UNIVERSITY OF GHANA

COLLEGE OF BASIC AND APPLIED SCIENCES

ASSESSMENT OF GASOLINE QUALITY MARKETED IN ACCRA METROPOLIS, GHANA

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DEPARTMENT OF CHEMISTRY

JULY 2015

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ASSESSMENT OF GASOLINE QUALITY MARKETED IN ACCRA METROPOLIS, GHANA

BY

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Declaration

I, hereby declare that this submission is my own work towards the award of MPhil Chemistry in the Department of Chemistry, University of Ghana and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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Abstract

Premium gasoline is often adulterated with cheaper products (adulterants) like domestic kerosene. Kerosene is more difficult to burn than gasoline and this result in the increase of tailpipe emissions and engine complexities. Having similar physical and chemical properties, the gasoline and kerosene cannot be distinguished easily leading to a complication in identification and quantification of the adulterant. Routine monitoring of gasoline at the pump has been pointed out as essential in the prevention of this adulteration and a number of possible methods have been reviewed as there is no standard method for the detection and quantification of kerosene in gasoline. Most of these methods are not utilized in developing countries like Ghana because they require either specialized laboratory, equipment or chemical hence their implementation involves huge financial budgets. A corollary of this is a need for cheaper and tailored method for monitoring kerosene adulteration in gasoline.

This study monitored gasoline adulteration with domestic kerosene in Accra Metropolis by exploring the differences in their acidity levels as a "fingerprint", determined by using an in-house, simple direct titration (SDT) method. Physicochemical properties of gasoline samples and other petroleum distillate fractions were studied after which simulation of gasoline adulteration with domestic kerosene was carried out and the acidity determined by the SDT method to obtain a calibration plot. The calibration standard was then utilized to estimate the amount of domestic kerosene (adulterant) present in 20 gasoline samples from some retail outlets in Accra Metropolis. Domestic kerosene in the range of 5 - 29% was found in 50% of the stations. This study therefore demonstrated that the method is feasible, cheaper, and does not require specialized laboratory or highly trained personnel to execute.

Key standard quality parameters of the commercial gasolines were also determined and their compliance with local and international specifications was evaluated. However the gasoline available in Accra Metropolis was found not to conform to standard specifications for Europe, Japan and India. 35% did not conform to specification of Ghana Standard Authority (GSA) as well.

Dedication

This work is dedicated to my lovely wife, Mrs. Wasila Ubeidalah and my children for their love, care, and moral encouragement.

Acknowledgement

Glory is to Almighty Allah, the Being above the reach of reason on whom I have depended.

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List of Abbreviations

AAMA	American Automobile Manufacturers Association
AIAM	Association of International Automobile Manufactures
AKI	Antiknock Index
ASTM	American Society for Testing and Materials
ATK	Aviation Turbine Kerosene
ATR	Attenuated Total Reflectance
BOST	Bulk Oil Storage and Transportation Company
CAP	Chemocapacitors
CDU	Crude Distillation Unit
CFR	Cooperative Fuel Research
CO	Carbon Monoxide
CP	Conducting Polymers
CSE	Centre for Science and Environment
DHA	Detail Hydrocarbon Analyzer
EEMF	Excitation Emission Matrix Fluorescence
EPA	Environmental Protection Agency
ETBE	Ethyl Tertiary Butyl Ether
EU	European Union
FBP	Final Boiling Point
FID	Flame Ionization Detector
GC	Gas Chromatography
GHAIP	Ghanaian Italian Petroleum Company
HACs	High Acid Crude Oils
HC	Hydrocarbons
IBP	Initial Boiling Point
KMO	Kaiser-Meyer-Olkin
LPG	Liquefied Petroleum Gas
MON	Motor Octane Number

MOS	Metal Oxide Semiconductors
MTBE	Methyl Tertiary Butyl Ether
NMR	Nuclear Magnetic Resonance
NOx	Nitrogen Oxides
OPEC	Organization of the Petroleum Exporting Countries
ON	Octane Number
PAHs	Polycyclic Aromatic Hydrocarbons
PCA	Principle Component Analysis
PM	Particulate Matter
RFGs	Reformulated Gasolines
RON	Research Octane Number
RVP	Reid Vapour Pressure
SDT	Simple Direct Titration
SFC	Specific Fuel Consumption
SPM	Suspended Particulate Matter

CHAPTER ONE

1 INTRODUCTION

1.1 BACKGROUND

Petroleum, a fossil fuel, supplies more energy to the world today than any other source. For thousands of years, the only sources of petroleum had been surface seeps or tar pits until 1858, when James Miller Williams made the first major commercial oil discovery in North America at Oil Springs, Ontario, he struck oil at a depth of only 18 metres. In the following year (1859), Colonel Edwin L. Drake discovered oil in Titusville, Pennsylvania by drilling to 21 metres. In today's industrialized society, petroleum means power and will hold the centre stage of economies for many years to come (Mather, 1947). Gasoline which had previously been considered a useless by-product of the distillation of crude oil has now taken on a new importance as advancements in technology made possible the mass production of the automobile in early years of the twentieth century (Fagan, 1991).

Gasoline is a mixture of several hundred organic volatile compounds, mainly hydrocarbons, ranged from four to twelve carbon atoms with boiling points in the range of 30 – 225 °C (Fialkov et al., 2008). The hydrocarbons present in gasoline are classified as paraffins (normal and branched), naphthalenes (cycloparaffins), olefins and aromatics. The physicochemical properties of gasoline largely depends on the nature of the crude oil from which it originates, the refining process be it distillation, alkylation, hydrocracking, catalytic cracking through which the gasoline is obtained, the end use for which it is

produced (automotive competitions, engine performance tests), and the environmental legislation like limits on benzene, aromatics, sulfur, lead, etc in place at the location of production and distribution (Barbeira et al., 2007; Flumignan et al., 2008; Takeshita et al., 2008). Gasoline also contains specified maximum levels of impurities and some minimum level of performance-enhancing additives. For example oxygenates like alcohols (mostly ethanol), ethers are added to gasoline to boost the octane rating (Barbeira et al., 2008).

As a result of industrialization and changes in lifestyle the urban metropolis growth is associated with increasing number of automobiles and in most growing cities gasoline or petrol driven vehicles comprise over 80% of the total vehicles registered. In Ghana, the transport sector accounts for over 80 percent of total consumption in 2003 (The World Bank, 2006; Yadav et al., 2013).

Transport fuels are often adulterated with other cheaper products or by-product or waste hydrocarbon stream for illegal profits. Adulteration may be as simple as adding regular-grade gasoline to the super-grade gasoline storage tank, which lowers the octane number of the super (Al-Ghouti et al., 2008). Premixed gasoline, a cheaper and lower quality gasoline mixed with lubricating oil is used to adulterate premium gasoline (Victor, 2014). Domestic heating and marine diesel fuels are often used to adulterate more expensive automotive diesel fuel (Kalligeros, et al 2001). Gasohol is adulterated by increasing the fraction of ethanol outside the specified range (Jorge and Barbeira, 2002; Pereira et al., 2006). Diesel is adulterated with kerosene, cyclohexane, crude hexane and turpentine oil (Patra and Mishra, 2002; Roy, 1999). Among the common adulterants for petroleum fuels, kerosene seems to be the most popular while industrial solvents, used lubricants and mixtures of hydrocarbons are the other possible alternatives (Taksande and Hariharan, 2006;

Wiedemann et al., 2005). For example, in Nigeria and Tanzania adulteration of gasoline and diesel fuel with kerosene is very common (Gawande and Kaware, 2013; Massawe et al., 2013; Osueke and Ofondu, 2011). Kerosene is a popular adulterant for gasoline because of its similarity in chemical composition due to the overlap in their production. These are mixed with almost no deviation in some specifications of the gasoline (Morello-Frosch et al., 2000).

Fuel adulteration has many effects especially on any vehicle that uses it. Adulterants alter the chemistry of the base fuel rendering its quality inferior to the required fuel quality for vehicles, moreover, it affects the combustion dynamics inside the combustion chamber of vehicles increasing the emissions of harmful pollutants significantly (Gawande and Kaware, 2013; Yadav et al., 2013). When kerosene is mixed with gasoline, it does not burn completely and accordingly releases more poisonous emissions like nitrous oxides, carbon II oxide (CO) and particulate matter (PM). This results in pollution, causing acute respiratory infections and other ailments (Roy, 1999). There is also a drastic increase in specific fuel consumption (SFC) and knocking tendency, hence reducing engine efficiency (Obodeh and Akhere, 2010; Usha et al., 2003). The diversion of domestic kerosene for adulteration with higher price fuels like gasoline drastically brings down its availability to the poor households, who turn to biomass for the purpose of cooking. The consequence is indoor air pollution and its attendant health effects (Gupta and Sharma, 2002).

Therefore, because of the various problems associated with gasoline adulteration with kerosene as enumerated by several studies, this work seeks to monitor gasoline adulteration

with kerosene in Accra Metropolis and offer a cheaper method of detecting the adulteration.

1.2 PROBLEM STATEMENT

Adulteration of transport fuel is a widespread issue among oil companies around the globe. In the United States of America biodiesel blends are adulterated with soy oil (Mahamuni and Adewuyi, 2009). In Greece, automotive diesel is adulterated with domestic heating and marine diesel (Kalligeros, et al 2001). The recent suspension by the Brazilian government of the state monopoly of fuel production and distribution, whilst it has created competition for stronger retail business given rise to significant changes in the fuel market in Brazil also opened the road to the criminal practice of adulteration of gasohol (Jorge and Barbeira, 2002; Pereira et al., 2006). In Southeast Asia diesel is adulterated with kerosene, cyclohexane, crude hexane and turpentine oil (Patra and Mishra, 2002; Roy, 1999). Gasoline is widely adulterated with kerosene. In Nigeria, adulteration of gasoline and diesel fuel with kerosene has been very rampant (Gawande and Kaware, 2013; Osueke and Ofondu, 2011). In Sri Lanka kerosene adulteration with diesel was found to be in the range of 0 to 35 % while its adulteration in gasoline in the range of 0 to 48 % in Colombo and its suburbs (Kulathunga and Mahanama, 2013). In Ghana gasoline adulteration with premix fuel and domestic kerosene is a common practice (Victor, 2014).

Currently the menace is a very flourishing business in developing countries where prices are usually regulated. Air pollution caused by adulterated fuel emissions, especially nitrogen oxides (NOx), carbon monoxide, hydrocarbons (HC), and suspended particulate

matter (SPM) has been a noteworthy matter. Running on gasoline mixed with kerosene leads to a substantive increase in air pollution, because of increased tailpipe emissions of harmful pollutants, as well as deterioration of performance and parts of engines. Some of these adulterations are done with almost no aberration in the analytical properties of automotive fuel hence may not show up in routine analytical tests. Laboratory techniques used in detecting adulteration are very expensive, time-consuming, require specialized personnel and only few are available. While a number of alternative techniques are available for detection and quantification of gasoline adulteration with kerosene, they require specialized equipments or chemicals which still make them not affordable for routine monitoring. In the light of this, monitoring gasoline adulteration on the market and exploring a cheaper, more precise, on-site method of detection and quantification of kerosene in gasoline becomes imperative.

1.3 JUSTIFICATION

Clean and green world is the requirement of today, and for this one should think and act as an environmentalist (Krishna et al., 2006). Many governmental regulations have been aimed at minimizing the environmental impact of the automobile. Most regulations initially focused on the automobile and have resulted in automotive technology which significantly reduces vehicle emissions compared to pre-control levels. With this type of progress already achieved via automotive technology, it was apparent that if further gains were to be made, it would be necessary to focus on cleaning up fuels that these vehicles

use. One of such change was the wide-scale introduction of unleaded gasoline (Renewable Fuels Foundation, 2009).

There are complaints by sections of the general public in Ghana about the increasing rate of fuel adulteration, which is causing damage to vehicle engines in the country and the environment (Attenkah, 2006).

Despite the threat posed by kerosene adulterated gasoline and the fact that recent engines demand specific quality, the scrutiny and enforcement of gasoline fuel standards in Ghana cannot be verified. To this end, a study of gasoline quality and its adulteration with kerosene on the market is needed. With the growing drive to deter fuel adulteration and the recognition towards lower vehicular emissions, a cheaper, more precise, on-site method of detecting motor gasoline fuel adulteration with domestic kerosene is needed. It will also prevent subsidized domestic kerosene diversion from the intended targets.

1.4 AIM

The objective of this work was to monitor gasoline adulteration with domestic kerosene sold in Accra Metropolis by the use of acidity, determined by using a new method, simple direct titration (SDT) method.

1.5 OBJECTIVES

The specific objectives are:

1) Monitoring acidity levels and pattern in petroleum fractional distillates from the refining of different crude oils.

2) To study acidity and physicochemical parameters of pure gasoline and kerosene.

3) Simulate adulteration of premium gasoline with domestic kerosene.

4) To develop a simplified in-house titration method (SDT method) for the determination of gasoline acidity and calibration standard.

5) Utilize the calibration standard (Linear regression) from 4 above to estimate amount of domestic kerosene (adulterant) present in gasoline from fuel retail outlets in Accra Metropolis.

6) To compare standard physicochemical properties of gasoline from the fuel stations with local and international specifications.

1.6 ORGANIZATION OF THE RESEARCH

The research is organized into five chapters. Chapter one gives the background, the problem statement, justification, aim, objectives, and organization of the research. Related literature is reviewed in chapter two. The review covers petroleum, petroleum products supply in Ghana, gasoline, kerosene, methods to check gasoline adulteration and quality

assessments of gasoline at fuel stations. Chapter three is methodology and that covers materials, sample collection, Physical and chemical properties (test methods) and data analysis. Chapter four is results and discussion. Chapter five concludes the thesis, and recommendations are offered.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 PETROLEUM

The term petroleum, which literally means “rock oil”, is commonly called crude oil. Various theories have been advanced over the years as to the origin of petroleum proposing an animal, vegetable, mineral and even meteoric origin. However, petroleum is believed to be formed from the remains of plants and animals that have been held under tremendous pressure in an aerobic environment for millions of years (Speight, 2002). It is not known exactly when humankind first used petroleum. It is known, however, that ancient people worshipped sacred fires that were fuelled by natural gas seeping to the surface through pores and cracks. It is also known that asphalt, a very viscous form of petroleum, was used to waterproof boats and heat homes as early as 6,000 BC. Asphalt was also used as an embalming agent for mummies and in the construction of the Egyptian pyramids around 3,000 BC. Thus petroleum's usefulness was recognized from the very beginnings of civilization.

2.1.1 Significance of petroleum

The reason that oil has such importance is that, it provides the fuel that runs the internal combustion engine. Petroleum's utility to humankind took a giant leap in the late 1800's when it replaced coal as the primary fuel for the machines of the industrial revolution (Fagan, 1991). It is projected by the World Oil Outlook (WOO) that developing countries

will experience a more dramatic increase in cars with an extra 800 million over the period 2010–2035 (OPEC, 2013). In today's industrialized society, petroleum means power. It provides the mechanical power to run machines and industries and also the political power that comes from being able to shut down the machines and industries of those who depend on you for their oil supply. As long as we depend on oil to fuel the engines of the world, it will continue to play a major role in our lives. Although oil is primarily an energy source, it is also used as a raw material in manufacturing many other products including; plastics, paints, fertilizers, detergents, cosmetics, insecticides, medicines, solvent for paints, insecticides and even food supplement (Fagan, 1991).

As a result of the role that petroleum plays, the organization of the Petroleum Exporting Countries (OPEC), a permanent, intergovernmental organization, was created at the Baghdad Conference on September 10–14, 1960, with the principal aim of safeguarding the collective and individual interests of its members and unifying the petroleum policies of its member countries. OPEC was founded at Iraq's invitation of Iran, Kuwait, Saudi Arabia and Venezuela. The Organization now comprises 12 Members: Algeria, Angola, Ecuador, the Islamic Republic of Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, the United Arab Emirates and Venezuela. The Organization has its headquarters in Vienna, Austria (Desta, 2003). Ghana has little domestic supply of crude oil; most of its crude oil demand is met by imports from Nigeria, supplements from Europe until the offshore discovery of crude oil in commercial quantities in July 2007 (Oswald and Amoah, 2011).

2.1.2 Characterization of petroleum

Crude oil is a complex combination of hydrocarbons consisting predominantly of paraffinic (straight and branched-chain alkanes), naphthenic (cycloalkanes or cycloparaffins), and aromatic hydrocarbons. Most commonly found naphthenes are five and six membered rings and occasionally a few rings with seven carbon atoms. Among these, methyl derivatives are the most abundant compounds as compared with the parent bicycle compounds. Crude oils contains up to 50% of such naphthenes. Aromatic compounds rarely amount to more than 15% of the crude oils. These are concentrated in heavy fractions such as gas oil, lubricating oils and the residuum. The alkyl derivatives of the benzene namely toluene and xylene are most common aromatic compounds in petroleum. The other derivatives of benzene include fused compounds, the di-aromatics (naphthalene) and tri-aromatics (Phenentherene or anthracene). Naphtheno-aromatic compounds have also been identified in crude oils. These compounds are abundant in shallow and immature crude oils. Many of these compounds can be related to steroid and triterpennoid structures (Yasin et al., 2013). The hydrocarbons in crude oil have carbon numbers that range from four (C4 or butanes), to large molecules containing more than sixty carbons. Sulfur, oxygen and nitrogen compounds, organometallic complexes notably of nickel and vanadium, and dissolved gases, such as hydrogen sulfide, are also found in crude oil. An “average” crude oil contains 84% carbon, 14% hydrogen, 1-3% sulfur, and approximately 1.0% nitrogen, 1.0% oxygen and 0.1% minerals and salts. Analytical studies indicate that similar hydrocarbons, heterocyclics, metals and other constituents, such as hydrogen sulfide, are present in all crude oils but their proportions vary depending on the crude source (API, 2011). Crude oil varies dramatically in colour, odour and flow

properties that reflect the diversity of its origin and the complexity increases with boiling range (Odebunm et al., 2002).

With crude oil cost accounting for about 80% of the refinery expenditures, processing cheaper crudes can have a very positive impact on refinery margins and is the single most important determinant for the profitability of an oil company (Hartmann, 2003). A reliable compositional characterization of petroleum is therefore important for the optimization of refining processes, products quality or slate and environmental issues. Crude oils can be fractionated into four different components based on solubility and polarity, namely, Saturates, Aromatics, Resins and Asphaltenes (SARA). Saturates are alkanes and cycloparafins, they are unreactive and therefore constitute stable products. Aromatics do not burn as clean as other hydrocarbons and can cause smoke and carbon deposits, as well as increases the luminosity of the combustion flame. Resins are polar molecules with heteroatoms (N, O, and S); whiles asphaltenes are similar to resin with polyaromatic core and higher molecular weight (Pasadakis et al., 2001). Asphaltenes play an important role in organic deposition during petroleum production and processing. Issues on asphaltenes and solid precipitation have always been highlighted as one of the major fouling precursors. A small change in maltenes component or temperature can initiate asphaltene dropouts (Deshannavar et al., 2010).

