2.9
Loss Ignition (water)	12.1	14.1	12.4

Table 4.3. Natural zeolite (NZ) samples physical properties.

	NZ-1	NZ-2	NZ-3
Specific gravity (gcm ⁻³)	2.38	2.20	2.16
Specific surface area (m ² g ⁻¹)	590	568	579
Cation exchange capacity (meg 100g ⁻¹)	186	169	176
Porosity (%)	81.2	76.8	78.5
Thermal conductivity (W mK ⁻¹)	0.73	0.77	0.75
pH	8.32	8.24	8.19

4.3.2 Physical properties and distillation tests results of products

The characteristics of the as-produced fuel were tested and the results are given in Table 4.4. It can be seen from this table that density, viscosity and water content of the WTO are in the range of standard diesel fuel; however, its flash point is lower than that of standard diesel fuel. It indicates that there is more volatile fuels exist in WTO. At the same time, its sulfur content is higher than that of standard diesel fuel, which is normal or an expected situation, since the vehicle tires contain high amount of sulfur. The sulfur amount in the as-produced WTO should be reduced down to the standard values so that it can be used as an engine fuel. The lower heating value (LHV) is another important characteristic of a fuel. The LHV of WTO is measured as 41,000 kJ/kg by using a bomb calorimeter (Leco AC350). It is found to be closer to the standard diesel fuel's LHV with a value of 42,700 kJ/kg in Turkish (TS-3082) and European (EN-590) standards. The three test results, regarding to distillation are given in comparison with the standard values. Among those, two of them indicate minimum and maximum distilled volumes at 250°C, the other one is related with maximum temperature at which 95 % of the fuel is distilled.

Table 4.4. Characteristics of diesel fuel [7] and WTO.

Properties	Diesel fuel TS3082-EN 590	WTO
Density at 15°C, kg/m ³	820-845	830
Viscosity at 40°C, mm ² /s	2-4.5	3.21
Water content, mg/kg	<200	130
Flash point, °C	>55	28.1
HHV, kJ/kg	42.70	41.00
Distillation		
Temperature at 250°C, max. volume (% v/v)	40	60
Temperature at 350°C, min. volume (% v/v)	85	80
Volume at % 95, max. temperature, °C	360	---

The distillation test is a chemical process, in which, two or more liquids with different boiling points can be separated from each other, or it is applied to indicate the evaporation temperature of each hydrocarbon that is present in any fuel. It is thought as a possible way to determine the quantity of hydrocarbons by comparing

them with standard petroleum fuels [21]. It can be understood from the distillation test results whether a fuel is heavy/light or not. In order to see the variation between the distilled temperatures versus distilled volume, a distillation test on the WTO sample was performed. The result shows that WTO is a mixture of different hydrocarbons, each of which evaporates at different temperature. The distillation temperature versus distilled volume graphic provides more appreciable ideas about the combustion and engine performance of a fuel sample, as an indication of how its ignition will take place [96]. It can be decided whether the fuel can be used in engines or not by looking at this distillation curve. Therefore, it is necessary to carefully examine the distillation curve to find out whether the distillation temperature of each WTO droplet is light or not. The distillation curve is directly related to the composition and chemical characteristics of the fuel. Thus, the engine performance can be predicted by the distillation curve, as well [97]. As a result of these considerations, the fuel sample's distillation test should be performed, and its distillation curve should be compared with other fuels' curves. It is understood from Figure 4.2 that the WTO produced in this study is lighter than standard diesel fuel. Thus, CaO and NZ-1 are used as catalysts to obtain fuels that are similar to gasoline and diesel fuels.

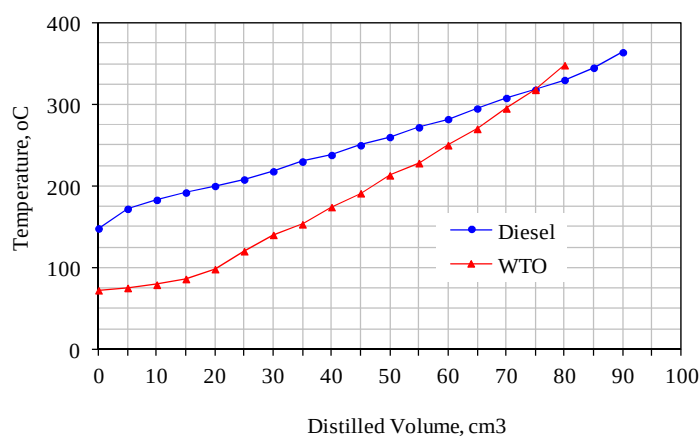


Figure 4.2. Distillation curve of WTO.

In order to examine the effects of CaO and NZ-1 catalysts on the as-produced WTO's distillation temperature, the CaO and NZ-1 were blended with waste tire at the mass basis of 2, 4, 6, 8 and 10 percentages, and their mixtures were then pyrolyzed. As a result, the WTO samples were produced. The as-produced WTO samples' distillation curves are depicted in Figures 4.3 and 4.4. These figures show

that the graphs from the WTO samples produced with CaO are closer to that of the diesel fuel than those produced with NZ-1. It can be observed from these figures that the distillation temperatures for both CaO and NZ-1 increase smoothly and gradually. This result is important because the starting ability and warm-up property of a fuel is evaluated by the evaporation temperatures of 20-70 % vaporization region of the distillation curves [12]. Each droplet of a fuel should be distilled in a regularly increasing temperature. A fuel sample that is distilled at a constant temperature or at a very narrow temperature band is not a desired fuel [12,95].

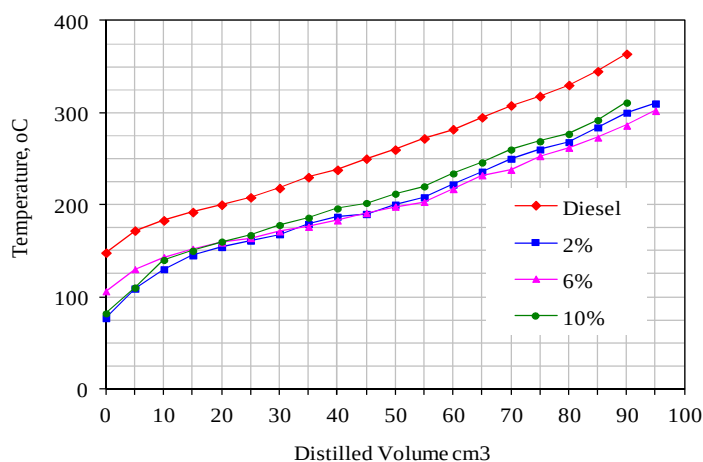


Figure 4.3. Effect of CaO amounts on distillation temperature of WTO.

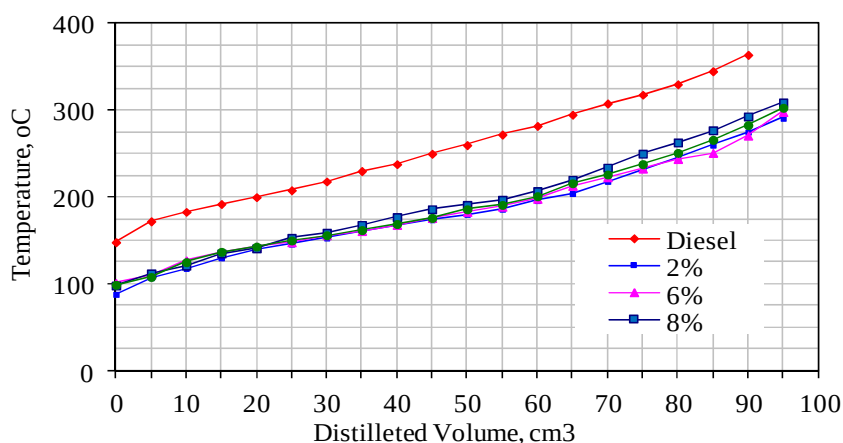


Figure 4.4. Effect of NZ-1 amount on distillation temperature of WTO.

Distillation graphs for a typical commercial diesel fuel and WTO-CaO and WTO-NZ-1 samples are shown in Figure 4.5 to decide which additive, CaO or NZ-1, is

more suitable for standard petroleum. The figure shows that the best WTO mixture graphs are obtained from these catalysts at the mass basis of 10 % of CaO and 8 % of NZ-1. However, the graph of WTO with 10 % of CaO is closer to the diesel fuel curve than the other one. As far as the distillation data are concerned, 10 % CaO was blended with WTO fractions with a similar boiling range of diesel fuel, which starts from 150 °C and ends at 360 °C [14]. The procedure for WTO fraction separation as light and heavy fuels is presented in the following two subsections. Thus, it can be concluded that the distillation temperatures for a huge amount of distilled volume for the CaO (10 %) sample are closer to the ones at diesel fuel graph. This indicates that WTO contains approximately 18 % lighter hydrocarbons (distilled by volume) than the hydrocarbons exist in the diesel fuel. It should be noted that the fuel that is lighter than diesel fuel can cause pre-ignition and detonation problems in the combustion chamber of an engine. Therefore, the light fuel presented in WTO should be removed, in order to burn the fuel sample without having any problems. As a result, it is considered that the pyrolytic liquid fuels can be used as engine fuels after upgrading and separating the as-produced WTO. It is observed that CaO is the more effective additive to produce engine fuel with a distillation curve that is closer to the commercial diesel fuel's distillation curve.

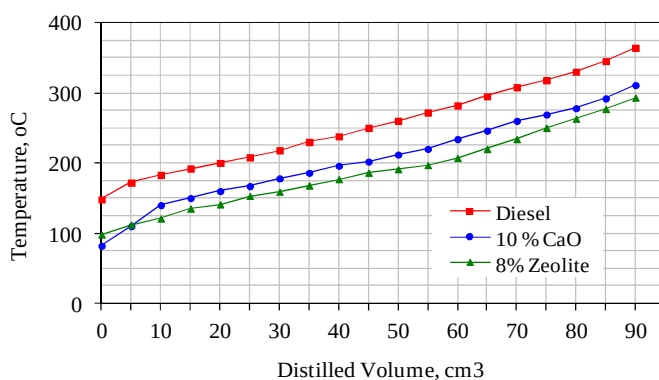


Figure 4.5. Distillation curves of 10 % CaO and 8 % NZ-1 on distillation temperature of WTO.

The 10% CaO and WTO mixture were put into the reactor, and then were heated from room temperature up to 150 °C. The first 18 % fraction of the total weight was collected into a burette, and the remaining sample was kept in the reactor. Some characteristic values of the light fuel sample are given in Table 4.5. The distillation curves for the collected light fuel, commercial standard gasoline fuel, and also

another gasoline fuel presented in reference [96] were depicted in Figure 4.6, in order to compare the as-produced sample's behavior with these samples. The figure shows that the as-produced light fuel is heavier than the other gasoline samples. However, the light fuel curve lies parallel to the other gasoline samples' curves. It is understood that the gasoline is a mixture of several volatile petroleum hydrocarbons that are composed of 4-12 carbon atoms, and whose distillation range varies between an initial boiling point of 40 °C and a final boiling point of 225 °C under atmospheric pressure. Many of the hydrocarbons have different boiling points. Thus, gasoline boils or distills over a wide range of temperature, unlike a pure compound like water, which boils at a single temperature. GLF's initial boiling point (54 °C) is within the range, but its final boiling point (253 °C) is higher than the standard 225 °C value. Characteristics and the tendency of distillation curve of a fuel used in engines are very important, thus the as-produced light fuel is named as gasoline like fuel (GLF). Since the as-produced light fuel resembles to those of standard gasoline samples that can be burned in SI engine.

Table 4.5. Some characteristics of the unleaded gasolines and GLF.

Properties	GLF	Unleaded gasoline	Unleaded gasoline
Density at 15°C, kg/m ³ (D1298)	740	780	742
Flash point, °C (D93)	20	-43	---
HHV, kJ/kg (D270)	42,163	43,890	43,000
IBP	54	34	43.5
10 vol %	74	53	55
50 vol %	121	92	102
90 vol %	188	154	174

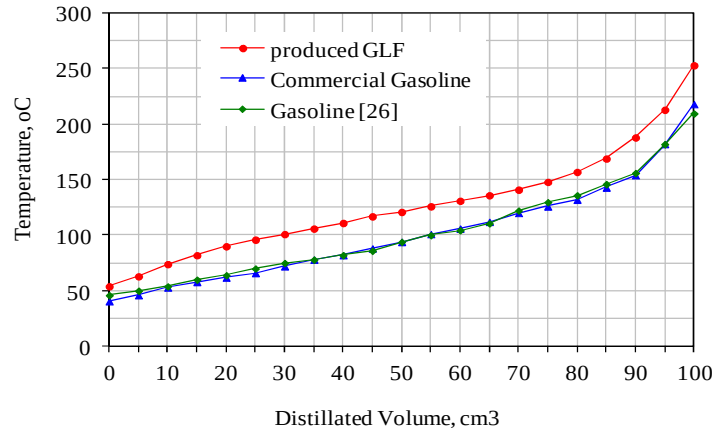


Figure 4.6. Distillation data for produced GLF and the other standard gasoline fuels.

After the first fraction; the light fuel was collected into a burette, and then the distillation temperature was slowly increased up to 450 °C, and finally the fuel was collected into another burette. The second fraction obtained by the distillation of the fuel mixture (10% CaO and WTO) was approximately 70 % of the total weight. The second fraction was distilled again, and its distillation curves' comparison with the ones from a commercial diesel fuel and some standard diesel fuel [98] were depicted in Figure 4.7. Since the characteristics and distillation test results of the fuels are very important, they were given in Table 4.6 and Figure 4.7 respectively. The table shows that the as-obtained fuel characteristics are reasonably close to the standard diesel fuel's values. For example, the lower heating value (LHV) is one of the most important properties. LHV of the as-produced heavy fuel is calculated as 43,214 kJ/kg by using an adiabatic bomb calorimeter. This value is slightly higher than the LHV of diesel fuel (42,700 kJ/kg) according to Turkish (TS-3082) and European (EN-590) standards given in Table 4.10. Also, the distilled volumes or temperatures that correspond to values indicated in these standards are given in Table 10. They found to be close to those of the standard diesel fuel. It is considered that the as-produced fuel's performance parameters will not decrease, contrarily they will increase. The distillation curve also supports this consideration. It is clear from the Figure 4.17 that the heavy fuel's curve resembles to and lies parallel to that of diesel fuels. Therefore, the as-produced heavy fuel is named as diesel like fuel (DLF). From these results, it can be concluded that the DLF can be used efficiently in diesel engines, and there will be no problems in the performance of the engine.

Table 4.6. Some characteristic of standard diesel fuel [7] and DLF.

Properties	Diesel fuel TS3082-EN 590	WTO
Density at 15°C, kg/m ³	820-845	825
Viscosity at 40°C, mm ² /s	2-4.5	3.09
Water content, mg/kg	<200	23
Flash point, °C	>55	130
HHV, kJ/kg	42,70	43,214
Distillation		
Temperature at 250°C, max. volume (%) v/v)	40	50
Temperature at 350°C, min. volume (%) v/v)	85	95
Volume at % 95, max. temperature, °C	360	---

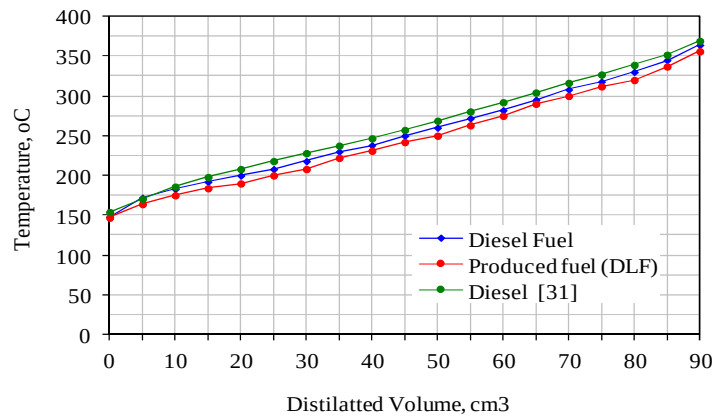


Figure 4.7. Distillation data for produced DLF and standard diesel fuels.

4.3.3 Ultimate analysis test results of products

The "ultimate analysis" provides the compositional information of the biomass in wt% of carbon, hydrogen, oxygen, sulfur and nitrogen, etc. That is, it gives the elemental composition information of any type of fuel. The heating capacity of any fuel is the most important property, since the size of any combustion system is designed according to the heating capacity of fuel to be used in the combustion system. It is known that the fuel's heating capacity basically depends on the carbon and hydrogen contents. Therefore, the ultimate analysis of WTO, GLF and DLF were performed to have an idea about content of WTO. The elemental composition is very important, since % values or the amount of elements exist in the fuel can give an idea about its volatility, heating capacity, combustion performance and its exhaust emissions. Therefore, the ultimate or elemental analysis of the WTO, GLF, DLF,

Gasoline and Diesel Fuels was performed and its results are shown in Table 4.7 [13,66,99]. It can be seen from the elemental analysis results in Table 4 that the total amounts of carbon and hydrogen in WTO, GLF and DLF were approximately close to that of in gasoline and diesel fuels. At the same time, the oxygen (O₂) amount was found to be very high, whereas the nitrogen (N₂) amount was low. The presence of O₂ and N₂ in any fuel is an undesired condition, since they do not have any heating value. But, the presence of O₂ increases the combustion performance. The H/C and O/C molar ratios were calculated from the elemental composition, and shown in Table 4.4. The WTO sample's ultimate analysis test results show that its combustion performance is high and emissions are in a reasonable range.

Table 4.7. Ultimate analysis of WTO, GLF and DLF with gasoline and diesel.

Elementals (wt%)	WTO	GLF	DLF	Gasoline	Diesel
C	79.49	80.44	81.31	85.4	86.58
H	9.04	10.06	11.28	14.1	13.29
N	0.38	0.28	0.52	200ppm	65ppm
O ^a	9.67	9.21	4.45	---	0.01
S	1.42	---	0.8	280ppm	0.11
H/C ^b	1.36	1.50	1.66	1.98	1.80
O/C ^b	0.09	0.08	0.04	---	---

^a Calculated by difference, ^b Calculation

4.3.4 FT-IR results of products

The FTIR spectrum of GLF is shown in Figure 4.8. The aromatic C-H stretching with alkenes' =C-H stretching vibration structure can be observed in the range from 3100 cm⁻¹-3000 cm⁻¹. The aliphatic -C-H stretching vibration bands were ranging between 2950 cm⁻¹ to 2800 cm⁻¹ with the same molecular arrangement, but with a different isomer structure. Also, the C=O stretching vibration bands, the alkene group's C=C stretching vibration and the ester-ketone bonds were ranging between 1750 cm⁻¹ and 1600 cm⁻¹. The bands distributed from 1550 cm⁻¹ to 1450 cm⁻¹ are related to aromatic C=C bending vibrations, which point out the presence of alkenes in the structure. The aliphatic -C-H bending vibration bands in the frequency range of 1400 cm⁻¹-1350 cm⁻¹ indicate the stretching alkynes and also the =C-H out of plane bending peaks around the 900 cm⁻¹-650 cm⁻¹ region point out the aromatic compounds and alkenes in the structure. The aromatic groups exhibit to increase intensity and concentration [22,26,100]. According to the FT-IR results, it can be

concluded that GLF is a really complex mixture, which contains both the aliphatic and aromatic compounds. Thus, it was proven that GLF is a good quality fuel to get combusted in a gasoline engine.

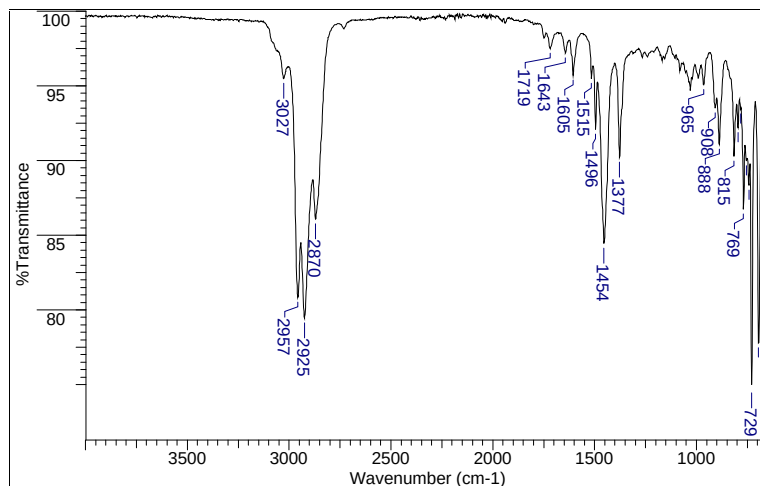


Figure 4.8. The FT-IR spectrum of GLF.

The FTIR spectrum of DLF is shown at Figure 4.9. The aromatic C-H stretching with alkene's =C-H stretching vibration structure were in the range of 3100-3000 cm^{-1} . The aliphatic -C-H stretching vibration bands range from 2950 to 2800 cm^{-1} with the same molecular arrangement and different isomer structure. And also C=O stretching vibration bands, alkene group's C=C stretching vibration and ester-ketone bonds were in the range between 1750 and 1600 cm^{-1} . The bands distributed from 1550 to 1450 cm^{-1} were concerned to aromatic C=C bending vibrations, and was clearly pointing out the presence of alkenes. The aliphatic -C-H bending vibration bands in frequency range of 1400–1350 cm^{-1} were indicating the stretching alkynes and also the =C-H out-of-plane bending peaks in the 900-650 cm^{-1} region were pointing out the presence of aromatic compounds and alkenes [22,26,100]. According to FT-IR results, it could be observed that DLF was a really complex mixture, which was containing the aliphatic and aromatic compounds in its structure. Thus, FT-IR test results proved that DLF was a good quality fuel to be combusted in a diesel engine.

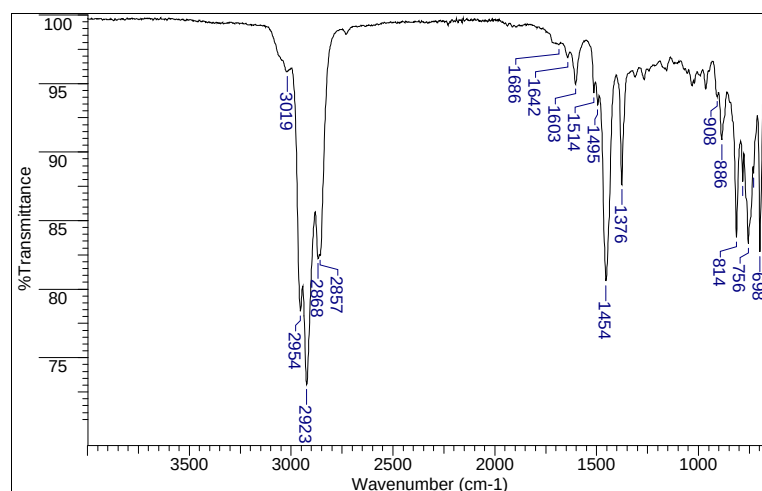


Figure 4.9. The FT-IR spectra of DLF.

4.3.5 GC-MS results of products

The GC–MS chromatogram of the WTO’s aliphatic subfraction is presented in Figure 4.10. The characteristic peaks identification were done by applying Probability Based Matching (PBM) algorithm on their spectra. The peaks’ identification quality outcomes were matched more than 90 % and were considered valid as was confirmed by Laresgoiti et al. [14]. Aliphatic subfractions of the WTO can be seen in Table 4.8. As it is observed from Table 4.5, n-pentane, alkanes, alkenes and branched hydrocarbons were determined in the aliphatic subfractions of the WTO samples, and they are predominantly composed of naphthalene, 1,4,6-trimethyl naphthalene, 2,7-dimethyl heptadecane, and 2,6,10,14-tetramethyl compounds. The WTO’s GC–MS analysis results were compared with the commercial diesel fuel ones and they were found to be similar to each other [101]. Also, WTO’s carbon subfractions distribution resembles to that of diesel fuel’s carbon subfractions distribution [101-102].

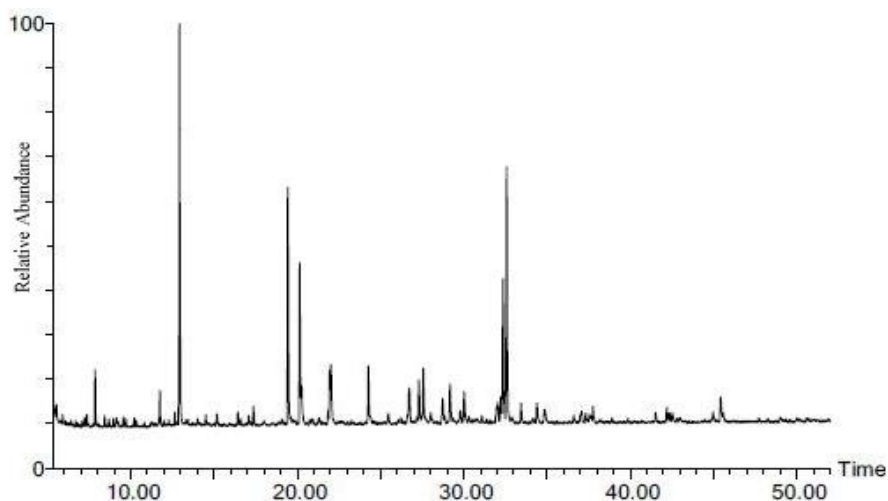


Figure 4.10. GC–MS chromatogram of aliphatic subfraction of WTO.

