

A MODEL FOR BLENDING MOTOR GASOLINE

CASE STUDY: TEMA OIL REFINERY LTD.

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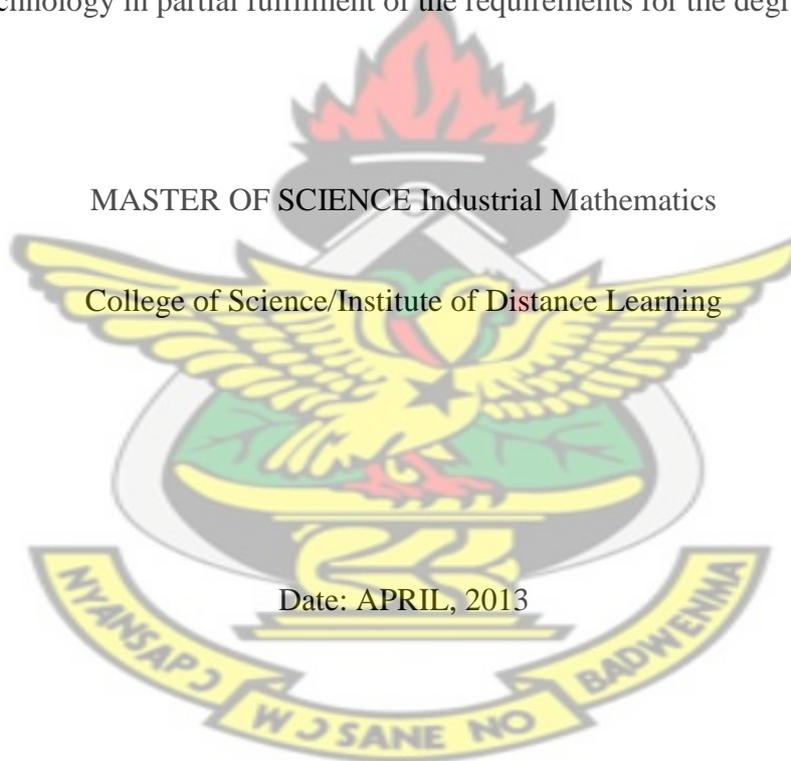
OKOTO ANSON FRANCIS (BSC. CHEMICAL ENGINEERING)

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Dr. E. Osei-Frimpong

Supervisor

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Dedication

I dedicate this work to the Almighty God, my dear wife Yvonne Owusu Ansah and three sons Obour , Boateng and Semanhyia Okoto Anson. I also dedicate the work to my mum Theresah Addo and my uncle Kenneth Addo.

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Declaration

I hereby declare that this submission is my own work towards the MSc/MPhil/PhD 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.

OKOTO ANSON FRANCIS

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Student Name & ID

Signature

Date

Certify by:

DR. E. OSEI-FRIMPONG

Supervisor(s) Name

Signature

Date

Certified by:

PROF. S.K. AMPONSAH

Head of Dept. Name

Signature

Date

and

Certified by

PROF. I.K. DONTWI

Dean, IDL

Signature

Date



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I will first of all like to say a big thank you to the Almighty God for seeing me through this research.

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Abstract

Without accurate blending correlations, any attempt to blend different gasoline cuts can be expected to achieve non-optimum results. The purpose of this work is to propose a method for predicting research octane numbers, Reid vapour pressure and the density for two component gasoline blends. A new mathematical model for blending of gasoline is presented in this paper. It is a model which combines the idea of linear blending and mixing problem to develop three first order ordinary differential equations. Numerical method specifically Runge-Kutta is applied to solve the presented models in our research by applying a written code in MATLAB Software. Also a generic analytical solution was generated to solve the equations. This new mathematical models for blending of motor gasoline is illustrated with some studies based on data from the Quality control department Tema Oil Refinery, Ghana.



CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THESIS

Petroleum, a fossil fuel, supplies more energy to the world today than any other source. Crude oil in its natural state has very few practical uses. However, when it is separated into its component parts by the process of fractionation or refining, those parts have almost unlimited number of applications. The United States is the world's leading consumer of petroleum; in 1994, Americans used 7,587,000 barrels of oil per day. Petroleum is formed from the remains of plants and animals that have been held under tremendous pressure for millions of years. Ordinarily, this organic matter would decompose completely with the help of scavengers and aerobic bacteria, but petroleum is created in an anaerobic environment, without the presence of oxygen. Over half of the world's known crude oil is concentrated in the Persian Gulf basin. Other major areas include the coasts of Alaska and the Gulf of Mexico. Petroleum products include gasoline. Gasoline is a mixture of hydrocarbons containing n-paraffins, olefins, naphthenes and aromatic (Chromatography Online, 2008). Motor gasoline is a mixture of lighter fractions of petroleum composed of hydrocarbons having boiling points in the range approximately 30°C to 215°C. Gasoline is a volatile, flammable liquid obtained from the refinement of petroleum, or crude oil. It was originally discarded as a by-product of kerosene production, but its ability to vaporize at low temperatures made it a useful fuel for many machines. Straight run stream from crude distillation unit (CDU) and cracked stream from fluidized Catalytic Cracker Unit (FCC) with the above boiling range are blended to obtain required motor gasoline