Crude oil types are typically differentiated by their density (measured as API gravity) and their sulfur content. Crude oil with high sulfur content is called sour crude while sweet crude has low sulfur content. Light (high API) or sweet crude oils are normally more expensive and have larger amount of low and medium fractions (high value products) such as LPG, naphtha and kerosene. Therefore, the lower the API of a crude oil, the lower the

value it has to a refiner as it will either require more processing or yield a higher percentage of lower-valued by-products such as heavy fuel oil, which usually sells for less than crude oil. There are basically four groups of crude oil based on API and sulfur. They are light-sweet (30-40° API, <0.5 wt% S), light-sour (30-40° API, 0.5-1.5 wt% S), heavy sour (15-30° API, 1.5-3.1 wt% S) and extra-heavy (<15° API and >3 wt% S) (Stratiev et al., 2010; Wiehe, 2008).

The commonly used industry standards of API gravity and sulfur, while important, do not adequately define a crude oil. Another important information of crude oil quality is the organic acid content. Their presence at high concentration may generate a number of problems at equipment operation and especially at crude oil atmospheric-vacuum distillation plants via their acid high corrosion activity. The total acid number of a crude oil is an indicator of the organic acids content in the crude oil. Crude oils with total acid number more than 0.5 mg KOH/g are mostly known to present much problems during processing (Yépez, 2005). High acid crude oils (HACs) represent the fastest-growing segment of global oil production. California, Brazil, North Sea, Russia, China, India and West Africa are known to supply HACs. As a result of lower prices of high acid crude oil feeds (total acid number over 0.5 mg KOH/g crude oil) their processing is one opportunity to increase crude oil processing profit and these types are often termed as opportunity crudes (Ooms et al., 2001; Stratiev et al., 2010).

Table 2.1: Physicochemical properties of some crude oils

PARAMETER	Forcados blend	Bonny light	Bonny midium	Gulf crude	Lagomar crude	Qua Iboe
Specific gravity @ 60/60°F	0.8808	0.8576	0.8845	0.8690	0.8960	0.8706
API gravity @ 60/60°F	29.1	33.4	28.4	31.3	26.4	31.0
Kinematic viscosity (cst) @100°F	7.00	7.16	7.01	5.69	4.49	9.86
Sulfur content (w/w %)	0.11	0.06	0.16	0.09	1.36	0.04
Pour point (°F)	+25	+85	+5	+35	-5	+35
Total acid content (mg KOH/g)	0.33	-	-	-	-	-
Water content (v/v %)	0.08	-	-	0.05	-	-

Source- Odebunm et al., 2013**.**

2.2 PETROLEUM PRODUCTS SUPPLY IN GHANA

Petroleum products marketed in Ghana include; premium gasoline, premix gasoline, liquefied petroleum gas (LPG), diesel, kerosene, aviation turbine kerosene (ATK), and residual fuel oil. Other petroleum products are; refinery gas, ethane, propylene, naphtha, distillate fuel oil, lubricants, white oil, grease, wax and bitumen (Energy Commission, 2006). All the petroleum products needed in Ghana were imported and distributed by the local branches of multinational oil companies like Texaco, Shell, British Petroleum, Mobil and Total until the establishment of Ghanaian Italian Petroleum Company (GHAIP) Ltd, which was licensed as a private limited liability company in 1960 as a fully owned Italian company. GHAIP was renamed as Tema Oil Refinery (TOR) in 1991 after the Government

of Ghana became the sole shareholder in 1977. TOR is able to meet only around 70 percent of Ghana‘s demand for petroleum products.

In September 1996, the state owned TOR acquired sole responsibility for importing crude oil and refined petroleum products into Ghana. According to the International Bank for Reconstruction and Development and The World Bank (2006), the liberalization of the petroleum sector has allowed private sector participation in the procurement of crude oil as well as the private import of refined products through tenders. Since the beginning of 2004, TOR ceased to have a monopoly on the importation of petroleum products, and from July 2004 it has been prohibited from importing petroleum products. In March 2004, private Oil Marketing Companies (OMCs) participated in the first competitive tender for gasoline with financing provided by a syndicate of banks (The World Bank, 2006). TOR’s maximum production capacity was 28,000 barrels of oil per day in 1990. By 2000 the production capacity had been expanded to 45,000 barrels per day to meet increasing demand. Yet annual diesel, gasoline and kerosene demand growth have been about two to three times the annual real GDP growth, whilst that of LPG has quadrupled. The implications are that gasoline and diesel demand have exceeded the country’s refinery capacity, increasing the risk of supply interruptions. If all the petroleum requirements of the nation are to be met from local refining, the total refinery capacity is projected to reach at least 115,000 barrels of oil per stream day by 2020. This can be achieved by expanding the Tema Oil Refinery to the required size by 2020. TOR was designed to process light and low-sulfur crude oils at a time crude oil prices were very low and tenable in neighbouring Nigeria. As a result of the total dependence on imported oil, the country maintains strategic stocks of petroleum products to minimize disruptions in economic activities in the event of external supply

problems (Energy Commission, 2006). Moreover, as the population of the country increases with a corresponding increase in the demand for petroleum products in the midst of bad roads, the government established the Bulk Oil Storage and Transportation Company (BOST) as a state owned company incorporated in 1993 as a limited liability company with the government of Ghana as the sole shareholder. BOST has the mandate to develop a network of Storage tanks and Pipeline infrastructure throughout the country and to keep strategic stocks for Ghana. It has depots across the country, most of which are linked to TOR or the Accra Plains depot by pipeline, to facilitate the transportation and distribution of petroleum products throughout the country. Until May 2001, BOST was responsible for the distribution of petroleum products from its strategically located depots which could be found in the Accra Plains, Mamiwater, Akosombo, Kumasi, Buipe and Bolgatanga. BOST was also made to announce revised petroleum prices on behalf of government (BOST, 2011).

Access to petroleum products in Ghana is satisfactory but has to be improved as the population grows. There are presently a total of 1,700 petroleum products retail outlets of which 37% are service stations, 20% are filling stations and 43% are reseller outlets. The total number of retail outlets represents an access ratio of 71 retail outlets per one million people. There are also vendors who sell mainly kerosene, in all rural communities thereby increasing the accessibility of petroleum products in most parts of the country. In addition to the service stations and reseller outlets, the Ministry of Energy, under the Rural Kerosene Distribution Improvement Project (RKDIP), has extended the reach of kerosene retail outlets to 1,540 rural communities by installing 5,000 litre capacity surface tanks for the retailing of kerosene (Energy, 2010). At the peak of high oil prices, nearly all

developing countries intervened with price-based policies to mitigate the price increase on the world market for at least one fuel. Policy reversals and postponement of price reform were common, governments that had earlier deregulated fuel prices or adopted automatic price adjustment mechanisms froze and subsidized retail prices, while others that had announced fuel price subsidy removal postponed price reform. Colombia in May 2008 postponed the removal of gasoline and diesel subsidies by a year. Both Jordan and Vietnam were to eliminate subsidies by 2007 but postponed (Kojima, 2013).

2.3 GASOLINE

Gasoline is a volatile and inflammable mixture derived from petroleum. Gasoline maybe colourless, pale brown or pink as the colour vary depending on the source (Carson et al., 1995; Ismayyir and Dawood, 2012). Gasoline is used as fuel for vehicles propelled by internal combustion engines in automobiles, planes, buses, boats, and also used as diluents, finishing agent, and industrial solvents (Pohanish, 1984). Other terms for gasoline are petrol and less commonly, motor spirit (Singh et al., 2000).

Typically, gasoline contains more than 100 compounds including small amount of benzene, toluene, and xylene (Renewable Fuels Foundation, 2009). However, as many as 1,000 compounds have been identified in some blends (Mehlman, 1990). How the gasoline is made (refinery process) greatly determines which chemicals and how much are present in the mixture and the actual composition varies with the source of the crude petroleum. Generally the composition is made up of Paraffins, Olefins, Naphthenes and Aromatics (PONA). Gasoline also contains specified maximum levels of impurities and some

minimum level of performance-enhancing additives (Barbeira et al., 2008; Carson et al., 1995).

The hydrocarbons constituents in this range are those that have 4 to 12 carbon atoms in their molecular structure. Some aromatics found in gasoline have high boiling points, they are also unstable, and the source of some residues and gums. Hence the levels of aromatics are often regulated (Wolf, 1995).

Gasoline varies widely in their physical and chemical properties, they normally boils between 30ºC -225ºC, **Figure 2.1**.

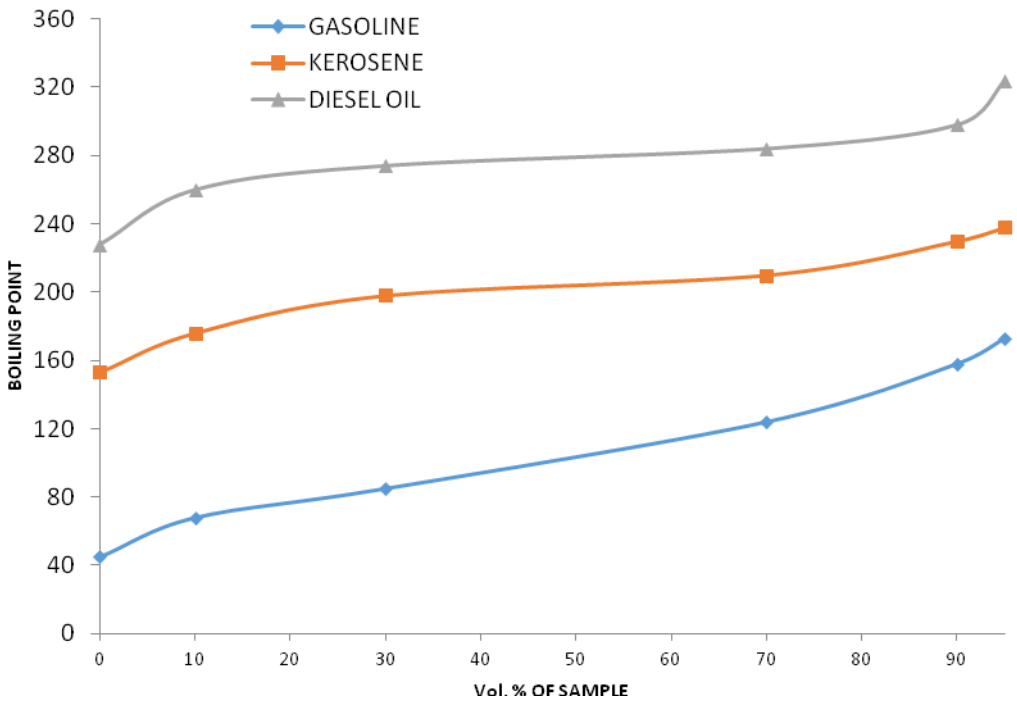

Figure 2.1: Distillation profile of gasoline, kerosene and diesel (Odebunm et al., 2002)**.**

A variety of specially formulated additives are added to gasoline to enhance its quality and performance, and to maintain standards during distribution and storage. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes (IARC, 1989). Many of these additives are also available in diluted forms as over-the-counter products for consumer addition (Renewable Fuels Foundation, 2009). In order to increase the gasoline's oxygen content the oil industry uses alcohols and ethers, both of which boost the octane rating, which was lowered with lower aromatics limits. Ethanol and Methyl Tertiary Butyl Ether (MTBE) are the primary oxygenates, with Tertiary Amyl Methyl Ether (TAME) and Ethyl Tertiary Butyl Ether (ETBE) used in limited quantities. Recently MTBE are not used as oxygenates due to their effect on the environment. The use of these Reformulated Gasolines (RFGs) is also as a result in limits on benzene, sulfur, and aromatics, and to achieve reductions in Volatile Organic Compounds (VOC), nitrogen oxides (NOx) and other toxics emissions (Wolf, 1995).

The composition of gasoline has changed significantly as commercial gasoline is produced by mixing different refinery streams at predefined concentration levels in order to meet quality market standards (Anderson, 2010). Automotive gasoline is graded based on the quality and the key distinctive quality parameter is the octane number, and more recently, the sulfur level (Adnan et al., 2013). Gasoline is a major profit generator for the petroleum industry where it represents about 70 % of refining profit (Singh et al., 2000). **Table 2.2** lists the common additives and why they are used.

Table 2.2: Gasoline additives and their uses

Additive	Purpose
• Detergents	➢ Eliminate or remove fuel system deposits
• Anti-icers	➢ Prevent fuel-line freeze up
• Fluidizer oil	➢ Used with detergents to control intake valve deposits
• Corrosion inhibitors	➢ To minimize fuel system corrosion
• Anti-oxidants	➢ To minimize gum formation of stored gasoline
• Metal deactivators	➢ To minimize the effect of metal-based components that may occur in gasoline
• Antiknock compounds (mostly organometallic compounds), e.g methyl cyclopentadienyl manganese tricarbonyl (MMT)	➢ To improve octane number

Source: Renewable Fuels Foundation, 2009

2.3.1 Gasoline production

James Miller Williams who made the first major commercial crude oil discovery refined the oil he produced and sold the product as lamp oil. In the following year, Colonel Edwin L. Drake discovered oil in Titusville, Pennsylvania. This discovery signaled the birth of the modern petroleum industry in the United State and numerous refineries were built to turn crude oil into kerosene for lamps and into lubricating oils for the machines of the industrial revolution. Gasoline was then considered a useless by-product until the invention of the gasoline engine in 1885 (Fagan, 1991).

Originally, “straight-run” gasoline was produced by simple distillation of crude oil without the use of chemical conversion processes. Shortly after 1900, motor vehicles began to appear in growing numbers, and gasoline began to have a marketable value as a refinery product. Around 1912, distillation of crude oil alone could not satisfy the rapidly growing

demand for gasoline. At this time, gasoline-range hydrocarbons were recovered from "wet" natural gas. However, only a limited amount of natural gasoline could be included in finished gasoline because of its high volatility and its relatively low anti-knock quality. Since then, petroleum refineries have developed several processes to contribute to the production of gasoline. In general, gasolines are blended from several petroleum refinery process streams that are derived by the following methods: direct distillation of crude oil, catalytic and thermal cracking, hydro cracking, catalytic reforming, alkylation, and polymerization. After the various gasoline streams have been blended, foul-smelling, corrosive, sulfur compounds are removed by hydrogenation (Lane, 1980). At present, the only commercial source of gasoline is petroleum, but it has been produced from shale oil, Athabasca tar sands, and by hydrogenation or gasification of coal (Sax and Lewis, 1987).

2.3.2 Quality of gasoline

2.3.2.1 Knock and Octane Number (ON) of gasoline

Knock is an abnormal combustion phenomenon that occurs in spark-ignition engines. Under normal operation, combustion of the air-fuel mixture within the engine cylinder is initiated by a spark and a flame front starts to propagate outwards. If the pressure and temperature of the unburned air-fuel mixture (ahead of the propagating flame front) reach high enough levels, spontaneous auto-ignition may occur in certain spots. This auto-ignition causes an extremely rapid release of much of the chemical energy stored in the unburned mixture, resulting in large pressure oscillations in the cylinder. In turn, these oscillations produce an audible metallic "pinging" sound and if severe enough, they can

cause major damage to engine components. This high sound which resembles knocking, is referred as “knocking”, the ability of a gasoline to resist knocking is rated as the octane number (Adnan et al., 2013; Heywood, 1988).

The ASTM defines two different types of ONs, the Research Octane Number (RON) and the Motor Octane Number (MON). Both methods use the same standard test engine but differ in the operating conditions. RON is measured in an engine running at 600 rpm and a fuel/air mixture at a temperature of 60°F, while MON is measured with the engine running at 900 rpm and a fuel/air mixture at a temperature of 300 °F (ASTM D-2699, 1999; ASTM D-2700, 1989). The average of RON and MON is known as the Antiknock Index (AKI) (Renewable Fuels Foundation, 2009). At octane levels below 100, the octane number of a given gasoline is the percentage by volume of isooctane in a blend with n-heptane that knocks with the same intensity at the same compression ratio as the gasoline when compared by one of the standardized engine test methods (Ghosh et al., 2006). RON values are typically 8 to 10 numbers higher than MON values and the difference between the RON and MON of a gasoline is called the “sensitivity”(Wolf, 1995).

Octane number is a direct function of the composition. Aromatics and branched iso-paraffins have higher octane numbers than the corresponding paraffins. Petrol RON and MON can have an important influence on engine performance and durability when the engine’s octane requirement is not satisfied (Barnett, 2001). Vehicles are designed and calibrated for a certain octane rating and when a customer uses gasoline with an octane rating lower than required, knocking may result. Engines equipped with knock sensors can handle lower octane ratings by retarding the spark timing, but this will increase fuel consumption, impair driveability and reduce power, and knock may still occur. Using

gasoline with an octane rating higher than recommended will not cause problems (AECC et al., 2014). Increasing the minimum octane rating available in the market place has the potential to help vehicles significantly improve fuel economy and, consequently, reduce vehicle CO_2 emissions. While the improvement will vary by power train design, load factor and calibration strategy, among other factors, vehicles currently designed for 91 RON gasolines could improve their efficiency by up to three percent if manufacturers could design them for 95 RON instead. Octane rating is becoming an especially important limiting factor in future efficiency improvements because new, more efficient engine designs, such as smaller displacement turbo-charged engines, are approaching their theoretical knock limits when using lower octane rated gasoline. Raising the minimum market octane to 95 RON will enable manufacturers to optimize power train hardware and calibrations for thermal efficiency and CO_2 emissions. All of these technologies and actions will be needed to meet the highly challenging fuel economy and CO_2 requirements emerging in many countries (Worldwide Fuel Charter, 2013).