Table 4.8. GC-MS characterization of the WTO.

Molecular Formula	Compound Name	RT (Min)	Area %
C ₆ H ₁₂ O ₄	1,2,4,5-Tetroxane, 3,3,6,6-tetramethyl	3.96	0.26
C ₆ H ₁₄	Pentane, 2-methyl	5.09	1.11
C ₇ H ₈	Toluene	10.32	0.51
C ₈ H ₁₀	Ethylbenzene	14.19	0.46
C ₈ H ₁₀	Benzene, 1,3-dimethyl	14.58	0.42
C ₉ H ₁₀	Benzene, 2-propenyl	22.31	0.07
C ₉ H ₁₂	5-Methylenecycloocta-1,3-diene	18.21	0.13
C ₉ H ₁₂	Benzene, 1-ethyl-4-methyl	18.67	0.26
C ₉ H ₁₂	Benzene, 1-ethyl-2-methyl	19.31	0.07
C ₁₀ H ₈	Naphthalene	31.17	0.29
C ₁₀ H ₁₄	Benzene, 1-methyl-3-(1- methylethyl)	21.44	0.46
C ₁₀ H ₁₆	D-Limonene	21.60	0.61
C ₁₁ H ₁₄	2-Ethyl-2,3-dihydro-1H-indene1,3,4,6	32.94	0.10
C ₁₂ H ₁₈	Benzene, 1-methyl-2-(1- ethylpropyl)	32.12	0.07
C ₁₂ H ₁₈	Benzene, hexyl	33.86	0.18
C ₁₁ H ₁₂	Naphthalene, 1,2-dihydro-3 methyl	34.31	0.25
C ₁₂ H ₁₄	(1-Methylenepent-2- enyl)benzene	34.70	0.21
C ₁₅ H ₂₄	1-(3-Methylbutyl)-2,3,4,5-tetramethylbenzene	34.92	0,62
C ₁₁ H ₁₄	1H-Indene, 2,3-dihydro-1,3- dimethyl	35.12	0.14
C ₁₁ H ₁₃ NO ₂	1,3,5-Trimethyl-2-(2-nitrovinyl)benzene	35.80	0.38
C ₁₂ H ₁₀	Biphenyl	39.33	0.60
C ₁₂ H ₁₂	Naphthalene, 1-ethyl-	39.84	0.99
C ₁₂ H ₁₂	Naphthalene, 2,7-dimethyl-	40.35	2.59
C ₁₃ H ₁₂	1,1'-Biphenyl, 2-methyl-	42.96	0.98
C ₁₃ H ₁₄	Naphthalene, 1,4,6-trimethyl-	44.22	3.43
C ₁₃ H ₂₈	Tridecane	35.04	0.12
C ₁₃ H ₂₀ O	(+)-3-Carene, 10-(acetylmethyl)	38.04	0.41
C ₁₄ H ₁₄	1,1'-Biphenyl, 2-ethyl-	46.49	0.99
C ₁₄ H ₁₆ O	5(6H)-Benzocyclooctenone,7,8-	37.86	0.99

	dihydro-8,8-dimethyl		
C ₁₄ H ₂₀	2,2,9,9-Tetramethyldec-5-ene-3,7-diyne	38.39	0.90
C ₁₅ H ₁₆	Benzene, 1,1'-(1,3- propanediyl)bis	48.07	0.99
	2-Naphthalenamine, 1,2,3,4- tetrahydro-		
C ₁₅ H ₂₁ N	N-methyl-1-(2- methyl-1-propenyl)-, trans	38.89	1.35
C ₁₆ H ₃₀ O	E-14-Hexadecenal	38.68	1.11
	Tetrabromopentacyclo[9.3.1.1(6,10).0(3		
C ₁₆ H ₂₀ Br ₄	,11).0(4, 10)]hexadecane	33.18	1.09
C ₁₇ H ₃₇ O ₃ P	Bis(2-ethylhexyl) methylphosphonate	36.98	0.88
C ₂₁ H ₄₄	Heptadecane, 2,6,10,14- tetramethyl	42.35	1.40
C ₂₁ H ₄₄	Eicosane, 10-methyl-	45.43	0.91
C ₂₁ H ₄₄	Eicosane, 10-methyl-	48.32	0.67

The GC–MS chromatogram of the GLF' aliphatic subfraction is presented in Figure 4.11. The characteristic peaks identification were done by applying Probability Based Matching (PBM) algorithm on their spectra. The peaks' identification quality outcomes were matched more than 90 % and were considered valid, once it was confirmed that their tentative assignments were in good agreement with the previously published GC/MS data of the similar products [14]. The molecular compounds identified in this subfraction are also listed in Table 4.6 to get an idea about the fuel's composition (the nature and compound types, etc.). As observed from Table 4.9, n-pentane, alkanes, alkenes and branched hydrocarbons were detected in aliphatic subfraction of GLF, and this subfraction predominantly contains pentane, 2-methyl, 2-pentene, 3-methylhexane, 1-heptenecyclopentane, 1-methyl-1,4-hexadiene, and 4-methyl compounds. The GLF sample's GC–MS analysis results were compared with gasoline fuel and they were found to be similar to each other [101]. Also, the GLF's carbon subfractions distribution resembles to that of gasoline fuel, as well [101-102].

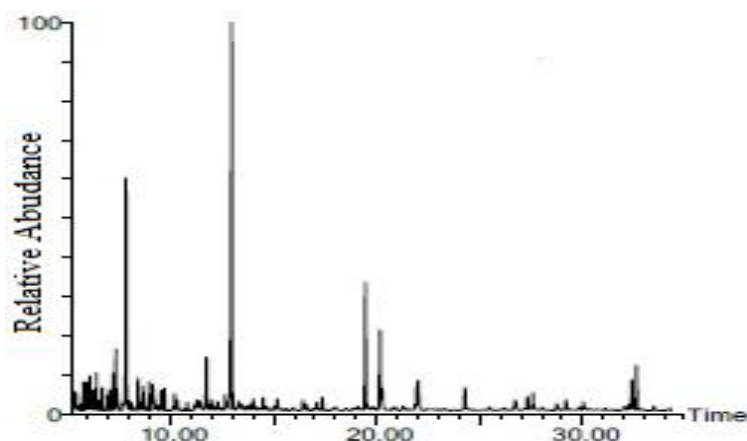


Figure 4.11. GC-MS chromatogram of aliphatic subfraction of GLF.

Table 4.9. Relative content of compounds at the aliphatic subfractions of GLF.

Molecular Formula	Compound Name	RT (Min)	Area %
C ₆ H ₁₄	Pentane, 2-methyl	5.38	0.42
C ₆ H ₁₂	1-Butene,2,3-dimethyl	5.42	0.40
C ₆ H ₁₂	1-Hexene	5.77	1.00
C ₆ H ₁₂	Hexane	5.91	0.69
C ₆ H ₁₂	2-Butene, 2,3-dimethyl	6.08	0.92
C ₆ H ₁₂	2-Pentene, 3-methyl	6.18	0.48
C ₆ H ₁₂	1,4-Pentadiene, 3-methyl	6.28	0.54
C ₆ H ₁₂	Pentane, 3-methylene	6.41	0.97
C ₆ H ₁₀	2,4-Hexadine	7.05	0.95
C ₇ H ₁₄	2-Pentene, 2,4-dimethyl	7.23	1.26
C ₆ H ₁₀	Cyclopentane, 1-methyl-	7.35	1.73
C ₆ H ₁₀	2,4-Hexadine	7.34	0.58
C ₆ H ₆	Benzene	7.84	6.63
C ₁₆ H ₂₀ Br ₄	2- Pentene-1-ol, 4-methyl-	8.34	1.13
C ₇ H ₁₄	1-Heptene	8.66	0.95
C ₇ H ₁₆	Heptane	8.94	0.95
C ₇ H ₁₂	1,4-Hexadine, 4- Methyl	9.13	1.61
C ₈ H ₁₆	1-Pentene, 2,4,4-trimethyl	9.55	0.69
C ₇ H ₁₂	2,4-Hexadine, 2-methyl-	9.71	0.76
C ₈ H ₁₆	2-Pentene, 2,4,4-trimethyl-	10.20	0.68
C ₇ H ₁₄	Cyclohexane	10.33	0.41
C ₇ H ₁₀	1,3,5-Hexatriene, 2-methyl-	11.29	0.59
C ₆ H ₁₂ O	Methyl Isobutly Ketone	11.41	0.64
C ₇ H ₁₂	2,4-Hexadiene, 3-methyl-	11.75	2.14
C ₇ H ₁₂	1-Ethylcyclopentene	11.98	0.42
C ₉ H ₂ O	Pentane, 2,4,4,4-tetramethyl	12.67	0.59
C ₇ H ₈	Toulene	12.98	18.24
C ₅ H ₆ S	Thiophene, 3-methyl-	13.29	0.62
C ₈ H ₁₆	1-Octene	14.01	0.41
C ₈ H ₁₈	Octane	14.50	0.53
C ₈ H ₁₄	2,4-Hexadiene, 2,3-dimethyl-	15.18	0.53
C ₈ H ₁₄	1,3-Dimethyl-1-cyclohexene	16.43	0.48
C ₈ H ₁₄	Cyclohexene, 1-ethyl-	17.09	0.42

C ₈ H ₁₀	Ethylbenzene	19.46	5.84
C ₈ H ₁₀	o-Xylene	20.16	3.69
C ₈ H ₁₀	Benzene, 1,3-dimethyl-	20.26	1.19
C ₈ H ₁₀	o-Xylene	21.95	0.98
C ₈ H ₈	Styrene	22.01	1.52
C ₉ H ₁₂	Benzene, (1-methylethyl)-	24.27	1.33
C ₉ H ₁₂	Benzene, propyl-	26.70	0.92
C ₉ H ₁₂	Benzene, 1-ethyl-4-methyl-	27.30	0.60
C ₉ H ₁₂	Benzene, 1-ethyl-3-methyl-	28.74	0.46
C ₁₀ H ₁₃ N	Azetidine,3-methyl-3-phenyl	29.17	0.67
C ₉ H ₁₂	Benzene, 1,2,3-methylethyl-	30.03	0.43
C ₁₀ H ₁₄	Benzene, 1-methyl-4-(1-methylethyl)-	32.38	1.45
C ₁₀ H ₁₆	Limonene	32.61	2.17

Aliphatic subfraction of the DLF was also obtained by using GC–MS chromatography and its results are shown in Figure 4.12. The molecular compounds identified in this subfraction are listed in Table 4.10, in order to get an idea about the DLF’s composition (the nature and compound types, etc.). As observed from Table 4.7, n-pentane, alkanes, alkenes and branched hydrocarbons determined in aliphatic subfraction of WTO, and such subfractions predominantly contain cyclohexene, 4-ethylbenzene, (1- methylethyl)-ethylbenzene, benzene, 1,2,3 trimethyl-benzene, butyl, 2,3-epoxycarane, 3,7,7 trimethyl-compounds. The DLF sample’s GC–MS analysis results were compared with diesel fuel and they were found to be similar to each other [101]. Also, the DLF’s carbon subfractions distribution resembles to that of diesel fuel, as well [101-102].

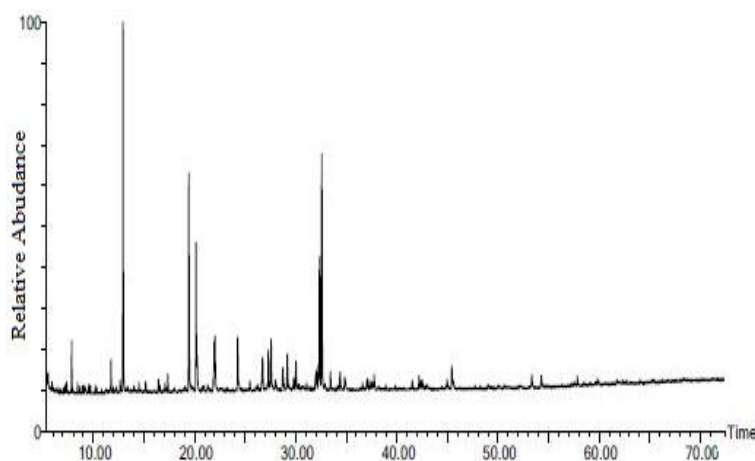


Figure 4.12. GC–MS chromatogram of aliphatic subfraction of DLF.

Table 4.10. Relative content of compounds at the aliphatic subfractions of DLF.

Molecular Formula	Compound Name	RT (Min)	Area %
C ₇ H ₁₂	2,4-Hexadiene, 2-methyl-	11.74	0.70
C ₇ H ₈	Toluene	12.92	7.03
C ₈ H ₁₂	Cyclohexene, 4-ethenyl	17.36	0.43
C ₈ H ₁₀	Ethylbenzene	19.43	4.80
C ₈ H ₁₀	o-Xylene	20.13	3.25
C ₈ H ₁₀	o-Xylene	21.94	1.04
C ₈ H ₁₀	Styrene	22.02	1.76
C ₉ H ₁₂	Benzene, (1- methylethyl)-	24.26	1.37
C ₁₀ H ₁₆	Santolinatriene	25.47	0.35
C ₉ H ₁₂	5-Methylenecycloocta-1,3-diene	26.73	1.12
C ₉ H ₁₂	Benzene, 1-ethyl-3-methyl	27.56	1.18
C ₉ H ₁₂	Benzene, 1-ethyl-2-methyl	28.73	0.76
C ₉ H ₂₀	Nonane	29.79	0.43
C ₉ H ₁₂	Benzene, 1,2,3 trimethyl-	30.02	0.88
C ₈ H ₁₆	2-Pentene,2,4,4-trimethyl	31.97	0.37
C ₁₀ H ₁₈	Cyclohexene, 1-methyl-4-(1-methylethyl)-	32.03	0.42
C ₉ H ₁₂	Benzene, 1,2,5-trimethyl-	32.22	0.50
C ₁₀ H ₁₄	Benzene, 1-methyl-2-(1-methylethyl)-	32.35	3.04
C ₁₀ H ₁₆	Limonene	32.57	5.35
C ₉ H ₁₀	Benzene, 2-propenyl-	33.43	0.51
C ₉ H ₈	Indene	34.39	0.63
C ₁₀ H ₁₄	Benzene, buthyl	34.85	0.65
C ₁₀ H ₁₆ O	2,3-Epoxy-carane,3,7,7 trimethyl-	37.07	0.49
C ₁₀ H ₁₂	Benzene, 2-ethenyl-1,3-dimethyl-	37.75	0.35
C ₁₀ H ₁₂	Benzene, 2-methyl-2-(2-propenyl-	42.19	0.35
C ₁₀ H ₈	Azulene	45.42	0.75
C ₁₁ H ₁₀	Naphthalene, 2-methyl-	53.32	0.55
C ₁₁ H ₁₀	Naphthalene, 1-methyl-	54.27	0.44
C ₆ H ₃ MnO ₅	Manganese, pentacarbonylmethyl-	67.64	0.36
C ₉ H ₁₆ BrNO	2-Piperidinone, N-[4-bromo-n-butyl-]	68.21	0.38
C ₁₃ H ₂₈	Decane, 6-ethyl-2-methyl	68.33	0.71
C ₄ H ₃ CoO ₄ Si	Cobalt, tetracarbonylsilyl	68.87	0.48
CH ₆ N ₄ O	Carbonic dihydrazide	69.49	0.37
C ₇ H ₅ MnO ₄	Manganese, pentacarbonylmethyl-, (oc-6-21)-	69.96	0.37
C ₁₀ H ₁₃ N ₃ O ₂	1-(4-Nitrophenyl)iperazine	70.04	0.36
C ₁₉ H ₃₆ O	2-Methyl-E,E-3,13-octadecadien-1-ol	70.04	0.34
C ₁₀ H ₂₁	1-Iodo-2-methylnonane	71.13	0.56
C ₁₉ H ₃₄ O ₃	Methoprene	71.14	0.79
C ₁₂ H ₁₆ N ₂ O ₃	Cyclobarbital	73.37	0.85

The general aliphatic product distributions based on carbon atom number can be seen in Figure 4.13. The tire pyrolysis oils are very complex mixtures of organic compounds. The compound components have been obtained from C₁ to C₂₆

structures. It indicates that lighter hydrocarbon components are increase steadily from C_4 to C_{12} , but they decrease from the C_{12} to C_{26} . The maximum yield rate of hydrocarbon occurs for the C_{12} and C_{13} samples. Hydrocarbons between C_{12} to C_{18} are higher than those of C_4 to C_{12} . Thus, hydrocarbons with C_{12} - C_{18} consist of a great amount of WTO, whose hydrocarbon content resembles to that of diesel fuel. It is observed that higher carbon content increases the density, the distillation temperature and WTO's heating value [26]. This indicates that a great amount of WTO has the characteristics of diesel fuel. As another case, when the WTO's aliphatic subfraction is compared with the diesel fuel's, it is found that their carbon distributions show similarities to each other [61]. The product's distribution includes C_4 - C_{12} , C_{13} - C_{21} and C_{23} - C_{26} , which is approximate to gasoline fuel, diesel fuel, light oil and waxes [103] respectively.

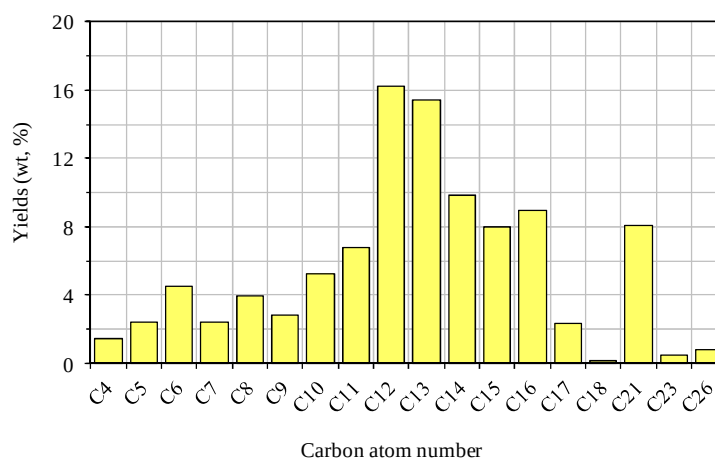


Figure 4.13. The carbon atom number distribution of WTO.

The typical use of GC-MS includes testing the purity of a particular substance, and/or separating the different components of a mixture (the relative amounts of each component). The two fractions of WTO were mixed with lime, and were analyzed with the GC-MS device. The GLF and DLF samples' general aliphatic product carbon atom number distributions can be seen in Figure 4.14. The GLF test results indicate the presence of seven carbon types at high hydrocarbon rates, and are given in Figure 4.14 and Table 4.9. The compound components have been obtained from C_4 to C_{12} range. The maximum yield rate of hydrocarbon occurs for the C_6 and C_8 range. As it can be seen in Figure 4.11, the compound components have been obtained from C_4 to C_{17} range. The hydrocarbons between C_{10} to C_{16} are higher than

those of C_4 to C_{17} . This indicates that a great amount of WTO resembles to the characteristics of diesel fuel. The second (DLF) fraction was found to have 12 and 13 carbons at high hydrocarbon rates that are given in Figure 4.14 and in Table 4.10. Increased carbon content increases its density and distillation temperature, and makes it close to diesel fuel's energy values. When its aliphatic subfraction is compared with that of diesel fuel, it is found that WTO's, their carbon distribution shows similarities to each other. The product's distribution includes C_4 to C_{12} and C_{13} to C_{17} samples, which are approximate to gasoline and diesel fuels, respectively. Based on the GC–MS analysis results, the GLF and DLF samples were found to resemble to the standard gasoline and diesel fuels, respectively.

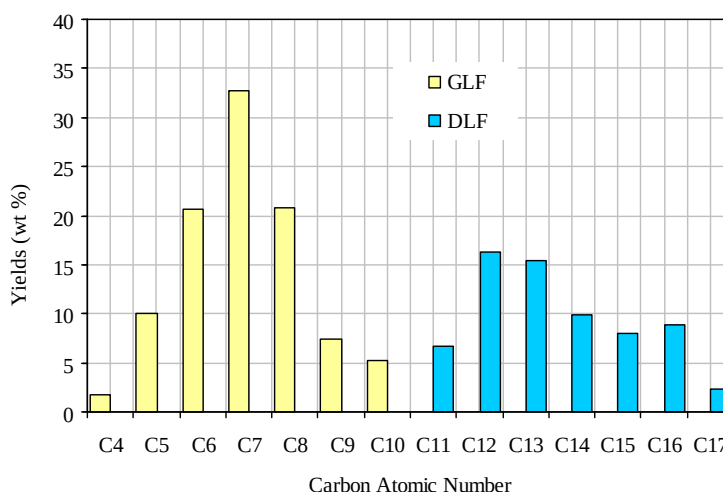


Figure 4.14. The carbon atom number distribution of GLF and DLF.

4.3.6 Pyrolysis time results of products

In this study, several pyrolysis processes were applied, and the optimum process conditions were obtained by producing plenty of WTO. The schematic of the pyrolysis process that was applied to tire rubber with additive samples were shown in Figure 4.15 which indicates the variation of pyrolytic temperature with time. It could be inferred from the figure that the heating rate was gradually increased with the pyrolytic time. At the same time, the sample temperature was gradually increased up to 450 °C in 300 min time intervals. Its temperature was kept stable at this point as the pyrolysis time reaches to 30 min.

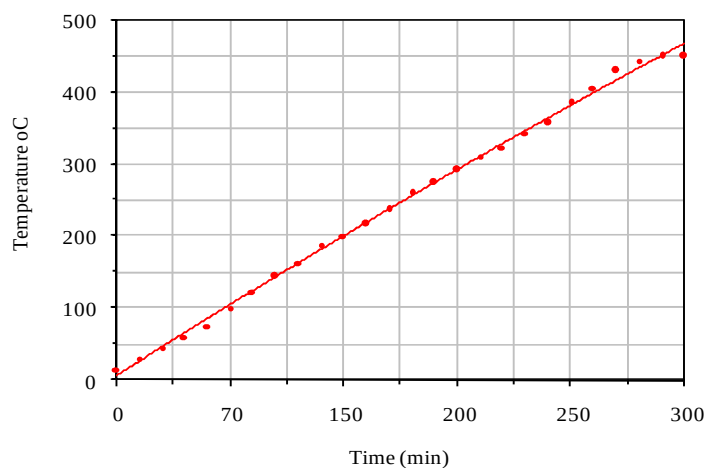


Figure 4.15. Variation of pyrolytic temperature with time for the waste tire.

The best curve is observed from the 10 wt% CaO mixture sample, which was separated into two fractions due to the temperature. Here, the first fraction between 54 °C to 150 °C is distilled into the collector tank. The first fraction's distillation curve raise a little bit up from the GF's curve. In Figure 4.16, the 10 wt% CaO-WTO mixture was first heated up to 45 °C for 60 min., and then its temperature was incrementally increased up to 150 °C for 120 min. Finally, its temperature was fixed at 150 °C for 40 min., in order to observe droplets dropping up to end of target temperature (150 °C). During the pyrolysis process, the mixer was active until the end. Here, the volatile compounds were condensed by a water condenser into a container.

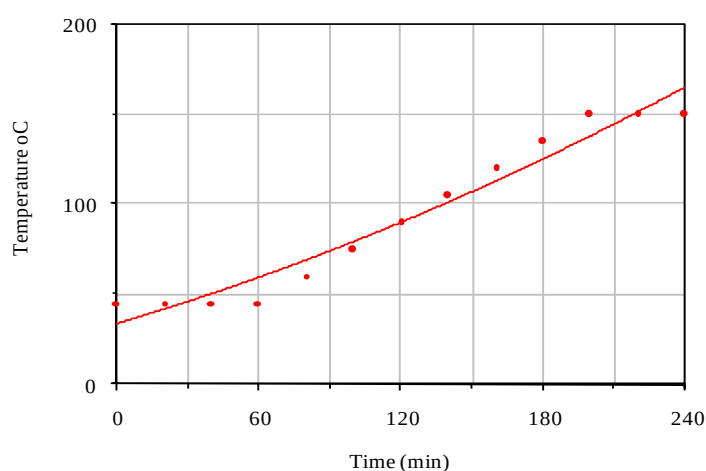


Figure 4.16. Variation of pyrolytic temperature with time for the GLF sample.