(www.speedfuels.com). Gasoline became the preferred automobile fuel because it releases a great deal of energy when burned, it mixed readily with air in a carburetor, and it initially was cheap due to a large supply. Costs have now increased greatly except where subsidized. Gasoline was first produced by distillation. A gasoline's octane number indicates its ability to resist knocking (premature combustion) and can be altered by changing the proportions of certain components. The compound tetraethyl lead, once used to reduce knocking, has been banned as toxic. Other additives include detergents, antifreezes, and antioxidants(www.answers.com). The first oil well in the United States was struck by Edwin L. Drake near Titusville, Pennsylvania, in 1859 at a depth of almost 70 feet (21 m). With the development of the four-stroke internal combustion engine by Nikolaus Otto in 1876, gasoline became essential to the automotive industry. Today, almost all gasoline is used to fuel automobiles, with a very small percentage used to power agricultural equipment and aircraft. Gasoline is one of the products derived from distilling and refining petroleum. Compounds of organic lead were added to gasoline in the past to reduce knocking in engines, but due to environmental concerns this is no longer common. Other chemicals are also added to gasoline to further stabilize it and improve its colour and smell in a process called "sweetening."

Produce gasoline from crude oil, it just removes the gasoline from other compounds in crude oil. Further refining processes are now used to improve the quality of the fuel. Refining petroleum Catalytic cracking is one of the most important processes in oil refining. This process uses a catalyst, high temperature, and increased pressure to affect chemical changes in petroleum. Catalysts such as aluminium, platinum, processed clay, and acids are added to petroleum to break down larger molecules so that it will possess the desired compounds of gasoline. Another refining process is polymerization. This is the opposite of cracking in that

it combines the smaller molecules of lighter gases into larger ones that can be used as liquid fuels. *Additives* Once gasoline is refined, chemicals are added. Some are anti-knock compounds, which react with the chemicals in gasoline that burn too quickly, to prevent "engine knock." In leaded gasoline, tetraethyl lead is the anti-knock additive. (Unleaded gasoline is refined further so the need for anti-knock additives is minimal.) Other additives (antioxidants) are added to prevent the formation of gum in the engine. Gum is a resin formed in gasoline that can coat the internal parts of the engine and increase wear. Gasoline is primarily a mixture of two volatile liquids, heptane and isooctane. Pure heptane, a lighter fuel, burns so quickly that it produces a great amount of knocking in an engine. Pure isooctane evaporates slowly and produces virtually no knocking. The ratio of heptane to isooctane is measured by the octane rating.

The greater the percentage of isooctane, the less knocking and the higher the octane rating. For example, an octane rating of 87 is comparable to a mixture of 87% isooctane and 13% heptanes (www.answers.com/topic/gasoline). Aromatics, olefins and naphthenic present in gasoline have the tendency to increase the octane rating of the gasoline as opposed to n-paraffin's which decrease the gasoline octane rating or octane number. The octane number is one of the essential measures of gasoline quality.

Reid vapor pressure (RVP) is a common measure of the volatility of gasoline. It is defined as the absolute vapor pressure exerted by a liquid at 100 °F (37.8 °C) as determined by the test method ASTM-D-323. The test method applies to volatile crude oil and volatile non viscous petroleum liquids, except liquefied petroleum gases.

The matter of vapour pressure is important relating to the function and operation of gasoline powered, especially carburetted, vehicles. High levels of vaporization are desirable for winter

starting and operation and lower levels are desirable in avoiding vapour lock during summer heat. Fuel cannot be pumped when there is vapour in the fuel line (summer) and winter starting will be more difficult when liquid gasoline in the combustion chambers has not vaporized. Thus, oil refineries manipulate the Reid Vapour Pressure seasonally specifically to maintain gasoline engine reliability. The Reid vapour pressure (RVP) differs slightly from the true vapour pressure (TVP) of a liquid due to small sample vaporization and the presence of water vapour and air in the confined space of the test equipment. That is, the RVP is the absolute vapour pressure and the TVP is the partial vapour pressure.. The mass density or density of a material is its mass per unit volume. In some cases (for instance, in the United States oil and gas industry), density is also defined as its weight per unit volume, although this quantity is more properly called specific weight(wikipedia.org). Crude oil contains more carbon than gasoline and the more process the gasoline the less carbon content it contains (Seddon, 2000). This issue is particularly pertinent when producing higher-octane gasoline. Such a fuel would produce improved vehicle engine efficiencies but at the considerable cost of carbon dioxide emissions in the refineries (Seddon, 2000). Blending is to mix or combine so the components are indistinguishable .Motor gasoline blending is the mechanical mixing of motor gasoline blending components. Mathematical modelling is a method of simulating real life situations with mathematical equations to forecast their future behaviour (www.businessdictionary.com) or a mathematical model is a description of a system using mathematical concepts and language. The process of developing a mathematical model is termed mathematical modelling. Mathematical model for motor gasoline blending is the mathematical presentation of gasoline blend components to allow investigation of key properties of the system and prediction of future outcomes to be carried out. In the first sixty years (60) after the process of petroleum refining was invented, the most important fraction

produced was kerosene, widely used as home heating product. The petroleum fraction slightly lighter than kerosene-gasoline-was regarded as waste product and discarded. Not until 1920s when the automobile became popular in the United States of America, did manufacturers find any significant use for gasoline. From then on, however, the importance of gasoline has increased with automobile use. Hence the blending of components to form gasoline of particular properties (www.bookrags.com). Volatility must be adjusted for the altitude and seasonal temperature of the location where the gasoline will be used (www.chevronwithtechron.com).

1.1.1 BRIEF DISCUSSION OF TERMS

Mixing problem is combining or blend of two or more components to form a uniform mixture.