Table 2.3: Octane model along with their pure-component RONs and MONs

	RON	MON		RON	MON
Paraffins			**Naphthenes**		
n-butane	94	89.6	cyclopentane	100	84.9
isobutane	102	97.6	cyclohexane	82.5	77.2
n-pentane	62	62.6	*m*-cyclopentane	91.3	80
i-pentane	92	90.3	C7 naphthenes	82.0	77
n-hexane	24.8	26	C8 naphthenes	55	50
C6 monomethyls	76	73.9	C9 naphthenes	35	30
2,2-dimethylbutane	91.8	93.4			
2,3-dimethylbutane	105.8	94.3	**Aromatics**		
n-heptane	0	0	benzene	102.7	105
C7 monomethyls	52	52	toluene	118	103.5
C7 dimethyls	93.76	90	C8 aromatics	112	105
2,2,3-trimethylbutane	112.8	101.32	C9 aromatics	110	101
n-octane	15	20	C10 aromatics	109	98
C8 monomethyls	25	32.3	C11 aromatics	105	94
C8 dimethyls	69	74.5	C12 aromatics	102	90
C8 trimethyls	105	98.8			
n-nonane	20	20	**Olefins/Cyclic Olefins**		
C9 monomethyls	15	22.3	*n*-butenes	98.7	82.1
C9 dimethyls	50	60	*n*-pentenes	90	77.2
C9 trimethyls	100	93	*i*-pentenes	103	82
n-decane	30	30	cyclopentene	93.3	69.7
C10 monomethyls	10	10	*n*-hexenes	90	80
C10 dimethyls	40	40	*i*-hexenes	100	83
C10 trimethyls	95	87	total C6 cyclic olefins	95	80
n-undecane	-35	-35	total C7d	90	78
C11 monomethyl	5	5	total C8d	90	77
C11 dimethyls	35	35			
C11 trimethyls	90	82	**Oxygenates**		
n-dodecane	-40	-40	MTBE	115.2	97.2
C12 monomethyl	5	5	TAME	115	98
C12 dimethyls	30	30	EtOH	108	92.9
C12 trimethyls	85	80			

Source: Ghosh et al., 2006

2.3.2.2 Volatility of gasoline

The ability of gasoline to change into vapour is very important since gasoline is metered in liquid form, but must atomize before it enters the cylinder of an engine. Gasoline that vaporize too readily (highly volatile) will cause decreased fuel flow to the engine, resulting in rough engine operation or stoppage known as vapour lock. Conversely, gasolines with

lower volatility may cause hard starting and poor warm-up and acceleration, as well as unequal distribution of fuel to the individual cylinders, which may cause knock, **Table 2.4**.

Table 2.4: Effect of gasoline volatility on vehicle performance

Volatility too low	Volatility too high
• Poor cold start • Poor warm up performance • Poor cold weather driveability • Increased deposits in crankcase, combustion chamber, and spark plugs • Unequal fuel distribution in carburetted vehicles • Potentially increased emissions	• Hot driveability problems/vapour lock • High evaporative emissions/ canister overload and purge • Fuel economy may deteriorate

Source: Renewable Fuels Foundation, 2009

Vapour pressure and distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting, warm up, and tendency to vapour lock with high operating temperatures or high altitudes. Maximum vapour pressure limits for gasoline are legally mandated in some areas as a measure of air pollution control. The distillation (volatility) characteristics of hydrocarbons have an important effect on their safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, properties, and the behavior of the fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapours (ASTM D-323, 1999; ASTM D-86, 2000).

2.3.2.3 Sulfur in gasoline

High sulfur levels in fuel affects many operating systems in vehicles, **Table 2.5**.

Table 2.5: Effects of sulfur on fuel sensitive technologies

Technology	Sensitivity to fuel quality	Key fuel parameter and threshold
On board diagnostics	medium	Sulfur < 150ppm
Lean burn	high	Sulfur < 30ppm
Stratified charge, gasoline direct injection	high	Sulfur < 30ppm
Advance catalyst formulation	high	Sulfur < 30ppm

Source: Renewable Fuels Foundation, 2009

Techniques used to reduce noxious emissions, or to reduce fuel consumption, are becoming very sensitive to contaminants in the exhaust stream and for gasoline vehicles. Sulfur content is the most critical parameter, primarily due to its effect on catalyst performance and durability (Barnett, 2001). Upon combustion, fuel sulfur is oxidized to sulfur oxides, primarily sulfur dioxide (SO_2) and some sulfur trioxide (SO_3). These are known to inhibit catalyst function of automobile exhaust catalyst; they may also be converted to acids and acid mists, that promote rusting and corrosion of engine parts and exhaust systems, and also increase particulate matter (Row and Doukas, 2008). Nitrogen Oxide (NO_X) decomposition potential is completely poisoned by sulfur; NO_X is a major pollutant of automobiles (Barnett, 2001).

Free sulfur or reactive sulfur in gasoline is determined in copper corrosion test; also sulfur in gasoline may also be in the form of mercaptant (Wolf, 1995). The American Automobile Manufacturers Association (AAMA) and the Association of International Automobile

Manufactures (AIAM) as well as the Coordinating Research Council recently conducted independent studies and their results support the conclusion that all in-use vehicles will experience improved emission control with lower sulfur gasoline. The Environmental Protection Agency (EPA) of the United States has therefore recommended the use of ultra low sulfur. The European Union (EU) has introduced environmental specifications aimed at providing sulfur free fuels (Row and Doukas, 2008; Worldwide Fuel Charter, 2013).

2.4 KEROSENE

The word kerosene which is derived from the Greek word 'keros', meaning 'wax' was discovered in 1853 by Abraham Gesner, a British physician. He developed a process to extract the inflammable liquid from asphalt, a waxy petroleum mixture. The term "kerosene" is a generic term referring to a fraction of crude oil that boils approximately in the range 145 to 300°C and consists of hydrocarbons approximately in the C9-C16 range. Kerosenes are the lighter end of a group of petroleum substances known as middle distillates, the heavier end being gas oils. They generally consist of a complex mixture of branched and straight chain paraffins and naphthenes (at least 70% by volume), aromatic hydrocarbons such as alkyl benzenes and alkylnaphthalenes (up to 25%) and olefins (less than 5% by volume) (EPA, 2011; Okonkwo et al., 2012). In the UK, kerosene is also known as paraffin and home heating oil. As a result of the higher proportion of paraffins which are saturated hydrocarbons, kerosenes are generally stable products (Chilcott, 2006). Kerosene lamps are widely used for lighting in rural areas, where electrical distribution is

not available or too costly for widespread use. Kerosene is therefore regarded as the petroleum fuel for the poor and rural communities (Energy Commission, 2006).

There are several refinery processes that make hydrocarbon streams suitable for blending kerosene-range products. Kerosene may be obtained either from the atmospheric distillation of crude oil (straight-run kerosene) or from cracking of heavier petroleum streams (cracked kerosene). The kerosenes can be further treated by a variety of processes to remove or reduce the levels of undesirable components, e.g. sulfur, nitrogen or olefinic materials. This additional processing also reduces compositional variation and enriches components that improve performance (cycloalkanes and isoalkanes). In practice, the major refining processes used are hydrodesulfurization (treatment with hydrogen to remove sulfur components), washing with caustic soda solution (to remove mercaptants and other sulfur-containing components), and hydrotreating (to remove olefins, sulfur- and nitrogen-containing components). For instance, hydrodesulfurized kerosene is obtained by treating a kerosene-range petroleum stock with hydrogen to convert organic sulfur to hydrogen sulfide, which is then removed. These subsequent treatments may blur the distinction between “straight-run” and “cracked” kerosenes (CONCAWE, 1996, 1995). While kerosenes are similar in composition, the precise composition of a specific kerosene-range refinery stream depends on the crude oil from which the kerosene was derived and on the refinery processes used for its production. Because they are complex petroleum derived hydrocarbons, substances in this category are typically not defined by detailed compositional data but instead by process history, physical properties, and product-use specifications (ASTM D-1655, 2001).

In Ghana, two main types of kerosene are available, domestic kerosene and aviation turbine kerosene (ATK) used as fuel for aircrafts (CDU, 2007). The acidity expresses the content of macromolecule organic acid normally because aviation kerosene doesn't contain water-soluble acid as leaving factory. Macromolecule organic acid mainly contains naphthenic acid; higher levels may corrode metal material seriously. Acidity of aviation kerosene is a critical requirement and must be certified before it is used. The acidity level in aviation fuel is capped at 0.015mg KOH/g. This is because above this threshold the jet engine parts can corrode leading to some vital parts of the jet engine becoming insulators instead of conductors. Acidity level of aviation kerosene therefore is a critical requirement and must be certified before it is used (Xing et al., 2008). It is important to note that kerosene is not a synonym for "jet fuels" which are a distinct class of petroleum distillate product containing a range of chemical additives (Chilcott, 2006).

2.5 METHODS TO CHECK GASOLINE ADULTERATION

The American Society for Testing and Materials International (ASTM International) has developed and documented the test methods for most of the widely used materials including petroleum products. Many ASTM tests for gasoline, kerosene, diesel and other petroleum products have been standardized and documented. Some of these tests involve determination of physical and chemical properties while others provide a measure of suitability of the fuel for use in automobiles from the point of engine performance / air pollution generated. Though no ASTM test is specifically designed to measure the adulteration of petrol and diesel with kerosene, some tests namely Density test, Evaporation test, Distillation test, Gas Chromatography, may be used to determine the

adulteration of fuel. The most traditional methods to qualitatively and quantitatively estimate fuel composition are gas chromatography (GC) (Pedroso et al, 2008) and high-performance liquid chromatography HPLC (Zinbo, 1984). These techniques involve the separation of mixtures of compounds by differential rates of elution by passing through a chromatographic column, governed by their distribution between a mobile and a stationary phase. Infrared spectroscopy has been reported for quantitative analysis of ethanol and methanol in fuels by using Attenuated Total Reflectance (ATR) (Battiste et al, 1981). Nuclear Magnetic Resonance (NMR) can be coupled with pattern recognition chemometric models as an analytical tool to determine the quality of gasoline. NMR spectroscopy has especially become a powerful tool for gasoline analysis without pre-treatment, mainly due to the fact that measurements are fast and can be automated, allowing the analysis of a large number of samples in a short period of time. In general, the typical chemical shifts in the spectrum are subdivided into regions and each one is associated with a specific molecular substructure, for example, aromatic, olefinic, and aliphatic hydrogen. A huge amount of data in NMR fingerprinting is produced, and chemometric analysis is frequently needed to extract the desired information (Monteiro et al., 2009). In another approach, related to origin determination purposes, Rigo et al. (2009) combined hydrogen nuclear magnetic resonance (1H NMR) fingerprinting of gasoline with pattern-recognition analyses to distinguish Brazilian commercial gasoline, processed in different states of Brazil (Rigo et al., 2009).

However, because fuel quality standards and test methods were not designed specifically for detecting adulteration, it means that it is possible to adulterate without violating the standards. The Centre for Science and Environment (CSE) in India after an independent

assessment of the fuel adulteration stated that checking for compliance with fuel quality standards does not necessarily imply testing for adulteration. It is important to differentiate between detection of adulteration and monitoring of non-compliance with fuel quality standards. This in other words means that compliance with fuel quality standards does not necessarily mean that fuels are not at all adulterated (Roychowdhury et al., 2002).

For more accurate detection, alternative testing methods and protocols have been adopted for surveillance over the world especially in areas where fuel adulteration is practiced. There have been a number of methods proposed for checking adulteration of petrol.

2.5.1 Spectroscopic methods

Multidimensional fluorescence techniques like synchronous fluorescence scan (SFS) and excitation emission matrix fluorescence EEMF are used in providing information about samples. For multi-fluorophoric systems, the importance of SFS and EEMF has been well-established (Patra and Mishra, 2002). The resulting excitation–emission data matrix provides a total intensity profile of the sample over the range of excitation and emission. SFS in particular has been found to be useful for the analysis and identification of oils (John, 1976).

Polycyclic aromatic hydrocarbons (PAHs) profile varies with the boiling range of the fuel. Low boiling gasoline contains PAHs with a lesser number of fused rings in a molecule, while the PAH fraction in diesel has a higher number of fused rings in a molecule. Hence the PAH profile in kerosene is different from petrol and diesel. Hence, the fluorescence fingerprints corresponding to different fuel compositions. PAHs have good molecular

fluorescence properties due to rigid π electron systems in the fused ring structures. This has been shown in a series of works by Patra (2002) and it was possible to introduce some analytical methods based on synchronous fluorescence techniques (Patra and Mishra, 2002a, 2002b). Furthermore, high fluorescence sensitivity allows their determination at very low concentrations. Synchronous fluorescence spectroscopy is a relatively simple and rapid approach for the simultaneous analysis of multi fluorophores. The adulteration of petrol and kerosene can be assessed with a significant accuracy using synchronous fluorescence spectroscopy (Eiroa et al., 2000).

Patra and Mishra (2002) discussed recent developments in various synchronous fluorescence methods for analysis of multi-component systems. Single-wavelength fluorescence measurement is limited in its ability to analyze complicated multi-component samples when they have severely overlapping emission and/or excitation spectra. This can be overcome by using synchronous fluorescence scan (SFS), where overlapping of spectra can be minimized. The selectivity of SFS can still be increased by taking derivative spectrum, applying different multivariate methods, selective fluorescence quenching, three-dimensional synchronous measurement or using some of these procedures in combination. The study showed kerosene shifts the SFS maximum of petrol towards the red, whereas, for diesel, a blue shift is observed. Calibration graphs obtained from SFS intensity measurement are found to be efficacious in the whole range (0–90% v/v) of kerosene, and gave a good linearity in the adulteration range generally found in the field (0–50% v/v) for petrol and diesel (Patra and Mishra 2002b).

2.5.2 Capacitance change method

Gas sensors based on capacitive properties or chemocapacitors (CAP) have been used in the study of organic volatile substances. The CAPs have been constructed in different geometries. The most common structure is planar with interdigitated electrodes having as sensitive layer conducting oxides (Ponce et al., 2009). The chemocapacitor is based on the change of capacitance caused by a change of dielectric constant, due the modifications in polarization properties of molecules and/or atoms inside the active layer by external perturbations, such as the interaction with volatile organic compounds (VOC). These layers are permeable for permitting the interaction between the analytes and the sensors (Pearce et al., 2003). This method has been used to study the composition of fuels. Using porous silicon as active layer they studied the dielectric response for methanol-water and ethanol-water. In both systems, increasing the alcohol concentration led to the elevation of the capacitance (Kim et al., 2000). Wiziack et al. (2002) used an array of eight capacitive polymeric sensors to discriminate gasoline, diesel, ethanol and some common fuel adulterants as toluene, hexane and water. These results depend on the polymeric material used as active layer and their interaction with organic volatile compounds (Wiziack et al., 2009).

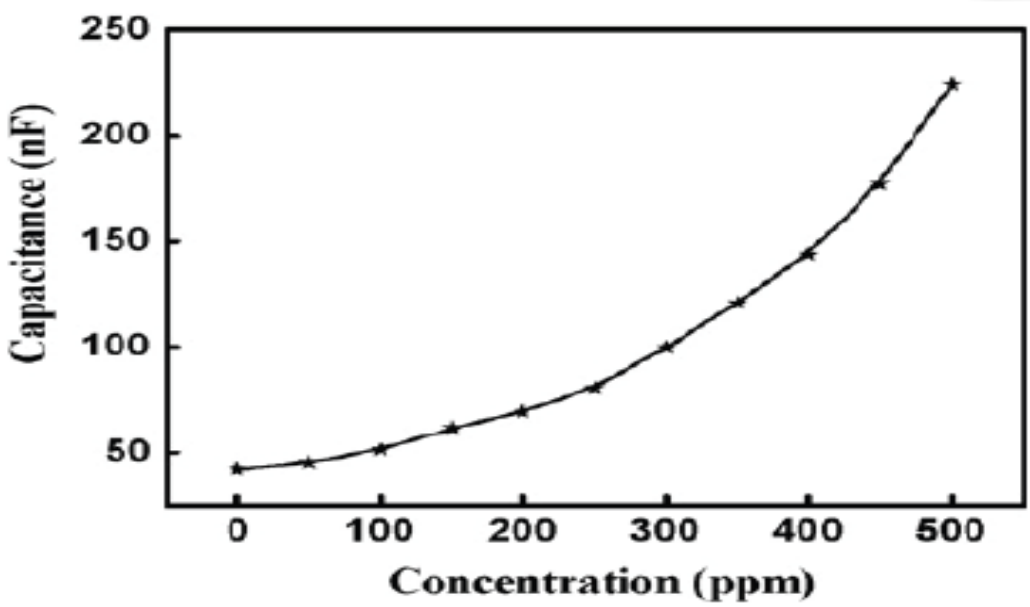

Figure 2.2: Change of capacitance with the concentration of ethanol at 200 Hz signal frequency (Li et al., 2007)

2.5.3 Refractive index method

A technique for detection/estimation of adulteration of gasoline/ diesel by kerosene using optical fibre sensor has been reported by Roy (1999). The method of Roy (1999) is particularly suitable for adulteration detection in petrol as its refractive index remains lower than that of core of the optical fibre even after mixing with 50% kerosene which results in smooth (and almost linear) variation of received power with % adulteration (Gupta and Sharma, 2002).

Brazil also suffers from fuel adulteration practice and studies focused on determining fuel composition by refractive index changes in optical fibres have been published. Thus, Falate

et al. (2005) studied the vapour of hydrocarbons and possible adulterants in gasoline. In their work they used fibre optics connected to long period gratings to measure changes in attenuation peak wavelength for ethanol gasoline mixtures in different proportions, and adulteration by addition of other solvents such as naphtha, turpentine and paint thinner in Brazilian commercial gasoline (Falate et al., 2005).

2.5.4 Extrinsic marker methods

The invention provides a method of detecting an adulterant in gasoline, aviation turbine fuel or diesel, with the help of a marker, wherein the adulterant is kerosene. The method involves detecting the presence of an organo sulphur marker in the fuel.

US Patent No. 5229298 (1992) disclosed a method of analyzing nitrogen bearing marker dye concentration in liquid fuels. The concentration of marker has been analyzed by gas chromatography equipped with nitrogen phosphorescence detector using trioctyl amine as internal standard. However, the markers disclosed here are prepared by various expensive protocols and method deals only with the detection of adulteration in gasoline fuels and not in the diesel fuels (Richfield, 1993). Also, US Patent No. 7858373 (2007) discloses various planar six membered cyanurate, isocyanurate or 1, 3, 5- triazine derivative markers to detect the adulteration in various liquid fuels such as commercial gasoline, diesel, biodiesel and ethanol blended gasoline. The presence of marker is determined by mass spectroscopy, as it displays the presence of characteristic m/z peaks of respective markers. However the disclosed markers are synthesized by various steps and hence marker is expensive and requires skilled chemist to understand the symmetry of the molecules and to analyze the data generated by the sophisticated mass spectroscopy (Haas, 2010).