The tire is brought from industrial waste. First, it was cleaned from dust and other impurities. Then it was charged to be liquefied at the reactor. Secondly, the WTO was mixed with an additive at a mass ratio of 10 % of CaO according to a previously explained study [104]. The WTO was heated up to 400 °C via slow pyrolysis for 270 min at an incrementally increased temperature at Figure 4.17. During pyrolysis, the mixer worked until the end of the process. The volatile compounds were condensed by water condenser into a container. At the end of the liquefaction process, the new derivation liquids were separated into fractions to be collected into different containers. The DLF properties and the distillation test were discussed to determine its use in a diesel engine or not, and after burning it in the engine. Finally, the DLF was burned in diesel engine. The DLF test results were compared with those of the diesel fuel.

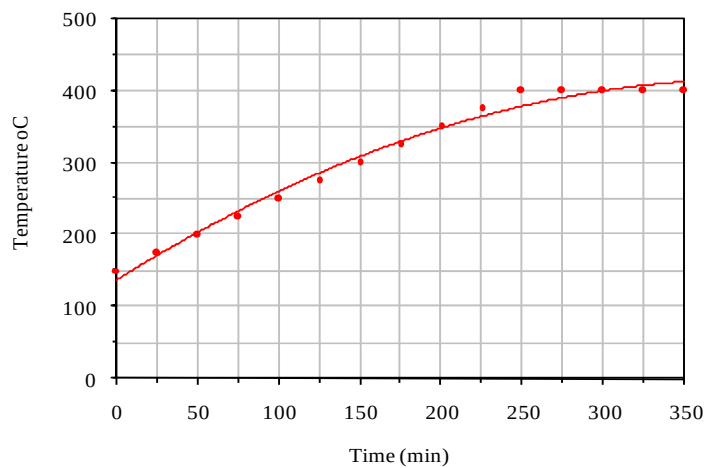


Figure 4.17. Variation of pyrolytic temperature with time for the DLF.

4.3.7 Regression analysis test results

Any experimental study needs a statistical method for modeling and to investigate the relationship between its variables. The regression analysis correlates the test parameters and predicts them for their best fit in the function.

The equipment selection, conditions, calibration, environment, observations, result reading and test planning can cause errors and uncertainties in the experiment. Thus, error and uncertainty analyses are used for physical quantities measurements.

This study was also evaluated by a linear regression model along with the experimental results, to investigate the influence of pyrolysis distillation temperature on the distilled volume, by using the SPSS version 22.0 statistical software. For this purpose, the GLF was used at the tests. The pyrolysis temperature variables were tested roughly at the temperature range from 54 °C to 196 °C. In the linear regression model, R^2 (adj.) and R^2 were found 95.3 % and 95.1 %, respectively, which could be considered as good results for GLF. The GLF's experimental results were close to the GLF's prediction results in linear regression model. Therefore, experimental standard was also proven to be accurate. The ANOVA and the t-tests were applied on CaO mixed WTO. Accordingly, the statistical significance value was found to be less than 0.05 ($0 < 0.05$). The ANOVA and t-test were valid by significance value. The linear regression model of GLF has the following mathematical formula:

$$V = -34.616 + 0.673 \times T \quad (4.1)$$

Thereby, the linear regression model of the measured distilled volumes and predicted distilled volumes were both presented in Figure 4.18, to observe these values comprehensively. Also, they were distributed and incrementally concentrated around a straight line. The distillation temperature was linearly increased along with the distillation volume and each bead exhibited that the experimental results are very close to a straight line. In addition to GF, GLF and prediction gasoline fuel were compared in Figure 4.19. As a result, all of these curves were found to be very close to each other.

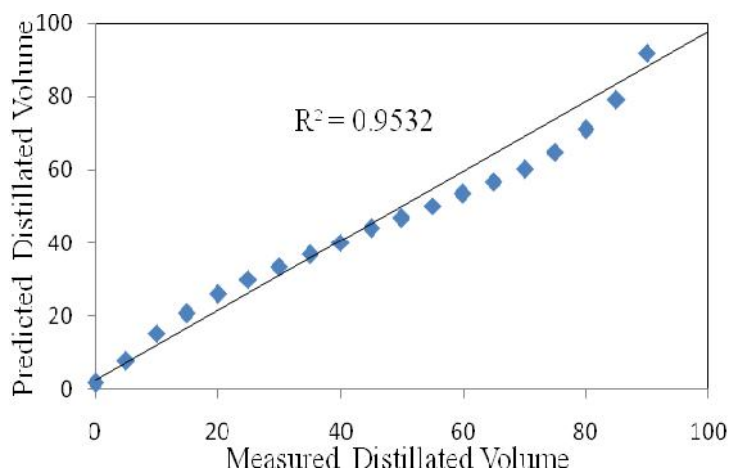


Figure 4.18. Comparison of measured distillated volumes and predicted distillated volumes by linear regression analysis of GLF.

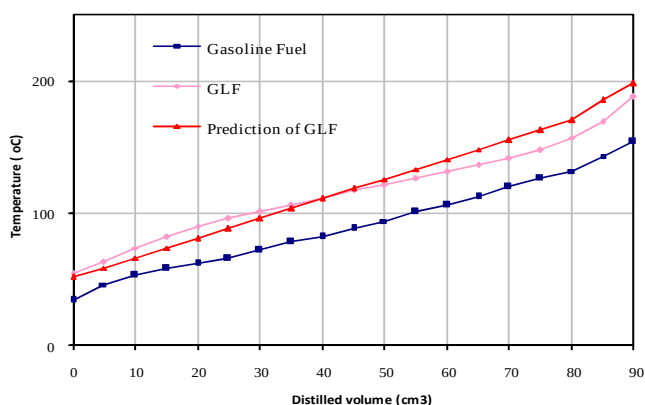


Figure 4.19. Comparison of GF, GLF and Prediction of GLF.

This study was also evaluated by linear regression model to investigate the influence of pyrolysis distillation temperature on the distilled volume with experimental results by using the SPSS version 22.0 statistical software. For this purpose, the DLF was used at the tests. The pyrolysis temperature variables were tested roughly at the temperature range from 145 °C to 345 °C. In linear regression model, R^2 (adj.) and R^2 were respectively 99.8 % and 99.5 % which were good results for DLF. Experimental results of DLF was close to the prediction results of DLF in linear regression model. Therefore, experimental standard was proven to be accurate. The ANOVA and t-test were applied on lime mixed waste tire oil. Accordingly, the statistical significance value was found less than 0.05 ($0 < 0.05$). The ANOVA and t-

test were valid by significance value. The linear regression model of DLF has the following mathematical formula:

$$V = -65.675 + 0.450 \times T \quad (4.2)$$

Thereby, the linear regression model of measured distilled volumes and predicted distilled volumes were both presented in Figure 4.20 to observe these values comprehensively. Also, they were distributed and concentrated around a straight line, incrementally. The distillation temperature was linearly increased with the distillation volume and each bead exhibited the experimental results to be very close to a straight line. In addition to diesel fuel, DLF and prediction diesel fuel were compared at Figure 4.21 As a result, all of these curves were found to be very close to each other.

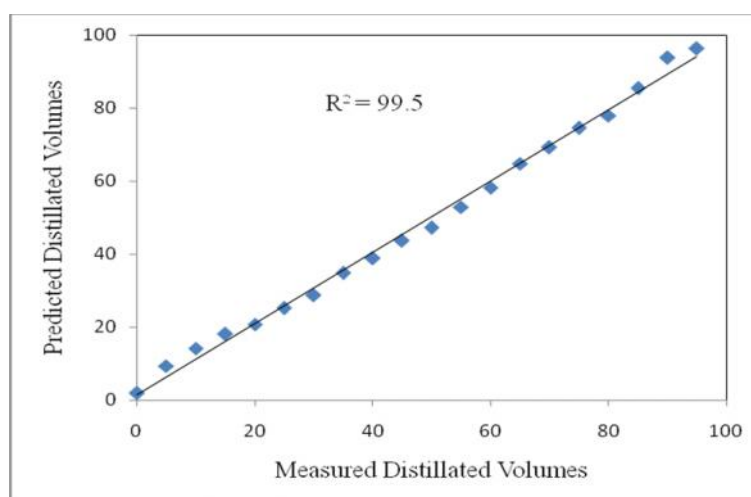


Figure 4.20. Comparison of measured distillated volumes and predicted distillated volumes by linear regression analysis of DLF.

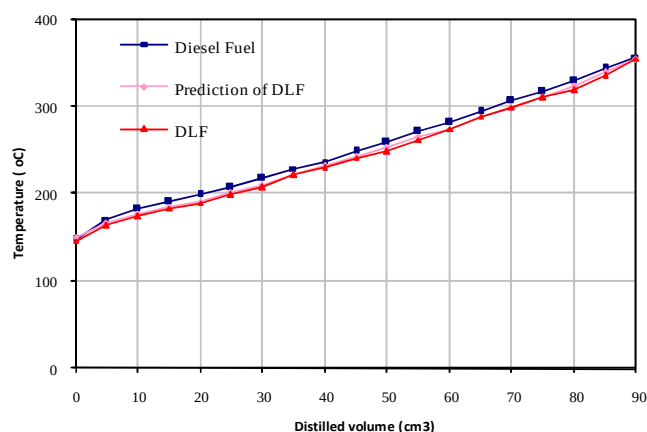


Figure 4.21. Comparison of DF, DLF and prediction of DLF.

4.4 Rotary kiln pyrolysis

4.4.1 Introduction

The waste tire is converted into light and heavy oils by using the rotary kiln reactor and then, the light and heavy oils are converted into GLF and DLF by using a batch reactor at 400 °C. At the first step, the waste tire is treated in the rotary kiln reactor to produce its non-condensable gas, carbon black and three fractions of oil components namely wax, heavy oil, and light oil. Afterwards the heavy oil and light oil are treated with NZ-1 and CaO with mass basis of 2 %, 6 %, and 10 %, individually and held on for 60 min. at 25 °C at batch reactor. Then, each sample is incrementally heated up to 400 °C and is reacted under thermal treatment. The aim of treating with such additives is to expose the chemical structure of the light and heavy oils to resemble standard fuels at a batch reactor. The wax is similar to sludge. It is mixed with the catalyst, as well. However, at the end of the process, the wax cannot be converted into standard fuels. Hence, there is no need to treat the sludge with any additives.

4.4.2 Physical properties and distillation tests results of products

Distillation test is an essential method which is beneficial for two or more fractions separated by different boiling points. Moreover, the evaporation temperature indicates each of these hydrocarbons. As a result, the distillation curve is directly

related to the composition and chemical characteristics of the fuel quality, since, each hydrocarbon has a strong influence on the distillation curve inclines and sudden point changes at certain temperatures. The distillation temperature curve versus distilled volume graphic gives brilliant ideas for the major chemical groups in fuel that are similar to standard fuels. Furthermore, the combustion and engine performances of fuel can be assumed and, also, how the ignition of fuel takes place can be indicated [95].

The structure of light and heavy oils is exposed by adding catalyst into them to resemble standard gasoline and diesel fuels. Thus, CaO and NZ-1 are mixed with light and heavy oils at 2, 6, and 10% weight ratios. As a result of the batch reactor process, the GLF and DLF are produced from light and heavy oils. The distillation test curves of gasoline, diesel fuels and CaO and NZ-1 mixture with light and heavy oil are given and compared in Figures 4.22 and 4.23. As observed from these figures, the best curves for the light and heavy oils are generated from the mixture with 10 wt% CaO, which is the most close to gasoline and diesel fuels curves than any others. As a result, the 10 wt% CaO is determined to be the best additive mixing ratio to produce and upgrade light and heavy oils into GLF and DLF.

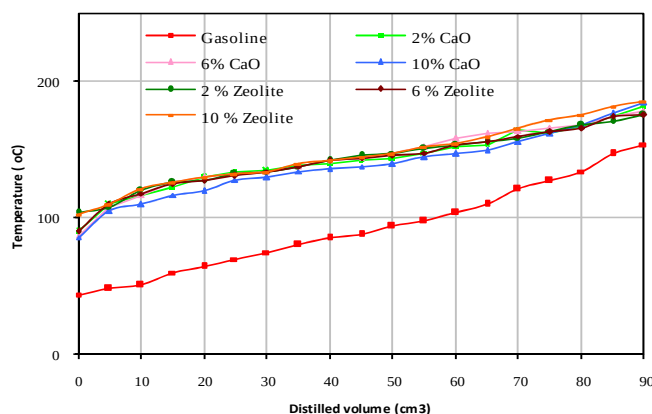


Figure 4.22. Effect of CaO & NZ-1 amounts on distillation temperature of light oil.

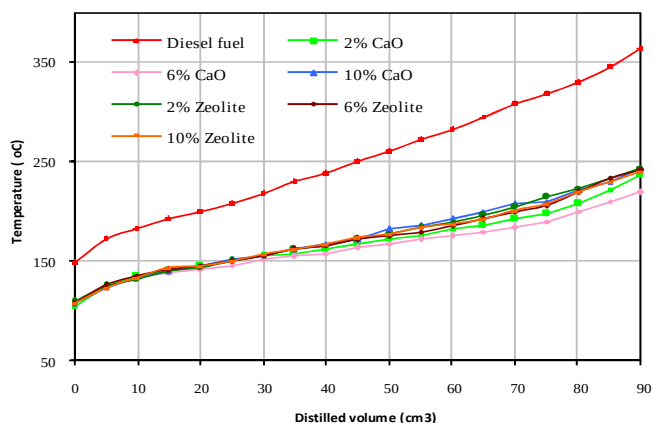


Figure 4.23. Effect of CaO & NZ-1 amounts on distillation temperature of heavy oil.

Density is another important parameter for the air–fuel mixture’s spread and uniform burning during the combustion. Here, the light oil has a lower density than that of gasoline but the heavy oil is in the range of diesel density. The viscosity affects the injection’s operation at low temperatures as the resistance of fuel. The higher viscosity causes poorer atomization in spraying and less accuracy for the injectors [105]. Here, the heavy oil sample is found in the range of diesel viscosity. The flash point indicates the lowest temperature of a volatile material to get vaporized to mix with air for ignition. The heavy oil is found to have a lower flash point than that of diesel. Therefore, the heavy oil sample needs to be treated with Na_2CO_3 catalyst to increase its flash point [106]. The higher amount of water content causes uncontrollable combustion, and worse than that, it can negatively affect the performance and emission values, as well. The heavy oil sample’s water content is lower than that of diesel fuel. The HHVs is a characteristic energy value for each substance in oil samples. The HHVs that is close to that of standard fuels which enables a good engine performance during combustion in a diesel engine. The HHVs of the light and heavy oil samples were found to be very close to that of standard fuels, which shown at Table 4.11.

Table 4.11. Thermo-physical of Light and Heavy Oils, Gasoline and Diesel

	Light Oil	Heavy Oil	Gasoline	Diesel
Density at 15°C (kg m^{-3})	742	827	780	820-845
Viscosity at 40°C ($\text{mm}^2 \text{s}^{-1}$)	---	3.16	---	2-4.5
Flash Point (°C)	---	---	-43	>55
Water (mg kg^{-1})	---	<200	---	<200
HHV (MJ kg^{-1})	43.316	42.548	43.890	42.700

Next, the light and heavy oils are mixed with NZ-1 and CaO additives with mass basis of 2 %, 6 %, and 10 %, individually. Besides, the oils are also exposed to pyrolysis to produce gasoline from the light oil and diesel from the heavy oil in the batch reactor. The characteristics of light and heavy oils' are analyzed as follow tests. Thus, light and heavy oil characteristics are tested for different parameters (density, viscosity, flash point and HHV) and the as-obtained results are shown at Table 4.12 in comparison with gasoline and diesel fuels. The GLF has lower density than that of gasoline but DLF is found to be in the range and also close to the lowest limit of diesel. The DLF viscosity is found to be in the range of diesel viscosity. The DLF has a lower flash point than that of diesel. Therefore, the heavy oils need to be treated with Na_2CO_3 catalyst to increase its flash point [106]. The water content in heavy oil sample is lower than that of diesel fuel. The HHVs of both the GLF and DLF were found to be very close to that of standard fuels. The physical and chemical analysis results from ultimate, sulphur, density, viscosity, flash point, HHV, and moisture are close to standards of gasoline and diesel fuel except the flash point of GLF which is higher than that of gasoline fuel, but DLF's is lower than that of diesel fuel. The sulphur content of DLF is higher than that of diesel fuel. Besides, the heavy oil and light oil are exposed to be converted into standard fuels in the batch reactor. Also, a small amount of mass loss, roughly 4-5 % of the total weight of mixture, is observed.

Table 4.12. Thermo-physical of GLF (10 wt% CaO-light oil blends) and DLF (10 wt% CaO-heavy oil blends), Gasoline and Diesel [13,66,99].

	GLF	DLF	Gasoline	Diesel
Density at 15°C (kg m^{-3})	745	830	780	820-845
Viscosity at 40°C ($\text{mm}^2 \text{s}^{-1}$)	---	3.12	---	2-4.5
Flash Point (°C)	21	24	-43	>55
Water (mg kg^{-1})	---	<200	---	<200
HHV (MJ kg^{-1})	43.216	42.148	43.890	42.700

4.4.3 Ultimate Analysis test results of products

The tire sample is firstly pyrolyzed in the rotary kiln reactor to produce three types of products namely the light and heavy oils and wax at a final temperature of 400 °C and with 10 °C/min heating rate. The properties of all fuel types should be available to determine their final area of use. Thus, light and heavy oil characteristics are tested for different parameters (elemental analysis) and the as-obtained results are

shown at Table 4.13 in comparison with gasoline and diesel fuels. The elemental analysis is done for the most common elements such as carbon (C), hydrogen (H), and nitrogen (N) in wt%. It is essential for organic compounds to contain carbon-carbon bonds. The H and C content in light and heavy oils are similar to that of standard fuels which also contain aliphatic and aromatic compounds. The N and S pollutant content comes from the tires' original elemental composition. Here, N generally destroys the ozone layer and gets dissolved in atmospheric water to cause acid rains. The light and heavy oils contain a little bit higher N content than that of diesel. While S is a major environmental pollutant which causes acid rains, as well. The heavy oil contains too much sulfur than that of diesel. Therefore, it's amount must be decreased by using oxidative desulfurization [107]. The high O amount in hydrocarbon affects the S and N compound yields. Thus, CO₂, SO₂ and NO_x will increase. The light and heavy oil samples are treated with CaO and NZ to decrease the as-mentioned S and N ratios [106].

Table 4.13. Thermo-physical of Light and Heavy Oils, Gasoline and Diesel [13,66,99].

Elemental Composition (wt%)	Light Oil	Heavy Oil	Gasoline	Diesel
C	77.98	81.14	85.79	86.58
H	11.78	9.81	14.21	13.29
N	0.48	0.41	---	0.01
O ^a	9.76	6.78	---	0.01
S	---	1.86	---	0.11

The C and H amount of GLF and DLF are a little bit lower than that of gasoline and diesel fuel, but the N and O contents are higher. Also, the S content of DLF is found to be too high than that of diesel, which shown at Table 4.14. Therefore, it must be decreased by applying oxidative desulfurization [107].

Table 4.14. Thermo-physical of GLF (10 wt% CaO-light oil blends) and DLF (10 wt% CaO-heavy oil blends), Gasoline and Diesel [13,66,99].

Elemental Composition (wt%)	GLF	DLF	Gasoline	Diesel
C	79.21	80.24	85.79	86.58
H	10.46	10.82	14.21	13.29
N	0.42	0.52	---	0.01
O ^a	9.91	6.78	---	0.01
S	---	1.64	---	0.11

^a Calculated by difference

4.4.4 FT-IR results of products

The FTIR spectra of GLF and DLF are presented in Figures 4.24 and 4.25. The C–H stretching vibration bands range from 3000 cm^{-1} to 2800 cm^{-1} and also C–H bending vibration bands among 1460 cm^{-1} and 1350 cm^{-1} show stretching alkenes. The $\text{C}\equiv\text{C}$ stretching vibration bands in the 900 cm^{-1} – 850 cm^{-1} frequency range determine the stretching alkynes and also the C=C-H out of plane bending peaks in the 900 cm^{-1} – 650 cm^{-1} region indicate the presence of aromatic compounds and alkenes. The aromatic groups exhibit an increase in their intensities, consequently with the concentration of the aliphatic peaks [22,26,100]. As a result of FT-IR, it can be observed that GLF and DLF are really complex mixtures that contain aliphatic and aromatic compounds. Thus, FT-IR test results prove that GLF and DLF is a good quality fuel to be combusted in gasoline and diesel engines.

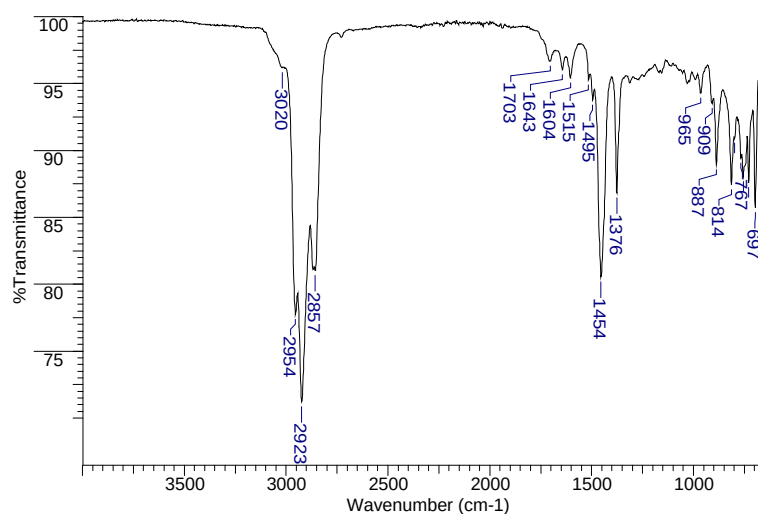


Figure 4.24. The FT-IR spectra of GLF.

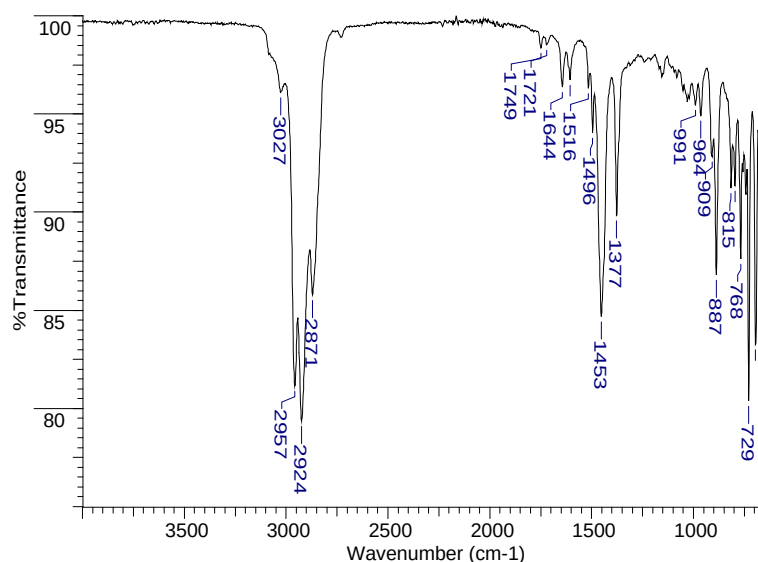


Figure 4.25. The FT-IR spectra of DLF.

4.4.5 GC-MS results of products

The GC–MS chromatogram of the WTO’s aliphatic subfraction is presented in Figure 4.26. The characteristic peaks identification were done by applying Probability Based Matching (PBM) algorithm on their spectra. The peaks’ identification quality outcomes were matched more than 90% and were considered valid as was confirmed by Laresgoiti et al. [14]. The molecular compounds are declared in Table 4.15 to have an idea about the chemical composition of GLF for GC-MS. Table 4.15 contains predominantly aliphatic compounds, single ring aromatic compounds, polyaromatic hydrocarbons (PAH) and others. The aliphatic compounds are alkanes such decane, and undecane. The single ring aromatics are benzene, ethyl-methyl and indene. The other hydrocarbons are limonene and cyclohexene [38,43,44,108]. The GC–MS analysis results of GLF are compared with standard fuels and are able to resemble them [101]. Furthermore, its carbon sub-fractions are similar to gasoline fuel carbon sub-fractions distribution [45,46,101,102]. The high carbon amount of GLF increases its density, distillation temperature and heating value, as well [26].