Differential equation is a mathematical equation for an unknown function of one or several variables that relates the values of the function itself and its derivatives of various orders. Differential equations play a prominent role in engineering, physics, economics, and other disciplines.

Differential equations arise in many areas of science and technology, specifically whenever a deterministic relation involving some continuously varying quantities (modelled by functions) and their rates of change in space and/or time (expressed as derivatives) is known or postulated. This is illustrated in classical mechanics, where the motion of a body is described by its position and velocity as the time value varies. An ordinary differential equation (ODE) is a differential equation in which the unknown function (also known as the dependent variable) is a function of a single independent variable. In the simplest form, the

unknown function is a real or complex valued function, but more generally, it may be vector-valued or matrix-valued: this corresponds to considering a system of ordinary differential equations for a single function.

Ordinary differential equations are further classified according to the order of the highest derivative of the dependent variable with respect to the independent variable appearing in the equation. The most important cases for applications are first-order and second-order differential equations

MATLAB (an abbreviation of MATrixLABoratory) is a computer algebraic package, registered trademark of computer software, now at version 7.10 (release R2010a) developed by the Math Works Inc. The software is widely used in many of science and engineering fields. MATLAB is an interactive program for numerical computation and data visualization. MATLAB is supported on Unix, Macintosh and 32Windows environments. MATLAB integrates mathematical computing, visualization, and a powerful language to provide a flexible environment for technical computing. The open architecture makes it easy to use MATLAB and its companion products to explore data, create algorithms and create custom tools that provide early insights and competitive advantages. Known for its highly optimized matrix and vector calculations, MATLAB offers an intuitive language for expressing problems and their solutions both mathematically and visually. Typical uses include:

- Numeric computation and algorithm development.
- Symbolic computation (with the built-in Symbolic Math functions).
- Modeling, simulation and prototyping.
- Data analysis and signal processing.
- Engineering graphics and scientific visualization.

MATLAB offers engineers, scientists, and mathematicians an intuitive language for expressing problems and their solutions mathematically and graphically. It integrates computation, visualization, and programming in a flexible, open environment. Complex numeric and symbolic problems can be solved in a fraction of the time required with other languages such as C, Fortran, or Java.

1.1.2 OVERVIEW OF BLENDING OF GASOLINE

Gasoline Blending is of ultimate importance in refinery economics. Traditionally, gasoline blending has been treated with some degree of simplification regarding physical property prediction. Frequently only a few properties have been seriously considered as blending constraints Gasoline blending is a refinery operation that blends different component streams into various grades of gasoline. Octane number is the property of gasoline that determines its knock ability. Typical grades include 83 octane (blended with oxygenated fuel such as ethanol, regular 87 octane, 92 octane and 91 octane. The Reid (Vapour pressure is set depending on the average temperature of the location the gasoline will be used (cold temperature require high RVP than warmer climates). These two specifications are the most significant and they are documented with each blend, to minimize octane giveaway potential. If the octane specification is 87.0 each 0.1 octane over this target value costs the refiner money.

1.1.3 ORGANIZATIONAL PROFILE OF TEMA OIL REFINERY LIMITED

Tema Oil Refinery (TOR) Limited is the only refinery in Ghana. It is authorized by its regulators to process crude oil and market petroleum products. The refinery is situated in Tema about 24kilometers east of the capital of Ghana, Accra. It was originally named the Ghanaian Italian Petroleum (GHAIP) company and incorporated as a private Limited

Liability Company under the company's ordinance (Cap 163) on December 12, 1960. It was 100% owned by ENI Group (Ente Nazionale Idrocarburi) of Italy. The Government of Ghana bought all the shares of GHAIP April 1977 and became sole shareholder.

In 1990, the name was changed to Tema Oil Refinery (TOR). TOR has a vision to become the first class petroleum refinery in Africa. TOR also has a mission to provide quality petroleum products and services primary in Ghana mainly through crude oil refining in a safe, efficient, cost effective and environmentally friendly manner to satisfy customer needs and to increase its shareholder value (www.tor@tor.com).

TOR has five departments under its production division; they are Waste Water Treatment, Residue Fluid Catalytic Cracker, Crude Distillation Unit, Utilities and Movement of Oil and Product. It is the Movement of Oil and Product department that does the blending of gasoline. In the case of Ghana's only Oil Refinery, the Tema Oil Refinery limited (TOR), the Crude Distillation Unit (CDU) processes the crude oil by fractional distillation into various products, such as the Liquefied Petroleum Gas (LPG), Light Gasoline, Heavy Gasoline, Gasoil, Kerosene (for domestic purposes), Aviation Turbine Kerosene (ATK), and Residue Fuel Oil (RFO) (CDU process manual, 2007).

There are two types of gasoline produced from the Crude Distillation Unit at TOR, which are the Light Gasoline and Heavy Gasoline. The Light Gasoline contains less of n-paraffins and more of aromatics, olefins and naphthenic as compared to the heavy Gasoline which contains more n-paraffin and less of aromatics, olefins and naphthenic (CDU process manual, 2007). This means that Light Gasoline has a higher octane number than heavy gasoline.

TOR's Residue Fluid Catalytic Cracking unit (RFCC) feeds on the RFO and cracks it further to higher quality products, such as LPG, Gasoline, Light Cycle Oil, Heavy Cycle Oil and

Clarified Oil. The Gasoline from the RFCC plant has a higher octane number than that of light and heavy Gasoline from the CDU- plant .The higher octane and the lower octane are then blended. (TOR RFCC process manual, 2008). TOR generates 80% of its power requirement internally and 20% from the national grid. The power is generated by steam turbine generators which together have 12 megawatts capacity. Currently only one, which is 5.5 megawatts, is operational.