2.5.5 Electrical conductivity method

There are several types of gas sensors based on the change in electrical dc resistance upon exposure to volatile compounds. They are known as chemoresistive sensors and are usually made from metal oxide semiconductors (MOS), MOS field-effect transistors (MOSFET) or, more recently, from conducting polymers (CP). Such sensors have been widely used to detect reducing and oxidizing gases as, for instance, petrol vapours in filling stations, ethanol in exhaled air etc (Gründler, 2007). CP based sensors have attracted much interest, specially for electronic noses, which are analytical instruments developed to mimic the human nose, and are basically formed by an array of dissimilar gas sensors, that generate different response patterns for different types of smells, attached to a pattern recognition system (Gardner and Bartlett, 1999). The reasons for using CPs for this purpose are that a huge number of different CPs can be synthesized, they respond to a wide range of volatile compounds and they operate at room temperature, which implies in low power consumption and hence, portability (Li et al., 2008). Interestingly, although poly*p*-xylylenes is known for its excellent insulating property, aryl-substituted derivatives become conducting upon doping and are highly stable to air and humidity, being very convenient for gas sensor. The sensors usually consist of thin (1 – 50 μm) doped polymer films deposited by spin-coating, drop–casting or other technique onto interdigitated electrodes. These, depending on the desired distance between digits can be obtained by several methods as, for instance, circuit printing (Li et al., 2008).

2.5.6 Ultrasonic technique

The effect of adulteration of petrol by diesel and diesel by kerosene on the speed of sound in the fuel sample has been investigated and has concluded that it is feasible to develop a cheap and easy to operate equipment which measures and uses the measured speed of sound to estimate the adulterants in fuel. Adulteration leads to the change in density as well as viscosity of the fuel. Since both of these parameters influence the speed of sound in a fluid, it is expected that the speed of sound in the adulterated fuel would be different from that in un-adulterated fuel (Gupta and Sharma, 2002).

2.5.7 Titration techniques

Phase titration method is one of the old methods used in detecting gasoline adulteration. The method was first investigated by Diamond et al (1988). The method suffered some setbacks and was later modified to a procedure showing considerable improvements. The approach was based on the differences between the solubility of petrol and kerosene in a water-based mixed solvent system arising from the variations in the hydrocarbon content (Diamond et al., 1989). A spectrophotometric titration permits effective end – point detection in turbid metric titrations, and the same approach can also be applied to the clarification titrations depending on removal of turbidity (Kimura et al., 1990). Hence Bahari et al thus used a rapid phase – titration procedure. The study described the objective of providing an alternative experimental procedure for a modified phase – titration method which shows major improvements over currently available approaches and has considerable potential as the basis of an infield method of analysis. The range of kerosene

adulteration covered (0 –20% v/v) represents the extremes of adulteration found in the field. They found that the calibration graphs are linear and are therefore especially efficacious for field applications. The method showed no significant dependence on temperature (Bahari et al., 1990).

2.6 QUALITY ASSESSMENTS OF GASOLINE AT FUEL STATIONS

In most growing cities, gasoline or petrol driven vehicles comprise over 80% of the total vehicles registered (Kathuria, 2002). It is therefore imperative that the standards for these fuels are regulated by governmental agencies. Unfortunately, in many countries people intentionally add cheaper organic substances in an attempt to raise profit margins (Pereira et al., 2006).

Pakistan is one of the countries that have witness a remarkable increase in the number of vehicles within a short period of time creating a corresponding demand for motor gasoline. However, refineries in the region are struggling to produce gasoline that meet the ever growing demand and also comply with the quality specifications of current automobile technology and the environment. Gasoline prices at the pump are mostly higher than other petroleum products making this expensive product attractive for adulteration as it offers higher profit margin. Consequently, gasoline quality issues gained great importance in Pakistan as the general public became conscious of related problems. Yasin et al (2008) took the onus and decided to appraise motor gasoline in the Multan District of Pakistan. Samples were taken from retail outlets of different marketing companies and the

physicochemical parameters tested using standard ASTM procedures that are generally used in the assay of gasoline worldwide. The study concluded that the stations gasoline conforms to the specification of Pakistan. However, the gas chromatographic results, showed the presence of heavier carbon chains (C14 and C15), in all the stations sampled. These heavier compounds are not part of gasoline composition and could be present as a result of mixing with heavier products like kerosene (Yasin et al., 2008). Hence despite the measurements of gasoline physicochemical parameters and their complaints with regulations, many adulterated gasolines are approved.

Thus in the work of Wiedmann et al (2005), physicochemical parameters like distillation temperatures, Motor Octane Number (MON), Research Octane Number (RON), Antiknock Indices values and ethanol percentage of gasolines obtained from different gas stations in the State of Rio de Janeiro were determined and the results were compared with the Brazilian National Petroleum Agency regulation standards. However the study integrated clusters analysis of the physicochemical parameters in the detection of adulteration in the gasoline. This provided more differences between samples resulting in better discrimination. It also offers an alternative bases for drawing conclusion other than quality specifications (Wiedemann et al., 2005).

The Centre for Science and Environment in India did an inspection of motor fuel quality at fuel dispensing stations, oil depots and tank lorries in the suburb of Delhi. In their initial assessment of existing quality monitoring prescribed by the Bureau of Indian Standards, fuel samples were deliberately adulterated and sent to the laboratory for analysis. The

findings indicated that the current fuel quality specifications and testing methods for fuel quality monitoring as prescribed by the Bureau are not adequate to catch adulteration. Limited set of tests were therefore adopted for study by the centre, leading to the discovery of stunning irregularities in gasoline samples (Roychowdhury et al., 2002).

Kerosene adulteration of commercial fuel (gasoline and diesel) was investigated in the city of Colombo in Sri Lanka. A method based on the polycyclic aromatic hydrocarbons (PAHs) profiles present in different fuel types was developed. Several analytical parameters were evaluated against the level of kerosene added to the synthetic mixtures. The linear regressions with high correlation coefficient were selected as the analytical parameters for the assessment of adulteration of the commercial samples. The results showed that twenty percent of the stations had not adulterated their gasoline and the levels estimated were less than 3 %, another twenty percent had adulteration levels around 15 %. Fifty percent of the stations had adulterations around 30 % and ten percent had an adulteration level as high as 48 %. Quantitative determination of adulteration was easier and more precise (Kulathunga and Mahanama, 2013).

In an adulteration identification study of gasoline from service stations in Riyadh, the Resonance Raman spectra and other two spectroscopic techniques were used to study the effects of popular adulterant by adding a known quantity of kerosene to pure gasoline. The fluorescence spectrum for kerosene shows great variation from gasoline and that provide a bases for identification as well as quantification of similar adulteration. The results revealed kerosene adulterations to the magnitude of 60% proportion of the kerosene (Reem, 2008).

In the work of Ozaki et al (2009), 40 gasoline samples from fuel service stations in Sao Paulo and had earlier been analyzed by a certified laboratory were subjected to an array of conducting polymers sensors, which provided better discrimination and classification of adulteration (Ozaki et al., 2009). Petrol stations across the city of Pune in India were found to have adulterated their gasoline and diesel fuels with kerosene in the range of 20-40 percent. The synchronous fluorescence scan technique, as mentioned earlier was employed in quantifying the amount of adulterant (Taksande and Hariharan, 2006).

In cognizance of the above, it is clear that there is no guarantee for gasoline quality at the point of sale, hence an urgent need for quality assessment of the product at fuel stations. Obviously, a tailor made method that is cheaper and more precise is necessary for effective appraisal of adulteration. Unfortunately, while the number of vehicles and fuel stations in Ghana has increased tremendously, studies on gasoline quality at the Ghanaian market cannot be verified. The next chapters reports on methods and findings of the assessment of gasoline quality in Accra Metropolis of Ghana.

CHAPTER THREE

3 METHODOLOGY

3.1 MATERIALS

All the chemical reagents used in this study were of analytical reagent grade and conform to the specifications prescribed by the committee on analytical reagents of the American Chemical Society for the testing of petroleum and petroleum products. The glassware were washed with soap solution, subjected to acid cleaning for about 3 days, rinsed with distilled water and dried in an oven.

3.1.1 Chemical reagents

The following chemical reagents were used; potassium hydroxide (KOH), anhydrous isopropyl alcohol, toluene, potassium acid phthalate, phenolphthalein indicator solution, p-naphtholbenzein indicator solution, dye and barium hydroxide.

KOH (pellets), barium hydroxide (powder) and potassium acid phthalate (powder) were obtained from AnalaR NORMAPUR, United Kingdom. Toluene and *p*-naphtholbenzein indicator solution were obtained from BDH, England. Anhydrous isopropyl alcohol was obtained from ALPHA CHEMIKA, Mumbai-India.

3.2 SAMPLE COLLECTION

Three different categories of samples were collected. The first category was for the examination of physicochemical properties of petroleum distillate fractions (fuels). 1.5 litres each of 15 petroleum fractions were sampled from the crude distillation unit (CDU) of Tema Oil Refinery (TOR). The 15 petroleum fractions consisted of light naphtha, heavy naphtha, kerosene, light gasoil, heavy gasoil, refined from three different types of crude oils; Forcados, Bonny Light and Brass River.

The second category was10 litres each of pure gasoline and domestic kerosene collected from TOR for adulteration simulation studies.

The third category was motor gasoline purchased from 20 fuel retail outlets in Accra Metropolis (**Figure 3.1**) and reference (control) samples collected from discharging ships at the Tema Harbour and TOR. Three (3) control samples each were gasoline sampled from different ships at the Tema harbour before discharging and market storage tanks at TOR (**Table 3.1**).

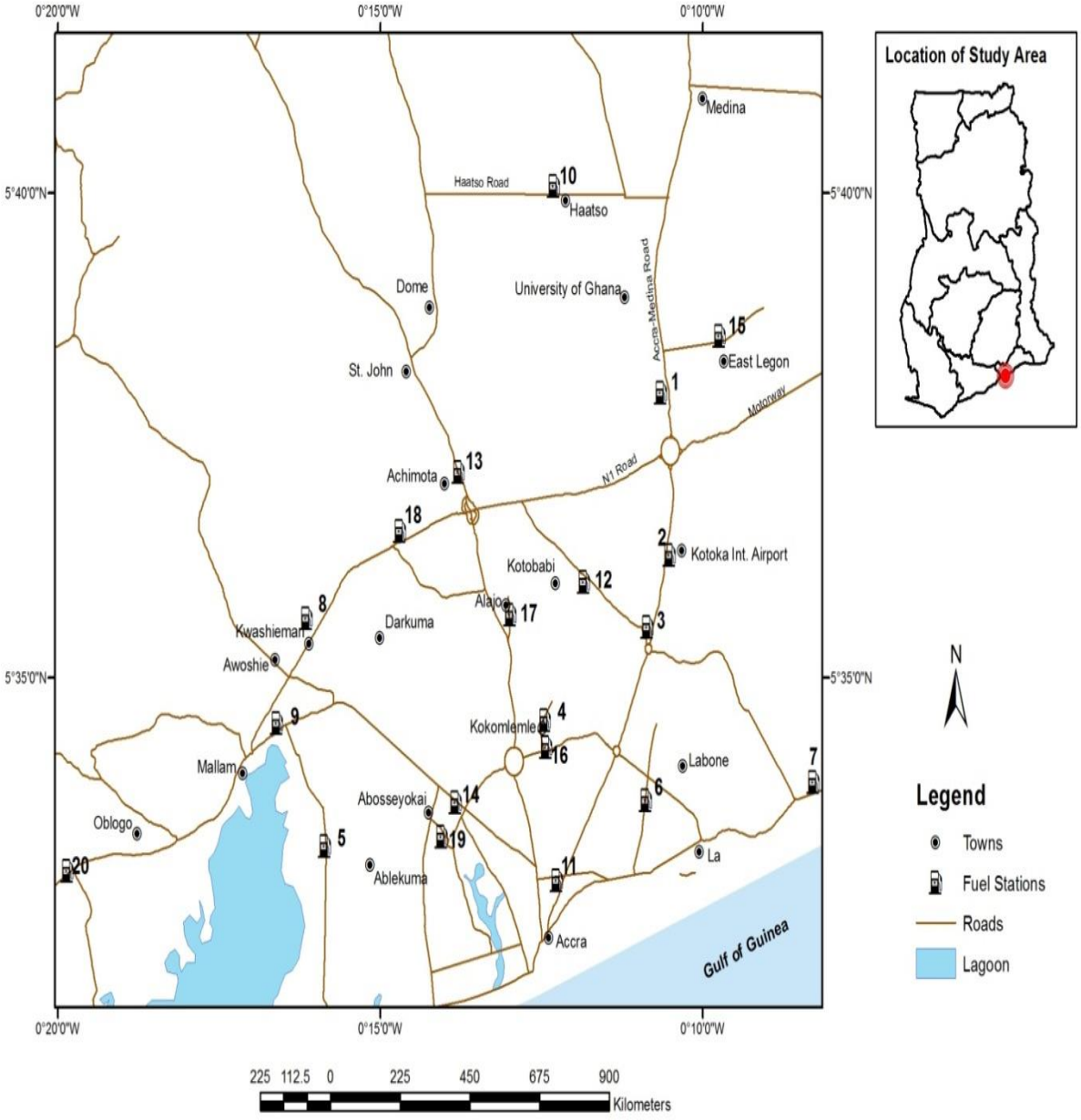

Figure 3.1: Map of study area, showing sampling locations (fuel stations)

Table 3.1: Gasoline samples from filling stations in Accra Metropolis and reference sites

Name of group	Site/Sample #	Location	Name of company
SHELL	1	East Legon	SHELL
	2	Kotoka airport	SHELL
	3	37	SHELL
	4	Kokomlemle	SHELL
	5	Dansoman	SHELL
GOIL	6	Osu	GOIL
	7	Labadi	GOIL
	8	Kwarshieman	GOIL
	9	Sakaman junction	GOIL
TOTAL	10	Haasto	TOTAL
	11	Makola	TOTAL
	12	Pigfarm	TOTAL
	13	Achimota	TOTAL
	14	Kanershie	TOTAL
MIXED	15	East Legon	SEL
	16	Circle	SO
	17	Alajo	NASONA
	18	Lapas	FRAGA OIL
	19	Abossey Okai	ALLIED OIL
	20	Weija	STAR OIL
SHIP	21	Tema Harbour	ELAN VITAL
	22	Tema Harbour	ESHIP EAGLE
	23	Tema Harbour	NISIDA
TOR	24	TOR	TOR
	25	TOR	TOR
	26	TOR	TOR

3.3 PHYSICAL AND CHEMICAL PROPERTIES

3.3.1 Monitoring of acidity levels and pattern of petroleum fractional distillates (Category 1)

The petroleum fractional distillates are light naphtha, heavy naphtha, kerosene, light gasoil and heavy gasoil. The acidity contents were determined as indicated below. In addition, the density, distillation temperatures and sulfur contents were measured to characterize the products.

Acidity of naphtha and kerosene

A weighed amount (95-105g) of sample was dissolved in titration solvent and titrated with alcoholic KOH to a colorimetric endpoint (ASTM D3242). The acidity was expressed as mg KOH/g (**Appendix 1**).

Acidity of gasoil

A weighed amount of the gasoil was dissolved in titration solvent and titrated to a potentiometric endpoint using a titroprocessor following ASTM method D664. The acidity was expressed as mg KOH/g (**Appendix 2**).

Density

Densities of all fractions were measured following ASTM method D1928. The fraction was brought to a specified temperature and a test portion transferred into a cylindrical container that had been brought to approximately the same temperature. The appropriate hydrometer, also at similar temperature, was lowered into the test portion and allowed to

settle. After temperature equilibrium was reached, the hydrometer scale was read and the temperature of the test portion taken. The observed hydrometer reading was reduced to the reference temperature at 15 °C.

Distillation temperatures

The ASTM method D86 was followed and the manual atmospheric distillation apparatus Herzog HDA 620 was employed. 100mL of sample was placed in a round-bottom flask and heated at a rate specified for a sample with its vapour pressure characteristics. Vapour temperatures were recorded when the first drop of condensate was collected (i.e. initial boiling point) and at recovered volumes of 5mL, 10mL, 15mL, 20mL, and every subsequent 10mL interval.

Sulfur

Sulfur was determined by ASTM D2622 method and the Horiba sulfur analyzer was used. A test portion of the petroleum fraction was placed in the X-ray beam of the apparatus and the intensity of the sulphur X-ray fluorescence was measured and used to calculate the sulphur content of the sample (ASTM D2622).

3.3.2 Pure gasoline and domestic kerosene (Category 2)

Acidity, density, distillation temperatures and sulfur content in pure gasoline and kerosene were measured according to the procedure in **3.3.1**; the hydrocarbon composition and RON of the pure gasoline were measured in addition.

Hydrocarbon Composition

Gas chromatography (GC) method was used and the sample preparation and injection was in accordance with ASTM D5134 employing Agilent 6890N Detail Hydrocarbon Analyzer (DHA), hyphenated with flame ionization detector (FID). The capillary column (DB-1) was of length 40m and diameter 0.099mm, a film thickness of 0.20µm with temperature limits of -60 ºC to 325 ºC. The flow rate inside the column was set at 1.3 ml/min. The temperature programmed 35ºC to 230 ºC was used as follows: Initial temperature of 35 ºC, held for 2.6 minutes, then ramp at 50 ºC/min to second temperature of 45 ºC, held for 3.0 minutes, ramp at 5 ºC/min to third temperature of 60 ºC, held for another 3.0 minutes, then ramp at 9.5 ºC/min to 200 ºC, held for just 1.0 minutes before it ramp to the final temperature of 230 ºC, with a total run time of 27.54 minutes. Each eluting peak was identified by comparing its retention time to a table of retention times, **Appendix 3.**

Research Octane Number (RON)

The standard test method for research octane number of spark-ignition engine fuel (ASTM D2699) was adopted. A standardized single cylinder, four-stroke cycle, variable compression ratio Cooperative Fuel Research (CFR) engine was used.

3.3.3 Gasoline adulterated with domestic kerosene

Simulated kerosene adulterated gasoline blends were prepared by adding different proportions of the pure domestic kerosene into the pure gasoline. Gasoline and kerosene

were mixed in: 100:00, 95:05, 90:10, 80:20, 70:30, 60:40 and 50:50 ratios. Density, distillation temperatures and sulfur content of these synthetic blends were studied. The measurements were in accordance with the procedure described in **3.3.1.**

The acidity of the adulterated gasoline was measured using the in-house SDT. The standard test method for acidity of kerosene (ASTM D3242) described in **3.3.1** was also employed to measure the acidity of the blends as a verification of the in-house SDT method described below.

Acidity of gasoline by simple direct titration (SDT) method

A known weight of the sample between 95 to 120g was taken into a 500ml Erlenmeyer flask. Two drops of p-naphtholbenzein indicator solution was added to the sample and the flask swirled to mix. The mixture was then titrated against a standardized 0.01N KOH to a definite colour change and the flask immediately covered. The colour change persisted for at least 10 seconds. The acidity is expressed as milligrams of potassium hydroxide per gram of sample (**Appendix 1**), required to titrate a sample from its initial colour in p-naphtholbenzein indicator solution to permanent colour change.

3.3.4 Gasoline from retail outlets and reference sites (Category 2)

Density, distillation temperatures and sulfur content of the commercial gasolines were measured according to the procedure in **3.3.1**; the in-house SDT method was adopted for the measurement of the gasoline acidity, hydrocarbon composition and research octane

number **(**RON) were measured as described in **3.3.2**. Vapour pressure was measured as follows.