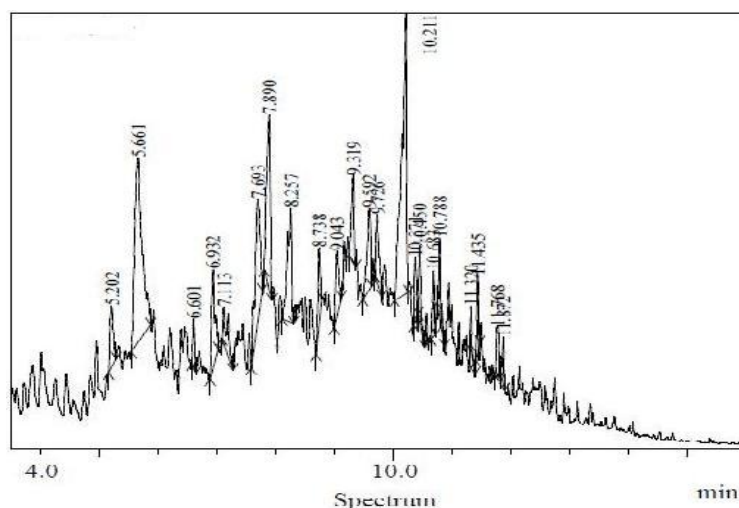


Figure 4.26. GC–MS chromatogram of aliphatic subfraction of GLF.

Table 4.15. Relative content of compounds at the aliphatic subfractions of GLF.

Molecular Formula	Compound Name	RT (Min)
C ₇ H ₁₂	Cyclopentene, 1,5-dimethyl	5.200
C ₇ H ₈	Benzene, methyl	5.663
C ₇ H ₈	Cyclopentene, 1,2,3-trimethyl-	6.60
C ₈ H ₁₄	1,3-Dimethyl-1-cyclohexene	6.933
C ₆ H ₇ Cl ₂ F	4-Fluoro-4,5-Dichlorocyclohexene	7.113
C ₈ H ₁₀	Benzene, ethyl-	7.692
C ₈ H ₁₀	p-Xylene	7.892
C ₈ H ₁₀	Benzene, 1,2-dimethyl-	8.258
C ₉ H ₁₂	Benzene, (1-methylethyl)-	8.738
C ₁₀ H ₁₆	3-Methyl-trans-3a,4,7,7a-tetrahydroindan	9.042
C ₉ H ₁₂	Benzene, 1-ethyl-4-methyl-	9.321
C ₇ H ₇ NO	Benzaldehyde, oxime	9.592
C ₉ H ₁₂	Benzene, 1,2,3-trimethyl-	9.725
C ₁₀ H ₁₆	dl-Limonene	10.213
C ₉ H ₈	Benzene, 1-propynyl-	10.371
C ₁₂ H ₁₆	Benzene, 1-methyl-4-(1-methylethyl)-	10.450
C ₁₀ H ₁₄	Benzene, 1-ethyl-3,5-dimethyl-	10.683
C ₁₀ H ₁₂	Benzene, methyl(1-methylethenyl)-	10.788
C ₁₀ H ₁₂	Benzene, 1-methyl-2-(2-propenyl)-	11.321
C ₁₀ H ₁₂	Benzene, 2-ethenyl-1,3-dimethyl-	11.433
C ₁₁ H ₁₄	1H-Indene, 2,3-dihydro-1,6-dimethyl-	11.767
C ₁₁ H ₁₄	1H-Indene, 2,3-dihydro-1,6-dimethyl-	11.871

The GC–MS chromatogram of the WTO’s aliphatic subfraction is presented in Figure 4.27. The characteristic peaks identification were done by applying Probability Based Matching (PBM) algorithm on their spectra. The peaks’ identification quality outcomes were matched more than 90% and were considered valid as was confirmed by Laresgoiti et al. [14]. The molecular compounds are listed at Table 4.16 to get an idea about the chemical composition of DLF for GC-MS. The chemical compound of

DLF, listed in Table 4.16, is composed of aliphatic compounds, single ring aromatic compounds, polyaromatic hydrocarbons (PAH) and others. The hydrocarbon compounds are determined from the aliphatic sub-fraction of DLF, and these sub-fractions include decane, undecane, alkenes, tridecane, hexadecane, octadecane, benzene, propyl, ethyl-methyl, indene, naphthalene, trimethylnaphthalene, tetrahydrophenanthrene, cyclohexane, ethenyl-methyl and hexadecanoic acid [38,43,44,108]. The GC–MS results of DLF are compared with commercial diesel fuel and they resemble to the commercial diesel fuel [101]. Additionally, its carbon sub-fractions are close to diesel fuel's carbon sub-fractions distribution [45,46,101,102]. The high carbon amount of DLF increase its density, distillation temperature and heating value, as well [26].

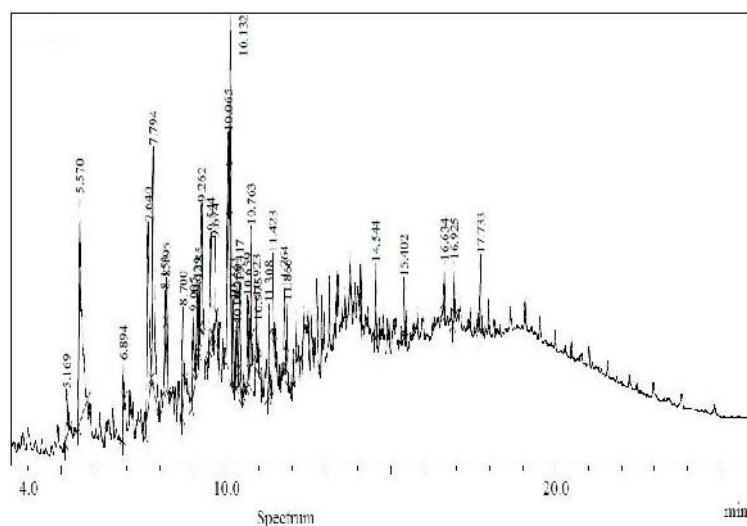


Figure 4.27. GC–MS chromatogram of aliphatic subfraction of DLF.

Table 4.16. Relative content of compounds at the aliphatic subfractions of DLF.

Molecular Formula	Compound Name	RT (Min)
C ₇ H ₁₂	Cyclopentene, 1,5-dimethyl-	5.171
C ₇ H ₈	Benzene, methyl-	5.571
C ₈ H ₁₄	1,3-Dimethyl-1-cyclohexene	6.892
C ₈ H ₁₀	Benzene, ethyl-	7.638
C ₈ H ₁₀	Benzene, 1,2-dimethyl-	7.796
C ₈ H ₈	Styrene	8.154
C ₈ H ₁₀	Benzene, ethyl-	8.196
C ₉ H ₁₂	Benzene, (1- methylethyl)-	8.700
C ₁₀ H ₁₆	3-Methyl-trans-3a,4,7,7a-tetrahydroindan	9.004
C ₉ H ₁₂	Benzene, propyl-	9.129
C ₁₀ H ₁₆	D-Limonene	9.183
C ₉ H ₁₂	Benzene, 1-ethyl-3-methyl	9.263
C ₇ H ₅ N ₅	Benzonitrile	9.546
C ₉ H ₁₂	Benzene, 1,3,5 trimethyl-	9.675
C ₁₀ H ₁₄	Benzene, 1-methyl-4-(1-methylethyl)-	10.067

C ₁₀ H ₁₆	D-Limonene	10.133
C ₉ H ₁₀	1H-Indene, 2,3-dihydro--	10.221
C ₉ H ₈	Methylenebenzocyclobutene	10.338
C ₁₀ H ₁₄	Benzene, 1-methyl-3-propyl-	10.350
C ₁₀ H ₁₄	Benzene, 1-methyl-4-(1-methylethyl)-	10.417
C ₁₀ H ₁₄	Benzene, 1-ethyl-2,4-dimethyl-	10.658
C ₁₀ H ₁₂	Benzene, 1-methyl-4-(1-methylethenyl)-	10.763
C ₈ H ₇ N	Benzonitrile, 2-methyl-	10.925
C ₁₁ H ₁₆	Benzene, 1-methyl-4-(1-methylpropyl)-	10.975
C ₁₀ H ₁₂	1H-Indene, 2,3-dihydro-5-methyl-	11.308
C ₁₀ H ₁₂	Benzene, 1-methyl-2-(2-propenyl)-	11.421
C ₁₁ H ₁₄	1H-Indene, 2,3-dihydro-1,6-dimethyl-	11.763
C ₁₁ H ₁₄	H-Indene, 2,3-dihydro-1,6-dimethyl-	11.867
C ₁₃ H ₁₄	Naphthalene, 1,6,7-trimethyl-	14.542
C ₁₆ H ₃₄	Hexadecane (CAS) n-Hexadecane	15.400
C ₁₆ H ₃₁ N	Hexadecanenitrile	16.633
C ₁₆ H ₃₂ O ₂	Hexadecanoic acid	16.925
C ₁₈ H ₃₅ N	Octadecanenitrile	17.733

By their evaporation points, the as-obtained gasoline and diesel fuels have found to possess hydrocarbon chains distributed from 4 to 12 and 8 to 24 atomic carbon numbers. The results in Table 4.16 indicate that GLF has C₈-C₁₀ distribution with a high rate, and the results in Table 4.17 indicate that DLF has C₁₀ and C₁₁ carbon distribution with a high rate. Based on the GC–MS analysis results, GLF and DLF are both found to resemble standard fuels. Hence, the great chemical amount in GLF and DLF indicates standard gasoline and diesel fuel characteristics [13,109].

The waste tire is converted into char about 35 wt%.The carbon black surface area and structure values are similar to the ones of commercial carbon black. Therefore, the char is analyzed to get an idea for a future study as a referral of an activated carbon absorbent material. The proximate, ultimate and HHV analyses are applied to the as-obtained carbon black were shown in Table 4.18. In consequence, the carbonblack is found to include a high content of carbon which increases with the combustion yields. On the other hand, the high volatile matter and the acceptable ash content are two important parameters that give good ideas to produce the above mentioned absorbents [110]. The proximate and ultimate analysis and HHV results have similarities with other researches [38].

Table 4.17. The ultimate, proximate and HHV analysis of char.

Ultimate Analysis (wt%)		Proximate Analysis (wt%)		HHV (MJ/kg)
C	89.86	MC	0.50	23.69
H	3.14	VM	74.09	
N	0.29	FC	15.06	
S	1.92	Ash	10.35	
O ^a	4.79			

^aBy difference, MC: Moisture content, VM: Volatile material, FC: Fixed carbon

The BET surface areas are measured to determine the pore structure. The pores are widened either by the release of volatiles, the collapse of carbon matrix or by the coalescence of micropores [111] under different heating rate conditions. Thus, mesopores of carbon black are developed by the extension of micropores. And also, the carbon black volatiles have enough duration to get diffused from structures [112,113]. In consequence, $S_{\text{BET-N}_2}$ is calculated to be 22.402 m²/g, and V_{total} is found 0.175 cm³/g, which is close to the literature values. Thus, it turns out to be a good idea to activate char to increase its pore volume and structure.

4.4.6 Pyrolysis time results of products

The pyrolysis conditions are affected by the heating rate, explosion duration and the final pyrolysis temperature and can change the characteristics of the products. The rotary kiln reactor temperature is increased 30 °C at each 25 min increment, once it is held for 85 min at 400 °C constant temperature. Afterwards, the light and heavy oils are mixed with different ratios of CaO and NZ-1 additives to produce GLF and DLF at a batch reactor. Firstly, the batch reactor temperature is incrementally increased from room temperature up to 150 °C with 20 °C to 25 min⁻¹ rate for the GLF sample. Secondly, the batch reactor temperature is incrementally increased from 150°C up to 400 °C with 25 °C to 25 min⁻¹ rate for the DLF sample. The relationship between temperature and the pyrolysis time is shown in Figure 4.28.

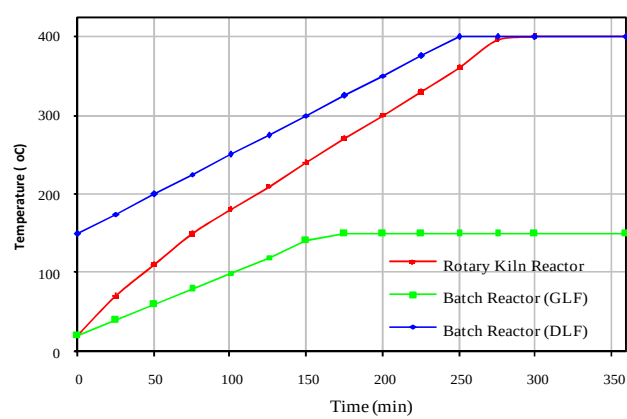


Figure 4.28. Variation of pyrolytic temperature with time for rotary kiln and batch reactor system.

CHAPTER 5

PERFORMANCE AND EMISSION TESTS OF GASOLINE LIKE FUEL AND IT'S BLENDS

5.1 Introduction

The engine performance and emission of spark ignition (SI) engine were tested by burning gasoline fuel (GF), gasoline-like fuel (GLF) (the 18 wt% of waste tire oil (WTO)) produced from 10 wt% Lime-WTO mixture, the mixture of GF and GLF with the amounts of 10 wt%, 20 wt%, 30 wt% and the blends of GLF and Turpentine with the amounts of 10 wt%, 20 wt%, 30 wt%. During the experiments, performance parameters such as brake torque (T), power (P_b), brake mean effective pressure (B_{mep}), brake specific fuel consumption (B_{sfc}), and brake thermal efficiency (η_{bt}) were tested. Furthermore, the exhaust gas temperature (EGT) and the engine emission parameters such as, nitrogen monoxide (NO), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and unburned hydrocarbon (HC) were analyzed.

The physico-chemical properties of eight samples and their distillation curves are valuable for combustion process. Thus, density, flash point, viscosity, lower heating value (LHV) test results and distillation graphs are given in Tables 5.1 and 5.2 with Figures 5.1 and 5.2. The characteristics of fuel and its distillation test give an idea that can be used in engine efficiently and also show similarities and differences from standard petroleum fuels. Otherwise, many problems can occur during the burning. The test results would enlighten how the combustion will take place in the engine combustion chamber. The GLF results compared with standard gasoline fuel are listed as follows [114]: and is summarized in Table 5.1 and 5.2, and also is explained briefly.

The gasoline fuel (GF)'s density value (742 kg m^{-3}) was close to that of GLF's (740 kg m^{-3}) [115]. The density test results suggest that the GF and the GF/GLF mixtures (at 10 wt%, 20 wt%, and 30 wt%) densities were defined at 741 kg m^{-3} as given in EN 228. The LHV of GF and GLF were obtained as 43 MJ kg^{-1} and 42.16 MJ kg^{-1} , respectively by using an adiabatic bomb calorimeter. The LHV of GF/GLF mixtures (at 10 wt%, 20 wt%, and 30 wt%) were close to each other and defined to be at $42.94\text{-}42.76 \text{ MJ kg}^{-1}$ range.

Density is the most valuable property for fuel samples. The Turpentine's density (880 kg m^{-3}) is higher than that of GLF (740 kg m^{-3}). The GLF's density is close to that of GF and given as 742 kg m^{-3} [115]. The density test results suggest that the GLF and GLF/Turpentine mixtures (10 wt%, 20 wt%, and 30 wt%) densities were defined to be at $754\text{-}782 \text{ kg m}^{-3}$ range as given in EN 228. The LHV of GLF and turpentine were obtained as 42.16 MJ kg^{-1} and 44.5 MJ kg^{-1} , respectively by using an adiabatic bomb calorimeter. The LHV of Turpentine was higher than that of GLF. By increasing the turpentine percentages in mixtures cause an increase in engine performances [116].

Table 5.1. Some characteristics of GF, GLF and their blends.

Parameters	Method (ASTM)	GF	GLF	GF+%10 GLF	GF+%20 GLF	GF+%30 GLF
Density (kg m^{-3})	D1298	742	740	741	741	741
Flash point ($^{\circ}\text{C}$)	D93	---	---	---	---	---
LHV (MJ kg^{-1})	D270	43	42.16	42.94	42.81	42.76
Distillation Range, ($^{\circ}\text{C}$)	D86					
IBP		34	54	40	41	42
10 vol. %		53	74	55	56	57
50 vol. %		94	121	112	121	127
90 vol. %		158	188	215	221	228
Final Point		218	253	233	236	258

Table 5. 2. Some characteristics of Turpentine, GLF and their blends.

Parameters	Method (ASTM)	Turpentine	GLF	GLF+%10T	GLF+%20T	GLF+%30T
Density (kg m^{-3})	D1298	880	740	754	768	782
Flash point ($^{\circ}\text{C}$)	D93	---	---	---	---	---
LHV (MJ kg^{-1})	D270	44.5	42.16	42.41	42.59	42.92
Distillation Range, ($^{\circ}\text{C}$)	D86					

IBP	150	54	54	57	57
10 vol.%	150	74	74	75	75
50 vol.%	153	121	134	138	145
90 vol.%	168	188	192	196	198
Final Point	180	253	251	250	252

Initial and final boiling points (IBP&FBP) determined the volatility of fuel samples or vice versa. The fuel sample's volatility can cause crank case dilution, fluctuating acceleration, cold plugging and bringing in engine temperature [116]. Thus, IBP and FBP might be close to GF to prevent those problems which were mentioned.

The distillation test results of GF, GLF, and GF/GLF mixture samples at 10 wt%, 20 wt% and 30 wt%, are shown in Figure 5.1. As can be seen from these results, the GLF mixed with GF behaves as a unique fuel. It is a significant result for the fuel sample to combust in the engine incrementally. These fuels' distillation curves rise smoothly and gradually as can be seen from Figure 5.1 [117]. These curves give an idea that combustion will occur without any problem. Thus, it is beneficial for both the economy and the environment to use GLF/GF mixture as a fuel.

The distillation test results of turpentine, GLF, and GLF/Turpentine mixtures at 10 wt%, 20 wt% and 30 wt%, are shown in Figure 5.2. Based on these test results; 85% of Turpentine was evaporated between 150°C to 160°C, which is represented with the horizontal line at the distillation curve since turpentine is rich with pure hydrocarbons. A horizontal distillation curve is not preferable, since an immediate burning can cause arise in high pressure. Additionally, Turpentine gets evaporated as a horizontal temperature line. It is also another big problem for the engine. It causes simultaneous combustion in the chamber. As a result of the combustion, the pressure and temperature in the chamber increase [66,115,117]. It is important for a fuel sample to get burned incrementally in the engine combustion chamber. As can be seen from GLF-Turpentine mixtures distillation test, turpentine is dissolved in GLF. The mixtures behave as unique fuels. It will not damage the engine and its components during combustion as observed from the curve. The results declared that no problems will occur in the SI engine. Thus, it has a positive effect on both the economy and the environment to use turpentine and GLF mixture as a fuel.

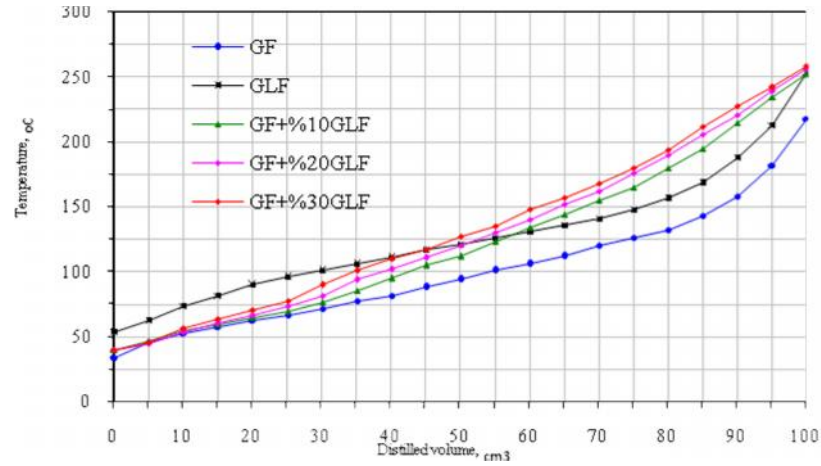
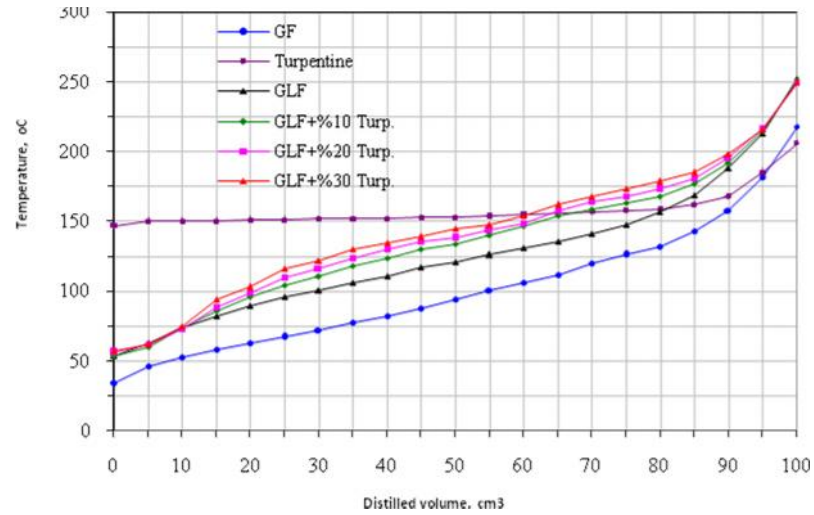


Figure 5. 1. Distillation curves of the GF, GLF and GF-GLF mixtures.



5.2. Performance test results of GF, GLF with GF-GLF and GLF-Turpentine blends

The fuel combustion effect on the engine was explained with the engine performance and the exhaust emission parameters. These parameters would indicate whether the fuel sample can be used efficiently in the engine, without causing any problems. Hence, the engine performance parameters are vital and should be carefully specified. The parameters include T , P_b , B_{mep} , B_{sfc} and η_{bt} . In addition to these, the engine parameters were also computed by the fuel and air expenditure, HHV_{fuel} , torque and speed.

The performance parameters (P_b , T , B_{mep} , η_{bt} and B_{sfc}) of GF/GLF blends (at 10 wt%, 20 wt% and 30 wt%) are given in Figures 5.3-5.7. As it is observed from those figures, there is a small difference between GF and GF/GLF blends. However, these samples' P_b , T , B_{mep} , and η_{bt} parameters were increased, whereas their B_{sfc} value was decreased at the maximum engine speed of 2500 rpm [118]. At this speed, the GLF and GLF/Turpentine samples with 10 wt%, 20 wt% and 30 wt% turpentine reached 93.6, 94.79, 95.83 and 96.94 Nm torque values, respectively. In consequence, their B_{sfc} values were decreased by adding Turpentine into GLF. The related highest B_{sfc} values of these samples at 2500 rpm were 211.41, 206.16, 200.26 and 196.72 g kWh⁻¹, respectively. It is obvious that the addition of more Turpentine into GLF caused an increase in P_b , T , B_{mep} and η_{bt} values while decreasing the B_{sfc} value. As discussed from the previous thermo-physical properties that were listed in Table 5.1, the HHV and the densities of GF and GF/GLF blends (at 10 wt%, 20 wt% and 30 wt%) were close to each other which get close the engine parameters.

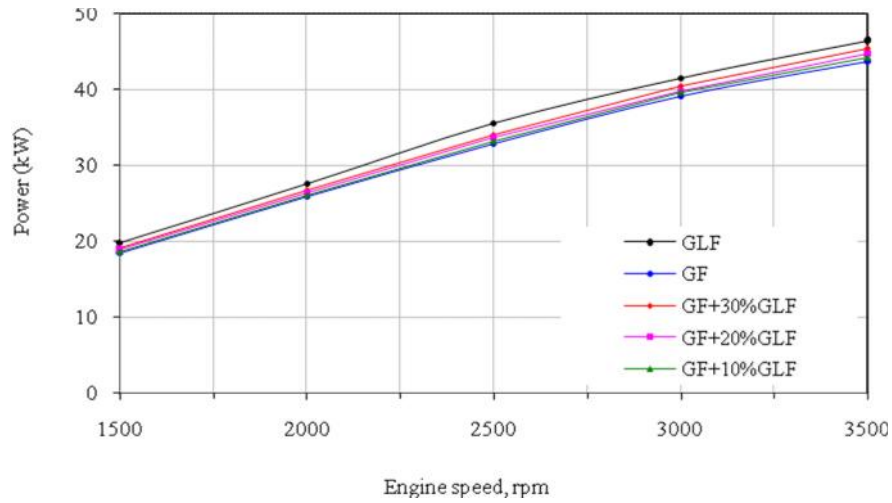


Figure 5.2. Effects of the GF, GLF and GF-GLF on power.