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1.2 PROBLEM STATEMENT

Gasoline need to be blended to meet certain quality specifications. Normally during blending the focus is on Research Octane number. The correct levels of Reid Vapour Pressure and density are also critical. Though the gasoline additive commonly used in blending is the MMT (Methycyclopentadieny Manganese Tricarbony). Environmentalist from the Ghana Environmental Protection Energy (EPA) are concerned about the manganese element emitted from this substance into the atmosphere. Their main argument is that the manganese is not biodegradable. In our case study, two streams of gasoline are produced. One stream with lower octane , reid vapour pressure and density and the other with higher octane, reid vapour pressure and density. For this reason there is the need to get a mathematical model to effectively predict the octane target and other critical factors like Reid Vapour Pressure and density to avoid octane booster addition.

1.3 OBJECTIVE OF THESIS

- The study seeks to develop a mathematical model for blending motor gasoline.

- To use the model to predict octane number, Reid vapour pressure of gasoline and density of gasoline blends

1.4 JUSTIFICATION OF THESIS

Gasoline revenues accounts for a good share of the profitability of refineries. Currently gasoline market continuous to experience expansion. This trend will persist in the near future. Carlos et al stated that gasoline production often yields 60-70% of a typical refinery's total revenue. Naturally, a higher octane gasoline sells higher than a lower octane gasoline. The quality of gasoline depends on the octane number and other critical factors like the density and Reid vapour pressure. Therefore it is economically good to blend to get a desired optimum gasoline to get a good price and also to improve the quality of the gasoline. To this end the mathematical model of gasoline bending is justifiable.

1.5 METHODOLOGY

In this study, the idea of material balance, mixing problem and linear blending is used to deduce first order ordinary differential equations. These models predict the density, Reid vapour pressure and research octane of gasoline blend and the equations is evaluated by explicit numerical method specifically Runge-Kutta method. MATLAB computer software program use to write an algorithm for the solution of the first order ordinary differential equations. The quality control department of Tema Oil Refinery will provide data for the validation of the model after they have done analysis on the samples taken from the gasoline

storage tanks. The data needed for the model are properties of the gasoline feed stocks from Tema Oil Refinery Ltd, the RVP, Density and RON.

1.6 SCOPE OF THESIS

This dissertation is limited to modeling differential equations to blend gasoline feed stock in Tema Oil Refinery Limited, Ghana. Two components are considered.

1.7 THESIS ORGANISATION

The thesis consists of the following five chapters, chapter one is introduction which covers background, problem statement, objective, justification, methodology, scope of thesis and thesis organization.

Chapter two reviews related research on gasoline blending models. Chapter three focuses on the methodology for the analysis of the differential equation obtained or derived for blending of motor gasoline. The derivation is from first principle using modelling via differential equation. A brief overview of Runge –Kutta numerical method and the software used MATLAB .Chapter four is data collection and analysis here by using available data from the Quality Control Department of Tema Oil Refinery Limited. We specifies the dependent variables in the blend. We solve the differential equations using Runge-Kutta method by writing a MATLAB code .

Chapter five concludes the thesis. We summarise the results of numerical solution and draws conclusion on the results obtained. Recommendations will be articulated

CHAPTER 2

REVIEW OF RELATED LITERATURE

2.1 Research Octane Number and Motor Octane Number

The Research Octane Number (RON) or the Motor Octane Number (MON) of an unleaded gasoline is one of the most essential measures of gasoline quality. The research octane number (RON) and the motor octane numbers (MON) of gasoline are measurements of its quality of performance as fuel. An octane number is a number which measures the ability of the gasoline to resist knocking. Knocking occurs when fuel combusts prematurely or explodes in an engine, causing a distinctive noise which resembles knocking (Smith, 2003). Engine knock is undesired, as it can cause damage to the engine, and it indicates that the engine is not running as efficiently as it could be. Many engines come with specific octane rating recommendations. Octane numbers are obtained by testing fuel in controlled circumstances. Two different types of octane number can be obtained: the Research Octane Number (RON) or Motor Octane Number (MON). These numbers are obtained by testing fuel in different circumstances, with the MON putting more stress on the engine to see how fuels perform in challenging circumstances. The octane number ratings on a gasoline pump often reflect an average value (Smith, 2003). It is the aim of refinery process engineers to predict correctly the octane ratings of blending unleaded gasoline.

The RON and MON of a gasoline are measurements of its performance quality. The octane number scale is based on the linear blending of isooctane and n-heptane. The octane number

of a gasoline is measured on a scale that ranges from that equivalent to isooctane, octane number of 100 to that of n-heptane octane number of 0.

Auckland and Charlock (1969) observed the saturates, aromatics (are cyclic compounds in which all ring atoms participate in a network of pi bonds, resulting in an unusual stability) and olefins (any unsaturated hydrocarbon containing one or more pairs of carbon atoms linked by a double bond) contents of unleaded gasoline affects the research or motor octane number. When the various gasoline components are blended together, the resultant octane number of the blend may have an octane number quite different from that of either component, even when the two components are of equal octane number.

2.1.1 Linear and Non-Linear blending

Linear blending is a blending problem where the objective function is linear and the constraints are also linear thus in optimization. In terms of equations the terms in the said equation should also be linear.