Vapour Pressure

The Stanhope-Seta equipment was used for measuring the Reid Vapour Pressure (RVP). The liquid chamber of the apparatus was filled with the chilled sample and the Reid method (ASTM D323) was followed.

3.3.5 Data analysis

The descriptive statistics and paired t-test comparisons of means were conducted to determine the different distribution of adulteration contents among the gasoline samples. Principal component analysis (PCA) was used to establish the source profiles of gasoline associated with different samples according to the distribution of adulteration contents. All statistical analyses were performed using SPSS version 17 for windows.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

Evaluation of gasoline quality is not a straight forward assignment. Comprehensive range of analytical protocols covered by international guides, mainly from the American Society for Testing and Materials (ASTM) International, involving the use of complex and expensive equipment are necessary for the assessment to appraise the quality. However, literature has shown that these standard protocols have not been able to adequately tackle most adulteration cases as some adulterated gasoline still comply with gasoline requirements. Thus a tailored method is required to deal with gasoline adulteration.

The determination of gasoline quality parameters such as research octane number (RON), sulfur content, distillation temperature, and the application of a new approach that utilizes acidity difference determined by in-house developed titration method to quantitatively measure kerosene adulterant in gasoline provide a comprehensive approach for assessing gasoline quality in Ghana.

Presently in Ghana, there is no realistic procedure for the measurement of gasoline doped with kerosene. In this work the adulterant was estimated using a calibration plot obtained by acidity differences between a reference and adulterated gasoline. An in-house simple direct titration (SDT) method was developed for the determination of gasoline acidity.

Initially, acidic content of petroleum fuel fractions was investigated to establish the levels and profile. These are the classes of fuels sold at the fuel stations. Thus the various kinds of crude oils (Forcados, Bonny Light and Brass River) processed into fractional distillates

were studied. Finally the quality of the gasolines was evaluated from the physicochemical parameters required by standards.

4.1 ACIDITY LEVELS AND PATTERN IN PETROLEUM FUEL FRACTIONS

The acidity in mgKOH/g expresses the total level of acids, mainly naphthenic acids that are present in a particular petroleum product or fraction (Xing et al., 2008). The levels of acidity in light naphtha, heavy naphtha, kerosene, light gasoil and heavy gasoil obtained from Forcados crude oil are shown in **Table 4.1**.

Table 4.1: Acidity and other parameters of distillate fractions from Forcados crude oil

PARAMETER	Light Naphtha	Heavy Naphtha	Kerosene	Light Gasoil	Heavy Gasoil
Acidity, mgKOH/g	0.0021	0.0044	0.0305	0.2359	0.4225
Density at 15 ºC, kg/m^3	666.5	754.5	814.6	867.8	883.2
DISTILLATION					
IBP ºC	30	53	143	235	255
10% recovery ºC	36	91	161	271	293
50 % recovery ºC	59	114	202	296	336
90% recovery ºC	90	140	238	348	372
FBP ºC	95	164	253	375	>380

The densities and distillation temperatures (from initial boiling point, IBP to final boiling point, FBP) characterized the various fractions. Acidity values ranged from 0.0021 to 0.4225 mgKOH/g. The acidity value of light naphtha was about half the value for the heavy naphtha as the two products are closely related and normally forms base fuel for gasoline. The acidity level of kerosene was about seven (7) times of heavy naphtha,

indicating a clear distinction between the two products. Light gasoil also had its acidity value about eight (8) orders of magnitude higher than the value for kerosene, distinguishing the different fuel fractions.

The range of acidity values of petroleum distillates from Bonny Light crude oil was from (0.0007 to 0.1383)mgKOH/g, heavy gasoil registered the highest acidity (**Table 4.2**).

Table 4.2: Acidity and other parameters of distillate fractions from Bonny Light crude oil

PARAMETER	Light Naphtha	Heavy Naphtha	Kerosene	Light Gasoil	Heavy Gasoil
Acidity mgKOH/g	0.0007	0.0014	0.0105	0.0789	0.1383
Density at 15 ºC, kg/m^3	700.3	772.9	822.0	858.8	863.4
DISTILLATION					
IBP ºC	38	105	153	183	187
10% recovery ºC	54	116	177	239	250
50 % recovery ºC	71	124	201	266	238
90% recovery ºC	94	141	232	288	337
FBP ºC	110	156	244	310	337

Here also, acidity value of kerosene was seven (7) multiples the value for heavy naphtha. This distribution reveals the clear distinction between kerosene and naphtha (gasoline range) fractions indicated earlier.

Petroleum fractions obtained from Brass River crude oil gave acidity values ranging from (0.0004 to 0.2342)mgKOH/g, **Table 4.3**.

Table 4.3: Acidity and other parameters of distillate fractions from Brass River crude oil

PARAMETER	Light Naphtha	Heavy Naphtha	Kerosene	Light Gasoil	Heavy Gasoil
Acidity mgKOH/g	0.0004	0.0007	0.0068	0.1235	0.2342
Density at 15 ºC, kg/m^3	717.5	776.9	820.9	861.4	874.8
DISTILLATION					
IBP ºC	40	105	140	192	210
10% recovery ºC	63	127	155	238	265
50 % recovery ºC	84	133	188	280	322
90% recovery ºC	124	145	217	336	378
FBP ºC	117	158	229	365	>390

Similar to the other crude oils, heavy gasoil was more acidic than any of the fractions. Accordingly, it was observed that acidity levels in each petroleum fractions obtained from the same crude oil increases with increasing boiling range temperatures and density. The higher the acidity the larger the density, **Tables 4.1- 4.3**. The levels of acidity however differ with the crude oil type. In all the Forcados crude oil had higher densities for all fractions as compared to Bonny Light and Brass River crude oils.

4.2 PHYSICOCHEMICAL PROPERTIES OF GASOLINE AND DOMESTIC KEROSENE

Detection and determination of fuel adulterations are very hard to evaluate. The detection of this malpractice becomes more difficult when the adulteration involves the addition of hydrocarbons, or their mixtures. Having similar chemical properties, the adulterant and fuel cannot be clearly distinguished. It therefore becomes imperative to know the properties of the fuel being adultered and the adulterant used or being investigated. **Table 4.4** indicates the acidity and other parameters of premium gasoline (fuel to be adulterated) and the domestic kerosene (adulterant), determined by standard ASTM methods.

Table 4.4: Physicochemical parameters of pure gasoline and kerosene

PARAMETER	Test method	Gasoline	Kerosene
Colour	visual	colourless	colourless
Acidity mgKOH/g	D3242	0.0040	0.0241
Density at 15 °C, Kg/m^3	D1298	726.2	820.7
Total sulfur, % mass, Max	D2622	8	263
DISTILLATION	D86		
IBP, °C		36	154
10 % recovery, °C		52	184
50 % recovery, °C		85	214
90% recovery, °C		156	236
FBP, °C, Max, °C		191	251
RON	D2699	91.4	
COMPOSITION	D5134		
Paraffins, %Vol.		47.93	
Olefins, % Vol.		33.37	
Naphthenes, % Vol.		9.48	
Aromatics, % Vol.		9.22	
Oxygenates, % Vol.		0.00	
Unknowns, % Vol.		0.27	
C4 %Vol.		2.23	
C5 % Vol.		27.90	
C6 % Vol.		25.38	
C7 % Vol.		13.60	
C8 % Vol.		20.53	
C9 % Vol.		7.14	
C10 % vol.		1.63	
C11 % Vol.		0.40	
C12 % vol.		0.06	
C13% Vol.		0.00	
C14% vol.		0.00	
>C14 % Vol.		0.00	

Regardless of the crude oil source or processing history, the major components of all kerosenes are branched and straight chain paraffins and naphthenes (cycloparaffins), which normally account for at least 70% by volume, aromatic hydrocarbons in this boiling range, such as alkylbenzenes (single ring) and alkylnaphthalenes (double ring) do not normally

exceed 25% by volume of kerosene streams, olefins are usually not present at more than 5% by volume (Obodeh and Akhere, 2010). The higher levels of paraffins in kerosenes, especially naphthenes resulted in higher acidity of kerosenes compared to gasolines. As indicated in **Table 4.5**, naphthenes in kerosene are around 28 %vol. compared to 9.48% vol. found in the gasoline. In all the physicochemical parameters studied were in agreement with specifications of the Ghana Standards Authority for premium gasoline and domestic kerosene.

Table 4.5: Chemical composition of kerosene

Fuel	Paraffins (%vol.)	Naphthenes (%vol.)	Olefins (%vol.)	Aromatics (%vol.)
Kerosene	55	28	0	16

Source: Fonseca et al., 2007

4.3 SIMULATION OF GASOLINE ADULTERATION WITH DOMESTIC KEROSENE

Extensive studies have been carried out on the effects of kerosene adulteration on gasoline. The addition of kerosene into gasoline changes the original composition of the gasoline, affecting its physicochemical properties in different ways. The effects on the gasoline include increased density, decreased volatility and reduced octane rating (Fonseca et al., 2007; Obodeh and Akhere, 2010;).

In this study, upon the addition of 5% of the domestic kerosene to the gasoline, the acidity value increased from 0.004 to 0.005mgKOH/g. This clearly indicated that domestic kerosene could increase acidity value of gasoline even in low volume owing to the higher levels of paraffins and naphthenes in kerosene. These compounds contribute significantly to acidity in petroleum fuels. 20% of the domestic kerosene in the synthetic mixture doubles the acidity from 0.004 to 0.008mgKOH/g. There was a sequential increasing in acidity of the gasoline resulted from increasing amount of the adulterant (**Figure 4.1**).

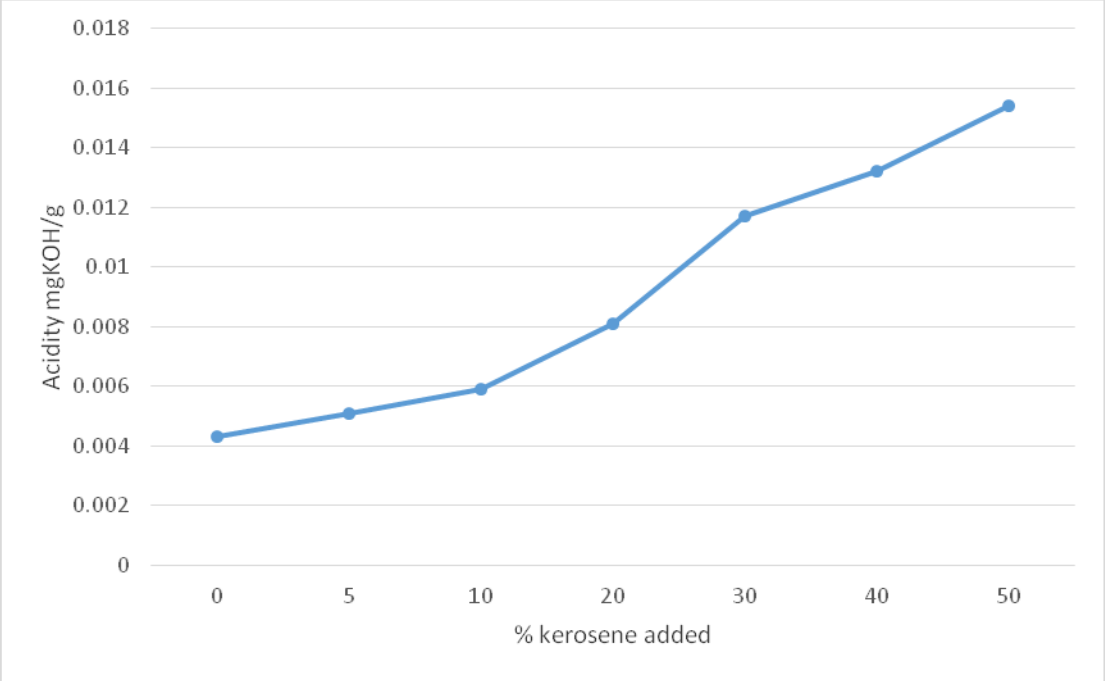

Figure 4.1: Relationship between % of kerosene in gasoline and total acidity

Distillation temperatures were also studied alongside the acidity as verification. It was observed that as the proportion of domestic kerosene (adulterant) in the gasoline increases

in the synthetic mixture, the distillation temperatures increase as well **Figure 4.2** and **Table 4.6**.

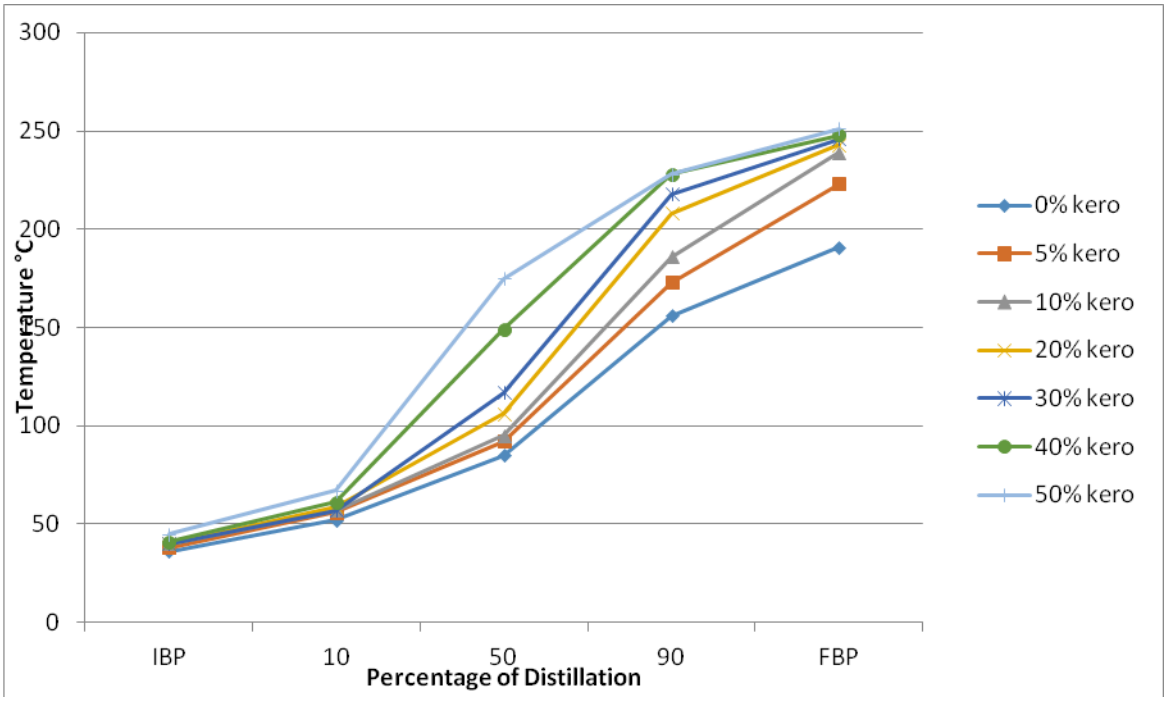

Figure 4.2: Variation of distillation curve of gasoline as a function of kerosene percentage

Table 4.6: Physicochemical parameters of gasoline adulterated with kerosene

PARAMETERS	0%vol. kerosene	5%vol. kerosene	10%vol. kerosene	20%vol. kerosene	30%vol. kerosene	40%vol. kerosene	50%vol. kerosene
Acidity, mgKOH/g (by SDT method)	0.004	0.005	0.006	0.008	0.012	0.013	0.015
Acidity, mgKOH/g (ASTM method)	0.004	0.005	0.006	0.008	0.011	0.014	0.016
Density at 15 °C, Kg/m^3	726.2	732.0	738.3	748.2	758.1	768.0	777.6
Total sulfur, ppm	8	57	66	78	92	113	121
IBP, °C	36	38	40	40	40	41	45
10% recovery, °C	52	56	57	59	59	61	67
50 % recovery, °C	85	92	95	106	117	149	175
90% recovery, °C	156	173	186	208	218	228	228
95% recovery, °C	170	202	210	223	228	232	238
FBP, °C	191	223	239	243	246	248	251

4.4 IN-HOUSE SIMPLE DIRECT TITRATION (SDT) METHOD OF DETERMINING ACIDITY OF GASOLINE

According to the American Society for Testing and Materials (ASTM), acidity or acid number is defined as the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample in a specific solvent or test conditions to a specific end point (ASTM D-664, 1995). Toluene and 2-propanol mixture is used as solvent in the ASTM test method for acidity in aviation turbine fuel (ASTM D3242). Where higher sample matrices prevent calorimetric end-point determination like in diesel and lubricating oil, equipments are employed for potentiometric end-point determination (ASTM D664). The use of expensive chemicals and equipments as pointed out earlier prevent the adoption of most methods reviewed for monitoring adulteration in many developing countries. Further, toluene is known to be toxic and may have an effect on human brain (Carson et al., 1995).

Comparatively, gasoline contains fewer matrices and for the purpose of "fingerprinting" the acidity of the gasoline and gasoline-kerosene mixtures were determined using an in-house direct titration method that does not involve the use of chemical solvent as used in the case of the ASTM method D3242. The results were compared with corresponding values obtained using the ASTM method D3242 as shown in **Table 4.6**. The acidity values obtained by the experimental method were numerically the same as that obtained by the standard ASTM method, (0%-20%) adulteration. The differences in values obtained by the two different methods in the other three (30 – 50%)

adulterated samples were all 0.001. The result of the simple direct titration method was closer to standard acceptable ASTM method value indicating high accuracy, leading to a high precision of the method over a range of measurements. As the percentage of the adulterant was increasing, the results of the SDT method were still close to the ASTM method values. The SDT method of acidity determination in gasoline was directly proportional to the concentration of the analyte in the sample. The linearity of the acidity and the percentage of kerosene as obtained by the SDT method ($R^2 = 0.9829$) indicated a strong correlation closer to R^2 of 0.9944 obtained as by the standard ASTM method (**Figures 4.3** and **4.4**).