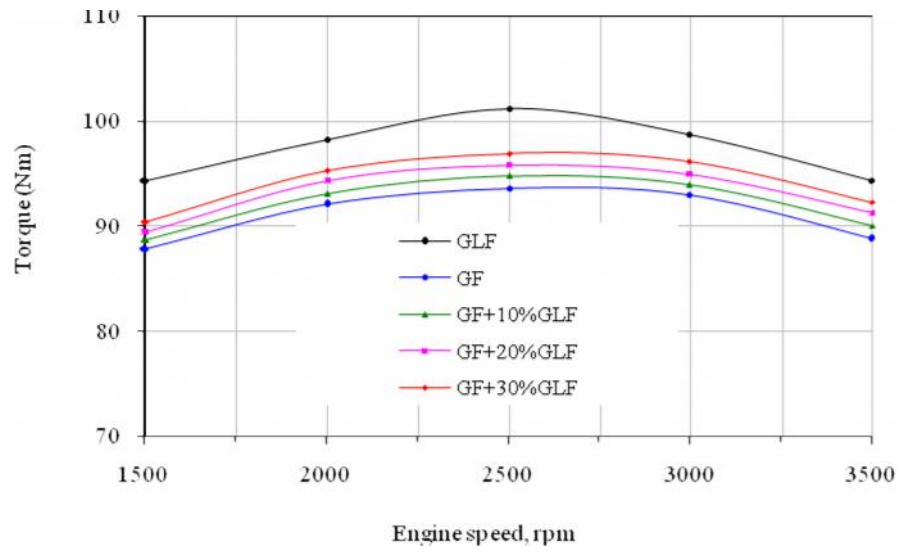


Figure 5.3. Effects of the GF, GLF and GF-GLF on torque.

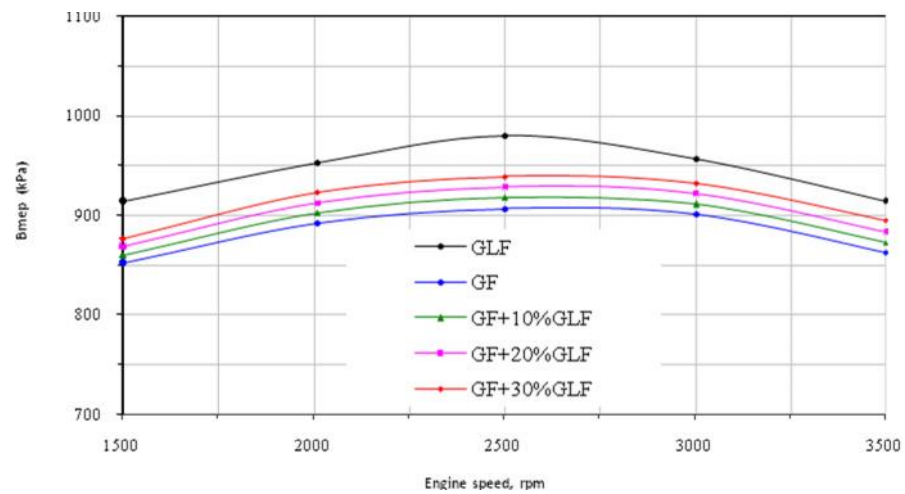


Figure 5.4. Effect of the GF, GLF and GF-GLF on Bmep.

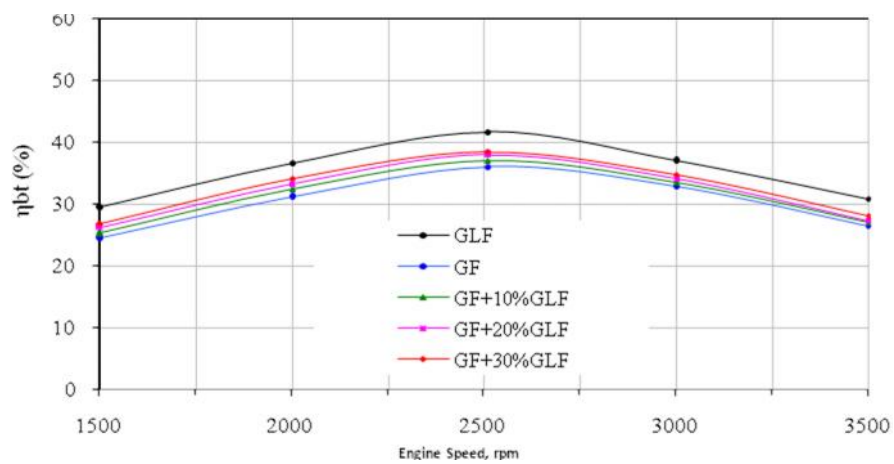


Figure 5.5. Effect of the GF, GLF and GF-GLF on η_{bt} .

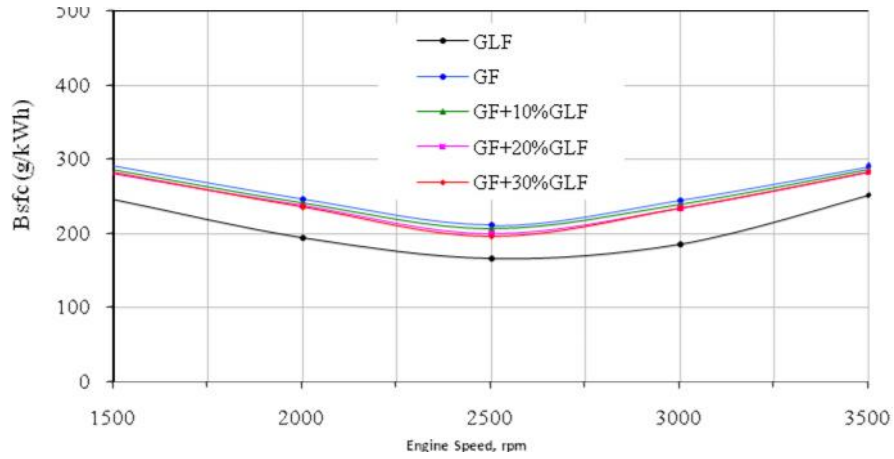


Figure 5.6. Effect of the GF, GLF and GF-GLF on Bsfc.

The performance parameters such as P_b , T , B_{mep} , η_{bt} and B_{sfc} of GLF/turpentine blend (at 10 wt%, 20 wt% and 30 wt%) are shown in Figures 5.8-5.12. Such parameters were all increased up to 2500 rpm, and then decreased at the maximum engine speed [67,69,119]. The T , B_{mep} and η_{bt} parameters reached to their maximum values at 2500 rpm, and the B_{sfc} went down to its minimum value for the fuel samples. The maximum torque (2500 rpm) values of GLF and the GLF/Turpentine samples at 10 wt%, 20 wt% and 30 wt% turpentine, were obtained as 101.2, 103.1, 105.1 and 106.3 Nm, respectively. In consequence, B_{sfc} values were decreased by adding turpentine into GLF. The related highest values of B_{sfc} were 166.16, 139.34, 119.13 and 98.92 g kWh⁻¹ at 2500 rpm. It is obvious that by adding more turpentine into GLF, it is possible to rise up the P_b , T , B_{mep} and η_{th} values, while decreasing B_{sfc} . This situation has positive effect on the engine performance. The two main points; (i) to increase P_b , T , B_{mep} and η_{th} (ii) in contrast to decrease B_{sfc} . As a consequence of both points; high density provides higher volumetric efficiency to engine [69] and higher HHV causes energy rise at the engine combustion chamber [118]. As discussed from the previous thermo-physical properties that were listed in Table 5.2, the HHV and the densities of GF and GF/Turpentine blends (at 10 wt%, 20 wt% and 30 wt%) were close to each other which get close the engine parameters.

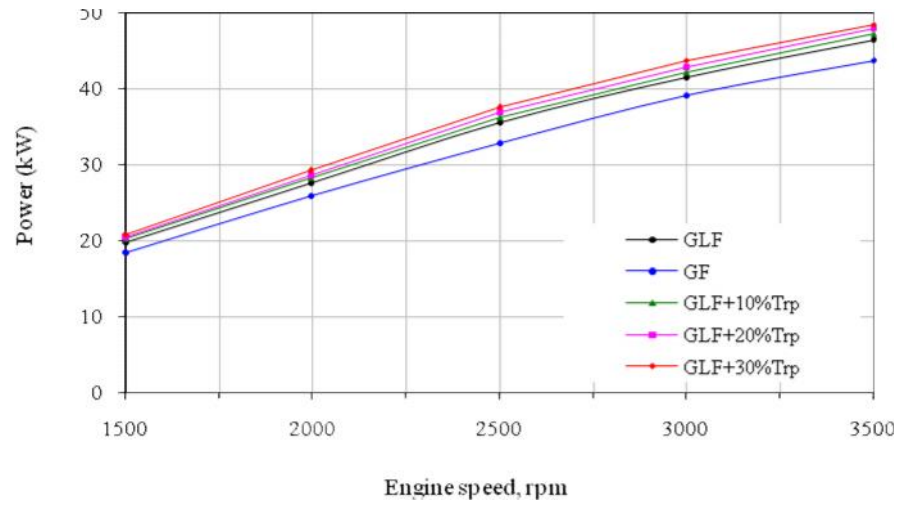


Figure 5.7. Effects of the GF, GLF and GLF-Turpentine mixture on power.

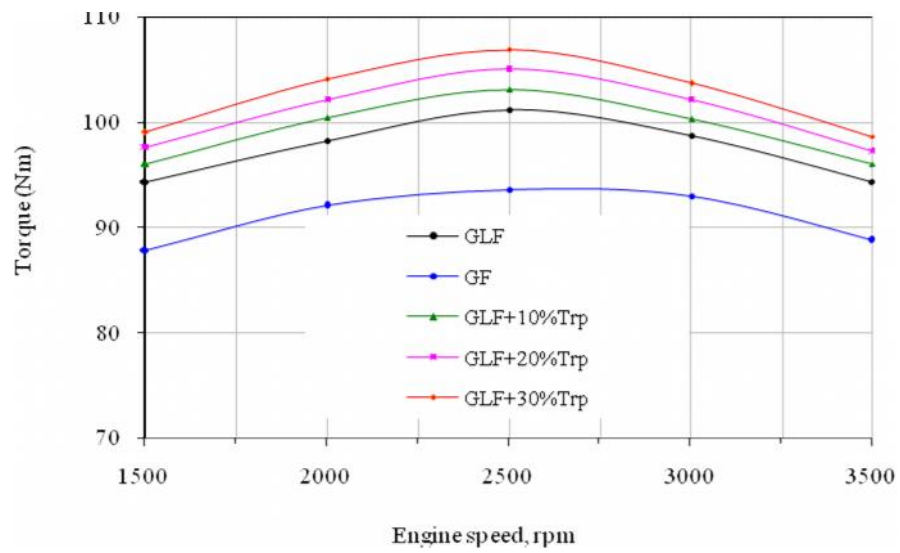


Figure 5.8. Effects of the GF, GLF and GLF-Turpentine on torque.

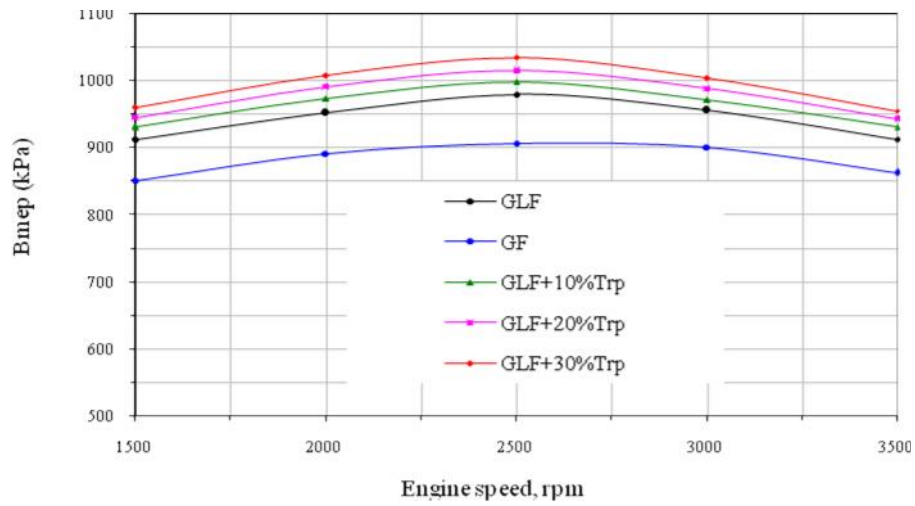


Figure 5.9. Effect of the GF, GLF and GLF-Turpentine on Bmep.

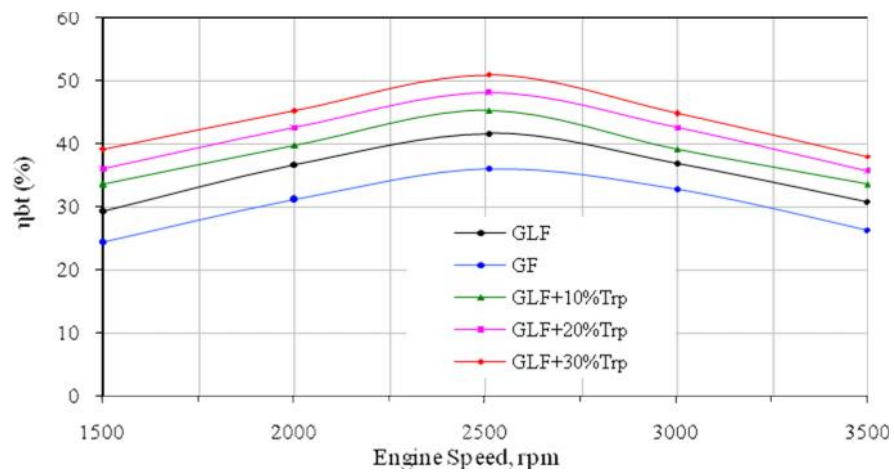


Figure 5.10. Effect of the GF, GLF and GLF-Turpentine on η_{bt} .

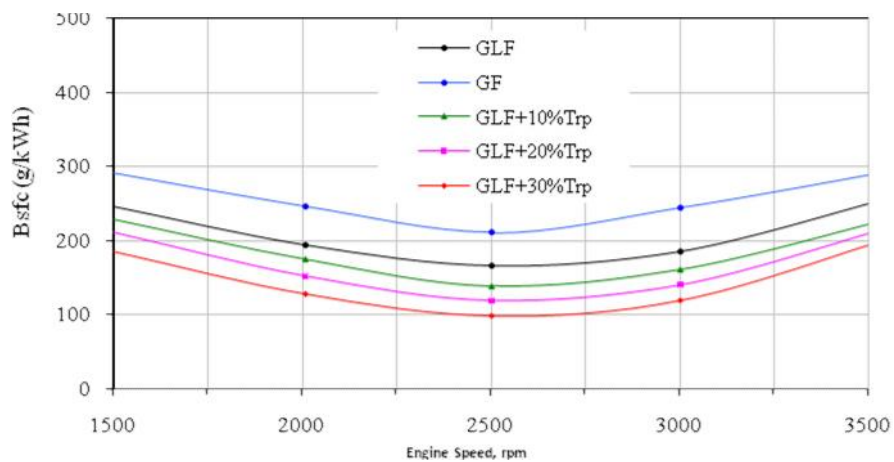


Figure 5.11. Effect of the GF, GLF and GLF-Turpentine on Bsfc.

5.3 The Emission test results of GF, GLF with GF-GLF and GLF-Turpentine blends

In this study, the exhaust gas temperature (EGT) and other engine emission parameters such as nitrogen oxide (NO), nitrogen dioxide (NO₂), carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂) and unburned hydrocarbon (HC) were analyzed by Testo 350 gas analyzer device. Collected test data were presented in graphical form and discussed below.

It is observed from Figures 5.13 and 5.14 that the highest EGT value was measured as 418°C by using the mixture of GF and 30 wt% GLF at 3500 rpm, while the maximum EGT value was measured as 515°C for the GLF and 30 wt% Turpentine blend. The EGT of GF/GLF and GLF/Turpentine mixtures were incrementally increased in the engine chamber, due to turpentine and GLF's high energy in the mixture and also their high distillation curves.

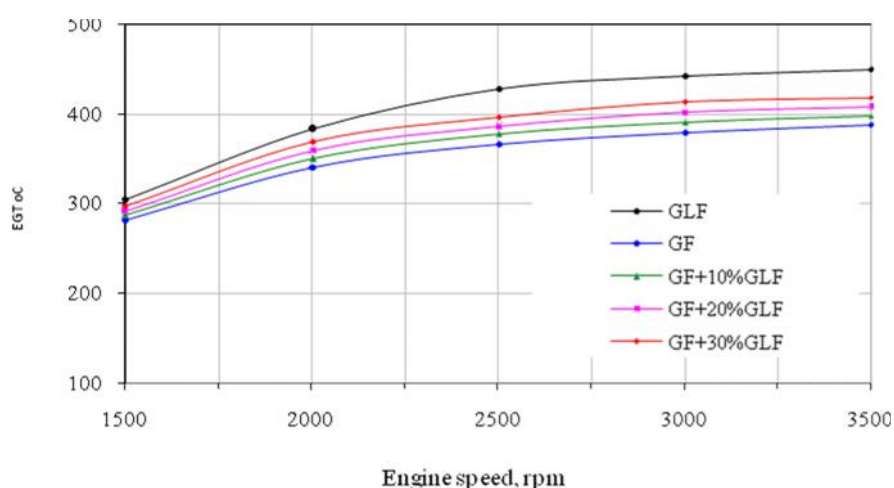


Figure 5.12. Effect of the GF, GLF and GF-GLF on exhaust temperature.

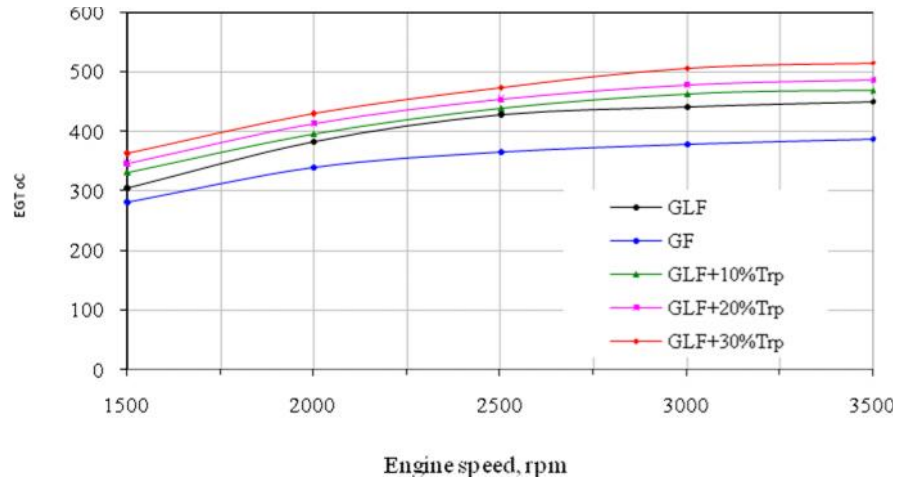


Figure 5.13. Effect of the GF, GLF and GLF-Turpentine on exhaust temperature.

Figures 5.15-5.19 indicate that CO_2 , CO, NO, NO_2 , and O_2 emissions were changed by engine speeds. By adding GLF into GF at 10 wt%, 20 wt% and 30 wt%, the CO_2 , NO and NO_2 emissions were started to increase while the CO emission was decreased. The maximum emission values were obtained at 2500 rpm.

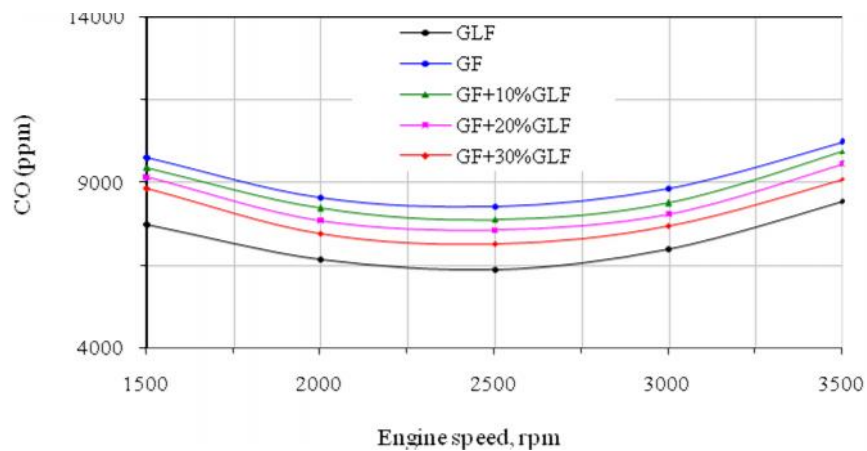


Figure 5.14. Effect of the GF, GLF and GF-GLF on CO emission.

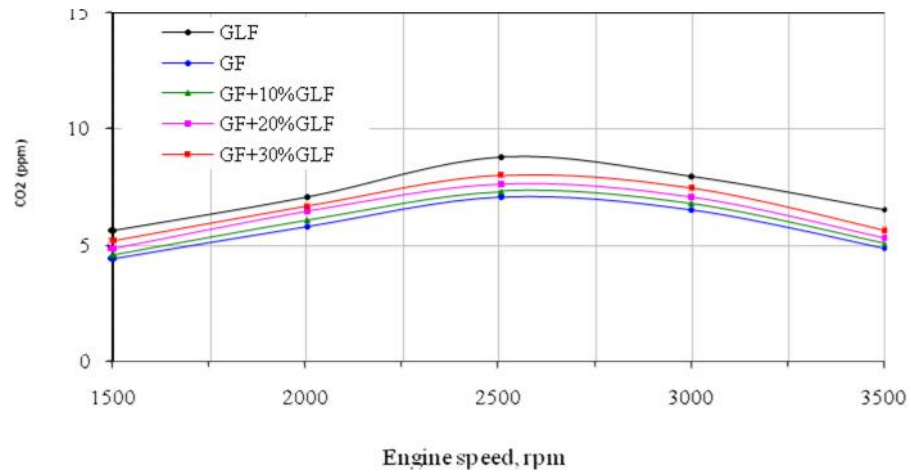


Figure 5.15. Effect of the GF, GLF and GF-GLF on CO2 emission.

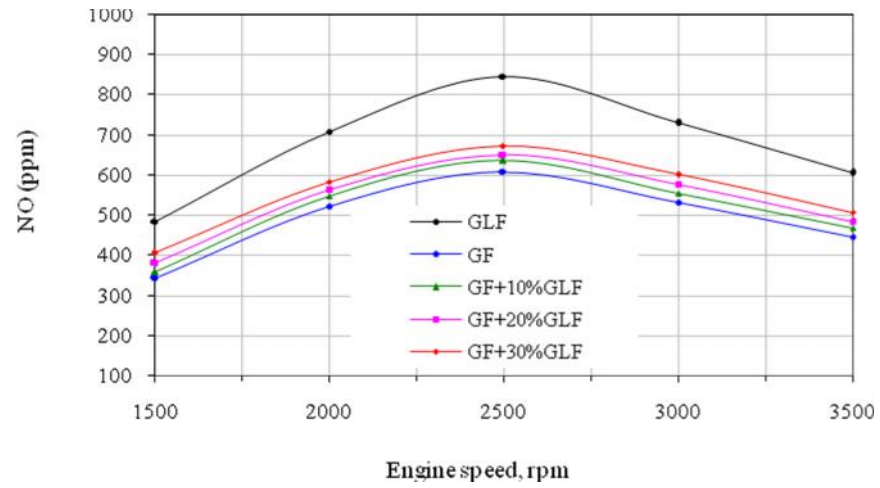


Figure 5.16. Effect of the GF, GLF and GF-GLF on NO emission.

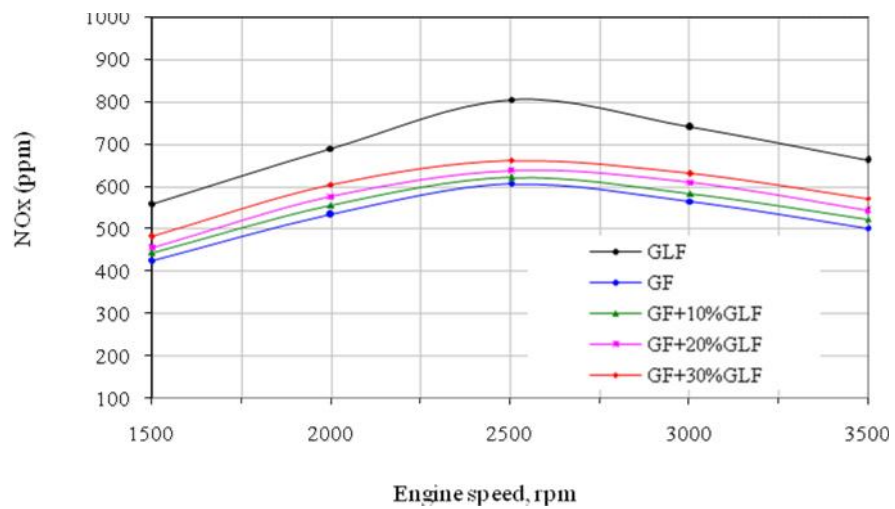


Figure 5.17. Effect of the GF, GLF and GF-GLF on NOx emission.