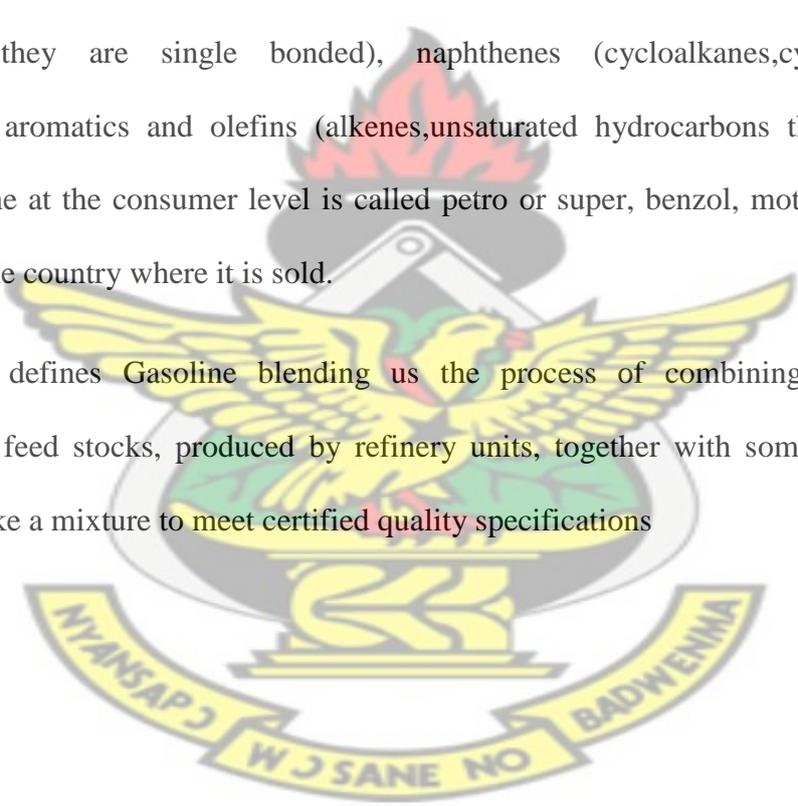
Rusin et al (1981) Stated for linear blending the octane number of a blend will be equal to the addition of the octane numbers of the components in proportion to their concentrations .In the light of Rusin et al. analysis, it is obvious that octane can be raised through refinery processes which increase alkylates or other high octane blending components, or through the use of gasoline additives such as ethanol, methyl tertiary butyl ether (MTBE), and organometallic compounds such as TetraEthylLead (TEL) and MethylcyclopentadienylManganese Tricarbonyl (MMT). It is also obvious that an accurate octane blending method is needed to optimize the blending and formulation of unleaded gasoline components.

For non-linear blending, the resultant octane number may be greater than, equal to or less than that calculated from the volumetric average of the octane numbers of the various blend components.

2.2 Gasoline Blending and Formulation

Gasoline is one of the main distillate obtained from crude oil in a refinery. It is a complex mixture of light hydrocarbons containing 5 to 10 carbon atoms and having a boiling range of 40 °C to 190 °C. A typical gasoline is predominantly a mixture of paraffins (alkanes, saturated hydrocarbons they are single bonded), naphthenes (cycloalkanes, cyclic saturated hydrocarbons), aromatics and olefins (alkenes, unsaturated hydrocarbons they are double bonded) gasoline at the consumer level is called petro or super, benzol, motor spirit or gas, depending on the country where it is sold.

Mourice(2009) defines Gasoline blending as the process of combining two or three components of feed stocks, produced by refinery units, together with some proportion of additives to make a mixture to meet certified quality specifications



