QUANTITATIVE ANALYSIS OF ETHANOL CONTENT AND KEROSENE ADULTERATION OF MOTOR GASOLINE IN ETHIOPIA, USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

MSC IN LASER SPECTROSCOPY

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MSC THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,

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This is to certify the thesis entitled" **Quantitative analysis of ethanol content and kerosene adulteration of motor gasoline in Ethiopia, using Fourier transform infrared spectroscopy"** submitted authors by Yordanos Fekede in partial fulfillment of the requirements for the degree of Master's in Physics with specialization (Laser spectroscopy). Therefore I recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the department.

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We, the undersigned members of that the Board of Examiners of the final open defence by Yordanos Fekede have read and evaluated her thesis entitled "**Quantitative analysis of ethanol content and kerosene adulteration of motor gasoline in Ethiopia, using Fourier transform infrared spectroscopy"** and examined the candidate. This is, therefore, certifying that the thesis has accepted in partial fulfilment of the requirements for the degree.

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This MSc Specialty or equivalent thesis has been submitted for examination with my approval as thesis advisor.

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List of abbreviation

ATR	Atenuated total reflectance
CNCS	Colleague of natural and computational sciences
CO	Carbon monoxide
CV	Cross validation
ESR	Electron spin resonance
ETBE	Ethyl teritiary amyl butyl ether
FIA	Fluorescent indicator absorption
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HC	Hydrocarbons
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
IR	Infrared
ISO	International standardization organization

MCT	Mercury cadmium telluride
MO	Molecular orbital
MON	Motor octane number
MTBE	Methyl teritiary amyl methyl ether
NIR	Near infra red
NMR	Nuclear magnetic resonance
PCA	Principal component analysis
PLS	Partial least square
PLSR	Partial least square analysis
PM	Particulate matter
RMSEP	root mean square error of prediction
RON	Research octane number
SIMCA	Soft independent modeling class analogy
UV	Ultraviolet
VIP	Variable importance projection

Abstract

The automotive sector in Ethiopia is a major player of economic growth and most activities rely on it. Gasoline is the most often utilized energy source used to power automotives with internal combustion engine; as a result its demand is growing from time to time. Due to the high demand, its quality is usually compromised. Among others, ethanol and kerosene are the most commonly added substances due to their cheaper price, and surplus availability compared to gasoline. According to ISO only 10% Ethanol should be added to gasoline to reduce greenhouse gas emission. However, in many countries including Ethiopia, there is no strict control on the amount of ethanol and the presence of kerosene in gasoline. Some random investigations showed that there are illegal adulteration practices on most gasoline stations [40]. Detecting adulterants and determining ethanol content can't be done by visual inspections due to their similarity and miscibility with the actual gasoline acquiring analytical techniques. This study aims to quantify ethanol content and kerosene adulteration in five gasoline brands from gas stations located in Hawassa city, Ethiopia using FT-IR spectroscopy. The ethanol content is determined by using the absorption peaks aroused from O-H and C-H stretching vibrations and the kerosene adulterations detected using absorption peaks in $1378Cm^{-1}$*and* $1460Cm^{-1}$ *region of IR spectrum. The later peaks are believed to be originated from the* CH_3 *bending vibration. The results obtained by FT-IR technique showed that there is an ethanol blending practice exceeding the limit set by ISO ranging from 2% to 9% and significant kerosene adulteration has also be detected. The results suggest that there are significant kerosene adulteration and ethanol blending noncompliance with gasoline quality standards in gasoline supply chain.*

Key words: Gasoline, ethanol, kerosene, FT-IR spectroscopy

contents

CHAPTER ONE

1. Introduction

1.1 Background of the study

Gasoline is one of the most widely used motor fuels. In general, gasoline is defined as a flammable liquid made from petroleum; consisting of a blend of refined hydrocarbons and other chemicals. It is mostly utilized as fuel in internal combustion engines found in automobiles. It is a highly refined product with a high density of energy[1]

However, certain blends or oxygenates can be added to gasoline without going over the limits set by national or international regulatory agencies in order to increase fuel efficiency and decrease greenhouse gas emissions. Ethanol is one of the additives used to blend in gasoline most frequently.

It is a colorless liquid that is combustible and volatile[2]. Ethanol is primarily used as an engine fuel and as a fuel additive. An industry advocacy group claims that using ethanol as fuel lowers dangerous tailpipe emissions of chemicals that cause ozone depletion, such as carbon monoxide, particulate matter, and oxides of nitrogen[3].

There are laws governing the use of ethanol as a gasoline additive in several nations, including Ethiopia. The maximum permissible ethanol level in gasoline is normally up to 10% by volume (E10), according to international organization for standardization (ISO)15376(2018), which establishes requirements and test procedures for ethanol used as blending component for gasoline. A few issues were found when the ethanol-gasoline quality was randomly inspected at different gas stations. However, using inferior gasoline and ethanol caused engine failure and unstable engine speed[4].

On the other hand, illegal gasoline adulteration with cheaper materials is a persistent problem worldwide, particularly in nations lacking robust regulations and effective control[5].

Some of the main culprits in gasoline adulteration are, waste industrial solvents, alcohols, mineral spirits, kerosene, rubber solvent, light and heavy petrochemicals, diesel, and paint thinner.

Kerosene, or paraffin, is the most common adulterant in gasoline. It is a liquid hydrocarbon that burns easily and is made from petroleum. It is extensively utilized as fuel in both homes and aircraft[6]. It is made up of hydrocarbon molecules, which normally have six to twenty carbon atoms per molecule, and is miscible in petroleum liquids[7]. Emissions of particulate matter (PM), carbon monoxide (CO), and hydrocarbons (HC) rise when kerosene is added to the fuel or gasoline mixture. One of the challenge in these adulterants is the difficulty of detecting them using conventional quality control procedures. Despite changing engine performance, adulteration will only marginally modify the physical and chemical properties of gasoline due to the nature of these solvents[8].

Since the excessive use of ethanol as fuel additive and the use of kerosene for fuel adulteration cause environmental pollution and affect engines performance, quantification of ethanol content and kerosene adulteration is needed. In the context of Ethiopia, where the automotive sector is a pivotal driver of economic growth and societal mobility, the accurate determination of ethanol content and the prevention of kerosene adulteration in motor gasoline are paramount concerns. Addressing these challenges requires advanced analytical methodologies that can offer reliability and accuracy and it can be done by spectroscopic techniques.

Spectroscopic methods involve the use of light matter interaction for both qualitative and quantitative study of atoms or molecules present in a sample. Their versatility, sensitivity and non-destructive analysis makes them preferable than the other methods. Fourier transform infrared spectroscopy is one of the most accurate spectroscopic techniques for fuel analysis that works by measuring the absorbance, transmittance or reflectance of infrared light by the sample.

This study endeavors to contribute to the comprehensive understanding of ethanol content and kerosene adulteration in motor gasoline in Ethiopia through the application of Fourier Transform Infrared (FTIR) spectroscopy.

1.2 Statement of the problem

The automotive sector in Ethiopia serves as a key driver of economic growth and social development, yet the quality of motor gasoline, vital for best internal combustion engine performance and for environmental safety, faces challenges such as ethanol content variability and unauthorized kerosene adulteration. These issues not only put engine efficiency and environmental protection in danger but also raise concerns about its compliance with national and international fuel quality standards. Ethanol content fluctuations across fuel stations need prompt inquiries into the accuracy of blending practices. Similarly, the illegal practice of kerosene adulteration remains inadequately studied prompting a research gap regarding the application of advanced analytical techniques, notably Fourier Transform Infrared (FTIR) spectroscopy, within the specific context of Ethiopia. Ensuring regulatory compliance among local fuel providers is essential, requiring examination of variations in ethanol content and kerosene adulteration to identify non-compliance issues and guide regulatory bodies in implementing targeted measures. This study aims to address knowledge gaps and proposes the application of FTIR spectroscopy to improve fuel quality assessments.

1.3 Research questions

As the researcher is interested in studying the variation of motor gasoline quality in Ethiopia, the following questions guided the investigation

1. What is the variability in ethanol content with in motor gasoline across different fuel stations in Ethiopia?

2. To what extent is kerosene adulteration present in motor gasoline in Ethiopia, if any?
3. Do local fuel providers in Ethiopia comply with national and international standards regarding ethanol content and prevention of kerosene adulteration in motor gasoline?

1.4 Objectives of the study

1.4.1 General objective

- ✓ The general objective of the study is to quantitatively analyze ethanol content and kerosene adulteration in motor gasoline in different gasoline stations in Ethiopia using Fourier transform infrared spectroscopy.

1.4.2 Specific objectives

The specific objectives of this study are:-

- ✓ To identify and quantify ethanol content and extent of kerosene adulteration in motor gasoline samples using FTIR spectrometer
- ✓ To assess the compliance of local fuel providers with established standards for ethanol content and prevention of kerosene adulteration in motor gasoline.
- ✓ To examine variations in fuel quality across different stations

1.5 The scope of the study

This research focuses on assessing ethanol content variability and unauthorized kerosene adulteration in motor gasoline in five different fuel providers (Taf oil, Tabarek, Noc, Total and Global oil) from gas stations located in Hawassa city, Ethiopia; using Fourier transform infrared spectroscopy.

1.6 Limitations of the study

Due to financial limit and time constraints:

- ✓ Only five gasoline samples from different fuel providers located in Ethiopia, such as; Taf oil, Tabarek, Total, Noc and Global oil are considered in this study.
- ✓ Only ethanol and kerosene contents are determined.

1.7 Significance of the study

This research holds crucial significance as it addresses critical challenges in the automotive sector of the country by delving into ethanol content variability and an unauthorized kerosene adulteration in motor gasoline. The study directly impacts engines performance, environmental sustainability and compliance with fuel quality standards. The outcomes are expected to inform regulatory bodies, fuel providers, and the public, promoting informed decision making. Furthermore, by proposing the application of FT-IR spectroscopy the study contributes to advancing analytical methodologies potentially influencing fuel quality assessment practice serving as a model for similar contexts. Ultimately, the research seeks to instigate positive changes ensuring higher fuel quality standards and promoting sustainable automotive practices in Ethiopia.