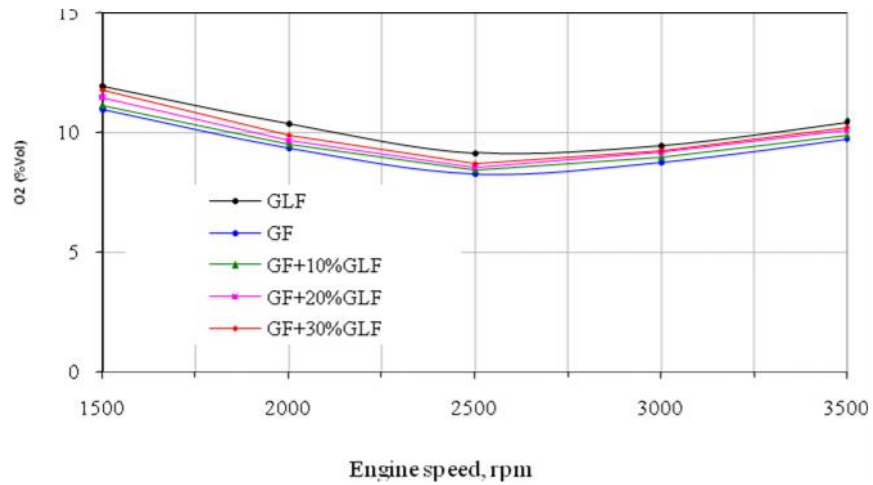


Figure 5.18. Effect of the GF, GLF and GF-GLF on O₂ emission.

Figures 5.20-5.24 shows the variations in CO, CO₂, NO, NO₂ and O₂ along with the engine speed, respectively. The Turpentine was added on GLF at 10 wt%, 20 wt% and 30 wt% ratios in order to cause an increase in CO₂, NO and NO₂'s emission values, while that of CO was decreased. The highest point for CO₂, NO and NO₂, and the lowest point for CO and O₂ were obtained at 2500 rpm speed. The curves fluctuated at different points.

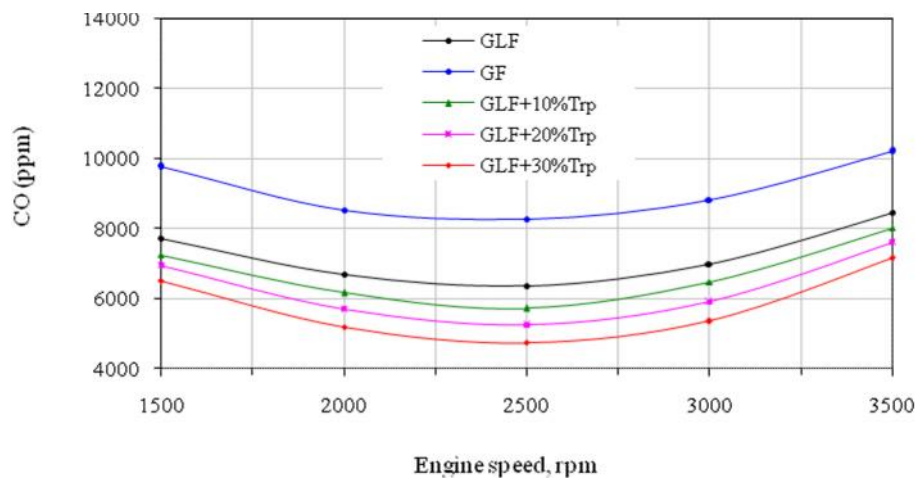


Figure 5.19. Effect of the GF, GLF and GLF-Turpentine on CO emission.

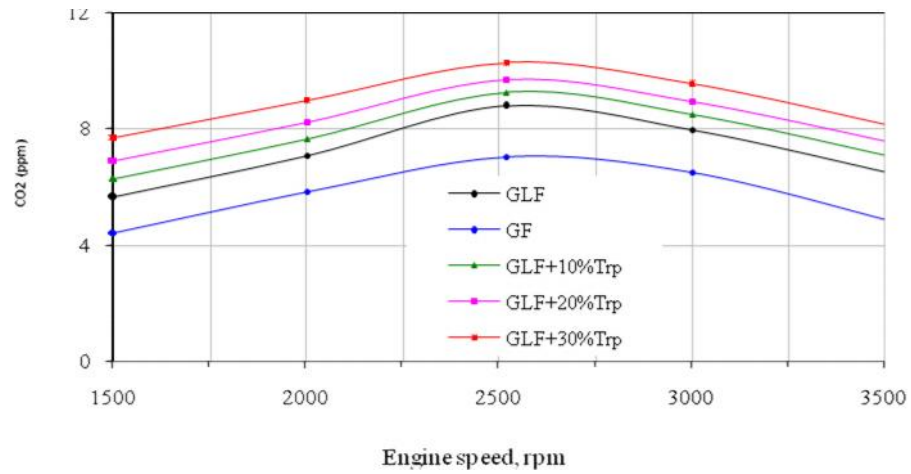


Figure 5.20. Effect of the GF, GLF and GLF-Turpentine on CO₂ emission.

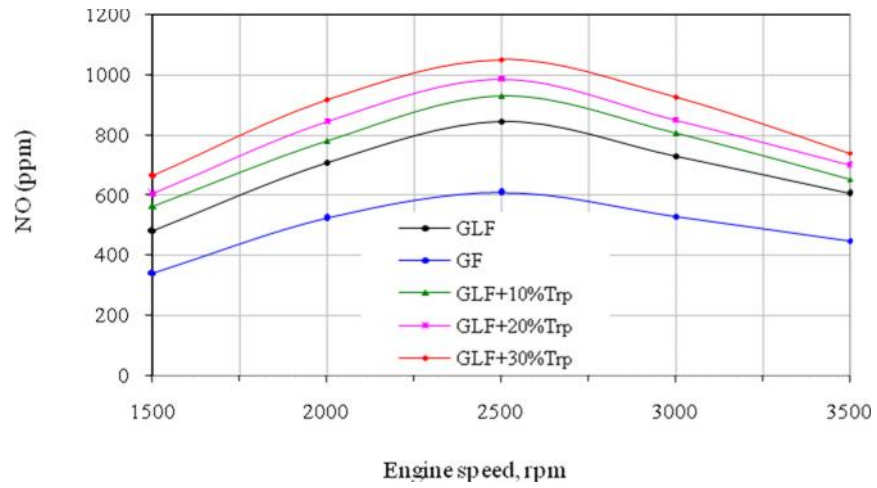


Figure 5.21. Effect of the GF, GLF and GLF-Turpentine on NO emission.

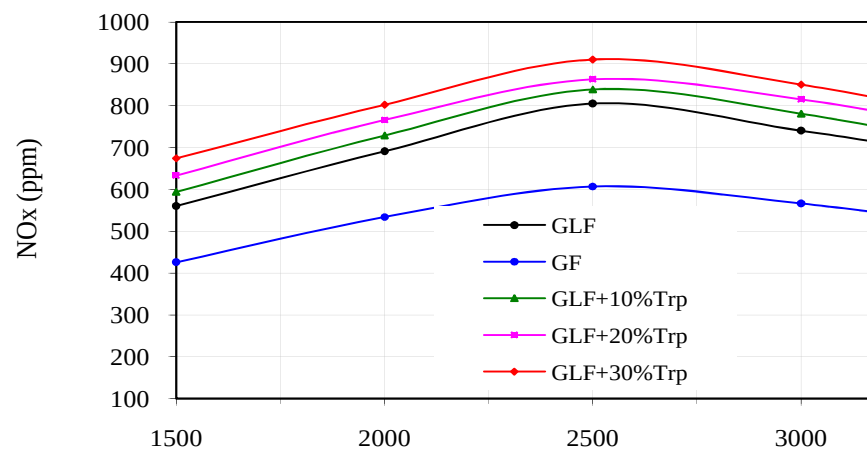


Figure 5.22. Effect of the GF, GLF and GLF-Turpentine on NO_x emission.

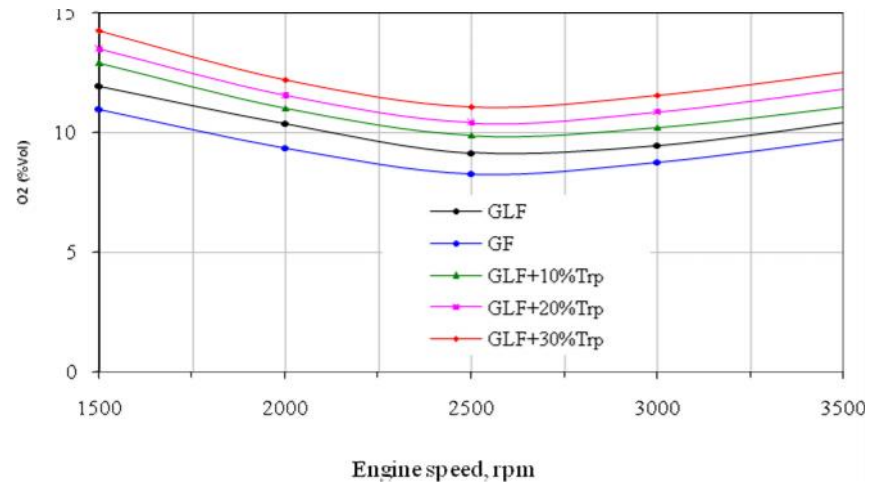


Figure 5.23. Effect of the GF, GLF and GLF-Turpentine on O₂ emission.

According to these factors, turpentine was detected to help the burning of GLF with a rich combustion including P_b , T , B_{mep} and EGT etc., except NO and NO_x emissions. The H_2O , O_2 , and N_2 emissions are not harmful for atmosphere and nature, whereas CO , CO_2 , and HC have harmful effects on the environment such as causing global warming and contributing to greenhouse gases. As much as possible, those gases should not be emitted into the environment or their emissions should be reduced under standard values. The source of CO emission was related with some factors such as physico-chemical specification [69], variations in air–fuel ratio and the engine chamber temperature [67], and also the oxygen deficiency, and insufficient time of combustion can be listed as other factors [118], all of which can cause incomplete combustion. The air–fuel ratio is the most essential parameter which leads to the emissions of CO , CO_2 and HC [67]. Thus, due to insufficient combustion, CO was thrown out without getting converted into CO_2 [120], since the CO decreases to minimum value when the O_2 amount reaches to the maximum value. It is clear that if the air–fuel ratio or the O_2 presence in combustion chamber is increased, the CO amount would be decreased.

For a good burning, the fuel has to be atomized, mixed and ignited completely. The atomization and mixing also have effects on the HC emission [120]. The fuel's viscosity and surface tension influence its penetration rate, and the maximum penetration and droplet size have effects on air–fuel ratio [67]. And also, since turpentine's density is higher than that of GLF, it increases the penetration and

droplet size of mixture [121]. This causes an unconcerned mixture and improper propagation of flame [121]. Consequently, the HC value increases up to 3000 rpm, then it increases slightly and finally it becomes smooth at Figure 5.25 and 5.26. Furthermore, the HC value is increased by adding GLF into GF and also by adding Turpentine into GF.

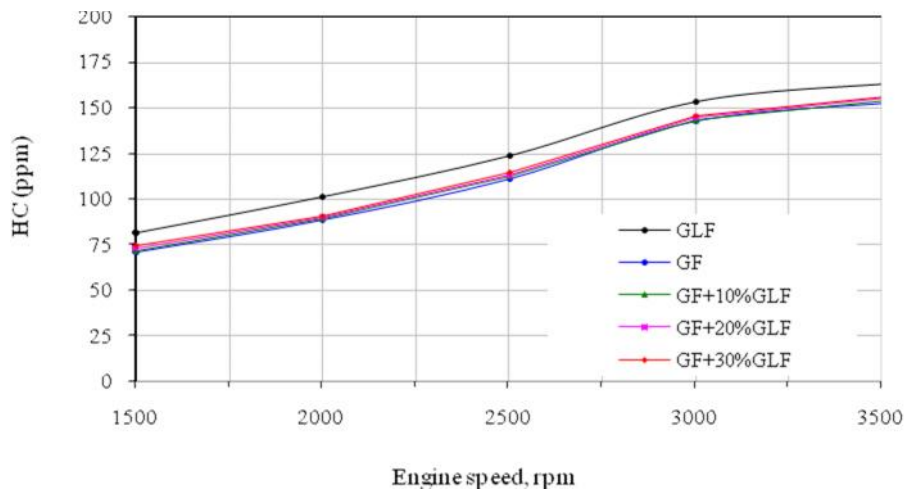


Figure 5.24. Effect of the GF, GLF and GF-GLF on HC emission.

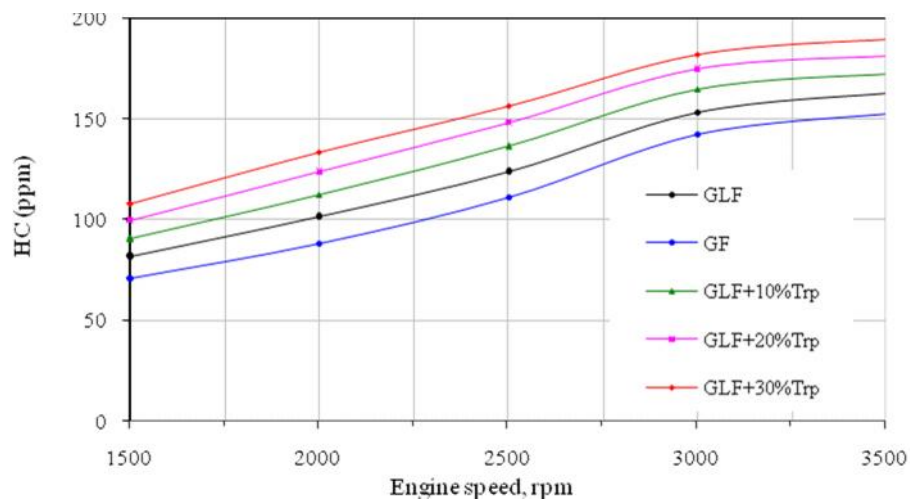


Figure 5.25. Effect of the GF, GLF and GF-Turpentine on HC emission.

CHAPTER 6

PERFORMANCE AND EMISSION TESTS OF DIESEL LIKE FUEL AND LOW SULFUR DIESEL LIKE FUEL

6.1 Introduction

This study aims to investigate both the engine performance and exhaust emission parameters obtained from a Diesel test engine. Diesel-like fuel (DLF) produced from waste tire oil (WTO) and low sulfur diesel-like fuel (LSDLF) is used in the diesel engine to obtain effect of the DLF on the engine performance and its emissions. The performance characteristics such as engine torque, engine power, brake specific fuel consumption (Bsfc), exhaust temperature and the emission parameters such as oxides of nitrogen (NO_x), sulfur dioxides (SO_2), carbon monoxides (CO) and total unburned hydrocarbon (HC) are tested. The DLF is obtained by using pyrolytic distilling unit that consists of a reactor, condenser, filters, collector, thermocouple and an electronic panel. The DLF contain high amount of sulfur, so it has to decrease to standard amount. The oxidative desulfurization (ODS) method was used to obtain lowest sulfur amount. The ODS were optimized by different parameters such as acid types, acid-hydrogen peroxide molar ratios, temperature, reaction time, ratio of water, methanol and acetonitril washing and extraction time. The sulfur was decreased from 8000 to 100 ppm after the treatment of ODS. The new product named as low sulfur diesel-like fuel (LSDLF).

6.2 Oxidative desulfurization of DLF

The sulfur level of DLF was decreased by using oxidative desulfurization methods. The ODS methods applied by changing experimental parameters such as acid types, acid-hydrogen peroxide molar ratios, temperature, reaction time, ratio of water, methanol and acetonitril washing and extraction time. The desulfurized DLF is

named as low sulfur diesel-like fuel (LSDLF). Physical and chemical properties and distillation test of the LSDLF were analyzed to compare with standard diesel fuel.

The effect of using HCl (37 %, from Merck Co.) and acetic acid (98 %, from Merck Co.), and also formic acid (85 %, from Merck Co.) was also used. Hydrogen peroxide (30 %, from Merck Co.) with hydrochloric acid, acetic acid and formic acid mixtures for all tests were freshly prepared each experiment. Then each product was washed with methanol, ethanol, acetonitril and de-ionized water at different mass ratios. The lowest sulfur sample was tested to determine its' physico-chemical properties and compositions.

Sulfur in DLF forms sulfur dioxide (SO_2) and sulfate (SO_4) particulate matter (PM) during combustion. These products were increased pollutants and mixed with water to cause acid rains which deteriorate environment and damage ozone layer. Thus, sulfur of the DLF has to decrease in minimum level. Therefore, ODS was applied to DLF for producing LSDLF. The HCl, formic acid and acetic acid were mixed with hydrogen peroxide in a 1:1 mole ratio, then added to 100 ml DLF and heated at 80 °C with continuous stirring for 3 hours, individually. Each sample was collected at different baker cooled at room temperature and firstly washed with 100 ml distilled water, a black precipitate was formed and upper layer of DLF separated from distilled water. Then each sample washed with 100 ml acetonitrile to remove sulfur. Each sample was analyzed to detect sulfur level. The formic acid has minimum sulfur level as 1628 ppm, shown at Figure 6.1.

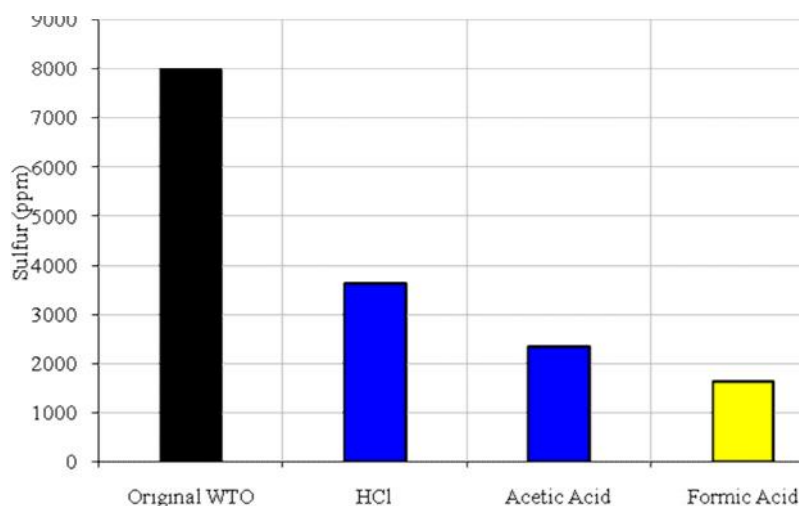


Figure 6.1. Selection of acids on sulfur removal.

The mole ratio of formic acid–H₂O₂ was changed to determine the lowest sulfur level of DLF. The best result was found 100 ppm at 1.76 H₂O₂ mmol/fuelg with 0.738 formic acid mmol/fuelg, which shown at Figure 6.2. Other parameters were fixed to optimize mole ratio of H₂O₂–formic acid mixture.

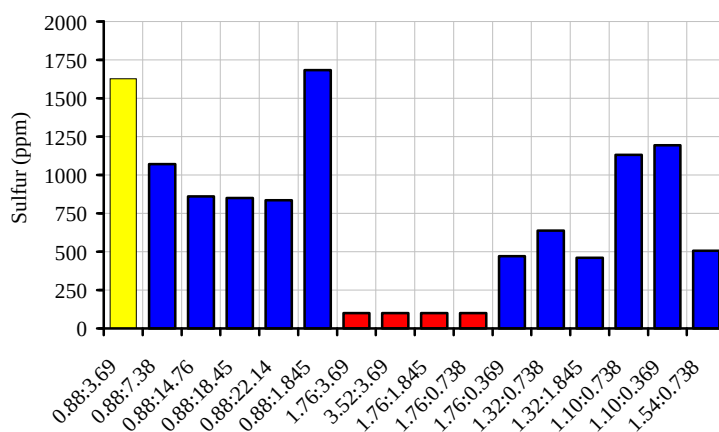


Figure 6.2. Optimization of the molar mixtures of H₂O₂–formic acid for sulfur removal.

At different distilled water, methanol and acetonitrile amount such as 5 ml, 10 ml, 15 ml and 20 ml were applied for sulfur removal, individually. But, desired sulfur decreasing cannot be satisfied. Figure 6.3 shown that sulfur cannot be remove by only using of distilled water, methanol and acetonitrile.

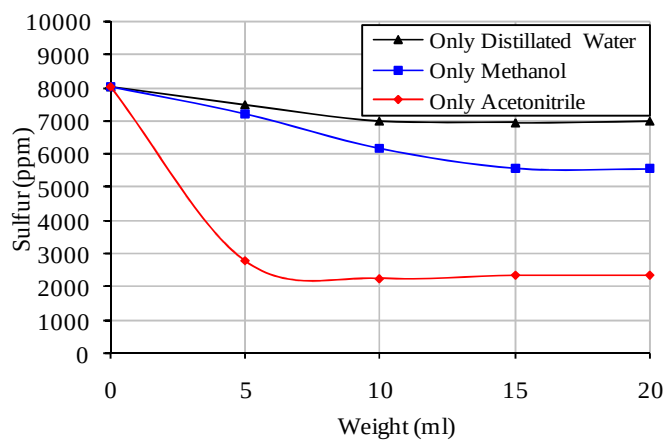


Figure 6. 3. Optimization of sulfur removal washing only by distillated water, methanol and acetonitrile.

At different temperature such as 40 °C, 50 °C, 60 °C, 65 °C, 70 °C and 80 °C were applied for sulfur removal. The best result was obtained at 70 °C, which shown at Figure 6.4. Other parameters were fixed to optimize temperature variations of H₂O₂–formic acid mixture.

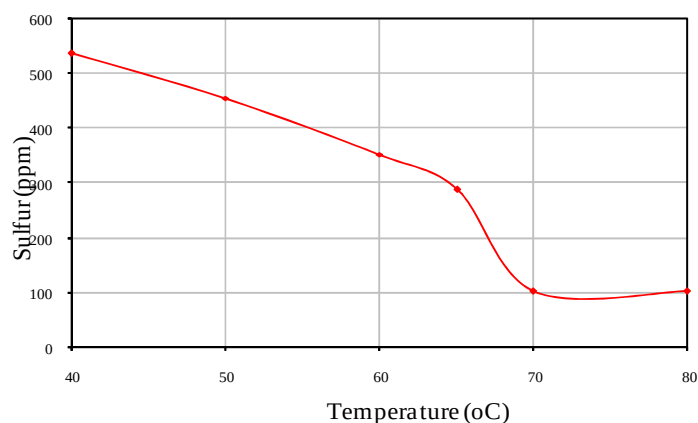


Figure 6. 4. Optimization of temperature variations for sulfur removal.

At different reaction time such as 30 min., 60 min., 90 min., 105 min., 120 min., 135 min., 150 min., and 180 min. were applied for sulfur removal, which shown at Figure

6.5. The best result was obtained at 120 min. Other parameters were fixed to optimize reaction time of H_2O_2 –formic acid mixture.

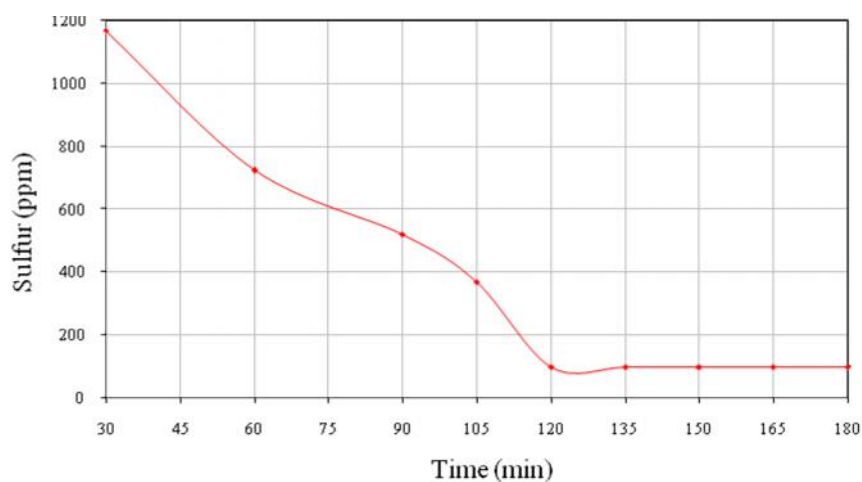


Figure 6. 5. Optimization of reaction time for sulfur removal.