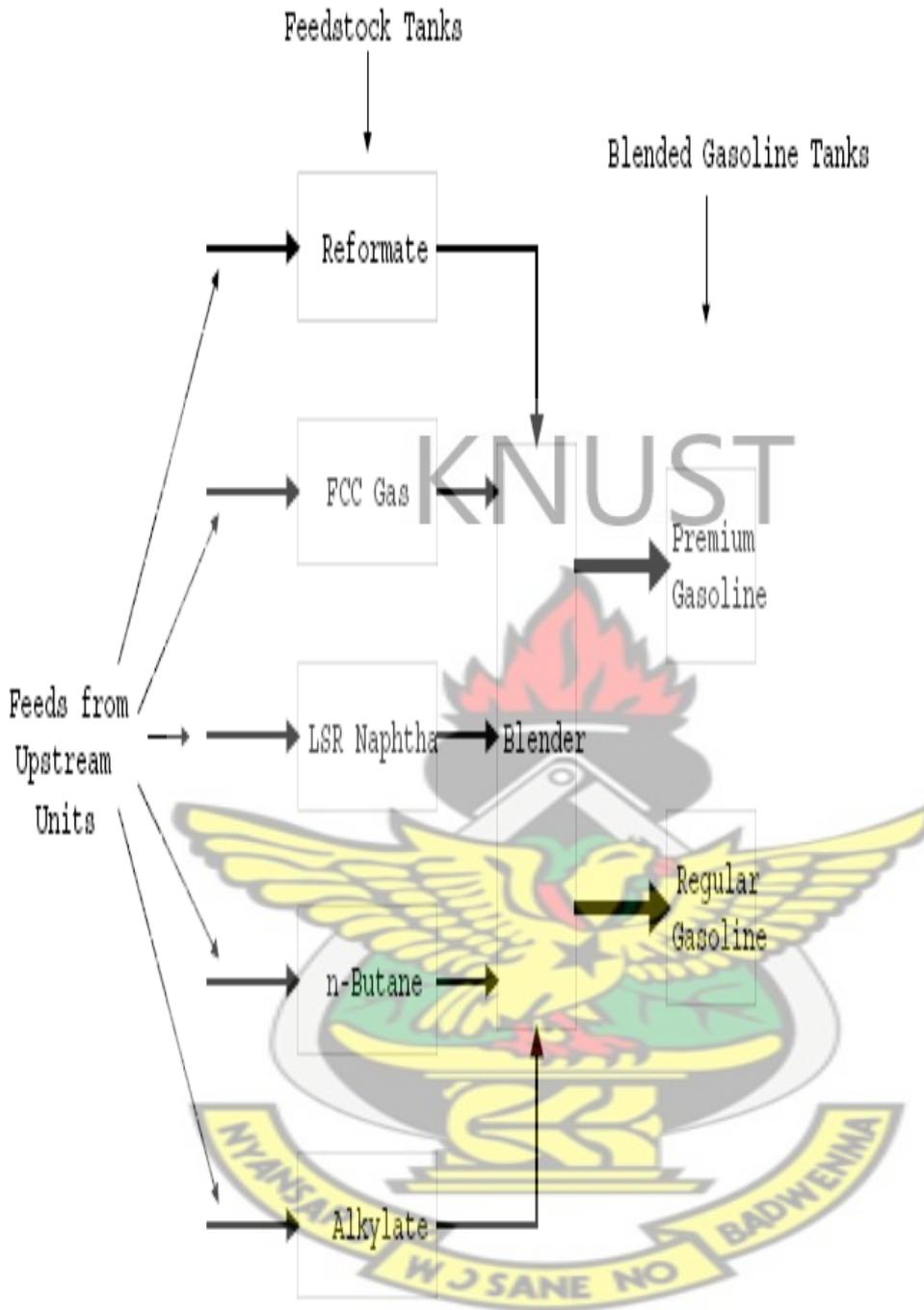


Figure 2.0. Flow chart for gasoline blending

In early stages of crude oil processing, most gasoline components are called naphtha. Modern reformulated gasoline is a blend of several refinery streams namely Catalytic Reformat, Hydrocracking, Straight Run Naphtha, FCC Gasoline, Visbreaker/ Coker Naphtha, Isomerate,

Alkylate, Oxygenate etc. At room temperature, hydrocarbons containing one to four carbon atoms are gases; those with five to 19 carbon atoms are usually liquids; and those with 40 or more carbon atoms are typically solids. Figure (1.1) below shows the typical carbon chain lengths found in the proposed HPV test plans and demonstrates the overlap that occurs.