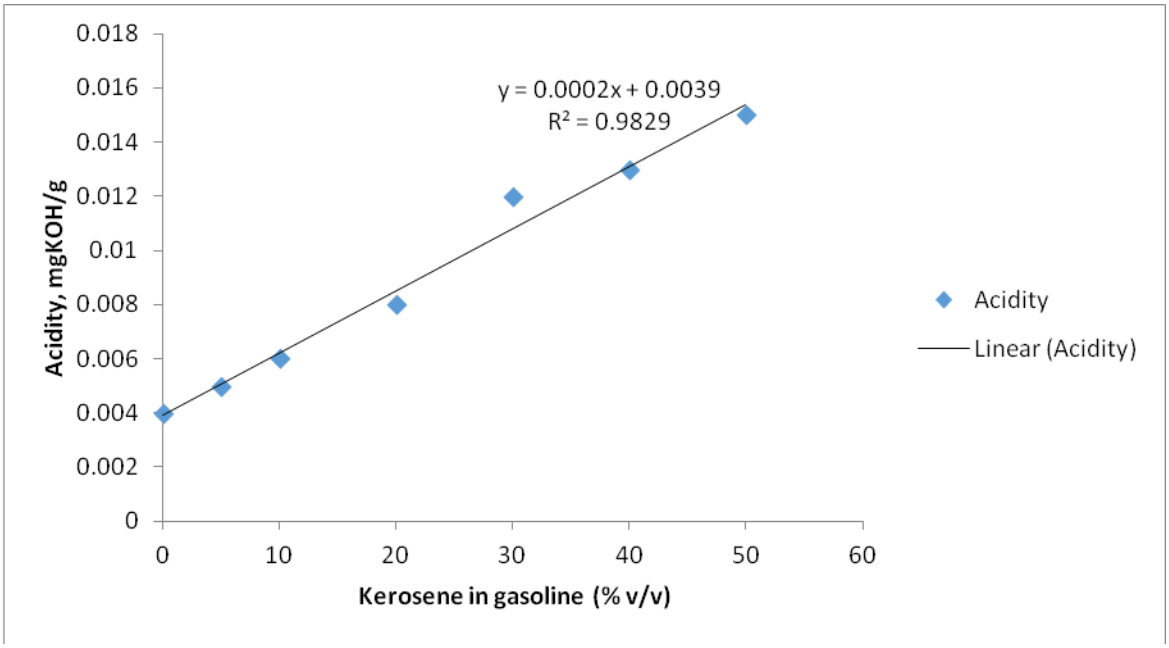

Figure 4.3: Calibration plot for acidity and adulterant level by SDT method

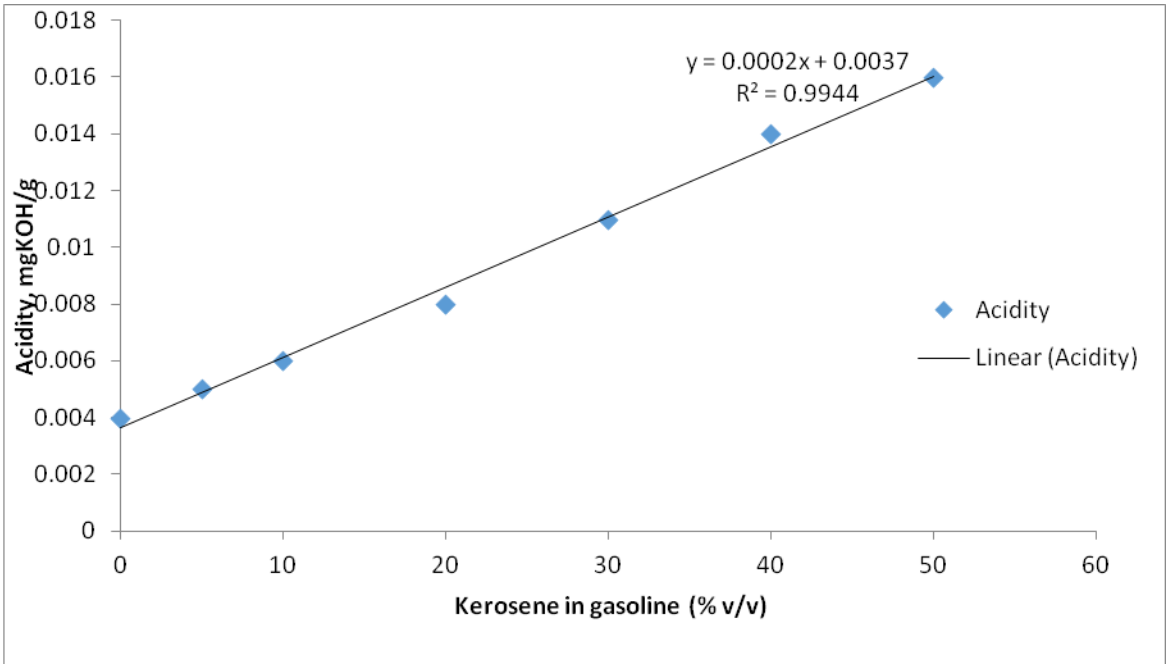

Figure 4.4: Calibration plot for acidity and adulterant level by ASTM method

4.5 ESTIMATION OF DOMESTIC KEROSENE ADULTERANT IN GASOLINE IN ACCRA METROPOLIS

The calibration standard for acidity and adulterant obtained by the SDT method shown in **Figure 4.3** was adopted for the estimation of the amount of the adulterant in the gasoline. The calibration obtained by the ASTM method was used to estimate the adulteration quantities for appraisal. The acidity levels of the gasolines from some of the filling stations were clearly higher than the reference samples and premium gasoline used for the adulteration simulation.

Overall, the highest adulteration of gasoline had adulteration content of 29% and 20% for SDT and ASTM methods respectively, registering the highest acidity. The reference samples had no adulteration, suggesting that the gasolines from the fuel station were doped. To make discussions understandable, samples of gasoline studied were grouped.

Shell filling stations samples

Four out of the 5 stations with shell brand had varied amount of domestic kerosene in the gasoline. Station 3, recorded the highest adulteration, with a higher acidity value resembling the simulated adulterated sample prepared. The domestic kerosene quantity estimated was 29%v/v, **Table 4.7**.

Table 4.7: Estimated levels of domestic kerosene in gasoline samples

Source	Sample Number	Acidty, mgKOH/g (y)	SDT (% Adulteration)	ASTM (% Adulteration)
SHELL	1	0.0067	14	10.0
	2	0.0045	3	2.7
	3	0.0097	29	20.0
	4	0.0053	7	5.3
	5	0.0030	-4.5	-2.3
GOIL	6	0.0052	6.5	5.0
	7	0.0074	17.5	12.3
	8	0.0051	6	4.7
	9	0.0053	7	5.3
TOTAL	10	0.0023	-8	-4.7
	11	0.0023	-8	-4.7
	12	0.0023	-8	-4.7
	13	0.0074	17.5	12.3
	14	0.0024	-7.5	-4.3
MIXED	15	0.0070	15.5	11.0
	16	0.0039	0	0.7
	17	0.0045	3	2.7
	18	0.0074	17.5	12.3
	19	0.0038	-0.5	0.3
	20	0.0022	-8.5	-5.0
SHIP	21	0.0015	-12	-7.3
	22	0.0007	-16	-10.0
	23	0.0035	-2	-0.7
TOR	24	0.0038	-0.5	0.3
	25	0.0036	-1.5	-0.3
	26	0.0030	-4.5	-2.3

GOIL filling stations samples

All the four stations were estimated to contain varied amounts of adulterant. Station 7 registered 17.5% v/v of domestic kerosene, the highest level among the group.

Total filling stations samples

One station (station 13) out of the five, representing 20% was estimated to contain 17.5%v/v of domestic kerosene.

Mixed filling stations samples

Three stations of the group representing 50% were estimated to contain some amounts of domestic kerosene. The group highest adulteration was found in station 18 with a quantity of 17.5%v/v.

Reference (Ship and TOR) samples

There was no adulterant detected in both ship and TOR samples. This affirms the method adopted in this study as the reference samples were not expected to be adulterated.

4.6 QUALITY EVALUATION OF GASOLINE SAMPLES FROM ACCRA METROPOLIS

Ghana has witnessed significant increase in the number of vehicles with a resultant proliferation of petroleum retail outlets especially in Accra. The increasing importance of fossil fuels such as gasoline to our society today cannot be over emphasized. Key gasoline quality parameters of the gasoline samples were measured. **Table 4.8** shows gasoline standard specifications for Ghana, Europe, Japan and India used to evaluate the quality of the samples.

Table 4.8: Gasoline standard specifications for Ghana, Europe, Japan and India

Property	Ghana(1)	EU(2)	Japan(3)	India(4)
Octane, RON, min	91	91	-	91
	-	95	96	95
Sulfur, wt/wt%, max	0.100	0.001	0.001	0.003
Reid Vapour Pressure, KPa, Max	65	50	78	-
DISTILLATION,				
10% evaporation ºC, Max	70	-	-	-
46 % evaporation ºC, Max	-	10	-	-
50 % evaporation ºC, Max	120	-	-	-
75% evaporation ºC, Max	-	100	-	-
90% evaporation ºC, Max	190		180	180
Final boiling point ºC, Max	225	-	-	195
COMPOSITION				
Aromatics %v/v, Max	-	35	-	35
Olefin %v/v , Max	-	18	-	10
Benzene %v/v, Max	1.5	1.0	-	-
Oxygenates wt/wt%	-	2.7	1.3	2-5
Density at 15 ºC, Kg/m^3	720-775	-	783 max	-
Ethanol	-	5.0	3.0	-
Methylcyclopentadienyl Manganese Tricarbonyl (MMT) mg/L, Max.	18	-	-	-

Source: Ghana Standard Authority (1), Row and Doukas, 2008 (2, 3, 4)

Table 4.9: Some quality indicators of the groups

Parameter	Shell	Goil	Total	Mixed	Ship	TOR
Average (RON)	90.96	91.20	91.12	90.82	91.60	91.47
Average (Sulfur, ppm)	113.60	238.75	61.00	138.2	105.00	309.67
Average (Aromatics, %v/v)	11.55	17.42	12.41	13.18	11.39	12.89
Average (Olefins %v/v)	27.61	26.46	28.99	31.25	28.70	30.21
Average (Benzene %v/v)	0.52	0.77	0.53	0.45	0.61	0.47
Average (Acidity, mgKOH/g)	0.0060	0.0060	0.0030	0.0050	0.0019	0.0030

The octane number (ON) is the most important property of gasoline used in evaluating its quality. ON is an indication of the thermal stability (antiknock characteristics) of the molecule which depends on its molecular structure as certain molecules tend to combust sooner and knock more than others. ON is therefore a direct function of the molecular composition of the gasoline fuel. The ON requirement in Ghana is a minimum of RON 91. The ship and TOR (reference samples) had the highest average RON values, while the fuel stations had lower RON values **Table 4.9.**

The more recent drive in fuel quality improvement focuses on sulfur reductions. Sulfur in fuel is found to be the main contributor to sulfur dioxide and particulate matter emissions. Sulfur is found to reduce the efficiency of exhaust after-treatment systems. The main evolution of petroleum fuel quality in the world is sulfur reduction (Welbeck, 2012). Reducing sulfur content of gasoline leads to a direct reduction in SOx emissions and also reduces VOCs, NOx and CO indirectly. The TOR had highest quantities of sulfur

determined in this study with an average of 309.67ppm as indicated above. This implies that more SOx, VOCs, NOx and CO would be emitted into the atmosphere. The limit of sulfur set by Ghana 0.100wt/wt%, (1000ppm) is very high compared to Europe and Japan is 0.001wt/wt%, (10ppm) and 0.003wt/wt%, (30ppm) for India.

While Europe, Japan and India have specifications for oxygenates, Ghana have no specification for oxygenates. Thus the samples measured contained no oxygenates.

Aromatics contribute highest to ON hence limiting the quantities of aromatics in gasoline has been a problem even though higher aromatics level increases the reactivity of emissions and also increases benzene levels, engine deposits and other VOCs. The quantities of aromatics in the gasoline samples were low. The averages (**Table 4.9)** were from11.39 to 17.42%v/v. Ghana has no limits on aromatics while the limit for Europe and Japan is 35%v/v maximum. These limits suggest that the range found was accommodating.

Even though Ghana has no limits on olefins, their levels are usually regulated as they result in engine fouling gums, high smoke and smog levels. The specifications of India and Europe for olefins are 10 and 18%v/v (max.) respectively. The lowest group average of olefins determined in the study was 26.46 %v/v.

The hydrocarbon constituents in gasoline range are those that have 4 to 12 carbon atoms in their molecular structure (Wolf, 1995). The hydrocarbon composition gives the number of carbon atoms in the compounds of the gasoline.

Benzene, a clear, colorless, flammable liquid is a known carcinogen with demonstrated increased incidence of several types of leukemia in exposed adults. Benzene has also been

shown to cause damage to DNA. The primary targets of benzene exposure in humans are the blood cell-forming system and the immune system. Dizziness, drowsiness, rapid heartbeat, disorientation, unconsciousness, headaches and loss of muscular control are some of the symptoms. Benzene levels were lower than 1.0%v/v in all filling station samples (EPA, 1998). The average amount of benzene in all the samples determined in this study was 0.58%v/v lower than the maximum limits of a Ghana (1.5%v/v) and Europe (1.0%v/v).

The volatility of gasoline plays significant role in the engine performance or driveability a vehicle under all conditions. Volatility is considered next to octane number in determining performance of gasoline engine. Gasoline which is too volatile vaporizes too easily and may boil in fuel pumps, lines or in carburetors at high operating temperatures. If too much vapour is formed, this could cause a decrease in fuel flow to the engine, resulting in symptoms of vapour lock, including loss of power, rough engine operation, or complete stoppage. Fuel economy could also deteriorate and evaporative emissions could increase (Renewable Fuels Foundation, 2009).The limits of gasoline volatility are therefore relative to the environmental temperature. The two main parameters used to control volatility limits are vapour pressure and distillation temperatures.

The RVP values ranged from 0.46 to 0.62 Kg/cm^2 which were below the maximum limit of 65KPa (0.66Kg/cm^2) set for Ghana. However, the vapour pressure does not give the overall volatility, but only indicate the volatility of the lighter components of the gasoline.

The distillation test provides volatility across the entire boiling range of the gasoline. The 10% evaporated temperature must be low enough to provide easy cold starting but high

enough to minimize vapour lock. The 50% evaporated temperature must be low enough to provide good warm up and cool weather driveability without being so low as to contribute to hot driveability and vapour locking problems. The 90% and end point evaporation temperatures must be low enough to minimize crankcase and combustion chamber deposits as well as spark plug fouling and dilution of engine oil.

The limits of distillation parameters for Ghana are 10%, 50% and 90% evaporated temperatures maximum values of 70, 120 and 190 °C respectively while the Final Boiling Point (FBP) maximum value is 225°C. For the 10% evaporated temperatures of the samples determined, the range was from 52 to 59°C, lower than the maximum limit of 70°C. The 50% evaporated temperatures of the samples ranged from 78 to 90 °C while the 90% evaporated temperatures were between 134 to 152°C. The FBP temperatures of the samples were in the range of 172 to 189°C.

Density is a function of the composition of the gasoline, the trend now is to narrow the density range of gasoline, to improve fuel economy, as it allow for better control of gasoline/air ratio in internal combustion engines and improve engine performance. It was observed during the simulation of gasoline adulteration with kerosene that density was not an effective parameter for evaluating gasoline quality as gasoline containing 40% kerosene had a density of 768.0Kg/m^3, which is within the specification range for gasoline in Ghana of 720-775 Kg/m^3.

Quality evaluation of Shell filling stations samples

The mean RON value for Shell stations was 90.96, **Table 4.10.** Station 1, with RON of 90.3 was the lowest among all the samples in this study and clearly below the GSA minimum limit of 91.0, Station 3 however recorded one of the highest RON (91.5) values among the filling stations.

Table 4.10: Physicochemical parameters of gasoline samples from Shell filling stations

PARAMETER	1	2	3	4	5	MEAN	STDEV.
Colour	Brown	Red	Red	Red	Red	0	0
Density at 15 ºC, Kg/m^3	733.3	735.7	729.6	727.6	739.2	733.1	4.7
RON	90.3	91.0	91.5	91.1	90.9	90.96	0.43
RVP, kg/cm^2	0.56	0.59	0.53	0.46	0.50	0.52	0.05
Total sulfur, ppm	74	47	101	156	190	114	59
DISTILLATION							
IBP, °C	37	37	38	40	39	38	1
10 %, °C	52	52	52	55	54	53	1
50 %, °C	82	85	79	83	85	82.8	2.5
90 %, °C	140	151	140	139	148	144	6
FBP, °C	184	187	182	194	198	189	7
Acidity, mgKOH/g	0.0067	0.0045	0.0097	0.0053	0.0030	0.006	0.003
COMPOSITION							
Paraffins, %Vol.	48.97	37.27	50.51	46.48	44.57	45.6	5.2
Olefins, % Vol.	28.32	32.23	18.33	31.84	27.33	27.6	5.6
Naphthenes, % Vol.	12.80	12.87	12.26	12.47	15.36	13.2	1.3
Aromatics, % Vol.	8.42	14.25	17.11	8.10	9.88	12	4
Oxygenates, % Vol.	0.00	0.00	0.00	0.00	0.00	0	0
Unknowns, % Vol.	1.49	3.37	1.69	1.11	2.86	2	1
C4, %Vol.	2.40	1.28	2.08	2.32	3.83	2	1
C5, % Vol.	26.80	20.41	28.07	25.49	17.80	23.7	4.4
C6, % Vol.	24.08	16.69	25.96	22.52	28.35	23.5	4.4
C7, % Vol.	12.92	13.55	19.56	16.21	12.82	15	3
C8, % Vol.	20.43	24.18	11.28	21.54	18.01	19	5
C9, % Vol.	8.30	12.94	8.42	6.98	10.60	9.4	2.3
C10, % vol.	3.01	4.74	2.24	3.16	4.00	3	1
C11, % Vol.	0.48	1.42	0.39	0.58	1.25	0.82	0.48
C12, % Vol.	0.09	1.42	0.09	0.10	0.48	0.44	0.58
C13, % Vol.	0.00	0.00	0.00	0.00	0.00	0	0
C14, % Vol.	0.00	0.00	0.11	0.00	0.00	0.02	0.05
>C14, % Vol.	0.00	0.00	0.10	0.00	0.00	0.02	0.05
Benzene, % vol.	0.35	0.52	0.43	0.70	0.61	0.52	0.14

The group had an average of 114ppm of sulfur. The sulfur level of the Shell group was far lower than the GSA maximum limit of 1000ppm even though they are above the limits of Europe and Japan (10ppm), and India (30ppm).

Even though Ghana has no limit on olefins, the levels found among the shell group (mean of 27.6%v/v) were generally high above the limits of Europe and India, 18 and 10%v/v respectively. This implies there would be high gum formation and engine fouling.

Station 3 was found to contain 0.11%v/v of compounds with 14 carbon atoms and 0.10%v/v of heavier compounds. This suggests adulteration with heavier products. The colour of the gasoline was also brown which could also be due to rust of underground tank.

The distillation curves of the Shell samples varied slightly at higher percentage recovery temperatures. However, the group curves were below the maximum limits set by the GSA (**Figure 4.5**).