At different distilled water amount such as 5 ml, 10 ml, 15 ml and 20 ml were applied for sulfur removal. The best result was obtained at 5 ml which shown at Figure 6.6. Other parameters were fixed to optimize reaction time of H_2O_2 –formic acid mixture.

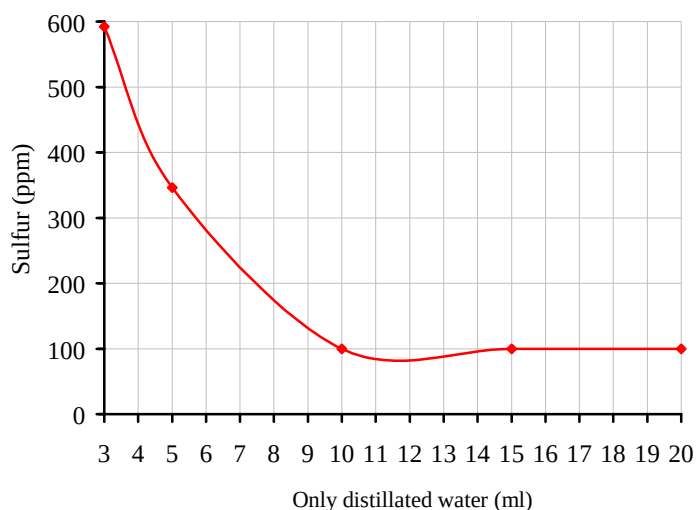


Figure 6. 6. Optimization of sulfur removal washing by different ratio of distilled water and constant acetonitrile.

At different acetonitrile amount such as 125 ml, 100 ml, 75 ml, 50 ml and 25 ml were applied for sulfur removal. The best result was obtained at 100 ml, which

shown at Figure 6.7. Other parameters were fixed to optimize reaction time of H_2O_2 –formic acid mixture.

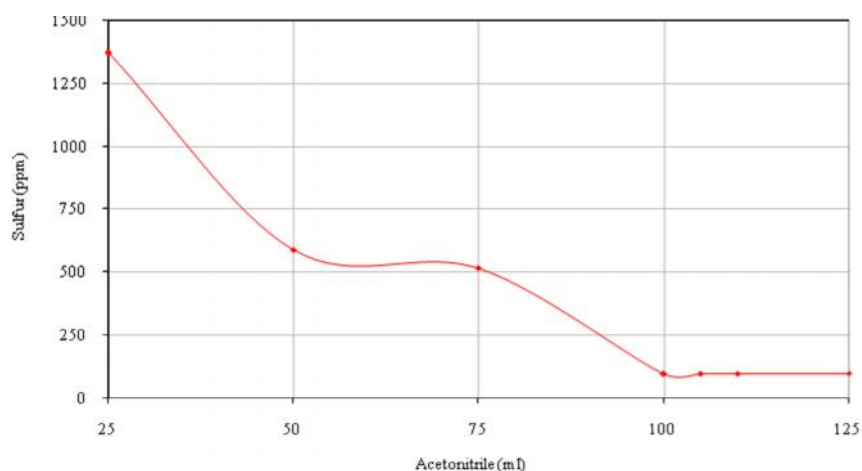


Figure 6. 7. Optimization of sulfur removal washing by different ratio of acetonitrile and constant distilled water.

The effect of distilled water extraction showed the same result at 1h and overnight, and the effect of acetonitrile extraction gave the same results after 1 h and overnight. This probably has to do with the solubility and phase separation of different hydrocarbons in DLF.

The elemental composition is also very important, since the % values or the amount of elements that exist in the fuel, can give an idea about its volatility, heating capacity, combustion performance and its exhaust emissions. Therefore, the ultimate or elemental analyses of LSDLF, DLF with diesel fuels were performed and their results are shown in Table 6.1 [13,66,99]. It can be seen from the elemental analysis results in Table 4.1 that the total amounts of carbon and hydrogen in LSDLF and DLF were approximately close to that of in gasoline and diesel fuels. At the same time, the oxygen (O_2) amount was found to be very high, whereas the nitrogen (N_2) amount was low. The presence of O_2 and N_2 in any fuel is an undesired condition, since they do not have any heating value. But, the presence of O_2 increases the combustion performance. The amount of O_2 improved and increased brake specific energy consumption [99]. The H/C, O/C molar ratios and the fuel's empirical formula were calculated from the elemental composition, and are shown in Table 6.1. The LSDLF sample's ultimate analysis test results show that its combustion

performance will be high and emissions will be in a reasonable range.

Table 6.1. Ultimate analysis of LSDLF, DLF with Diesel [7].

Elementals (wt%)	DLF	LSDLF	Diesel
C	81.31	81.176	86.58
H	11.28	12.942	13.29
N	0.52	0.572	65ppm
O ^a	4.45	5.308	0.01
S	0.8	0.002	0.11
H/C ^b	1.66	1.66	1.80
O/C ^b	0.04	0.04	---
Empirical Formula ^b	CH _{1.66} O _{0.04}	CH _{1.66} O _{0.04}	---

^aCalculated by difference, ^bCalculation

Aliphatic subfractions of the DLF were also obtained by using GC–MS chromatography and its results are shown in Figure 6.8. The molecular compounds identified in these subfractions are listed in Table 6.2, in order to get an idea about the DLF's composition (the nature and compound types, etc.). As observed in Table 6.2, n-pentane, alkanes, alkenes and branched hydrocarbons were determined to be present in aliphatic subfraction of LSDLF, and such subfractions predominantly contained cyclohexene, 4-ethylbenzene, (1- methylethyl)-ethylbenzene, benzene, 1,2,3 trimethyl-benzene, butyl, 2,3-epoxycarane, and 3,7,7 trimethyl-compounds. The LSDLF sample's GC–MS analysis results were compared with diesel fuel and were found to be similar to each other [101]. Also, the LSDLF's carbon subfractions distribution resembles that of diesel fuel [101-102].

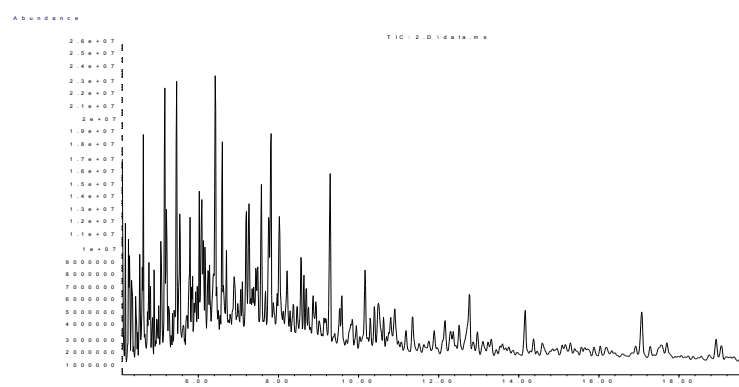


Figure 6. 8. GC–MS chromatogram of aliphatic subfraction of LSDLF.

Table 6.2. Relative content of compounds at the aliphatic subfractions of LSDLF.

Molecular Formula	Compound Name	RT (Min)	Area %
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C ₇ H ₁₂	2,4-Hexadiene, 2-methyl-	11.74	0.70
C ₇ H ₈	Toluene	12.92	7.03
C ₈ H ₁₂	Cyclohexene, 4-ethenyl	17.36	0.43
C ₈ H ₁₀	Ethylbenzene	19.43	4.80
C ₈ H ₁₀	o-Xylene	20.13	3.25
C ₈ H ₁₀	o-Xylene	21.94	1.04
C ₈ H ₁₀	Styrene	22.02	1.76
C ₉ H ₁₂	Benzene, (1- methylethyl)-	24.26	1.37
C ₁₀ H ₁₆	Santolinatriene	25.47	0.35
C ₉ H ₁₂	5-Methylenecycloocta-1,3-diene	26.73	1.12
C ₉ H ₁₂	Benzene, 1-ethyl-3-methyl	27.56	1.18
C ₉ H ₁₂	Benzene, 1-ethyl-2-methyl	28.73	0.76
C ₉ H ₂₀	Nonane	29.79	0.43
C ₉ H ₁₂	Benzene, 1,2,3 trimethyl-	30.02	0.88
C ₈ H ₁₆	2-Pentene,2,4,4-trimethyl	31.97	0.37
C ₁₀ H ₁₈	Cyclohexene, 1-methyl-4-(1-methylethyl)-	32.03	0.42
C ₉ H ₁₂	Benzene, 1,2,5-trimethyl-	32.22	0.50
C ₁₀ H ₁₄	Benzene, 1-methyl-2-(1-methylethyl)-	32.35	3.04
C ₁₀ H ₁₆	Limonene	32.57	5.35
C ₉ H ₁₀	Benzene, 2-propenyl-	33.43	0.51
C ₉ H ₈	Indene	34.39	0.63
C ₁₀ H ₁₄	Benzene, buthyl	34.85	0.65
C ₁₀ H ₁₆ O	2,3-Epoxy-carane,3,7,7 trimethyl-	37.07	0.49
C ₁₀ H ₁₂	Benzene, 2-ethenyl-1,3-dimethyl-	37.75	0.35
C ₁₀ H ₁₂	Benzene, 2-methyl-2-(2-propenyl)-	42.19	0.35
C ₁₀ H ₈	Azulene	45.42	0.75
C ₁₁ H ₁₀	Naphthalene, 2-methyl-	53.32	0.55
C ₁₁ H ₁₀	Naphthalene, 1-methyl-	54.27	0.44
C ₆ H ₃ MnO ₅	Manganese, pentacarbonylmethyl-	67.64	0.36
C ₉ H ₁₆ BrNO	2-Piperidinone, N-[4-bromo-n-butyl-]	68.21	0.38
C ₁₃ H ₂₈	Decane, 6-ethyl-2-methyl	68.33	0.71

The characteristics of the produced fuel were tested and the results are given in Table 6.3. It can be seen from this table that density, viscosity and water content of the LSDLF are in the range of standard diesel fuel. However, its flash point is lower than that of standard diesel fuel. This indicates that more volatile fuels exist in LSDLF. The lower heating value (LHV) is another important characteristic of fuel. The LHV of LSDLF was measured as 42,760 kJ/kg by using a bomb calorimeter (Leco AC350). It was found to be closer to the standard diesel fuel's LHV, with a value of 42,700 kJ/kg in Turkish (TS-3082) and European (EN-590) standards. The cloud and pour point were near to standard. The corrosion test was slight tarnish which can not wear out the engine. The three test results regarding distillation are given in comparison with the standard values. Among those, two of them indicate minimum

and maximum distilled volumes at 250 °C, and the other one is related to the maximum temperature at which 95 % of the fuel is distilled.

Table 6.3. Characteristics of diesel fuel [7] and LSDLF.

Properties	Diesel fuel TS3082-EN 590	LSDLF
Density at 15°C, kg/m ³	820-845	837
Viscosity at 40°C, mm ² /s	2-4.5	3.98
Water content, mg/kg	<200	---
Flash point, °C	>55	43
HHV, MJ/kg	42.70	42.76
Cloud point	D-97	12
Pour point	D-2500	15
Corrosion test	D-130	1a-1b
Distillation		
Temperature at 250°C, max. volume (% v/v)	40	55
Temperature at 350°C, min. volume (% v/v)	85	95
Volume at % 95, max. temperature, °C	360	---

The FTIR spectrum of LSDLF is shown at Figure 6.9. The aromatic C-H stretching with alkene's =C-H stretching vibration structure were in the range of 3100-3000 cm⁻¹. The aliphatic -C-H stretching vibration bands range from 2950 to 2800 cm⁻¹ with the same molecular arrangement and different isomer structure. And also C=O stretching vibration bands, alkene group's C=C stretching vibration and ester-ketone bonds were in the range between 1750 and 1600 cm⁻¹. The bands distributed from 1550 to 1450 cm⁻¹ were concerned to aromatic C=C bending vibrations, and was clearly pointing out the presence of alkenes. The aliphatic -C-H bending vibration bands in frequency range of 1400–1350 cm⁻¹ were indicating the stretching alkynes and also the =C-H out-of-plane bending peaks in the 900-650cm⁻¹ region were pointing out the presence of aromatic compounds and alkenes [22,26,100]. According to FT-IR results, it could be observed that LSDLF was a really complex mixture, which was containing the aliphatic and aromatic compounds in its structure. Thus, FT-IR test results proved that LSDLF was a good quality fuel to be combusted in a diesel engine.

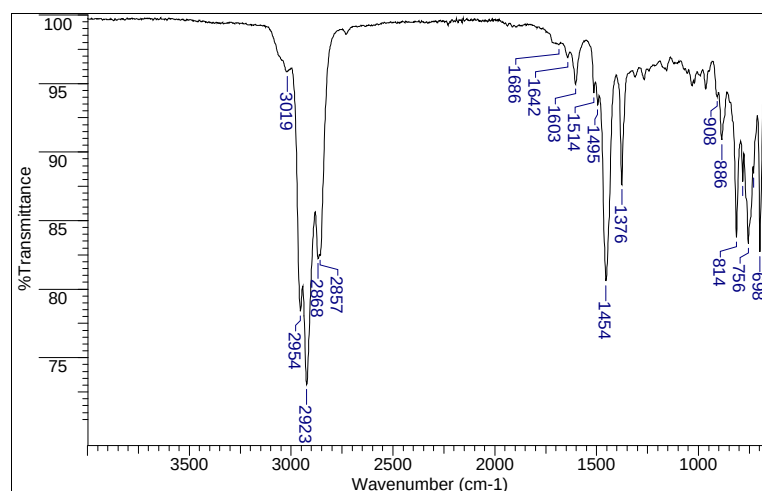


Figure 6. 9. The FT-IR spectra of LSDLF.

This study was also evaluated by linear regression model to investigate the influence of pyrolysis distillation temperature on the distilled volume with experimental results by using the SPSS version 22.0 statistical software. For this purpose, the DLF was used at the tests. The pyrolysis temperature variables were tested roughly at the temperature range from 145 °C to 345 °C. In linear regression model, R^2 (adj.) and R^2 were respectively 99.7 % and 99.4 % which were good results for LSDLF. Experimental results of LSDLF were close to the prediction results of LSDLF in linear regression model. Therefore, experimental standard was proven to be accurate. The ANOVA and t-test were applied on lime mixed waste tire oil. Accordingly, the statistical significance value was found less than 0.05 ($0 < 0.05$). The ANOVA and t-test were valid by significance value. The linear regression model of LSDLF has the following mathematical formula in Eq. 6.1:

$$V = -62.793 + 0.455 \times T \quad (6.1)$$

Thereby, the linear regression model of measured distilled volumes and predicted distilled volumes were both presented in Figure 6.9 to observe these values comprehensively. Also, they were distributed and concentrated around a straight line, incrementally. The distillation temperature was linearly increased with the distillation volume and each bead exhibited the experimental results to be very close to a straight line. In addition to diesel fuel, LSDLF and prediction diesel fuel were compared at Figure 6.10. As a result, all of these curves were found to be very close to each other.

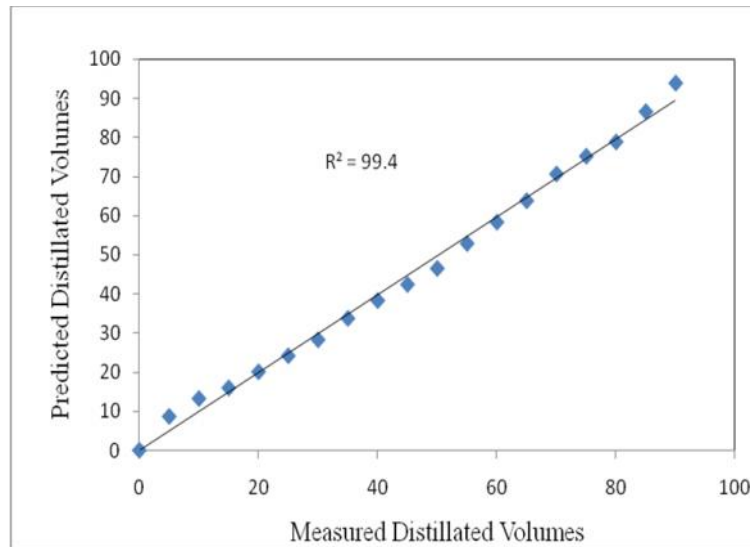


Figure 6. 10. Comparison of measured distillated volumes and predicted distillated volumes by linear regression analysis of LSDLF.

The variation between the distilled temperatures versus distilled volume, a distillation test on the LSDLF sample was performed. The result shows that LSDLF is a mixture of different hydrocarbons, each of which evaporates at a different temperature. The distillation temperature versus distilled volume graphic provides more appreciable data about the combustion and engine performance of a fuel sample, as an indication of how its ignition will take place [96]. It can be determined whether the fuel can be used in engines or not by looking simply at this distillation curve. Therefore, it is necessary to carefully examine the distillation curve to find out whether the distillation temperature of each LSDLF droplet is light or not. The distillation curve is directly related to the composition and chemical characteristics of the fuel. Thus, the engine performance can be predicted by the distillation curve, as well [97]. As a result of this consideration, the fuel sample's distillation test should be performed and its distillation curve compared with other fuels' curves, which was shown at Figure 6.11. From these results, it can be concluded that the LSDLF can be efficiently used in diesel engines, and there will be no problems in engine performance.

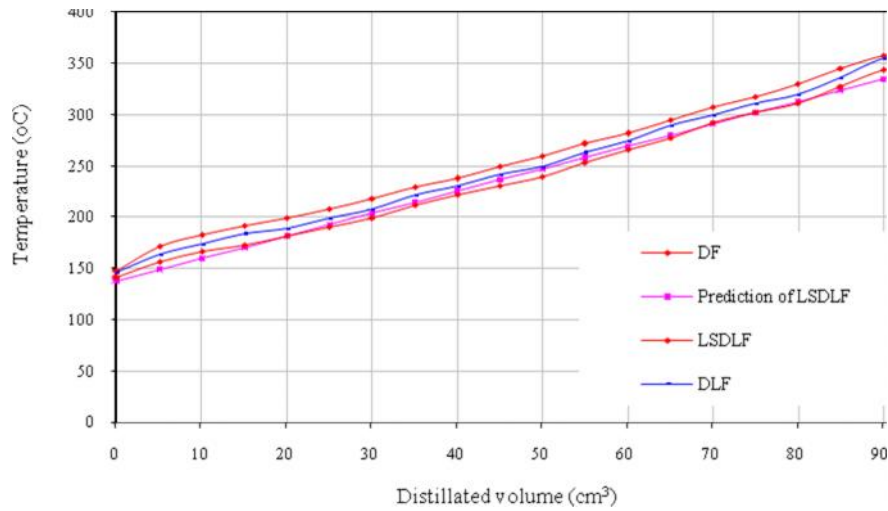


Figure 6. 11. Comparison of Diesel, LSDLF and Prediction of LSDLF.

6.3 Performance test results of DF, DLF and LSDLF

The fuel combustion effect on the engine was explained with the engine performance and exhaust emission parameters. The parameters would give an idea that can be used efficiently and without causing any trouble. Hence, the engine performance parameters are vital and should be specified. These parameters are brake torque (T), brake power (P_b), brake mean effective pressure (Bmep), brake specific fuel consumption (Bsfc) and the brake thermal efficiency (η_{th}). In addition to these, engine parameters were computed by fuel and air expending, LHV_{fuel} , torque and speed.

Figures 6.12-6.16 show variations of power, torque, Bmep, η_{th} and Bsfc along with the engine speed. It was observed that torque and Bmep were increased with the engine speed and reached the maximum value at 1500 rpm, whereas the Bsfc reached the minimum value at the same speed. The maximum torque value for the LSDLF, DLF and diesel around at 1500 rpm were observed. The thermal efficiency for both sample fuels was shown in Figure 6.15, in order to support the findings presented in Figures 6.15 and 6.16. Therefore, the Figures clearly showed that the LSDLF, DLF does not seem to have any inconvenience. The Bsfc is the ratio of mass fuel consumption to effective brake power and inverse to the η_{th} [122]. The Bsfc increases by the brake power increases up to 2500 rpm engine speed. The Bsfc was increased by friction, heat losses and deterioration at high speeds [123]. The

performance curve of the LSDLF, DLF was the same with the performance curve of the diesel fuel. The power, torque, and Bmep of the DLF were found to be very close to diesel fuel at Figures 6.12-6.14. Additionally, thermal efficiency for diesel was seemed to be higher than that of LSDLF and DLF in Figure 6.14, because Figure 6.15 shows that the Bsfc of the LSDLF and DLF was higher than diesel. So, it is a disadvantageous criterion for the LSDLF and DLF's fuel consumption. Finally, it was understood that the LSDLF and DLF could be combusted safely in diesel engines as observed from Figures.

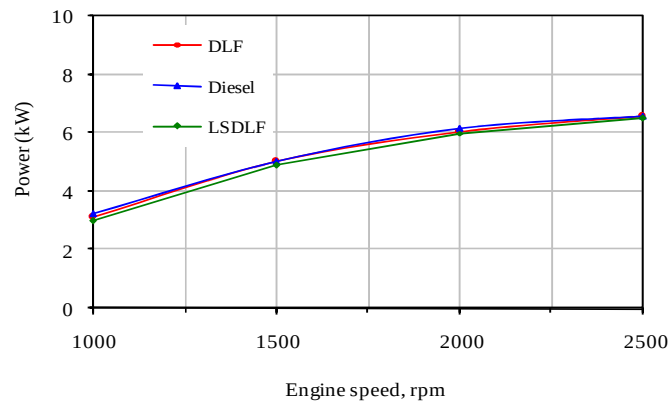


Figure 6. 12. Effects of the LSDLF, DLF and diesel on engine power.

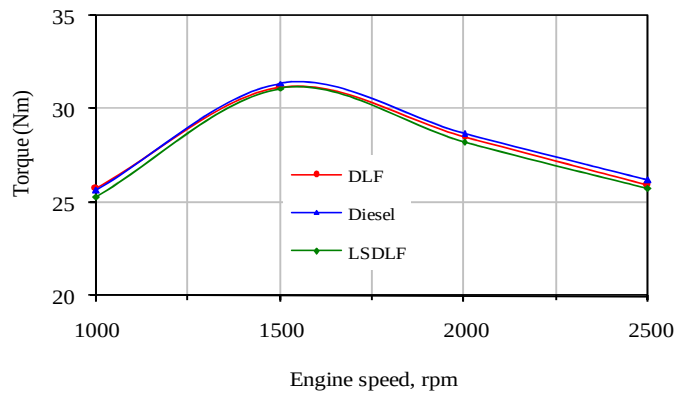


Figure 6. 13. Effects of the LSDLF, DLF and diesel on engine torque.

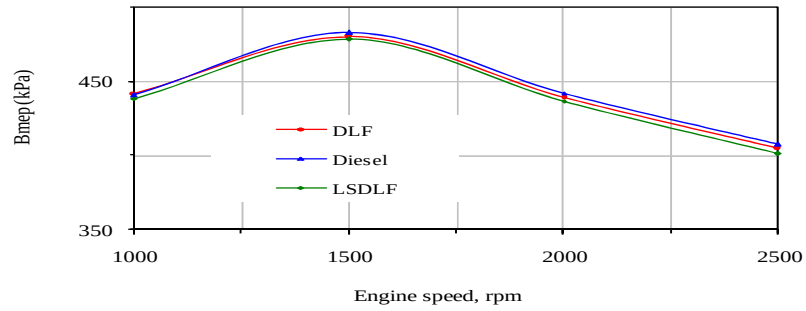


Figure 6. 14. Effect of the LSDLF, DLF and diesel on the Bmep.

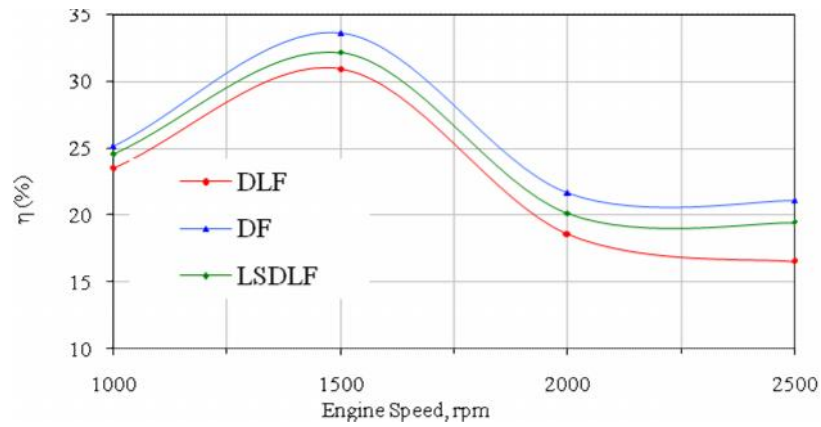


Figure 6.15. Effect of the LSDLF, DLF and diesel on the η_{th} .