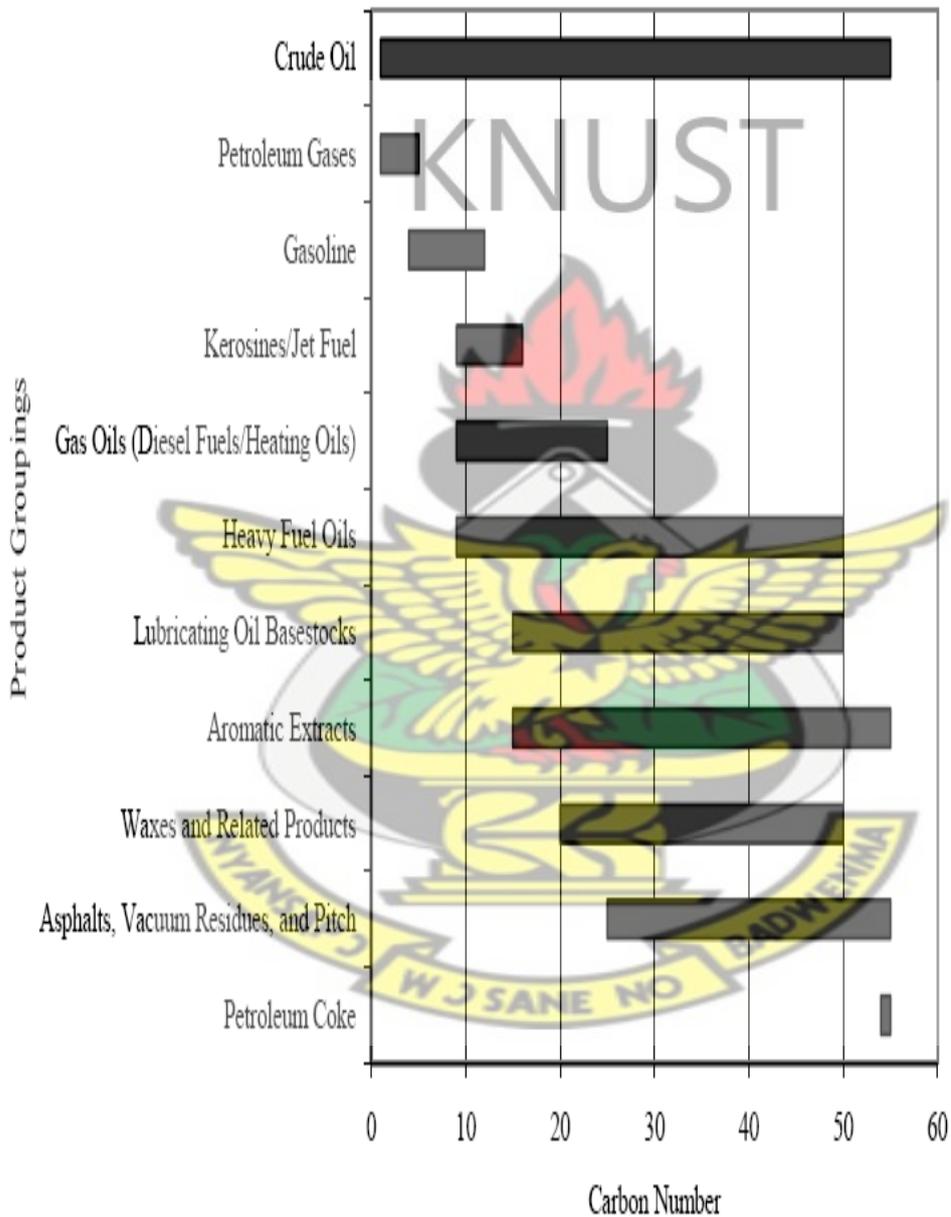


Fig 2.1 Typical Carbon Chain Lengths (USEPA, 2001)

The product application and customer acceptance set detailed specifications for various gasoline properties which in turn determine which refinery streams are suitable for a specific.

Below is the table for Gasoline specifications and their importance:

Table 2.0 Gasoline Specifications and their Importance

Specifications	Importance
Antiknock Index (AKI)	
Research Octane Number (RON)	Low to medium speed knock and run-on
Motor Octane Number (MON)	High speed knock/Part-throttle knock
Fuel Volatility	
Vapor Liquid (V/L) Ratio	Vapor lock
Distillation	Cool weather drivability, hot start and hot drivability, vapor lock, evaporative losses, crankcase deposits, combustion chamber and spark plug deposits
Vapor Pressure (VP)	Low temperature starting, evaporative losses, vapor lock
Copper Corrosivity Stability - Fuel System corrosion	
Existent Gum	Induction system deposits, filter clogging
Oxidation Stability	Storage life
Sulfur Content	Exhaust emissions, engine deposits and engine
Metallic Additives	Catalyst & oxygen sensor deterioration
Temperature for Phase Separation	Water tolerance of blended fuels

2.2.2 Hydrocracking

Hydrocracking is the process by which hydrocarbon molecules of petroleum are broken into simpler molecules, as of gasoline or kerosene, by the addition of hydrogen under high pressure and in the presence of a catalyst (American Heritage Science Dictionary, 2005). This cracking process is assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydro-treater, the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms. This permits wide variations in yields of gasoline and furnace oils to meet seasonal demand changes and can effectively process hard to crack stocks. However since hydrocracked stocks lack the high octane olefins present in catalytically cracked stocks, they must be reformed.

2.2.3 Reforming process

Reforming process convert low octane gasoline range hydrocarbons into higher octane ones. Thermal reforming has been almost completely replaced by catalytic reforming. Most reforming catalysts are bimetallic catalysts consisting of platinum with another promoting metal, such as rhenium Hood(1973) and Lane(1980).

2.2.4 Alkylation

Alkylation is a process in which an alkyl group is added to or substituted in a compound, as in the reaction of alkenes with alkanes to make high-octane fuels or it converts refinery gases into gasoline range liquids of exceptionally high antiknock quality. The octane number of alkylate depends primarily upon the kind of olefins used and upon operating conditions. This method is costly and is not commonly used in gasoline production (OSHA, 2008).

2.2.5 Sulphuric acid alkylation process

Sulphuric acid alkylation process, the feedstock, thus, Propylene, Butylene, Amylene and Iso-Butane enters the reactor and contacts the concentrated sulfuric acid catalyst. The reactor is

divided into zones, with olefins fed through distributors to each zone, and the sulfuric acid and Iso-butananes flowing over baffles from zone to zone. The reactor effluent is separated into hydrocarbon and acid phases in a settler, and the acid is returned to the reactor. The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, deisobutanized, and debutanized. The alkylate obtained from the deisobutanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock. The iso-butane is recycled to the feed (CDU, 2008).