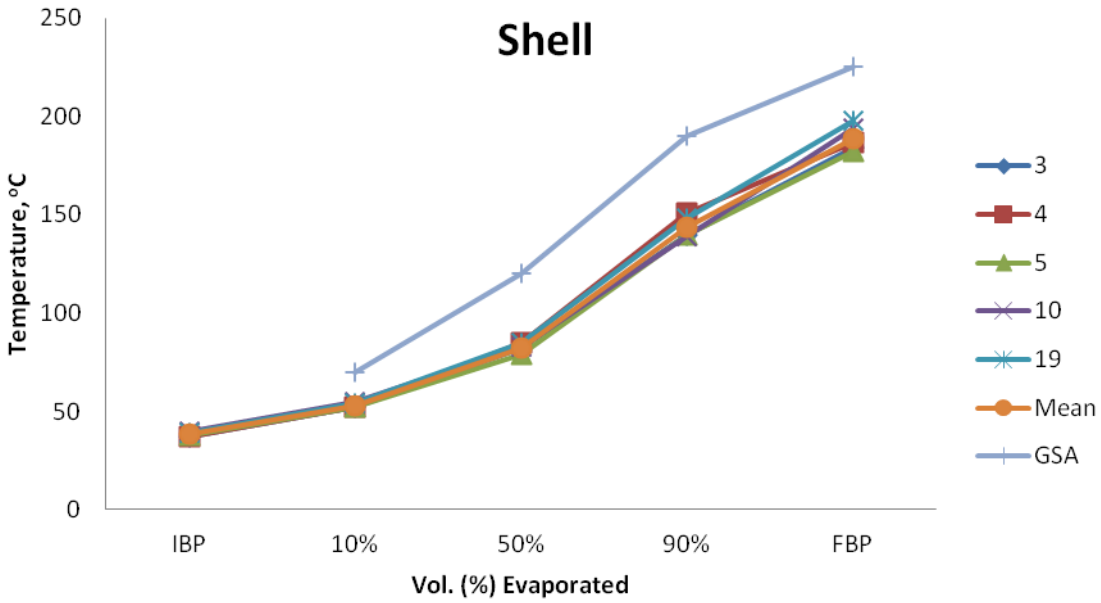

Figure 4.5: Distillation curves of Shell samples and GSA limits

Quality evaluation of GOIL filling stations samples

Goil stations had an average RON of 91.20, the highest among the filling stations groups, **Table 4.11**. All the samples of the group conform to the minimum requirement of 91 set by GSA.

The GOIL group had the highest sulfur levels among the filling stations groups with an average of 239ppm of sulfur. As pointed out earlier, it implies that more SOx, VOCs, NOx and CO would be emitted into the atmosphere, yet the sulfur level of the GOIL group was lower than the GSA maximum limit of 1000ppm.

Table 4.11: Physicochemical parameters of gasoline samples from GOIL filling stations

PARAMETER	6	7	8	9	MEAN	STDEV.
Colour	Red	Red	Red	Red	0	0
Density at 15 ºC, Kg/m^3	730.2	729.1	727.1	728.5	728.73	1.29
RON	91.3	91.0	91.5	91.0	91.200	0.245
RVP, kg/cm^2	0.56	0.59	0.53	0.50	0.55	0.04
Total sulfur, ppm	262	236	222	235	238.75	16.76
DISTILLATION						
IBP, °C	37	37	38	39	38	1
10 %, °C	52	52	52	54	53	1
50 %, °C	82	85	79	85	82.75	2.87
90 %, °C	140	151	140	148	144.75	5.62
FBP, °C	184	187	182	198	187.75	7.14
Acidity, mgKOH/g	0.0052	0.0074	0.0051	0.0053	0.006	0.001
COMPOSITION						
Paraffins, %Vol.	46.91	35.85	52.46	38.42	43.41	7.66
Olefins, % Vol.	31.80	26.66	17.61	29.76	26.46	6.23
Naphthenes, % Vol.	10.81	14.19	11.12	11.51	11.91	1.55
Aromatics, % Vol.	9.37	23.30	16.70	20.31	17.420	6.007
Oxygenates, % Vol.	0.00	0.00	0.00	0.00	0	0
Unknowns, % Vol.	1.11	3.72	2.09	3.39	2.578	1.205
C4, %Vol.	1.72	4.82	2.30	1.07	2.48	1.64
C5, %Vol.	24.79	12.30	30.72	23.01	22.71	7.68
C6 , %Vol.	22.67	20.22	27.77	19.92	22.65	3.63
C7 , %Vol.	15.17	22.05	17.10	17.65	17.993	2.907
C8 , %Vol.	24.29	14.10	10.06	13.76	15.55	6.11
C9 , %Vol.	8.52	13.22	8.32	12.37	10.608	2.551
C10 , %Vol.	1.55	5.82	1.39	6.13	3.723	2.605
C11 , %Vol.	0.18	1.94	0.20	1.75	1.018	0.959
C12 , %Vol.	0.00	1.62	0.06	0.95	0.658	0.775
C13, %Vol.	0.00	0.18	0.00	0.00	0.05	0.09
C14, %Vol.	0.00	0.00	0.00	0.00	0	0
>C14, % Vol.	0.00	0.00	0.00	0.00	0	0
Benzene, % vol.	0.52	0.98	0.72	0.85	0.77	0.20

The olefins level for the group was similar to the shell group indicated above, with a mean of 26.56%v/v.

Station 7 was found to contain 0.18%v/v of compounds with 13 carbon atoms. The rest of the samples had compounds with a maximum of 12 carbon atoms.

The distillation curves of the GOIL samples showed similarities at the lower percentage temperatures giving rise to a unified curve at the lower end but varied at the higher percentage recovery temperatures. The distillation curves of the GOIL samples were below the maximum limits set by the GSA (**Figure 4.6**).

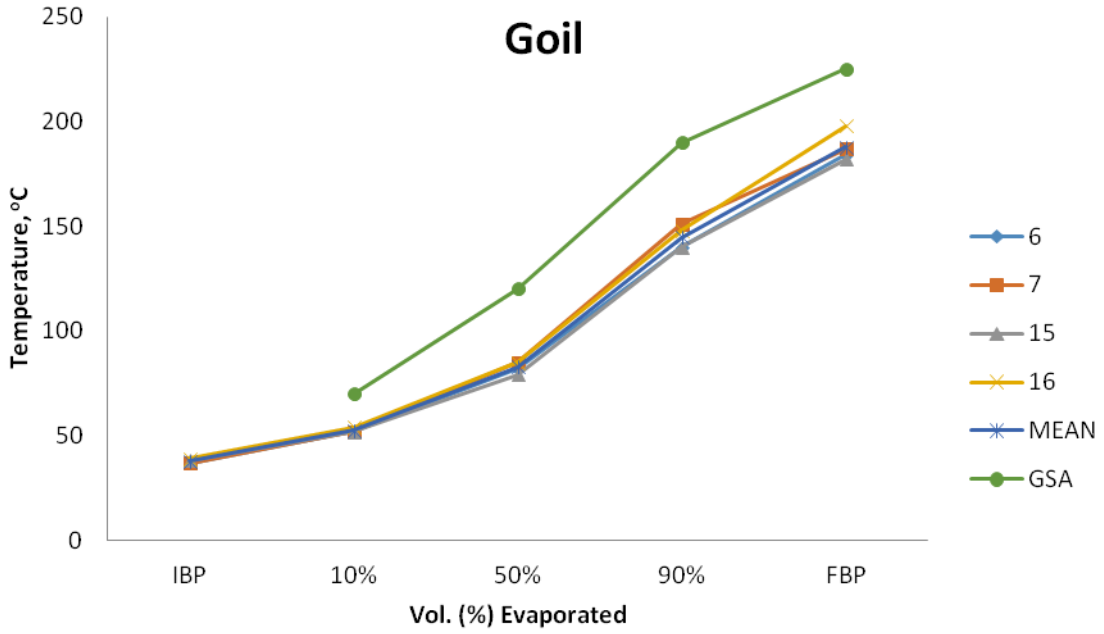

Figure 4.6: Distillation curves of GOIL samples and GSA limits

Quality evaluation of Total filling stations samples

The group had an average RON of 91.12. The RON values among the group were almost the same. The sulfur levels of the Total group were the lowest, an average of 61ppm indicating their emissions would be lower. However, the mean olefins value of 27.6%v/v was similar to the groups mentioned earlier.There were no heavier compounds recorded among the samples from Total stations. The distillation curves of the Total samples showed much uniformity, **Table 4.2 and Figure 4.7**.

Table 4.12: Physicochemical parameters of gasoline samples from Total filling stations

PARAMETER	10	11	12	13	14	MEAN	STDEV.
Colour (Visual)	Red	Red	Red	Red	Red	0	0
Density at 15 ºC, Kg/m^3	738.1	733.3	729.9	730.8	728.6	732.14	3.75
RON	90.8	91.5	91.1	91.1	91.1	91.12	0.25
RVP, kg/cm^2	0.53	0.53	0.56	0.52	0.52	0.53	0.02
Total sulfur, ppm	8	17	156	9	10	61.00	82.35
DISTILLATION							
IBP, °C	38	38	37	39	37	37.8	0.8
10 %, °C	53	52	52	53	53	52.60	0.55
50 %, °C	85	82	80	82	83	82.40	1.82
90 %, °C	150	146	141	141	147	145.00	3.94
FBP, °C	191	187	181	179	184	184.40	4.78
Acidity, mgKOH/g	0.0023	0.0023	0.0023	0.0074	0.0024	0.003	0.002
COMPOSITION							
Paraffins, %Vol.	40.93	45.65	43.12	47.45	47.12	44.85	2.78
Olefins, % Vol.	32.32	27.74	30.08	29.81	25.02	28.99	2.75
Naphthenes, % Vol.	12.56	10.70	11.47	13.60	12.58	12.18	1.12
Aromatics, % Vol.	12.28	14.99	13.55	7.61	13.63	12.41	2.85
Oxygenates, % Vol.	0.00	0.00	0.00	0.00	0.00	0	0
Unknowns, % Vol.	1.87	0.92	1.78	1.55	1.65	1.55	0.38
C4 %Vol.	2.36	1.87	0.78	2.87	2.32	2.04	0.79
C5 % Vol.	15.58	27.89	29.24	26.88	24.00	24.72	5.46
C6 % Vol.	21.41	25.00	24.59	22.32	24.12	23.49	1.55
C7 % Vol.	12.42	23.09	23.00	14.28	11.83	16.92	5.66
C8 % Vol.	27.15	12.08	13.15	20.74	19.69	18.56	6.15
C9 % Vol.	9.14	5.13	5.78	8.32	9.79	7.63	2.07
C10 % vol.	8.51	3.70	1.53	2.59	4.06	4.08	2.67
C11 % Vol.	0.99	0.24	0.00	0.36	1.23	0.56	0.52
C12 % Vol.	0.56	0.07	0.17	0.08	1.31	0.44	0.53
C13% Vol.	0.00	0.00	0.00	0.00	0.00	0	0
C14% vol.	0.00	0.00	0.00	0.00	0.00	0	0
>C14 % Vol.	0.00	0.00	0.00	0.00	0.00	0	0
Benzene, % vol.	0.26	0.70	0.78	0.44	0.46	0.53	0.21

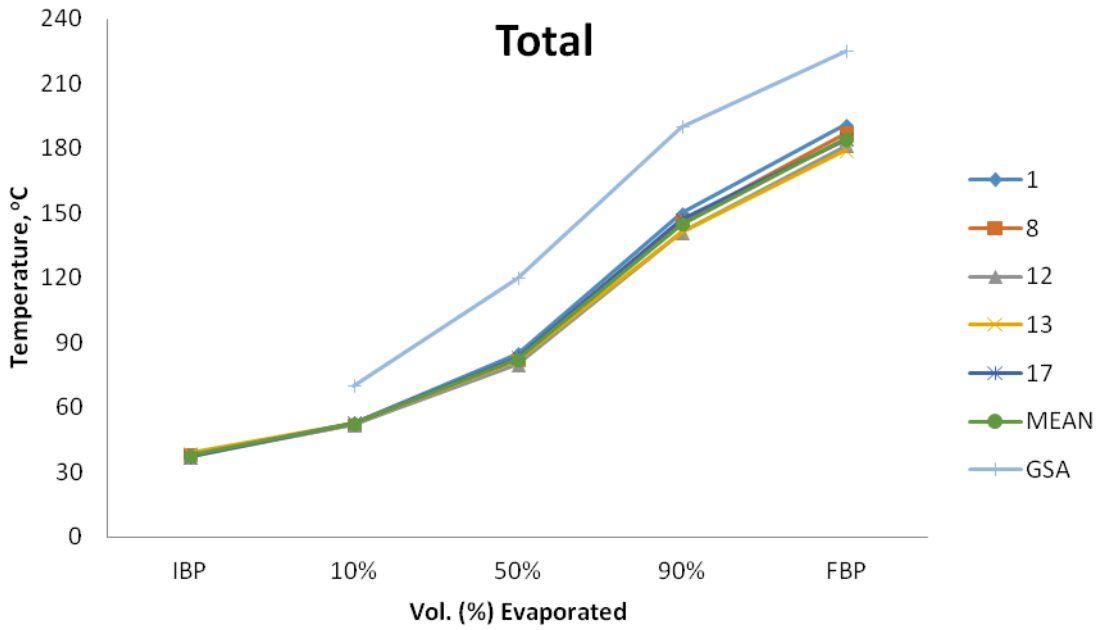

Figure 4.7: Distillation curves of Total samples and GSA limits

Quality evaluation of Mixed filling stations samples

The mixed group of filling stations consisted of different brands, they had a mean RON of 90.82, the lowest compared to the other groups of filling stations. Most of the stations in this group did not conform to the minimum requirement of RON 91 set by GSA. However, there were no heavier compounds recorded among the samples from the mixed filling stations.

Table 4.13: Physicochemical parameters of gasoline samples from Mixed Filling Stations

PARAMETER	15	16	17	18	19	20	MEAN	STDEV.
Colour	Red	Red	Red	Red	Red	Red	0	0
Density at 15 °C, Kg/m^3	727.6	736.3	732.3	729.7	731.3	729.2	731	3
RON	90.8	90.7	90.6	91.0	91.0	90.8	90.8	0.2
RVP, kg/cm^2	0.62	0.50	0.46	0.59	0.53	0.56	0.54	0.06
Total sulfur, ppm	173	9	227	152	65	74	138.2	68.5
DISTILLATION								
IBP, °C	37	39	38	37	38	37	37.7	0.8
10 %, °C	52	54	55	52	52	52	52.8	1.3
50 %, °C	78	85	85	85	79	82	82.3	3.2
90 %, °C	134	148	143	151	140	140	142.7	6.1
FBP, C	172	198	190	187	182	184	185.5	8.7
Acidity, mgKOH/g	0.0070	0.0039	0.0045	0.0074	0.0038	0.0022	0.005	0.002
COMPOSITION								
Paraffins, %Vol.	47.98	36.65	37.20	48.04	46.05	42.27	43.0	5.2
Olefins, % Vol.	30.28	32.64	37.18	28.70	27.17	31.52	31.3	3.5
Naphthenes, % Vol.	12.86	12.75	10.32	8.00	11.28	11.53	11.1	1.8
Aromatics, % Vol.	7.75	14.58	14.01	15.26	12.77	14.68	13.2	2.8
Oxygenates, % Vol.	0.00	0.00	0.00	0.00	0.00	0.00	0	0
Unknowns, % Vol.	1.14	3.37	1.29	0.69	2.72	1.91	1.85	1.02
C4 %Vol.	2.23	1.27	2.57	3.06	2.69	0.98	2.13	0.83
C5 % Vol.	27.90	18.67	16.19	19.78	27.20	30.75	23.42	5.94
C6 % Vol.	25.38	16.16	21.14	17.36	25.37	24.85	21.71	4.17
C7 % Vol.	13.60	14.08	16.72	11.08	20.96	20.37	16.14	3.94
C8 % Vol.	20.53	25.53	27.60	33.76	8.62	13.00	21.51	9.41
C9 % Vol.	7.14	13.29	11.34	11.41	8.47	6.77	9.74	2.65
C10 % vol.	1.63	4.90	2.03	2.47	3.13	1.05	2.54	1.36
C11 % Vol.	0.40	1.38	0.45	0.40	0.61	0.18	0.57	0.42
C12 % vol.	0.06	1.35	0.08	0.00	0.23	0.14	0.31	0.51
C13% Vol.	0.00	0.00	0.00	0.00	0.00	0.00	0	0
C14% vol.	0.00	0.00	0.00	0.00	0.00	0.00	0	0
>C14 % Vol.	0.00	0.00	0.00	0.00	0.00	0.00	0	0
Benzene, % vol.	0.44	0.52	0.13	0.26	0.47	0.88	0.45	0.26

The sulfur levels for the group were also far below the GSA maximum limit of 1000ppm, as the mean was 138ppm. The distillation curves of the mixed stations were scattered indicating diversity in sources, **Figure 4.8**.

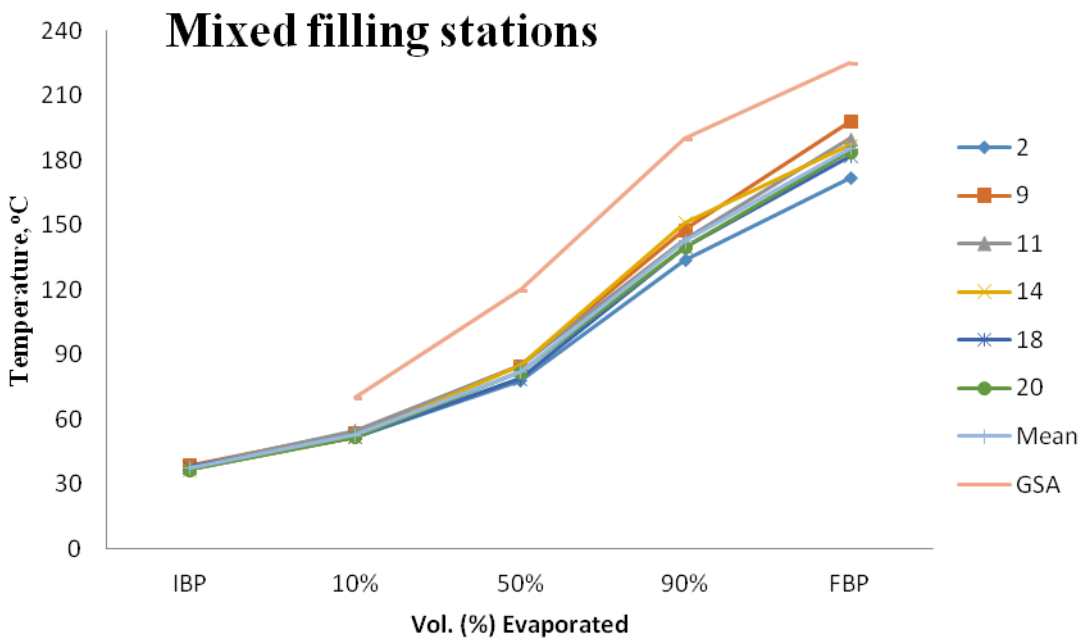

Figure 4.8: Distillation curves of mixed filling stations samples and GSA limits

Quality evaluation of Ship (reference) samples

The mean RON for the ship reference samples was 91.6 with a standard deviation of 0.1, hence all the samples conform to the GSA limit of minimum RON of 91.