CHAPTER TWO

2. Theoretical background

2.1 Optical spectroscopy

Optical spectroscopy is specific type of spectroscopy that examines how materials interact with light in different regions of electromagnetic spectrum [9]. This method entails analyzing how materials absorb, emit or scatter light within these specific wavelength ranges to obtain information about the composition, structure and properties of materials. It is a versatile and powerful tool for studying a wide range of materials from simple molecules to complex systems. Optical spectroscopy typically relies on six phenomenon absorption, fluorescence, phosphorescence, emission, scattering and chemiluminescence.

Absorption involves absorption of photon or radiation leading to the excitation of an atom or molecule or transition from a lower state to a higher one. This specific transition that occur is determined by the energy of the photons. Emission is a phenomenon in which a photon is generated causing an atom or molecule that is in an excited state to return to its ground state. When an atom or molecule in an excited state transits to a lower energy level, the extra energy is often emitted as a photon that process is called emission [10].

Emission of light after the absorption of a photon is known as photoluminescence, while that occurs after a chemical reaction is called chemiluminescence. Luminescence refers to the spontaneous emission of radiation from electrically or vibrationaly excited species that is not in thermal equilibrium with its surroundings. Specifically it involves the emission of light resulting from the direct excitation of emitting species by light. Fluorescence and phosphorescence are common forms of photoluminescence. Fluorescence occurs when radiation is emitted from first excited single state (S1) that is achieved by absorbing photons, while phosphorescence occurs when light is emitted from triplet state (T1) after inter-system crossing takes place [11].

Scattering or Raman spectroscopy is based on the analysis of inelastically scattered light [12]. It is a phenomenon in which light interacts with the vibrational modes of a molecule leading to a shift in the energy of scattered photons and the shift provides information about the vibrational energy levels of molecules allowing for identification of chemical bonds and molecular structure.

2.1.1 Electromagnetic radiation

Electromagnetic radiation, also commonly known as light, represents a type of energy that exhibits characteristics of both waves and particles. Certain features of electromagnetic radiation, like its refraction during the transition between different mediums are most effectively understood by considering light as a wave. Conversely aspects such as absorption and emission are better explained by regarding light as a particle [13]. Nevertheless the dual models of wave and particle behavior provide a useful description of electromagnetic radiation.

2.1.1.1 Wave nature of light

When studying effects like reflection, refraction, interference and diffraction electromagnetic radiation is commonly represented as a wave composed of electric and magnetic fields oscillating perpendicular to each other. The vibrations in the electric and magnetic fields occur at right angles to each other and to the waves travel direction [10].

An illustration below depicts an instance of plane-polarized electromagnetic radiation, characterized by a solitary oscillating electric field and a solitary oscillating magnetic field.

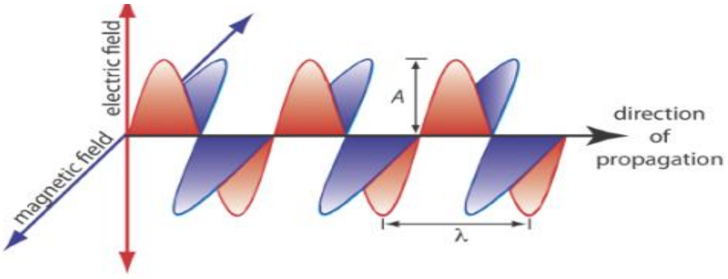

Figure 2.1 Electromagnetic wave

2.1.1.2 Particle nature of light

In many interactions between radiation and matter it is often beneficial to view light as composed of photons or discrete packets of energy. The energy of the photon can be connected to its wavelength, frequency and wave number through the equation[13]

$$E = hv = \frac{hc}{\lambda} = hc\bar{v}$$

Where h represents planks constant (6.626*10^{-34}J s) the wave number ($\bar{v}$) and frequency (v) are directly related to the energy (E) of a photon, while the wavelength (λ) is inversely proportional to the energy. The radiant power of radiation beam is directly proportional to number of photons emitted per second.

2.1.1.3 Electromagnetic spectrum

Electromagnetic spectrum is a range of all possible frequencies of electromagnetic radiation extending from long wavelength radio waves to micro waves and infrared light to visible light (very small part of electromagnetic spectrum to UV light to higher energy X-rays, gamma rays and cosmic rays)[14].

Each region of the spectrum corresponds to a specific range of wavelengths or frequencies with unique properties and interactions with matter.

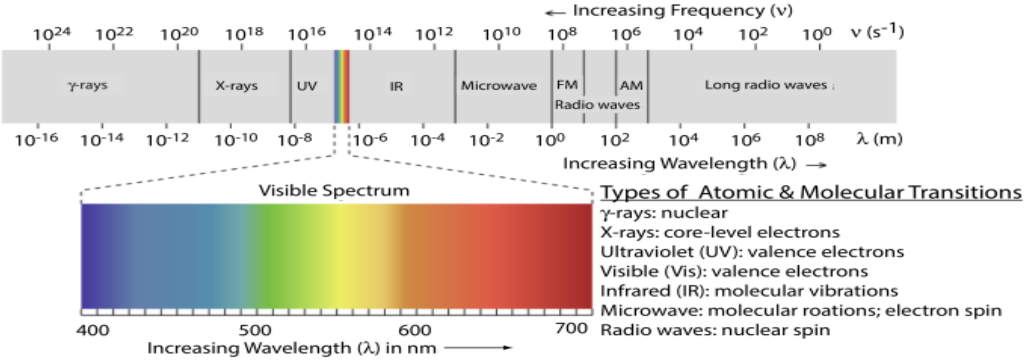

Figure 2.2 Electromagnetic spectrum

2.1.1.4 LASER

The term laser originates from the abbrivation for “light amplification by stimulated emission of radiation’’. It uses a process that enhances or amplifies light signals[15]. Lasers produce tightly focused, intense and coherent beams of radiation due to their ability to amplify light[10]. The working principle of laser relies on absorption, stimulated emission, population inversion and amplification. According to quantum theory atoms can only have energies in specific discrete states. Typically atoms are in their lowest energy state, known as ground states. When intense light from source interacts with a substance it can excite atoms from ground state to higher energy levels through absorption. After a short period at the higher level the atom returns to its ground state emitting photon in a process known as spontaneous emission. If an atom in an excited state is hit by an external photon with the exact energy needed for spontaneous emission the external photon combines with the one emitted by the excited atom both photons are then released from same excited state and this phenomenon is known as stimulated emission and it plays crucial rule in laser operation.

When the material is not externally stimulated, there's a higher concentration of atoms in the lower energy level or ground state compared to the upper level. However, when the upper level surpasses the lower level in population, known as population inversion, it deviates from the usual occupancy pattern, which is crucial for laser operation. For stimulated emission to occur, the upper energy level or metastable state must have a prolonged lifetime, allowing atoms to remain in that state longer than in the lower level. Therefore, to sustain laser action, the pumping mechanism (external excitation) must maintain a greater population of atoms in the upper energy level relative to the lower level[16].

2.2 Molecules and their Electronic structure

The electronic configuration of molecules refers to how electrons are arranged within the molecule, including their distribution among different atomic orbitals and their interactions. This configuration plays a crucial role in determining the chemical characteristics and behavior of the molecule. In molecules, electrons are distributed among different molecular orbitals based on the valence electrons contributed by each atom. This electronic structure is commonly explained using molecular orbital theory, which involves the combination of atomic orbitals to create molecular orbitals that house electrons.

The goal of molecular orbital theory is to describe the structure of molecules by applying principles akin to those used for atoms, such as orbitals, electron configurations, and diagrams. When atoms bond by sharing electrons to form single, double or triple bonds, their individual atomic orbitals merge to produce molecular orbitals. For effective combination, these molecular orbitals need to have similar energy levels, overlap efficiently, and be in close proximity. In a specific example, two atoms each contribute one electron from their outer shell, leading to the sharing of their valence electrons through the overlap of their 1s orbitals.

When atomic orbitals come together to create chemical bonds, they give rise to an equivalent number of molecular orbitals. The overlapping of two s orbitals results in the formation of two new orbitals: one with lower energy than the original s orbitals (bonding MO) and one with higher energy than the original s orbitals (antibonding MO) [16].

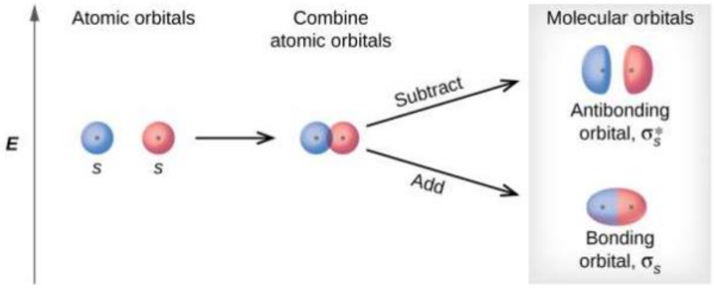

Figure 2.3 Diagram representing molecular orbital theory

When two orbitals from different atoms interact positively, they generate a fresh molecular orbital that fosters bonding. This lower-energy bonding molecular orbital contributes to the molecule's stability. Conversely, when orbitals from distinct atoms interact negatively, they produce a new molecular orbital that encourages anti-bonding. This anti-bonding orbital undermines the stability of the molecule.