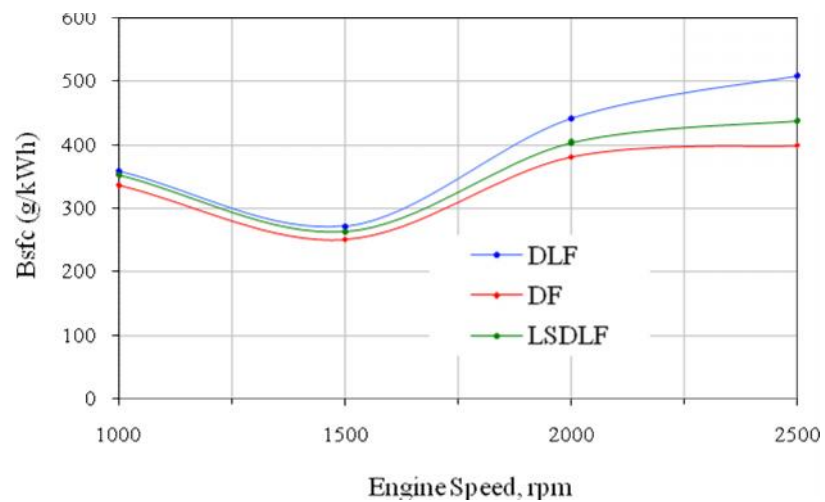


Figure 6.16. Effect of the LSDLF, DLF and diesel on Bsfcc.

6.4 The Emission test results of DF, DLF and LSDLF

The exhaust temperature and emission values are extremely significant for the engine performance. Thus, the exhaust temperature was measured continuously during the experiment. The exhaust temperature of the LSDLF, DLF and diesel fuel, which were very close to each other, was presented along with the engine speed variations in Figure 6.17. The exhaust temperature change between 358 °C to 450 °C for the LSDLF was compared with the change between 394 °C to 458 °C for diesel, indicating a significant change in its value. If any fuel has high distillation temperature, it increases the burning temperature in engine. Accordingly, the higher diesel temperature values correspond to the higher distillation temperatures. Thus, the higher combustion temperature affects the increase in the exhaust temperature. A high exhaust temperature is not preferable, due to the high heat transfer amount into the environment. At a finite value, engine's thermal efficiency decreases with high heat transfer. So, the performance parameters can be agitated by thermal efficiency.

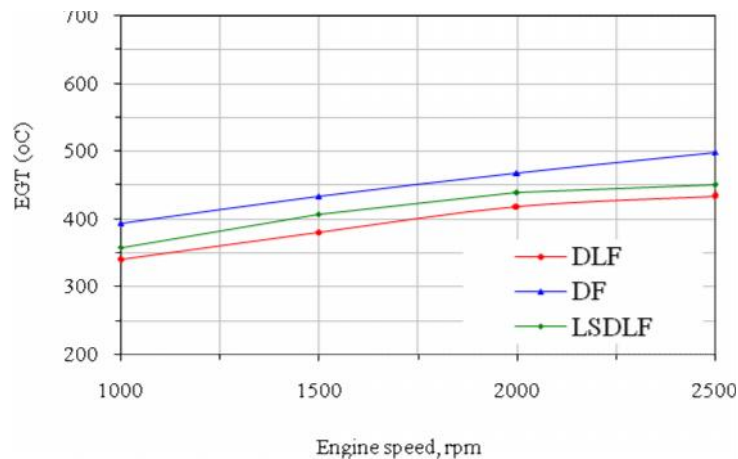


Figure 6.17. Variation of EGT with engine speed.

The exhaust emission results were analyzed, in their relation with sulfur dioxide (SO₂), carbon monoxide (CO), carbon dioxide (CO₂), nitrogen monoxide (NO), nitrogen oxides (NO_x) and oxygen (O₂), by a gas analysis device. The SO₂, CO, CO₂, NO, NO_x and O₂ values were verified with both DLF and diesel engine speeds in Figures 6.18-6.24. The SO₂ values of LSDLF and DLF were observed to be higher than that of diesel fuel, as shown in Figure 6.18. As seen from Table 4.4, the sulfur presence in DLF was higher than diesel fuel, which had a direct effect on SO₂ emissions at engine combustion. The sulfur was remarkable in the environment due

to the fact that sulfur compound gases reacted with water vapor and formed sulfuric acid (H_2SO_4) in the atmosphere. The sulfur rains are detrimental to nature from all aspects. Thus, the sulfur amount in DLF must be decreased to the standard values as named LSDLF. The LSDLF has 100 ppm of sulfur amount.

In an ideal burning, CO, CO_2 , NO and NO_x emissions should not be produced after combustion. Such emissions have toxic effect on the environment, as shown in Figures 6.19-6.24. Emission values of these gases for LSDLF and DLF were found slightly higher than that of diesel fuel for all engine operations. The O_2 emission value of LSDLF and DLF was quite close to that of diesel fuel as shown in Figure 6.23. The carbon and nitrogen elements were also present in the fuel. The air and fuel were reacted to produce CO_2 and N_2 . The excess O_2 was also released in the emissions. The engine emissions are affected by fuel characteristics [124]. The air-fuel ratio, engine temperature [123], inadequacy of oxygen and the minimum combustion time [116] can lead to incomplete combustion. The air-fuel ratio is the other main parameter that affects CO, CO_2 and HC emissions [125]. The CO, CO_2 , NO and NO_x values reached their minimum and maximum points between 1500 to 2000 rpm. Figures 6.19 and 6.22 clearly show that these emissions were reduced at 2500 rpm engine speed. The highest and the lowest points of the Figures are the inflections on the curves. The increase in CO amount in combustion chamber was influenced by the deficiency of oxygen and the minimum time of combustion cycle at high speed [116]. The fuel physical properties as density, viscosity, surface tension affect on atomization which determine HC emission. Figure 6.24 shows that HC of LSDLF and DLF and diesel fuel were closed to each other's [121].

High emission values, which lead to energy losses and ambient pollutions, are not desirable. In addition, compared to diesel fuel, the low O_2 amount in LSDLF and DLF exhaust could be explained by low air-fuel ratio. It was obviously seen that by decreasing the CO amount, the air-fuel ratio could be increased. As result of ignition, if CO and NO_x emissions were highly decreased, then both the energy consumption and also, the trouble effect on the environment would decrease. So, it also contributes positively to the economy.

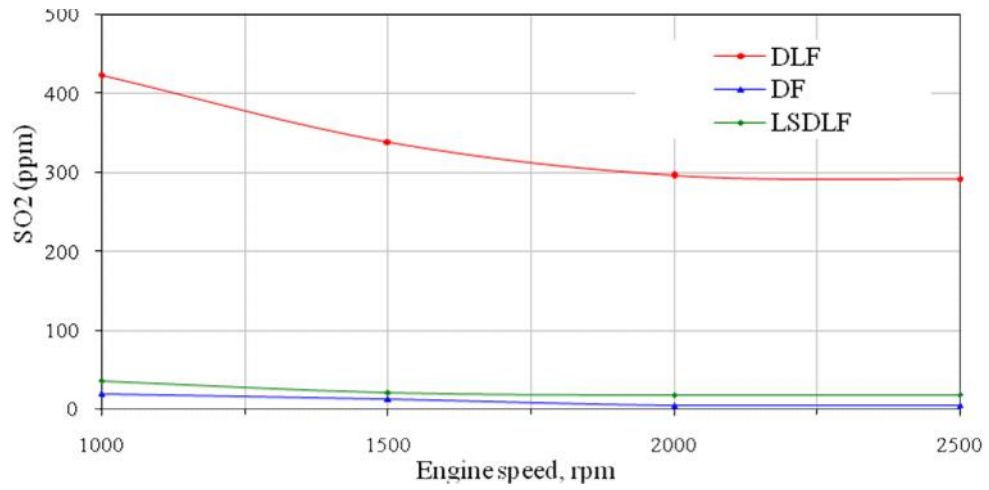


Figure 6.18. Variation of SO₂ emission with engine speed.

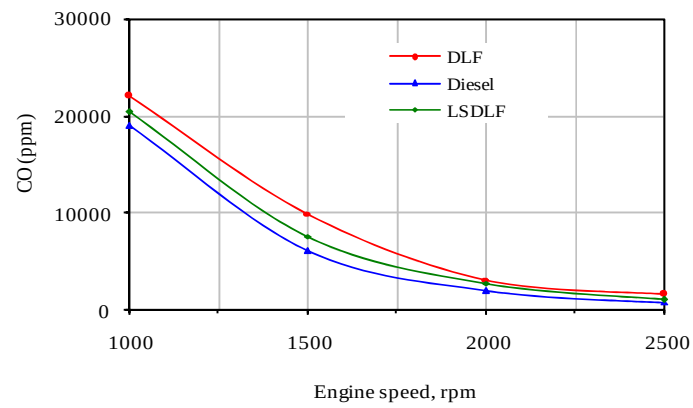


Figure 6.19. Variation of CO emission with engine speed.

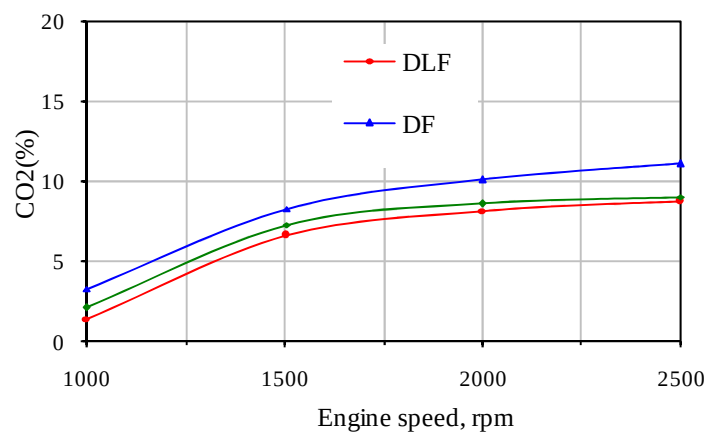


Figure 6.20. Variation of CO₂ emission with engine speed.

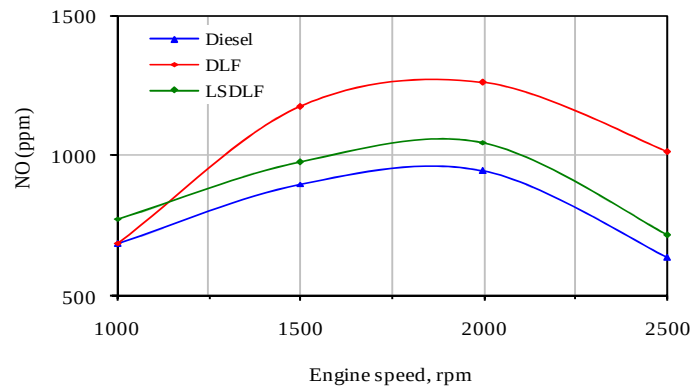


Figure 6.21. Variation of NO emission with engine speed.

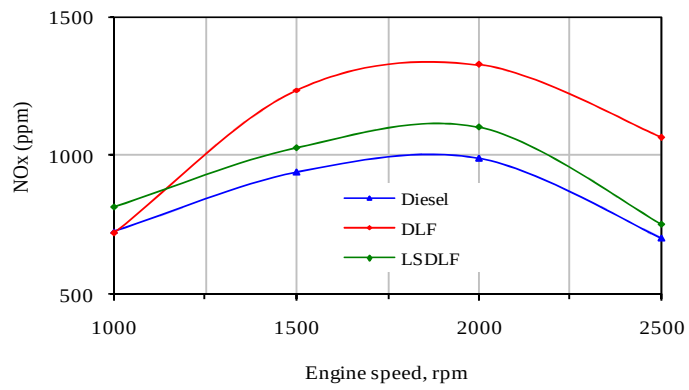


Figure 6. 22. Variation of NOx emission with engine speed.

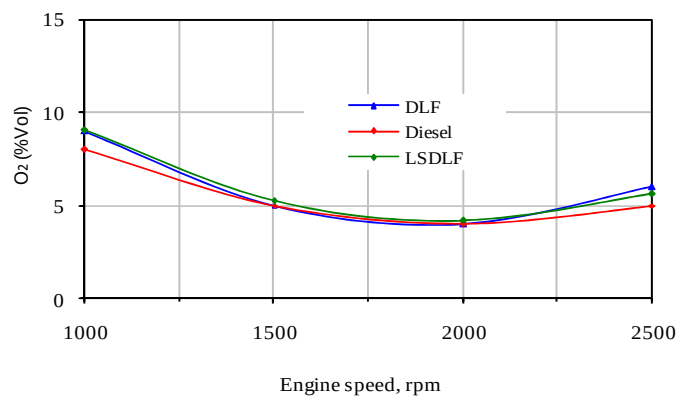


Figure 6. 23. Variation of O2 emission with engine speed.

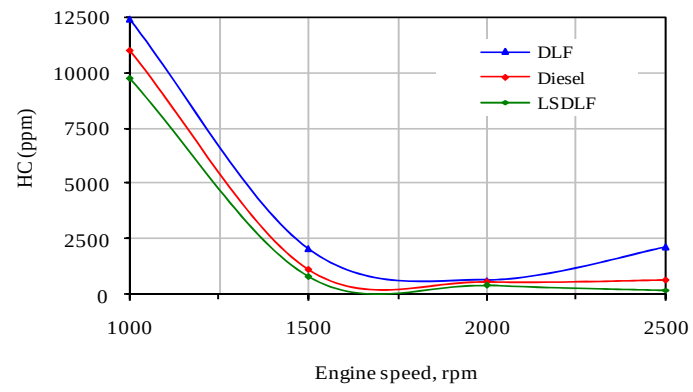


Figure 6. 24. Variation of HC emission with engine speed.

CHAPTER 7

THE ECONOMIC ANALYSIS

7.1 Introduction

The production cost for waste tire pyrolysis was determined for five cases. The waste tire converted to waste tire to oil (40 wt% of WTO), carbon black (42 wt% of CB_p), and non-condensable gas (18 wt% of Gas), than to convert liquid product as GLF (18%), DLF (70%) and residue of the pyrolysis (12%). The waste tire cost is 0.026 \$/kg, lime cost is 0.05 \$/kg and the energy cost (electricity) is 0.116 \$/kWh in Turkey. An economic chain of calculations were done for energy unit costs, feedstock and other parameters were listed in Tables 7.1.

The general formula described as:

$$\text{Total sample production} = \text{Daily production} \times \text{days} \times \text{Life of fuel production system} \quad (1)$$

$$\text{Amortization of the pyrolysis unit} = \text{Total fuel production} / \text{Cost of system} \quad (2)$$

$$\text{Energy cost} = \text{Used total power} \times \text{unit cost of energy} \quad (3)$$

$$\text{The cost of raw material} = \text{Energy cost} / \text{raw material weight} \quad (4)$$

$$\text{Total cost} = \text{Energy cost} + \text{the cost of raw material} + \text{Amortization} \quad (5)$$

The main part of pyrolysis unit cost is 14,333 \$. The main part can be used for 10 years as full load of production [7]. The pyrolysis unit loads 20 kg of each day to produce 8 liters of WTO and 3.6 L_N m⁻³ of Gas. The next step, 20 liters of WTO expose with 10 %wt CaO to produce 3.6 liters of GLF and 14 liters of DLF.

The Eq. 1 used as:

$$\text{The WTO production} = 20 \times 260 \times 10 = 520,000 \text{ liters (or kg)}$$

$$\text{The GLF production} = 3.6 \times 104 \times 10 = 3,744 \text{ liters (or kg)}$$

$$\text{The DLF production} = 14 \times 104 \times 10 = 1,248 \text{ liters (or kg)}$$

The Gas=3.6*260*10=9,360 L_N m⁻³ (or liter)

Total=534,352 liters (per year)

The Eq. 2 used as:

Amortization of the pyrolysis unit=13,310 \$/534,352 liters =0.025 \$/liters (per year)

Table 7.1. The experimental economic analysis of electricity.

Equipments	Power (kW)	Experiment Time (h)	Total Power (kWh)
Reactor (WTO)	8	4.5	36
Mixer (WTO)	0.2	4.5	0.9
<u>Total WTO Cost</u>			<u>36.9</u>
Reactor (N-Gas)	8	1.5	12
Mixer (N-Gas)	0.2	1.5	0.3
<u>Total Gas Cost</u>			<u>16.4</u>
Reactor (GLF)	8	2	16
Mixer (GLF)	0.2	2	0.4
<u>Total GLF Cost</u>			<u>16.4</u>
Reactor (DLF)	8	4	32
Mixer (DLF)	0.2	4	0.8
<u>Total DLF Cost</u>			<u>32.8</u>

7.2 The Unit cost of WTO

The WTO unit cost as follow:

The Eq. 3 used as:

Energy cost = 36.9 kWh*0.116 \$/kWh= 4.280 \$

The Eq. 4 used as:

The cost of raw material= 4.2804 \$/8 kg = 0.535 \$/kg

The Eq. 6 used as:

Total cost = 0.535+0.026*0.4+0.025= 0.570 \$/liter of WTO

7.3 The Unit cost of Gas

The Gasunit cost as follow:

The Eq. 3 used as:

Energy cost = 16.4 kWh*0.116 \$/kWh= 1.902 \$

The Eq. 4 used as:

The cost of raw material= $1.9024 \text{ \$}/3.6 \text{ L}_N \text{ m}^{-3} = 0.528 \text{ \$}/\text{L}_N \text{ m}^{-3}$

The Eq. 6 used as:

Total cost = $0.5284+0.026*0.18+0.025= 0.558 \text{ \$}/\text{L}_N \text{ m}^{-3}$ of Gas

7.4 The Unit cost of GLF

The GLFunit cost as follow:

The Eq. 3 used as:

Energy cost = $16.4 \text{ kWh}*0.116 \text{ \$}/\text{kWh}= 1.902 \text{ \$}$

The Eq. 4 used as:

The cost of raw material= $1.9024 \text{ \$}/3.6 \text{ liter} = 0.528 \text{ \$}/\text{liter}$

The Eq. 6 used as:

Total cost = $0.5284+0.570*0.18+0.025= 0.656 \text{ \$}/\text{liter}$ of GLF

7.5 The Unit cost of DLF and LSDLF

The DLFunit cost as follow:

The Eq. 3 used as:

Energy cost = $32.8 \text{ kWh}*0.116 \text{ \$}/\text{kWh}= 3.804 \text{ \$}$

The Eq. 4 used as:

The cost of raw material= $3.8048 \text{ \$}/14 \text{ kg} = 0.271\text{\$/kg}$

The Eq. 6 used as:

Total cost = $0.271+0.570*0.7+0.025= 0.695 \text{ \$}/\text{liter}$ of DLF

The desulfurization of DLF was done by using formic acid and hydrogen peroxide with washing acetonitrile. Firstly, formic acid (0.01 L)-hydrogen peroxide (0.2 L) mixed with DLF (1000 L) at 70 °C, then, washed triple with acetonitrile (1 L). The cost of formic acid (0.01 L), hydrogen peroxide (0.02 L) and acetonitrile (1 L) are 0.003 \$/L, 0.02 \$/L and 1 \$/L. And also, the price of electricity for 70 °C, for 120 min., is 0.2 \$/kWh. So, the total price of LSDLF is 1.918 \$/L. However, acetonitrile can be recycled, so the price decrease to 0.918 \$/L. The main part of pyrolysis unit cost is 11,477 \$. The main part can be used for 10 years with a full load production [7]. Amortization of the pyrolysis unit is 0.157 \$/L. The costal results for a pilot scale system of Gas ($0.407 \text{ \$}/\text{L}_N \text{ m}^{-3}$) is lower [126]. However, GLF (0.333 \$/L) and

LsDLF's costs (0.918 \$/L) [127] are higher than that of commercial petroleum fuels. The unit price for electricity and the dollar exchange rate are also high in Turkey. If a power plant is built, natural gas or coal can be used as alternative heating sources for the beginning of pyrolysis, and then N-Gas based pyrolysis can be used as a recovery energy source.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

The waste tire was pyrolyzed in the previous studies. In this work, three main topics have been discussed deeply; the production of fuel from waste tire, performance and emissions, and desulfurization method. The results were given as follow sub-sections with future works.

8.2 Production of gasoline and diesel-like fuels from waste tire oil by using rotary kiln reactor

The waste tire is firstly pyrolyzed in a rotary kiln reactor to obtain more gas, light liquid, heavy liquid, wax products, and less carbon black at their maximum yields as, 25%, 12%, 8%, 35% and 20% of the total weight (4 tones). The light and heavy oils are blended with CaO and NZ additives at mass basis of 2%, 6%, and 10% in a batch reactor, and are distilled at 400°C. The light oil mixture resembles to gasoline like fuel and named as GLF and the other one is similar to diesel like fuel and called as DLF, which can be combusted in engines. The physical and chemical properties of GLF and DLF are analyzed and were found to resemble standard petroleum fuels.

8.3 Production of gasoline and diesel-like fuels from waste tire oil by using batch reactor

This waste tire was exposed by using the catalytic distillation method to obtain engine fuels. Waste tire oil (WTO) product that had a 40% ratio was produced with 42% char, while the remaining 18% was released into the atmosphere as a gaseous by product. The WTO was mixed with two additives, namely naturel zeolite and

lime, at different mass ratios (mass basis of 2%, 4%, 6%, 8%, 10%). Each fuel sample was exposed to pyrolytic distillation to obtain light and heavy fuel products. Characteristics of the as-produced fuels were determined and their distillation tests were investigated. As a result of these tests, the lime mixture fuel sample at 10 wt% ratio showed the best results, acquired the optimum distillation temperatures and was close to diesel fuel. This mixture was categorized as light and heavy fuels according to its distillation test results. Characteristics of those light and heavy fuels resembled those of gasoline and diesel fuel, which were named as gasoline-like fuel (GLF) and diesel-like fuel (DLF), respectively. Fractions of the as-produced fuels were 18 wt% of WTO for the light fuel, and 70 wt% for the heavy fuel. The other product was 12 wt% of residues.

8.4 Performance and Emissions of the GLF Mixed with Turpentine and Gasoline Fuel

The engine performance and emission of spark ignition (SI) engine were tested by burning gasoline fuel (GF), gasoline-like fuel (GLF) (the 18 wt% of waste tire oil (WTO)) produced from 10 wt% Lime-WTO mixture, the mixture of GF and GLF with the amounts of 10 wt%, 20 wt%, 30 wt% and the blends of GLF and Turpentine with the amounts of 10 wt%, 20 wt%, 30 wt%. During the experiments, performance and emissions parameters were tested. The GLF added into GF has increased the P_b , T , $Bmep$, and η_{bt} values, and conversely, the $Bsfc$ value was decreased with the increasing amount of GLF in GF. Also, the EGT of GF was increased as well. Furthermore, the CO_2 , NO and NO_x were increased, while CO was decreased. And also, the HC and O_2 values were increased by adding GLF into GF. The increased Turpentine amount in GLF caused an increase in P_b , T , $Bmep$, η_{bt} values, however it caused a decrease in $Bsfc$ value. The EGT was increased incrementally in the engine. Besides, the CO_2 , NO and NO_x were increased, while CO was decreased. The HC and O_2 were also increased by adding more Turpentine.

8.5 Performance and Emissions of the DLF and LSDLF

This study aims to investigate both the engine performance and exhaust emission parameters obtained from a diesel test engine. Diesel-like fuel (DLF) produced from

waste tire oil (WTO) is used in the diesel engine to obtain effect of the DLF on the engine performance and its emissions. The DLF sulfur removed and named as low sulfur diesel-like fuel (LSDLF) which is used in the diesel engine to obtain effect of the LSDLF on the engine performance and its emissions. The chemical and physical properties of LSDLF and DLF were observed to be similar to diesel fuel. The LSDLF and DLF were burned in engine without any trouble. According to LSDLF and DLF burning test results; its torque, power and Bmep were similar to diesel fuel, while its Bscf value was higher than that of diesel fuel, and its thermal efficiency was lower than that of diesel fuel. The cost of LSDLF was estimated to be 0.918\$/l. The DLF's sulfur content was found to be far higher than the standards; thus, its value must be decreased. Therefore, desulfurization, as the most popular, easy and high efficiency method applied DLF and the LSDLF was 100 ppm.

8.6 Recommendation for future works

The followings can be suggested for future studies:

1. During the pyrolysis, consumption of electricity was so much high. Thus, a new alternative energy sources needs.
2. The pyrolysis time is long. So, an alternative technique such as solvent extraction require for industrial usage.
3. The gas of batch pyrolysis need to store at a tank and then, it will be use again for pyrolysis instead of electricity.
4. The oxidative ODS removes some organic compounds and by washing acenotrile cause to absorbed some useful chemicals. Thus, a new catalyst can be use instead of ODS.
5. A different types of additives add into GLF and DLF to improve engine parameters.

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