The sulfur levels of the ships samples vary. The mean of 105ppm sulfur was lower than the filling stations except the total group.

Olefins levels among the ships samples were similar to those from the filling stations.

The composition of all the ship samples was in the range of C4 to C12. There were no C13 and heavier compounds present **(Table 4.14)**.

Table 4.14: Physicochemical parameters of gasoline from ships

PARAMETER	21	22	23	Mean	STDEV.
Acidity, mgKOH/g	0.0015	0.0007	0.0035	0.0019	0.0014
Colour	Undyed	Undyed	Undyed	-	-
Density @ 15°C, kg/m^3	724.3	730.2	725.7	726.733	3.038
RVP, kg/cm^2	0.61	0.51	0.56	0.6	0.1
Sulphur, ppm	162	81.0	72.0	105.00	49.568
RON	91.7	91.6	91.5	91.600	0.473
DISTILLATION,					
IBP , °C	36	35	36	36.000	1.528
10%, °C	49	52	53	52.667	2.309
50%, °C	73	88	90	87.333	6.557
90%, °C	137	146	149	140.667	14.844
FBP, °C	169	186	188	181.000	16.643
COMPOSITION					
Paraffins, % Vol.	52.46	47.22	50.67	46.283	3.994
Olefins, % Vol.	17.61	28.65	29.99	28.697	9.105
Naphthenes, % Vol.	11.14	14.58	10.52	12.817	1.933
Aromatics, % Vol.	18.79	8.40	8.72	11.387	6.358
Unknowns, % Vol.	2.09	3.75	0.83	2.223	1.465
C4, % Vol.	2.30	0.26	2.49	1.683	1.236
C5, % Vol.	30.72	23.51	27.10	27.270	3.391
C6, % Vol.	27.77	23.51	23.76	25.013	0.725
C7, % Vol.	17.10	15.76	16.91	16.590	6.358
C8, % Vol.	10.06	20.83	21.30	17.397	1.465
C9, % Vol.	8.32	6.84	5.39	6.850	1.506
C10, % Vol.	1.39	4.14	1.70	2.410	0.172
C11, % Vol.	0.20	0.47	0.52	0.40	0.25
C12, % Vol.	0.06	0.46	0.00	0	0
C13, % Vol.	0.00	0.00	0.00	0	0
C14, % Vol.	0.00	0.00	0.00	0	0
>C14, % Vol.	0.00	0.00	0.00	0	0
Benzene, % Vol.	0.30	0.85	0.67	0.61	0.28

The distillation curves of the ships samples were below the maximum limits set by the GSA. There were significant variations however in the distillation curves among the ships samples indicating diversity in source and refining processes employed in obtaining the various gasoline samples (**Figure 4.9**).

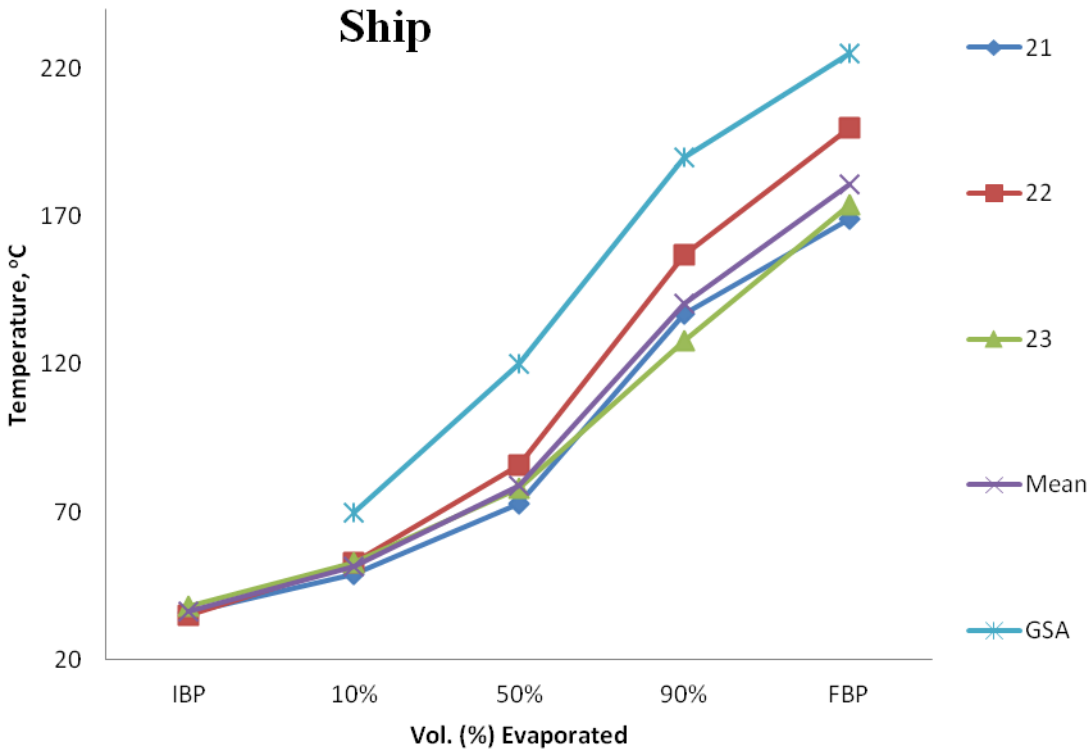

Figure 4.9: Distillation curves of Ship samples and GSA limits

Quality evaluation of TOR (reference) samples

The mean RON value for the TOR group was 91.47. Like the ships reference samples the TOR gasolines were of higher RON than the filing stations, and all the RON values among the reference group satisfy the requirement of the GSA.

With a mean of 309ppm of sulfur, the TOR sulfur levels were however higher than the filing stations. This implies the crude oil used in the production had higher sulfur levels.

Olefins levels among the TOR samples were generally similar to those from the filling stations. The levels of benzene in the TOR samples were low as the aromatics were also low, as was the case of the filling stations.

The composition of all the TOR samples is in the range of C4 to C12. There were no C13 and heavier compounds present.

Like the filling stations all the distillation curves of the gasolines from TOR were below the maximum limits set by the GSA. The distillations curves also showed great similarity as the source was the same, **Figure 4.10**.

Table 4.15: Physicochemical parameters of gasoline samples at TOR

PARAMETER	24	25	26	Mean	STDEV.
Acidity, mgKOH/g	0.0038	0.0036	0.0030	0.004	0.003
Colour	Undyed	Red	Red	-	-
Density @ 15°C, kg/m^3	735.1	737.4	737.2	736.57	1.27
RVP, kg/cm^2	0.53	0.56	0.59	0.56	0.03
Sulphur, ppm	153	344	432	309.67	142.63
RON	92.0	91.3	91.1	91.47	0.47
DISTILLATION,					
IBP , °C	37	35	36	36	1
10%, °C	53	52	53	52.667	0.577
50%, °C	84	88	90	87.333	3.055
90%, °C	152	146	149	149	3
FBP, °C	185	186	188	186.333	1.528
COMPOSITION					
Paraffins, % Vol.	40.96	47.22	50.67	46.283	4.922
Olefins, % Vol.	27.45	28.65	29.99	27.813	1.271
Naphthenes, % Vol.	13.35	14.58	10.52	12.817	2.082
Aromatics, % Vol.	17.04	8.40	8.72	11.48	4.899
Unknowns, % Vol.	1.19	1.15	0.20	0.85	0.56
C4, % Vol.	2.57	2.34	1.74	2.217	0.429
C5, % Vol.	25.13	25.07	28.15	26.117	1.761
C6, % Vol.	21.59	26.74	25.09	24.47	2.63
C7, % Vol.	23.39	13.34	13.79	16.840	5.677
C8, % Vol.	13.43	23.42	24.37	20.407	6.061
C9, % Vol.	6.42	5.07	4.14	5.210	1.146
C10, % Vol.	4.42	2.42	2.46	3.100	1.143
C11, % Vol.	1.08	0.36	0.12	0.5	0.5
C12, % Vol.	0.08	0.99	0.00	0.36	0.55
C13, % Vol.	0.00	0.00	0.00	0	0
C14, % Vol.	0.00	0.00	0.00	0	0
>C14, % Vol.	0.00	0.00	0.00	0	0
Benzene, % Vol.	0.72	0.31	0.43	0.49	0.21

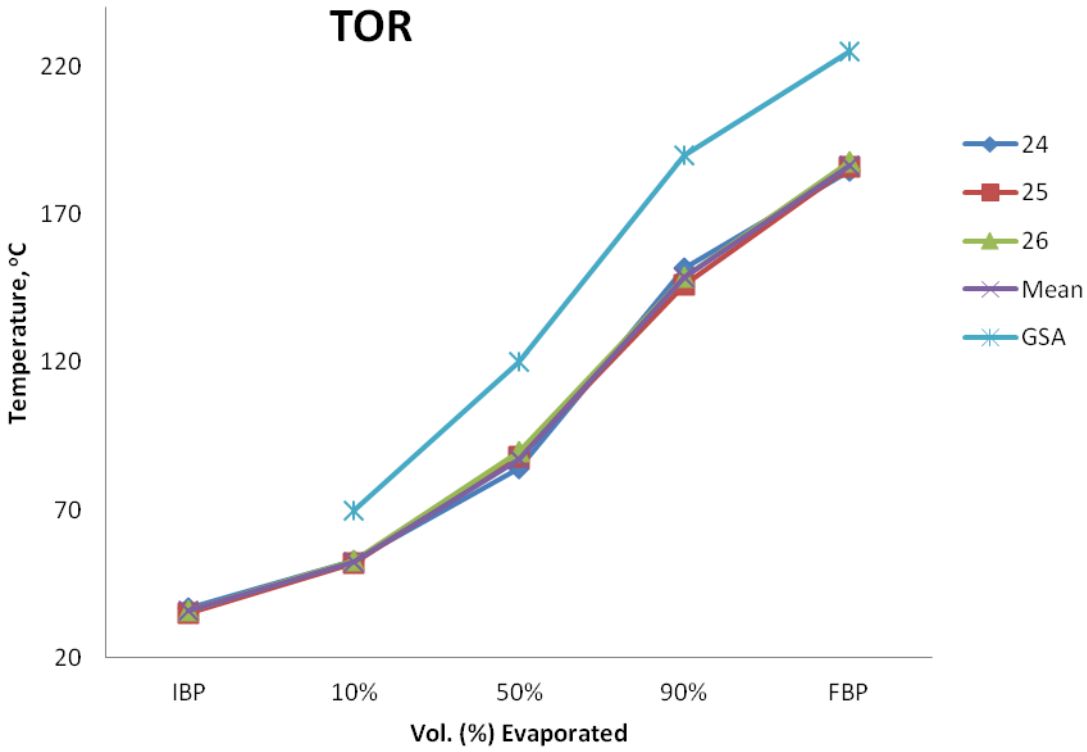

Figure 4.10: Distillation curves of TOR samples and GSA limits

4.7 MULTIVARIATE STATISTICAL EVALUATION OF GASOLINE ADULTERATION IN GREATER ACCRA, GHANA

Principal Component Analysis (PCA)

For PCA, the value of KMO (Kaiser-Meyer-Olkin) measure of sample adequacy was 0.75, which meets the limit of 0.600 conventionally held as a critical value. Bartlett's test of sphericity showed that principal component analysis could be applied to the data at the $p < 0.01$ level. Two principal components were identified using Varimax with Kaiser Normalization for the gasoline samples. The principal components accounted for 91.80% of the total variance in the dataset.

The first component (PC1), which explained 48.70% of the total variance with an eigenvalue of 2.92, was most dependent on samples from ship, TOR and Total. This component comprises the unadulterated groups implying that, gasoline bought from such outlets have little or virtually no adulteration content.

The second component (PC2), which explained 43.10% of the total variance with an eigenvalue of 2.59, was mainly dominated by samples from Shell, Goil and Mixed. This component comprises the adulterated filling stations implying that, gasoline bought from such outlets have some degree of adulterated content (**Table 4.16**).

Table 4.16: Varimax rotated factor loadings matrix and communalities obtained from principal component analysis for gasoline adulteration.

Variables	Component 1	Component 2
TOR	0.950	
Ship	0.978	
Shell	0.580	0.970
Goil	0.263	0.887
Total	0.874	0.419
Mixed	0.354	0.773
Eigenvalue	2.923	2.585
Explained Variance (%)	48.714	43.085
Cumulative Variance (%)	48.714	91.799

The effects of gasoline adulteration by kerosene raise several environmental and health concerns. Some adulterants increase emissions of harmful pollutants. These include tail pipe emissions of hydrocarbons (HC), carbon monoxide (CO) due to incomplete combustion, oxides of nitrogen (NO_x) and particulate matter (PM). Emissions which fall into the category of unregulated emissions are benzene and polyaromatic hydrocarbons (PAHs), which are known carcinogens. Benzene depends mostly on fuel composition and catalyst performance. PAHs in the exhaust are due to the presence of PAHs in the fuel and in part due to PAH formation by fuel combustion in the engine in the case of gasoline. Amounts of pollutants emitted also depend on parameters such as air-to-fuel ratio, engine speed, engine load, operating temperatures, whether the vehicle is equipped with a catalytic converter and the condition of the catalyst. There is an indirect adverse effect on the society and this is through the loss of tax revenue via the large scale diversion of kerosene

designated for household use in Ghana for adulteration in gasoline. This singular activity can deprive people kerosene used for cooking.

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The conclusions drawn from this study are as follows:

- Acidity levels of various petroleum distillate fractions were dependent on the type of crude oil.
- The acidity of premium gasoline was far lower than that of kerosene.
- The accuracy and precision of the in-house simple direct titration (SDT) method developed was high, hence the correlation coefficient of the linear regression was also high.
- All the fuel stations examined, 40% had lower levels of adulteration (3-10% of domestic kerosene); while 20% had significant adulteration (14-29% of domestic kerosene).
- The acidity method of "fingerprinting" gasoline adulteration is cheaper, simple, and reliable.
- The gasoline available in Accra Metropolis did not conform to standard specifications for Europe, Japan and India. 35% also fail to meet the requirements set by the Ghana Standards Authority (GSA).
- The principal component data analysis discriminated gasolines from ships, TOR and Total fuel stations as one component largely unadulterated, while the other

component dominated by gasolines from Mixed stations, GOIL and Shell stations as largely adulterated.

5.2 Recommendations

The following recommendations are made to promote the scope of knowledge on monitoring of gasoline adulteration and quality;

- A detailed study of the acidity of gasolines is recommended. This study demonstrated that acidity of gasoline, which is not measured as a quality requirement is a sensitive parameter that offers an easier and cheaper means of monitoring gasoline contamination and adulteration.
- Continuous quality monitoring and enforcement should be undertaken to protect the environment and the consumer.
- It is also recommended that Ghana should explore the use of oxygenates in gasoline. Oxygenates increases octane number significantly, they also reduces emissions of carbon monoxide, nitrogen oxides and hydrocarbons. It will also offer an opportunity to reduce the dependence on fossil fuel which is expensive and untenable.

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Appendices

Appendix 1 Calculation of acidity by calorimetric titration:

Acidity, mg of KOH/g = (K× N × 56.1)/W

Where:

56.1 = Molar mass of KOH,

K = Volume of KOH solution required for titration of the sample mL,

N = normality of the KOH solution, and

W = weight of sample used, g.

Appendix 2 Calculation of acid number (acidity) by potentiometric titration:

Acid number, mg of KOH/g = [(A-B) N X 56.1]/W

Where:

A = Volume of KOH solution required for titration of the sample, mL.

B = Volume of KOH solution required for titration of the blank, mL.

N = normality of the KOH solution, and

W = weight of sample used, g.

Appendix 3 Retention times of some hydrocarbon standards by gas chromatography

RETENTION TIME/MIN	STANDARD	RETENTION TIME/MIN	STANDARD
1.576	i-butane	5.289	2-methyl-2-hexene
1.652	n-butane	5.527	3 – ethylpentane
1.678	2, 2 - dimethylpropane	5.871	methylcyclohexane
1.689	t – butane – 2	5.972	1, 1, 3 – trimethylcyclopentane
1.834	3 – methylbutene – 1	6.277	ethylcyclopentane
1.928	i-pentane	6.316	2, 2, 3 – trimethylpentane
2.006	pentene – 1	6.386	2, 4 – dimethylhexane
2.047	2 – methylbutene – 1	7.000	2, 3, 4 – trimethylpentane
2.077	n-pentane	7.386	2,3-dimethylhexane
2.110	isoprene	7.628	2 – methylheptane
2.126	t – pentene – 2	7.685	4-methylheptane
2.184	3, 3 – dimethylbutene – 1	7.685	4 – methylheptane
2.357	2, 2 – dimethylbutane	7.923	3 – methylheptane
2.535	4 – methylpentene – 1	8.356	2, 2, 5 – trimethylhexane
2.658	cyclopentane	8.998	n-octane
2.670	2, 3 – dimethylbutane	10.301	1, 1, 4 – trimethylcyclohexane
2.717	2 – methylpentane	11.751	1, 4 – dimethylbenzene
2.884	2 – methyl – 1, 4 – pentadiene	12.351	2-methyloctane
2.943	3 – methylpentane	12.927	1, 2 – dimethylbenzene
3.109	n-hexane	13.998	n-nonane
3.135	t – hexene – 3	14.401	i – propylbenzene
3.175	t – hexene – 2	15.501	3,6-dimethyloctane
3.209	2 – methylpentene – 2	15.768	1, 4 – methylethylbenzene
3.318	c – hexene – 2	15.832	1, 3, 5 – trimethylbenzene
3.416	3, 3 – dimethylpentene – 1	16.323	1, 2 – methylethylbenzene
3.484	2, 2 – dimethylpentane	16.793	1, 2, 4 – trimethylbenzene
3.534	methylcyclopentane	17.564	1, 2, 3 – trimethylbenzene
3.589	2, 4 – dimethylpentane	17.812	2, 3 – dihydroindene
3.953	benzene	18.395	1, 3 – diethylbenzene
3.981	3 – methylhexene – 1	18.564	1, 3 – dimethyl – 5 – ethylbenzene
4.168	cyclohexane	19.065	1, 3 – dimethyl – 4 – ethylbenzene
4.564	3-methyhexane	19.944	1, 4 – ethyl – i – propylbenzene
5.191	n-heptane	20.019	1,2,3,5-tetramethylbenzene