When two hydrogen atoms form a hydrogen molecule (H_2), their individual 1s orbitals combine to create two molecular orbitals: a bonding orbital (σ1s) and an anti-bonding orbital (σ*1s). In H_2, the two electrons from each hydrogen atom occupy the bonding orbital, leaving the anti-bonding orbital unoccupied in the ground state [17]

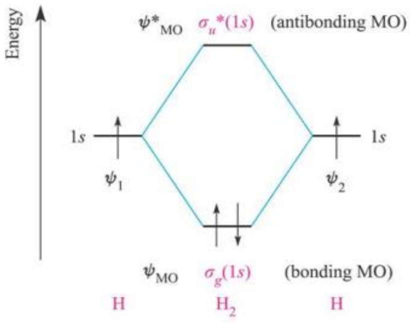

Figure 2.4 Molecular orbital diagram of H_2

The electron arrangement of carbon is, $1s^2 2s^2 2p^2$ totaling twelve electrons in a carbon atom. Consequently, the electronic configuration of the C_2 molecule in its ground state is $\sigma(1s)^2$ $\sigma^*(1s)^2$ $\sigma(2s)^2$ $\sigma^*(2s)^2$ $\pi(2px)^2$ $\pi(2py)^2$.

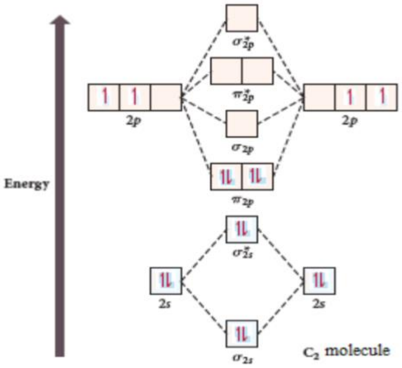

Figure 2.5 Molecular orbital diagram of $\mathbf{C_2}$

2.3 Molecular spectra

Molecular spectroscopy involves the study of how molecules interact with electromagnetic radiation, leading to transitions between their rotational, vibrational, and electronic energy levels. Molecular spectra are more complex than atomic spectra and can result in various types of spectra depending on the changes that occur when a molecule absorbs or emits a photon:

Changes in rotational quantum number produce rotational spectra in the far infrared and microwave regions, changes in both vibrational and rotational quantum numbers create vibrational-rotational spectra in the near infrared region, changes in electronic energy levels, along with vibrational and rotational energy levels, give rise to electronic spectra in the visible and ultraviolet regions, changes in nuclear spin quantum number in a magnetic field lead to nuclear magnetic resonance (NMR) spectra, changes in resultant spin direction in a magnetic field result in electron spin resonance (ESR) spectra in the microwave region. Nuclear transitions generate Mossbauer spectra in the gamma rays region.

Overall, a molecule possesses translational, rotational, vibrational, electronic, spin, and nuclear energies, with the total energy being the sum of all these components:

$E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{el} + E_{spin} + E_{nuclear}$

All the energies mentioned are quantized except for translational energy. The significant difference in mass between the electron and nucleus allows for their motion to be considered separately, leading to the Born-Oppenheimer approximation. According to this approximation, the total energy can be expressed as the sum of rotational, vibrational, and electronic energies ($E_{total} = E_{rot} + E_{vib} + E_{el}$). Translational energy is omitted from this expression as it is considered to be very small and negligible [18].

2.3.1 Transition probability

In an atom or molecule, when exposed to an electromagnetic wave such as visible light, it can cause the electric or magnetic properties to oscillate. If the frequency of this oscillation matches the energy difference between two specific states (Ψ_1 and Ψ_2), the interaction is considered resonant. This resonance occurs when the induced electric or magnetic moment aligns with the transition moment. In quantum mechanics, the transition probability of a molecule moving from one state (Ψ_1) to another (Ψ_2) is represented by $|M_{21}|^2$, where M_{21} is known as the transition dipole moment. Mathematically, this transition moment can be expressed as

$$M_{21} = \int \psi_2 \mu \psi_1 d\tau$$

The ψ_1 and ψ_2 are two different eigenstates in one molecule, M_{21} is the electric dipole moment operator. If we have a system with n molecules and each has charge q_n, and the dipole moment operator is can be written as:

$$\mu = \sum n q_n x_n$$

the x_n is the position vector operator [18][19].

2.3.2 Oscillator strength

When electromagnetic radiation interacts with an atom or molecule, it can cause the absorption or emission of radiation, leading to a transition between different energy levels. The oscillator strength quantifies the likelihood of absorption or emission of electromagnetic radiation during such transitions. A higher oscillator strength indicates a more prominent transition. It is defined as the ratio of the transition rate in quantum mechanics to the absorption or emission rate in classical mechanics for a single electron oscillator with the same frequency as the transition. The oscillator strength, denoted as f, is directly related to the square of the transition dipole moment $f \propto (\mu)^2$, where (μ) represents the transition dipole moment, $\mu = \sum_i e_i . r_i$ with e being the electronic charge and r indicating the extent of charge displacement. The concept of oscillator strength is utilized to compare transition strengths across different quantum mechanical systems, enabling calculations of dipole moment matrix elements, transition probabilities, assessment of theoretical models, and determination of impurity concentrations [18].

2.3.3 Vibrational selection rules

Vibrational selection rules are a set of guidelines that dictate the permissible transitions between different vibrational energy levels within a molecule. These rules are based on principles of energy conservation and quantum mechanics. The primary selection rule in vibrational spectroscopy states that a molecule must exhibit a variation in its dipole moment during a vibration in order for that vibration to be considered infrared active. Homo-nuclear molecules, lacking a permanent dipole moment and experiencing no change in dipole moment during vibration, are thus deemed infrared inactive. Conversely, heteronuclear diatomic molecules such as HCl are classified as IR active due to their dipole moment changes. Interestingly, certain vibrations in molecules like carbon dioxide, which lack a dipole moment, can still be considered infrared active. The specific vibrational selection rules include the requirement that transitions involve a change of ±1 in the vibrational quantum number (v), allowing molecules to move between adjacent vibrational levels. In the case of linear molecules, additional conditions apply, such as specific requirements for symmetric and antisymmetric vibrational modes. For diatomic molecules, transitions are only permitted if there is a change of ±1 in the vibrational quantum number. [20]

2.3.4 Frank-Condon principle

Frank-Condon principle explains that during an electronic transition, the speed of the transition is significantly faster than the movement of the nucleus, allowing us to treat the nucleus as stationary. The likelihood of a vibrational transition occurring between two states is higher if these states have a significant overlap. This principle clarifies why some peaks in a spectrum are intense while others are weaker or not visible in absorption spectroscopy.

$$M = \int \psi_e' \ (r, R_e) \ . \ \mu_e . \psi_e''(\mathrm{r}, R_e)\mathrm{dr} \int \psi_v' \ (R) . \psi_v''(R) dR$$

The second integral in the equation provided represents the vibrational overlap between two distinct eigenstates. The square of this integral is known as the Franck-Condon factor, which influences the contribution of vibrational transitions to the overall transition probability. It indicates that for a significant vibrational contribution, there must be a substantial overlap between the vibrational ground state and the excited state [21].

$$\text{Franck} - \text{Condon factor} = |\psi_v'(R)\psi_v''(R)dR|^2$$

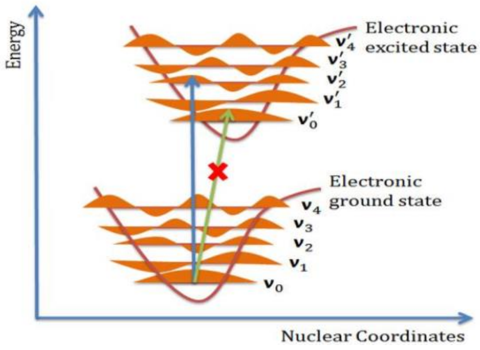

Figure 2.6 Franck - Condon energy diagram

2.4 Spectroscopy for quantitative determination

Lambert's law, formulated by Johann Heinrich Lambert, asserts that within a uniform medium, the decrease in light intensity as it traverses a substance is directly proportional to the initial intensity of the incoming light. This relationship can be mathematically represented as $-dI/dx \propto I$, where I denotes the intensity of the incident monochromatic light and -dI/dx indicates the reduction in intensity across a small distance dx within the medium. Specifically, $-dI/dx = kI$ (where k is the constant of proportionality, known as the absorption coefficient) which relies on the properties of the absorbing medium. To determine the integrated absorption coefficient, it is necessary to integrate the equation, leading to the following result.

$$\log I/I_0 = -K_1 x \quad (K_1 = k/2.303)$$

This equation is integrated form of Lambert's law where k_1 is integrated absorption coefficient or extinction coefficient of the substance or absorptivity of the substance.

Beer's law, established by August Beer, states that when a solution is exposed to monochromatic light, the decrease in light intensity as it passes through the solution is directly related to both the initial intensity of the incident light and the concentration of the solution. Mathematically the law says:

$-\frac{dI}{dx} \propto Ic$ where c is the concentration of solution, –dI/dx is decrease in the intensity of light on passing through solution of thickness dx.

$-\frac{dI}{dx} = \varepsilon Ic$ (ε = constant of proportionality = molar absorption coefficient)

The molar absorption coefficient is influenced by the characteristics of the absorbing substance and the wavelength of the light employed. To calculate the integrated absorption coefficient, it is necessary to integrate the aforementioned equation.

log I/I_0= –ε1 c x (where, ε1 = ε /2.303)

This formula represents the integrated version of Beer's law, where ε1 stands for the integrated absorption coefficient or molar extinction coefficient of the absorbing solution, also known as molar absorptivity. Lambert-Beer's law, sometimes referred to as Beer-Lambert-Bouguer law or simply Beer's law, states that the absorbance of light is directly proportional to the thickness and concentration of the absorbing medium (solids) for a specific material. Mathematically, this relationship can be expressed as:

$$\text{Absorbance} \propto c\,x$$

$$\text{Absorbance (A)} = \varepsilon_1 c\,x$$

$$A = \log I_0/I = \varepsilon_1 c\,x$$

2.5 Vibrational / IR spectroscopy

One of the spectroscopic techniques based on the interaction between light rays and the chemical molecule under study is infrared (IR) spectroscopy. It involves identifying chemical compounds by analyzing how they absorb infrared radiation and interact with their chemical bonds. The primary technique utilized is absorption spectroscopy, which takes advantage of the unique vibrational frequencies of molecules that correspond to specific energy levels. This method

provides valuable insights into the functional groups found within molecules. Radiation in a certain region of the electromagnetic spectrum (at a specific frequency) is employed in infrared spectroscopy. The infrared portion of the electromagnetic spectrum lies between 12800 and 10 cm^{-1}; the near infrared region is between 12800 and 4000 cm^{-1}; the mid-IR is between 4000-200 cm^{-1}; and the far-IR is between 200 and 10 cm^{-1}[22].

Several groupings have distinctive peaks in the IR spectrum. As such, it aids in the examination of the characteristic groups that are present in the material whose spectrum have examined, hence aiding in the examination of the substance's structure. The fact that the characteristic group peaks change as the molecular structure does is equally significant to us. For instance, the C=O group produces a peak in the infrared spectrum between 1900 and 1600 cm^{-1}, but the molecule's structure affects the peak's side in this range[23].

2.5.1 Factors affecting IR frequency

Vibrational frequencies depend on various factors including the nature of the vibration, bond strength, atom masses, and electronegativity. Different types of vibrations, like stretching versus bending, exhibit differences in frequency, with stretching requiring more energy. Bonds with higher bond orders, such as double or triple bonds, vibrate at higher frequencies compared to single bonds due to their increased strength specifically, according to hooks law the strength of a bond, as measured by its force constant, directly influences the vibrational frequency of that bond.

$$\bar{\upsilon}= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu= \frac{m_{1*}\, m_2}{m_1+m_2}$$

Bonds with greater strength exhibit higher force constants and consequently have higher vibrational frequencies.

$$\mathbf{C{\equiv}C > C{=}C > C{-}C}$$

Moreover, lighter atoms vibrate faster than heavier ones, leading to higher frequencies for bonds involving lighter atoms as we can see from the above equation.

$$\mathbf{H{-}C > C{-}C, \qquad H{-}O > C{-}O}$$

Electronegativity influences the intensity of the peak rather than the frequency itself, affecting the absorption intensity by altering bond polarity. Bonds with greater polarity, such as C-O bonds, exhibit stronger absorption intensity compared to less polar bonds like C-C bonds.

2.5.2 The four regions of infrared spectrum

The IR spectra can be categorized into four main regions spanning approximately 4000-2800, 2800-1900, 1900-1200, and 1500-400 cm^{-1}. The first segment, above 2800 cm^{-1}, predominantly reflects X-H bonds, particularly bonds involving hydrogen. Here, triple bonds occur slightly lower in frequency compared to double bonds, followed by single bonds. This last segment, also known as the fingerprint region, can be intricate with overlapping peaks.

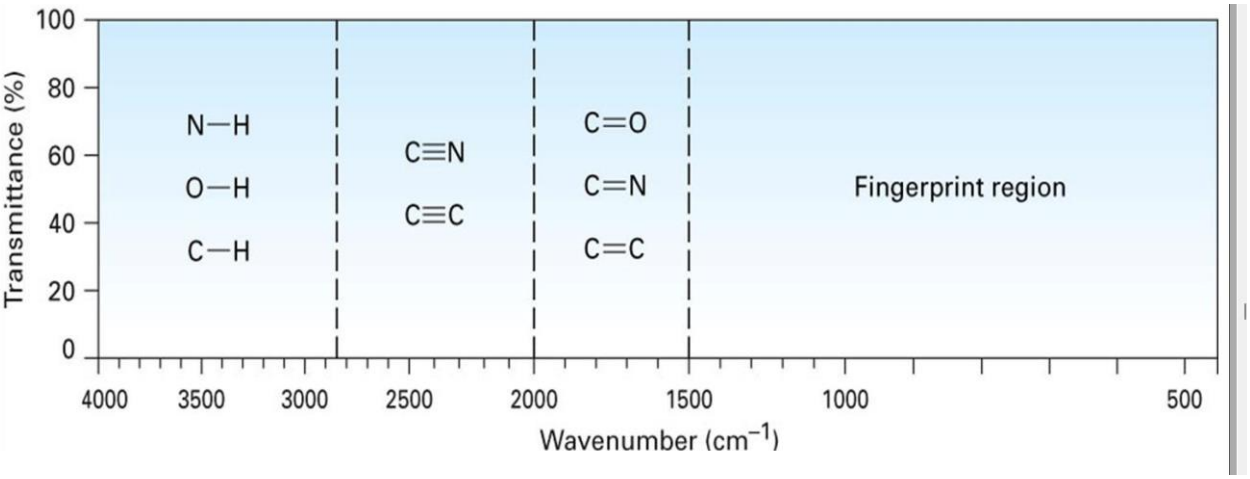

Figure 2.7 The four regions of infrared spectrum

In the X-H region, encompassing C-H, N-H, and O-H bonds, frequencies correspond to the energies of the respective bonds. Notably, the O-H bond exhibits the highest frequency due to its superior strength. An important characteristic of this region is its sensitivity to hydrogen bonding, particularly evident in alcohols and carboxylic acids, which broaden the bands.

Extensive hydrogen bonding can significantly widen the O-H band from roughly 100 cm to as much as 600 cm. The triple bond region houses alkynes, around 2200-2100 cm^{-1}, and nitriles, slightly higher in frequency. Nitriles exhibit strong bands owing to the strong bond dipole caused by the electronegativity of nitrogen, while alkynes display weak to moderate bands.

The double bond region is intricate, accommodating various double bonds like C=O, C=C, N=O, and C=N. The carbonyl functional group (C=O) is particularly informative, being common across many functional groups, with distinct vibrational frequencies.

Lastly, the C-X region is dedicated to single bond vibrations. However, its complexity stems from the multitude of single bonds within a molecule, making interpretation challenging. Nevertheless, akin to fingerprints being unique, the fingerprint region of the IR spectrum is distinctive for each molecule [24].

2.5.3 Types of vibrations in molecules

Molecular shape alterations, such as bond stretching, bond bending, and internal rotation around single bonds, leads to changes in a molecule's dipole moment as it vibrates or rotates. Infrared absorption specifically happens when the infrared radiation interacts with a molecule experiencing a change in dipole moment during its vibrational or rotational movements. This absorption occurs only when the incoming infrared photon possesses enough energy to enable the transition to the subsequent allowed vibrational state to occur ($\Delta E = h\nu$).

The way infrared radiation interacts with substances can be explained by alterations in molecular

dipoles linked to vibrations. Vibrations may entail modifications in bond lengths (stretching) or bond angles (bending). Certain bonds can stretch symmetrically within a plane or asymmetrically out of a plane. Bending vibrations can occur either within a plane (like scissoring or rocking) or out of a plane (like wagging or twisting).

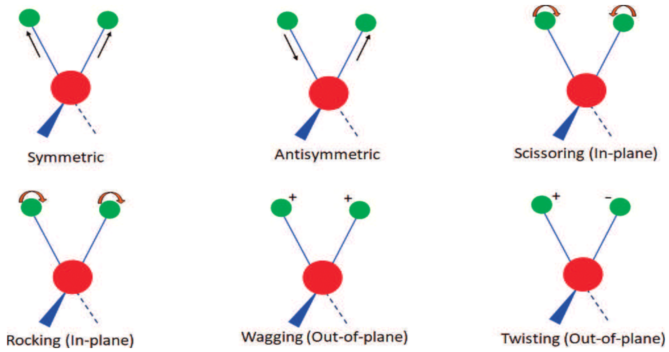

Figure 2.8 Types of molecular vibrations

2.6 Fourier transform infrared spectroscopy (FT-IR)

2.6.1 Principles

FT-IR short for Fourier transform infrared spectroscopy is favored technique in the field of infrared spectroscopy. During this process infrared radiation is directed through a sample with some being absorbed and some transmitted. IR absorption induces alteration in the vibrational energy levels of molecules where each functional group with in a molecule absorbs IR radiation at distinct frequencies. The strength of absorption bands correlates directly with the concentration of the absorbing species in the sample. This characteristic behavior enables the identification of specific chemical bonds [13].

An FT-IR spectrometer acquires spectrum by initially capturing interfrogram of the sample signal through an interferometer. Subsequently, it employs Fourier transform technique to convert the raw interferogram data into a spectrum thereby achieving resolution (see Fig.2.9 below). The resulting spectrum reflects the molecular absorption and transmission characteristics of the sample creating a unique molecular fingerprint. Just like fingerprints no two distinct molecular structures yield the same IR spectrum.

2.6.2 Instrumentation

The FTIR spectrometer acquires an infrared spectrum by initially capturing an interferogram of a sample signal with an interferometer, followed by applying a Fourier Transform to the interferogram to generate the spectrum. Ft-ir uses interferometers instead of dispersive elements. An interferometer utilizes the method of combining multiple waves to identify variations between them. The FTIR spectrometer employs a Michelson interferometer for this purpose.

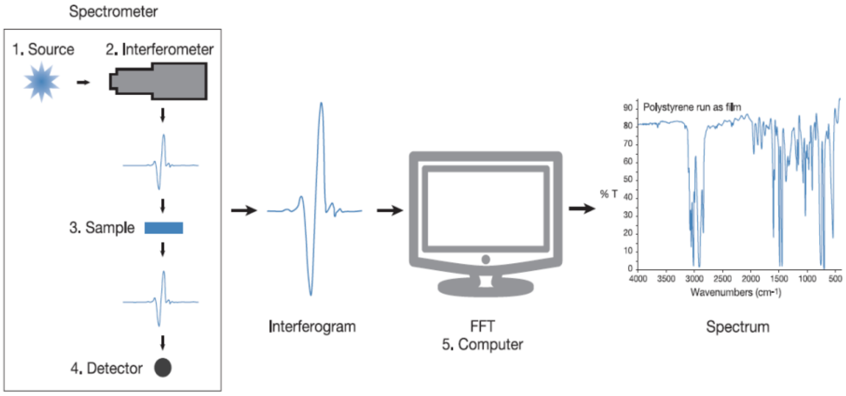

Figure 2.9 FTIR simple block diagram for instrumentation of - spectroscopy (thermo scientific inc.2013)

2.6.3 Components of FT-IR spectrometer

i. Light source

The infrared (IR) source is typically a solid material that is heated to 1200K using an electric current, covering the mid-IR range (2-25 µm). Silicon carbide is often used for this purpose as it mimics the output of a black body. To produce near-IR radiation (1-2.5 µm), a higher temperature source like a tungsten-halogen lamp is required. For far-IR wavelengths beyond 50 µm, a mercury discharge lamp is preferred due to its higher output compared to a thermal source. In compact IR detection devices, micro IR sources have been developed, functioning similarly to thermal sources but with a smaller heating element that fits within the detector's size. This compact design allows for quick heating and cooling, enabling electronic modulation of these IR sources instead of relying on an external wave chopper. A recently developed IR source is the quantum cascade laser. It involves a distributed feedback laser that produces a specific wavelength with a tuning range of less than 0.1% of the central wavelength. Other variations of this laser have wider tuning capabilities or function as broad-spectrum sources. While the quantum cascade laser is not ideal for Fourier-transform infrared spectroscopy (FTIR), it is highly effective for quickly acquiring IR spectra.[25]

ii. Sample cells

Transmission mode: In transmission mode measurements, glass or quartz cuvettes are unsuitable for creating sample cells in IR spectroscopy due to their strong absorption across most of the IR spectrum. Instead, alkali metal halides like KBr and NaCl are frequently chosen as they offer transparency in the IR region[25].

Attenuated total reflectance (ATR) mode: The ATR technique, employed in FTIR spectroscopy for sample analysis, utilizes a sample cell containing a high refractive index crystal, like diamond, germanium, or zinc selenide. When infrared light enters the crystal at an angle surpassing the critical angle, it experiences total internal reflection within the crystal. However, the interface between the crystal and the sample generates an evanescent wave, causing some infrared radiation to penetrate into the sample and interact with its molecules. Thus, the ATR sample cell facilitates the interaction between infrared light and the sample through total internal reflection, enabling the measurement of absorption spectra that reveal the sample's chemical composition and structure[26].

iii. Interferometer

The interferometer comprises a beam splitter, a stationary mirror, and a movable mirror. In mid-IR spectroscopy, potassium bromide or calcium fluoride is commonly used for the beam splitter due to the strong absorbance of glass and quartz in this range. Reflective materials such as silver, gold, and aluminum are suitable for the mirrors in the IR beam path. Half of the beam is directed to the fixed mirror for reflection, while the other half passes through to the moving mirror. The discrepancy in path lengths between the two arms of the Michelson interferometer is referred to as the optical path difference or retardation. By adjusting the position of the moving mirror, the retardation changes, altering the interference pattern of the IR beam. The resulting signal detected in relation to retardation is known as an interferogram. At zero retardation, where constructive interference occurs for all wavelengths, the signal reaches its peak. This zero retardation point corresponds to total constructive feedback [25].

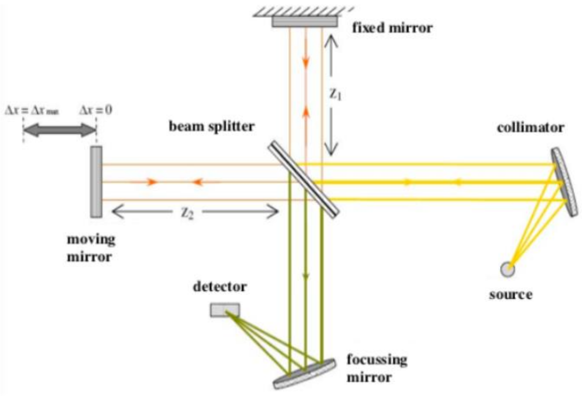

Figure 2.10 Simple interferometer

iv. Detector

The pyroelectric detector is commonly preferred and extensively utilized in numerous FTIR applications due to its excellent detection threshold, rapid response time, and cost-effectiveness. In cases where enhanced sensitivity is needed, the mercury cadmium telluride (MCT) detector can be utilized, but it necessitates a cooling system to sustain its heightened sensitivity. Thermoelectric cooling may be suitable for compact setups, while liquid nitrogen cooling is recommended for applications requiring even greater precision [25]

2.7 Gasoline and it's quality

Gasoline is made from crude oil by refining it. It is a liquid fuel that is mostly used to power automobiles with internal combustion engines. It's among the most often utilized energy sources. Gasoline accounted for 54% of transportation sources and 46% of all petroleum products utilized in 2018. In fact, motor gasoline is the most common energy source for transportation and will stay so at least until 2040 [27]. Although the chemical makeup of gasoline is complicated, organic molecules including aromatic hydrocarbons, cycloalkanes, and alkanes make up the majority of its composition. The precise constituent of gasoline can change based on a number of variables, including the refinement process and the crude oil source but commonly between 4 to 12 carbon atoms per molecule.

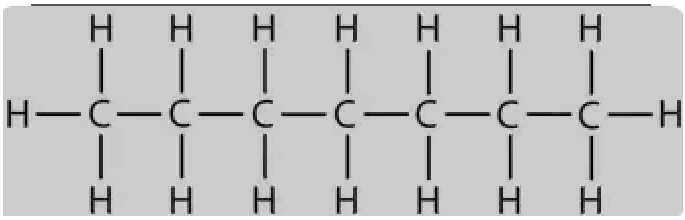

Figure 2.11 Representative chemical structure of gasoline

Unlike pure compounds, like water, which boils at a single temperature, gasoline boils and distills throughout a range of temperatures. To obtain a distillation curve, gasoline must boil between 30°c and 202°c [28]. The set of rising temperatures at which gasoline evaporates for a predetermined sequence of rising volume percentages 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 98.5–99% as the ultimate endpoint is known as the gasoline distillation curve[29].

The copper corrosion test, volatility (starting and vapor lock), vapor pressure (environmental control), motor octane number (MON), and research octane number (RON) are crucial In addition to improving gasoline octane ratings, additives like ethanol, methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE), and other oxygenates also boost performance, guard against oxidation and rust formation, and lower carbon monoxide emissions [30].

On the other hand, overuse of these oxygenates, particularly ethanol, can lead to plastic part deformation, rust in engine metal parts, and fuel system corrosion. The international organization of standards (ISO)15376(2018) states that 10% by volume is normally the maximum amount of ethanol that can be added to gasoline[4]. On the other hand, adulterants that release hydrocarbons, carbon monoxide, and particulate matter into the air, such as waste industrial solvents, alcohols, mineral spirits, and kerosene, pose a health concern and pollute the environment.

2.7.1 Ethanol blending

Ethanol (C_2H_5OH) also known as ethyl alcohol is a clear colorless liquid[2] that is commonly used as solvent, fuel, and in the production of alcoholic beverages. It is a type of alcohol that is produced through the fermentation of sugars by yeast, from ethane by hydration process and as a byproduct of beer production. Ethanol has wide range of industrial applications including as a biofuel additive, in pharmaceuticals and as a solvent in various chemical processes. Ethanol has gained significant attention as a renewable and environmentally friendly alternative to fossil fuels, particularly in the context of biofuels and sustainable energy production its production from renewable feed stokes contributes to reducing greenhouse gas emissions and dependence on non-renewable resources but excessive use of ethanol in fuel system affects engines performance and may damage the engine[4].

2.7.2 Gasoline adulteration with kerosene

When illegal compounds are added to gasoline, it's known as gasoline adulteration. This can result in lower fuel quality and perhaps engine damage. It's a chain of problems that can be harmful to cars and the environment alike. The term "adulterants" refers to the foreign materials that, when added, change and lower the fuel's quality. Kerosene, alcohol, and other inferior fuels are common adulterants in gasoline that can impair a vehicle's economy and performance.

In the Ethiopian context, Kerosene is believed to be a common adulterant to the gasoline. In terms of boiling points, kerosene is a refined product that is in between gasoline and diesel fuel. It is frequently used as fuel for lighting, heaters, and jet engines. As dual-purpose kerosene, it can be made from straight-run kerosene, which is produced by distilling crude oil under atmospheric pressure, or from cracked kerosene, which is produced by catalytic, thermal, or steam cracking of heavier petroleum streams [31]. The World Health Organization advises "governments to immediately stop promoting its household use" because kerosene is a fuel that pollutes the environment. High concentrations of dangerous particulate matter found in kerosene smoke increase the risk of diseases like cancer and asthma [32].

2.7.3 Review of related literatures on ethanol and kerosene detection and quantification

A study on determination of ethanol in gasoline showed that an infrared spectrum with the O-H and alkane C-H absorptions can be used to readily quantify the proportion of ethanol in hexanes in a laboratory experiment. Hexanes and standard ethanol solutions were made, and the infrared spectra of these solutions are gathered. To create a standard curve that shows the percentage of ethanol, the areas under the O-H and C-H absorptions are utilized. The model ethanol in hexanes calibration system's results for the analysis of ethanol in gasoline compare favorably to advertised values and to values found by water extraction, indicating that the results were reasonably consistent with the advertised values [33].

Research has been conducted on the quick identification of adulterant kerosene in diesel and gasoline [34]. By analyzing gasoline and diesel samples, estimating the intensity of adulteration comparing the detection limits of Fourier Transform Infrared (FTIR) and Fluorescent Indicator Absorption (FIA), and assessing the detection aptitude of the techniques, an attempt has been made in this study to develop a combination analytical tool for the quick detection of kerosene adulteration. In seven carefully chosen areas in Eldoret, Kenya, suspected tampered gasoline and fuel were meticulously gathered. References were followed all the way from the shipper's dispensing station to the Eldoret pipeline depot. In order to compare the adulteration contour, arrays of six blend combinations of kerosene with either gasoline or diesel were made in bespoke proportions. FTIR spectroscopy, fractional distillation, FIA, and density tests were conducted in order to be characterized. With the lowest densities of 0.7373 and 0.8199 Kg/l for gasoline and diesel, respectively, compared to 0.7374 and 0.8345 Kg/l for the standards, the results indicated a significant change in density at different levels, potentially indicating adulteration. As can be seen from the sample distillation end points of 234.0^0C for gasoline, which represents an increase of 20.0^0C, and 382.0^0C for diesel, which represents a fall of 4.0^0C, fractional distillation gave an appropriate signal for adulteration. The initial qualitative data from FTIR was represented by peaks in the 2950–3200cm^{-1} range, whose intensities changed with adulteration. FIA was able to classify samples as olefins, saturates, and aromatics, yielding thorough qualitative data. Thus, the study fronts Fractional distillation, density testing, FTIR, and FIA methods for rapid determination of adulterant kerosene.

Research has been conducted on the identification and measurement of diesel adulteration in Moroccan gasoline through the use of chemometric instruments and Fourier transform infrared spectroscopy [35]. In order to identify and measure gasoline adulteration with diesel, transform-infrared spectroscopy (FTIR) was used in conjunction with chemometric methods, principal component analysis (PCA) and partial least squares regression (PLSR) in particular. The procedure consists of preparing 100 mixes in total, after which each sample's FTIR fingerprints were recorded. PCA was utilized to confirm that mixtures and pure products may be identified from one another and to ensure that there are no anomalies. When PC1 and PC2 alone were used, almost 98% of the overall variability could be accounted.

Based on infrared spectra, the PLSR model has demonstrated its ability to predict gasoline adulteration in the concentration range of 0 to 98% (w/w). It has an acceptable calibration and prediction error (root mean squared error of calibration = 0.63 and root mean square of external

validation and/or prediction = 0.69) and a high significant coefficient of determination (R2 = 99.25%).

Additional research conducted in India examined an often occurring instance of adulteration of Euro IV diesel fuel with low-quality subsidized kerosene. To produce a preliminary assessment of the adulteration, diesel samples contaminated with kerosene were subjected to analyses for density, viscosity, atmospheric distillation, aniline point, total sulfur, and cetane index. Chromatographic [gas chromatography (GC) and high-performance liquid chromatography (HPLC)] and high-resolution mass spectrometric (HRMS) analysis were performed to detect the fingerprint regions in samples because these methods were inadequate in identifying the diesel adulteration even with up to 40% kerosene. Diesel fuel can be contaminated with kerosene, which can be detected using primary evidence provided by total sulfur, aniline point, and

Atmospheric distillation (recoveryat250°C). The ratio of n-C10 to n-C12 increased significantly, and decreased from n-C15 to n-C20 through GC. The contaminated samples exhibited a noteworthy rise in alkylbenzene content, as indicated by the HRMS data. In adulterated diesel samples, a strong connection was found between the results of the HPLC and HRMS for saturates, mono, di, and tri+-aromatics. In every sample that was acquired via HPLC and HRMS analysis, the Student's t test revealed a strong connection between the values of the various hydrocarbon groups [36].

To give a clearer interpretation and increase the accuracy of ethanol level detection in gasoline. They invented near-infrared spectroscopy, a quick analysis technique based on effective characteristic spectra. Based on the molecular structure of ethanol, five effective distinctive spectral bands were used, and four modeling approaches were then developed. Variable importance projection (VIP) spectra, NIR complete spectra, and the four modeling techniques were employed in the analysis and modeling process. To achieve optimal model performance, the model was constructed using the effective characteristic spectra, excluding the interference spectra of aromatic hydrocarbons. External validation as well as internal cross validation were used to further assess the model. The evaluation parameters of the model were as follows: the correlation coefficient of internal cross-validation (RCV 2) was 0.9995, the root mean square error of prediction (RMSEP) was 0.5572, the correlation coefficient of external prediction validation (RP 2) was 0.9995, and the root mean square error of cross-validation (RMSECV) was

0.6193. In comparison to the full spectrum and VIP spectra models, the effective characteristic spectra model had bigger RCV 2 and RP 2 values and reduced RMSEP and RMSECV values. As a result, the most accurate model that could quickly analyze the amount of ethanol in gasoline was the effective characteristic spectra model [37].

In a different investigation, four potential adulterants kerosene, diesel, naphtha, and premix in gasoline were identified qualitatively and quantitatively using FTIR analysis in conjunction with chemometric (multivariate) approaches. To calibrate the model, synthetic admixtures were created by combining gasoline with different amounts of adulterants. The chemometric techniques used were partial least square (PLS) regression and soft independent modeling class analogy (SIMCA) classification. The kind of adulterant present was predicted by the SIMCA classification model at an error rate of 6.25% for kerosene and naphtha and 12.5% for premix. On the other hand, no prediction error for diesel-contaminated sample classification was noted. For every adulterant, the concentrations could be predicted using the PLS regression model with prediction errors less than 5% [38].

Study in Kenya aimed to use FTIR spectroscopy to evaluate the adulteration of automobile gasoline in Nairobi, Kenya. The FTIR data indicated that adulteration occurred at central locations, such as storage tanks prior to distribution to retailers or at retailer points, with adulteration ranging from 7.825 ± 1.275 % to 17.464 ± 0.574 %. The sulfur readings for a few samples indicated that there was a chance of adulteration with high sulfur solvents such as fuel and kerosene. The amount of lead in a few unleaded gasoline samples was examined. The sulfur readings for a few samples indicated the possibility of adulteration with high sulfur solvents such as fuel and kerosene. The amount of lead in a few unleaded gasoline samples was examined. The results showed that although there was lead in the gasoline, it was not beyond the Kenya Bureau of Standards' threshold, indicating that the environmental impact of lead is still not fully addressed. This work led to the development of a new technique that required less time for analysis, was quick, and had a high sample through put [39].

CHAPTER THREE

3. Materials and methods

3.1 Instrument and apparatus

- FT-IR spectrometer (Perkinelmer FT-IR spectrometer)
- Volumetric flasks
- Pipettes
- Beakers
- Computer with software

3.2 Reagent and chemicals

Chemicals:- Ethanol (97%)
Kerosene (pure)

Ethanol (97%) was obtained from parachem chemicals and equipment suppliers; kerosene was obtained from selam car oil suppliers.

3.3 Sample collection

Gasoline samples were collected from fuel stations corresponding to five different fuel providers such as; Taf oil, Global oil, Total oil, Noc oil, and Tebarek oil, located in Hawassa city, Ethiopia. The samples were drawn directly from the pump into the bottle and well crooked to prevent loss of light hydrocarbons, labeled immediately and stored in safe and dry place in Hawassa university physics laboratory.

3.4 Cleaning

Volumetric flasks, pipets, beakers and all glass bottles went through a cleaning process using water and detergent, followed by rinsing with both regular water and ultimately with distilled water.

3.5 Sample preparation

Ethanol was extracted from gasoline by dehydration (ethanol recovery) method water was added to gasoline and the water and ethanol formed layer to the actual gasoline, the gasoline remained on the top and the ethanol and water settled to bottom. After extracting ethanol from the gasoline different solutions of ethanol in gasoline were prepared by first preparing standard,1%, 2.5%, 5%, 10%, 25%, and 50% of ethanol in gasoline and labeled as $E_{1,}$ $E_{2.5}$, E_5 E_{10}, E_{25}, E_{50}. Similarely, different concentrations of kerosene in gasoline (1%, 3%, 5%, 10%, 30%, 50% and 85%) were prepared by accurately measuring their volume and labeled as K_1, K_3, K_5, K_{10}, K_{30}, K_{50} and K_{85} and moved to CNCS central laboratory for FTIR measurement.

3.6 Calibration standards for ethanol

The FT-IR spectra of seven ethanol gasoline standards were obtained (see Fig 4.3). The spectral regions around 3144-3705cm^{-1} wave number corresponds to absorption due to stretching vibration of O-H bond from ethanol. The spectral region around 2770-3144cm^{-1} corresponds to absorption due to stretching vibration of C-H bonds of gasoline and ethanol. The areas of these spectral regions were determined using origin software. During analysis, uniformity was maintained across all standards and samples measured by ensuring consistency in peak identification and baseline correction. Then the ratio of the areas under O-H peak to the area under the C-H peak was calculated and a standard curve correlating the percentage of ethanol to the ratio of the areas were subsequently produce a calibration curve to facilitate quantitative analysis.

3.7 quantification of ethanol content in gasoline samples

The FT-IR spectra of the five gasoline samples (Taf oil, Global, Total, Noc and tebarek) were obtained for quantification of ethanol content. The areas under O-H and C-H peaks were determined and the ratios of the areas were calculated.

The ethanol percentage in gasoline sample was then determined using the following equation

%Ethanol = [(area of O-H peak)/(area of C-H peak) – (y-intercept)]/ slope

3.8 Calibration standards for kerosene

The FT-IR spectra of four kerosene gasoline standards were obtained and peaks at $1378 Cm^{-1}$ and $1460 Cm^{-1}$ were recorded and analyzed to determine respective areas. The specified regions for each peak and the baseline correction performed by the origin software remained uniform across all standards. The sum of peak areas were calculated and a standard curve of percent kerosene versus the peak areas was produced for quantitative analysis,

3.9 Determination of kerosene content in gasoline samples

The FT-IR spectra of the five gasoline samples were obtained for determination of kerosene content and the area under the peaks responding to increase in concentration of kerosene were determined and the sum of the areas was then calculated. The percentage kerosene in gasoline sample was then calculated by the equation

%kerosene = [sum of peak areas – (y - intercept)]/slope

CHAPTER FOUR

Result and discussion

The analytical region of infrared spectra of the pure gasoline shows a series of peaks from around 2770Cm^{-1} to 3000Cm^{-1}which is C-H stretching bond due to the hydrocarbons present in gasoline.

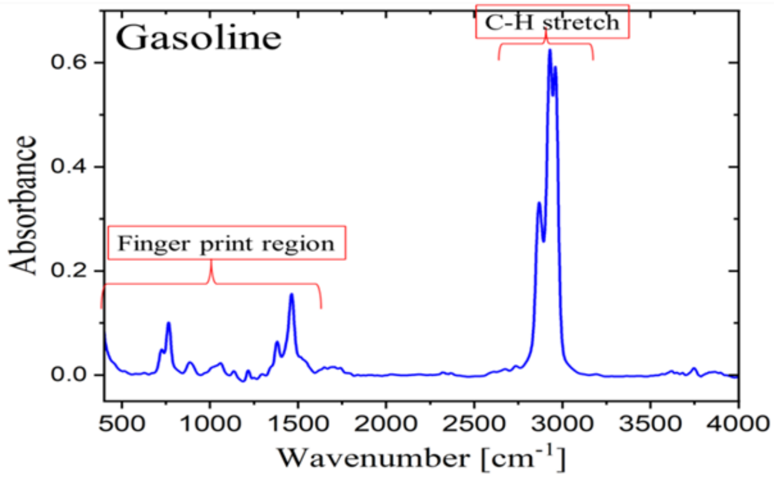

Figure 4.1 IR spectra of gasoline

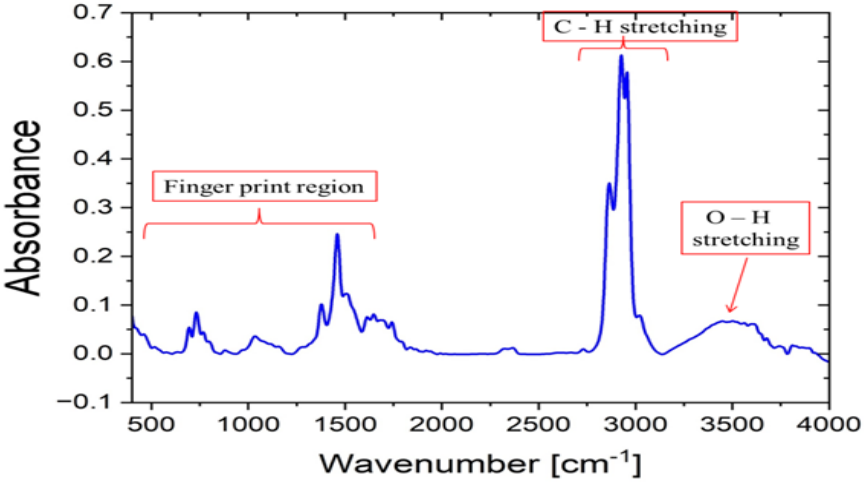

Figure 4.2 Representative IR spectra of ethanol gasoline standard (10% ethanol in gasoline)

Fig 4.2 is the representative infrared spectra of ethanol gasoline standards containing 10% ethanol by volume. In the analytical region a broad and strong peak in region of $3144Cm^{-1}$ to $3705Cm^{-1}$ is shown which corresponds to O-H stretching vibrations due to the hydroxyl group present in ethanol and there is peak combined alkane groups with gasoline's C-H peaks.

In ethanol gasoline standards, initially when ethanol is added in small amount (1%) to gasoline a sharp peak appears around $3000Cm^{-1}$ to $3100Cm^{-1}$ wave number region and as more ethanol is added to the gasoline this peak becomes less intense and combines with gasoline's C-H peaks with increasing ethanol concentration as shown in the figure below. This shows the peak intensities of ethanol's C-H peaks may be influenced by the presence of O-H group leading variations in intensity compared to gasoline C-H peaks and overlapping of ethanol's C-H peak with those of gasoline.

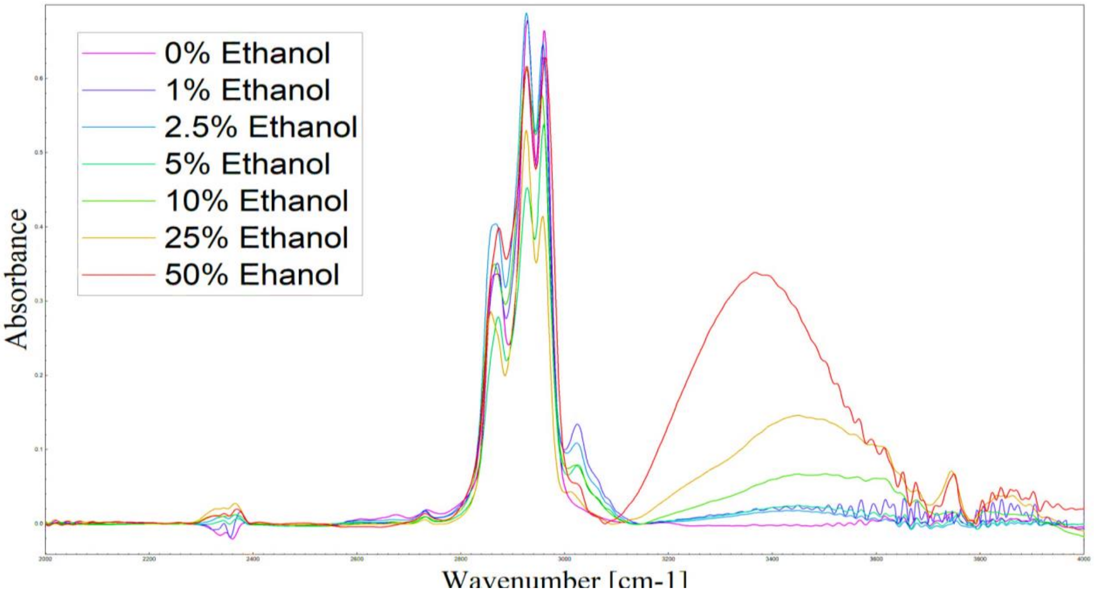

Figure 4.3 FT-IR spectra of gasoline and ethanol gasoline standards (0%, 1%, 2.5%, 5%, 10% , 25%, and 50%)

The calibration of those ethanol gasoline standards ranging from 0%(just gasoline) to 50% the ratio of the areas under O-H peak to the area under C-H peak versus percent ethanol formed is linear as shown in the figure below with R^2 value of 0.99892.

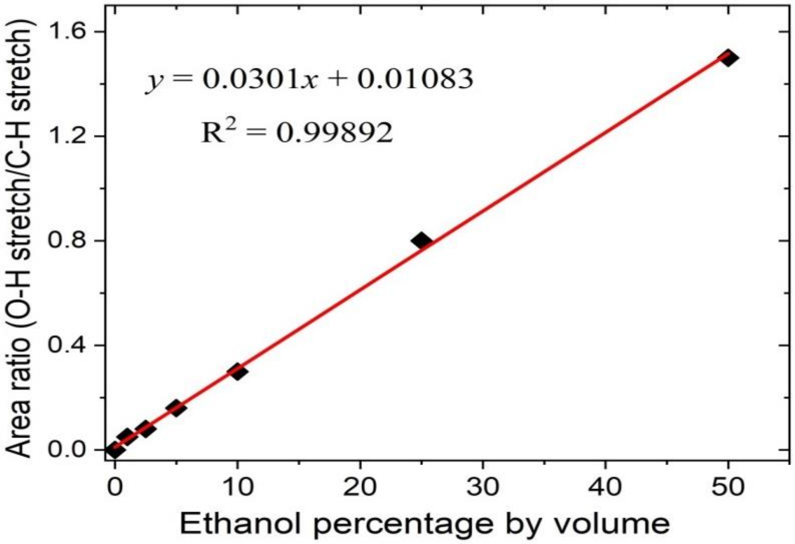

Figure 4.4 Calibration curve of area ratio (O-H stretch/C-H stretch) against ethanol percentage of gasoline standard with ethanol

The results of my quantitave analysis on the gasoline samples based on the calibration shows a notable variations in ethanol content among the gasoline samples collected from five different stations, namely Global, Noc, Tebarek, Taf oil, and Total, as shown in Table 4.1 below.

Table 4.1 Gasoline stations and their determined percentage of ethanol

Name of gasoline Stations	Ethanol content(%)
Global	18.7
Noc	9.44
Tebarek	12.6
Taf oil	18.5
Total	12.5

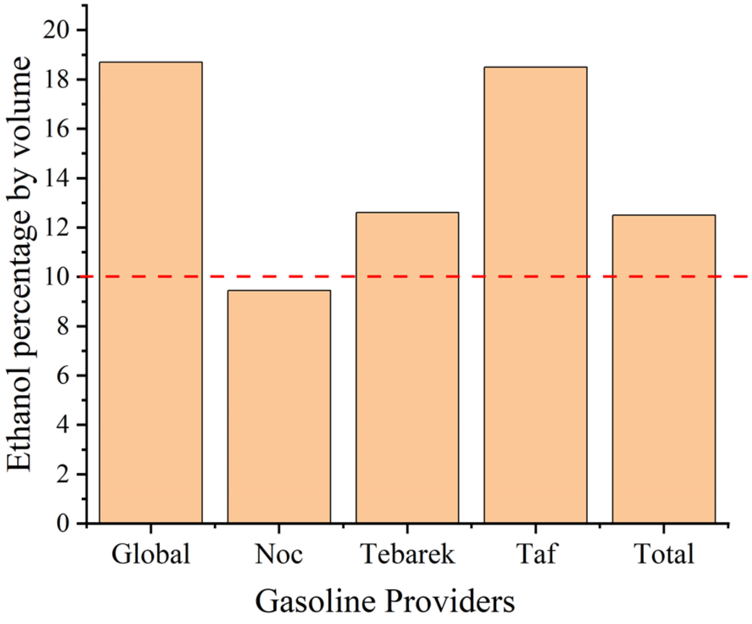

Figure 4.5 The percentage of ethanol by volume obtained from randomly selected gas stations from five different gas providers. The horizontal red dash line indicates the maximum allowed ethanol percentage set by ISO.

These findings indicate that four out of five stations namely Global, Taf oil, Total and Tebarek exceeded the maximum allowed limit of ethanol which is set at 10% by ISO, two of them with 2% and the others by around 9% and one of the stations, Noc is almost consistent with the permissible limit. And the observed variability in ethanol content among the sampled stations hints at underlying differences in fuel blending practices, supply chains, or storage conditions. As discussed in literature ethanol, when added to gasoline exceeding limits set by national or international regulatory agencies raises concerns about engine performance and fuel efficiency.

Visual identification of the functional groups of kerosene and gasoline is difficult. This is due to the similarities in structure of hydrocarbon in kerosene and gasoline. As a result determination of kerosene contents in gasoline is complex. However, by preparing different concentrations of kerosene in the gasoline(The gasoline sample utilized in this study for calibrating kerosene already contained certain percentage of kerosene to ensure accurate calibration and analysis the spectra of the sample used was recorded initially and the gasoline kerosene standards were prepared and used for calibration of kerosene taking into account the initial presence of kerosene in the gasoline). It is shown that there is an increase in absorption level at 1378Cm^{-1} and 1460Cm^{-1} in the fingerprint region of Ir spectra of kerosene gasoline standards. The only peaks that consistently respond to the amount of kerosene added are the two peaks which are located in the finger print region (i.e 1378 cm-1 and 1460 cm-1).

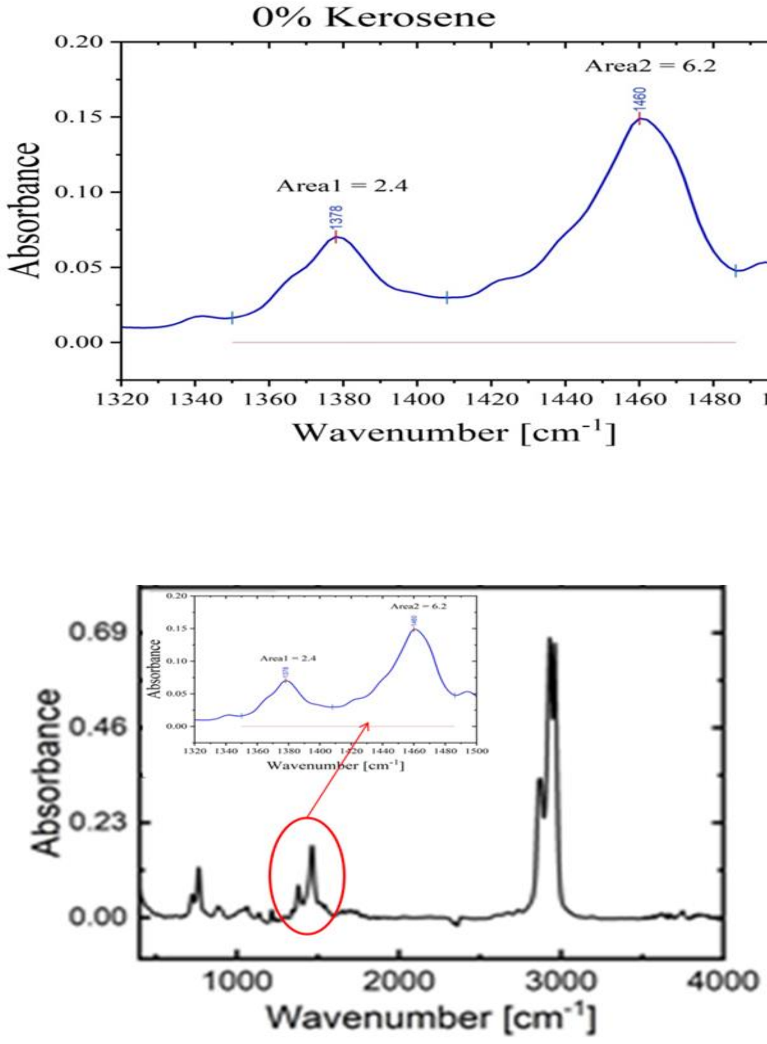

Figure 4.6 Recorded peaks of gasoline

As shown in the figure below, Fig 4.7, as the concentration of kerosene increases the absorption at the two peaks increases and the areas under these peaks are determined and their sum was calculated and a calibration curve was formed for quantification of kerosene adulteration in the gasoline samples.

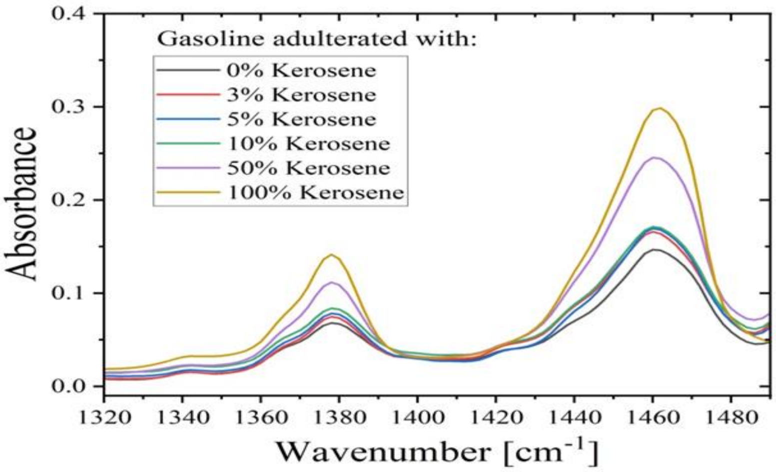

Figure 4.7 Recorded peaks of kerosene gasoline standards

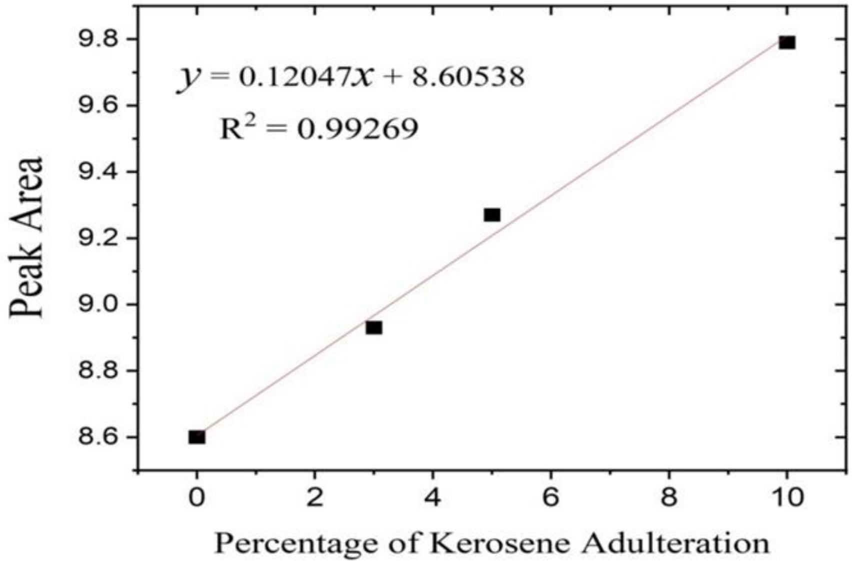

Figure 4.8 Calibration curve of peak areas against percentage of kerosene of gasoline standards with kerosene

The calibration formed is linear with R^2 value of 0.993 and using this calibration the amount of kerosene adulteration in gasoline samples were calculated. The result reveals a prevalence of kerosene adulteration across these sampled stations. The highest levels of kerosene adulteration was detected at stations Tebarek and Total conversely the station labeled Global exhibited relatively lower level of kerosene adulteration which is still illegal because even minor levels of adulteration can have detrimental effects on engine performance, emission and overall vehicle efficiency. The intermediate levels of adulteration detected at Noc and Taf oil.

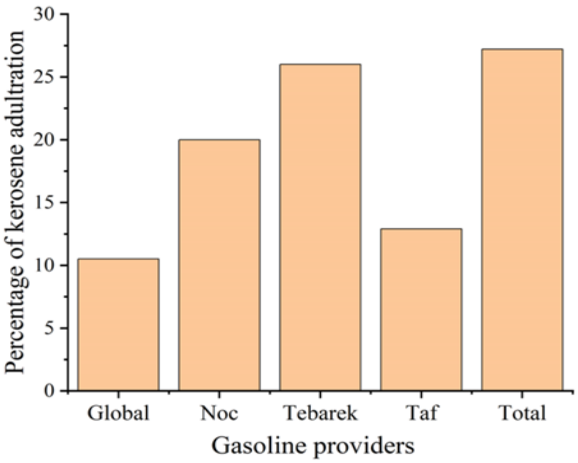

Figure 4.9 The percentage of kerosene adulteration by volume obtained from randomly selected gas stations from five different gas providers

CONCLUSION

This study highlights the variability in ethanol content and detection of kerosene adulteration in motor gasoline among gasoline samples from five different stations in Ethiopia. The analysis revealed that four out of five stations exceeded the maximum allowed limit of ethanol in gasoline with values ranging from 2% to 9% and detected illegal gasoline kerosene adulteration on all gasoline samples from the stations in significant amounts. This adulteration and blending practices could be from the primary suppliers, supply chain, or from the stations and that needs further investigation. Several reports in the literature indicated that excessive ethanol gasoline blending practices affects engines performance and causes engine failure and unstable engine speed. On the other hand illegal kerosene adulteration in gasoline causes environmental pollution by emitting particulate matter, carbon dioxide, and different hydrocarbons and in this case the sampled stations ethanol blending practice and illegal kerosene adulteration lowering the quality of gasoline being used shows that there are no stricter regulations on gasoline blending and adulteration practices and due to the scarcity of gasoline the consumers do not question the quality of the gasoline at all.

Finally, since the quality of gasoline affects engines performance and environmental safety there should be more stricter regulations on ethanol limit in gasoline and avoiding kerosene adulteration and a timely follow up in stations is also important to protect the environment, the consumers and their engines.

RECOMMENDATIONS

In this study five gasoline samples were analyzed to quantify ethanol content and kerosene adulteration using FT-IR spectroscopic technique further research should conducted encompassing extensive range of gasoline stations and determining other adulterants and oxygenates using either FT-IR or other techniques. Understanding the source where excessive ethanol blending and illegal kerosene adulteration was practiced to implement targeted interventions is important so that the regulatory agencies will know whom to take a measure on. The agencies can also use the analyzed data from this study to make stricter regulations on the sampled gasoline stations in this study.

Consumers should also make informed decision about the quality of gasoline they are using to avoid damage on their engine and to protect their environment from hazardous emission.

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