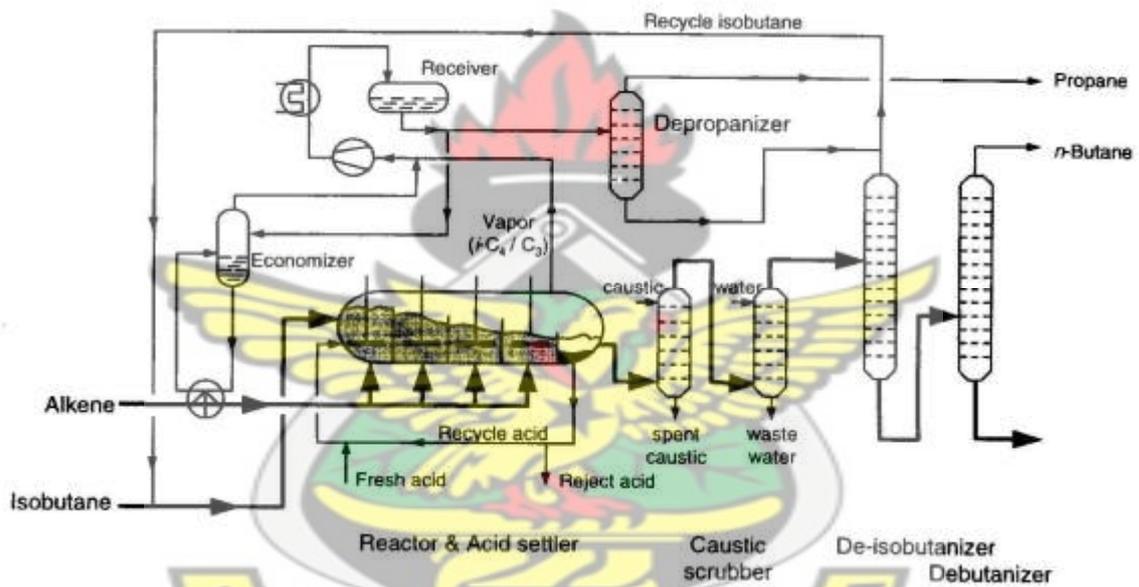


Figure 2.2 Sulphuric Acid Alkylation Process (RFCC, 2008)

2.2.6 Polymerization

Polymerization combines two or more low molecular weight olefin gases into higher molecular weight olefin liquids suitable for gasoline blending or for use as chemical feed stocks (RFCC, 2008). However, because olefinic liquids have low antiknock quality and the reactants, olefin gases, are valuable chemical feeds, the polymerization process is no longer

widely used to produce gasoline blend streams (RFCC, 2008). In view of lead phase out schedules adopted, various options for octane enhancement have been explored.

The need for high quantity fuels, having increased resistance to knock over a wide range of engine operating conditions is of paramount significance in current engine operation. Careful refining and blending of fuel components can produce a fuel of sufficiently increased knock resistance to satisfy engine requirements under certain stressed conditions.

2.3 Anti-Knock Performance in an Internal Combustion Engine

Knock-free engine performance is as important as good drivability. Octane number is a measure of a gasoline's antiknock performance, its ability to resist knocking as it burns in the combustion chamber. There are two laboratory test methods to measure the octane number of a gasoline. One yields the Research octane number (RON); the other, the Motor octane number (MON). RON correlates best with low speed, mild-knocking conditions; MON correlates best with high-speed and high-temperature knocking conditions and with part-throttle operation. For a given gasoline, RON is always greater than MON. The difference between the two is called the sensitivity of the gasoline (Downs and Walsh, 1949).

2.4 Octane Rating or number

An essential characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as detonation. Octane rating is measured relative to a mixture of 2, 2, 4- trimethylpentane (an isomer of octane) and n-heptane. There are a number of different conventions for expressing the octane rating therefore; the same fuel may be labelled with a different number, depending upon the system used. Two compounds were chosen, heptane (C_7H_{16}) and 2,2,4-trimethylpentane

$(\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3)$. Heptane has a high affinity to auto-ignite in an engine, so it was given an octane number of 0. In contrast 2, 2, 4-trimethylpentane has a low affinity to auto-ignite, so it was given a rating of 100. A compound that is less likely to auto-ignite than pure 2, 2, 4-trimethylpentane would have an octane rating of more than 100.

In 1912 was usual noise in the spark ignition internal combustion engine. The noise was called “knocking”, which destroyed the engine then relatively fast. Kettering assigned Thomas Midgley, Jr. to the task of finding the exact cause of knock in internal combustion engines (Midgley, 1993). They used a Dobbie-McInnes monograph to demonstrate that the knock did not arise from pre ignition, as was commonly supposed, but arose from a violent pressure rise after ignition. The monograph was not suitable for further research, so Midgley and Boyd developed a high-speed camera to see what was happening. They also developed a “bouncing pin” indicator that measured the amount of knock ((Midgley, 1989).

2.5 Some Gasoline models

Also it has been common to assume linear predictors for properties, in the sense that values of blend properties are given by linear combinations – in weight or volume basis – of correspondent values of the cuts. This also implies that the blending becomes a linear programming problem, trivially solved by standard techniques. Obviously, depending on the extension of simplification adopted in connection with blend property prediction, the notion of optimal blending may become meaningless. The oil products are manufactured by blending two or more different fractions whose quantities and physicochemical properties depend on the crude oil type, the way and conditions of processing. The quality of the oil products (fuels) for sale has to comply with the current standards for liquid fuels, and the produced quantities have to comply with the market needs. It is in producer's interest to do

the blending in an optimal way, namely, to satisfy the requirements for the oil products quality and quantity with a maximal usage of the available fractions and, of course, with a maximal profit out of the sold products.

The optimization of refinery products blending is accomplished by applying linear programming. The problem is solved by using the spread sheet solver WHAT'S BEST! Julija Risticl etal. (1999).

Pasadakis N. (2006) used Artificial Neural Network (ANN) models have to determine the Research Octane Number (RON) of gasoline blends produced in a Greek refinery. The developed ANN models use as input variables the volumetric content of seven most commonly used fractions in the gasoline production and their respective RON numbers.. The predicting ability of the models, in the multi-dimensional space determined by the input variables, was thoroughly examined in order to assess their robustness. Based on the developed ANN models, the effect of each gasoline constituent on the formation of the blend RON value was revealed

Albahri T. A, (2003) Proposed a theoretical method for predicting the octane number of pure hydrocarbon liquids. The method is based on a structural group contribution approach and requires no experimental procedure or knowledge of the physical or chemical properties only the chemical structure of the molecule. The results of two different sets of structural groups derived from the Joback group contribution approach are tested and compared. The method is notable for the absence of any theoretical procedure which has previously been used to estimate the pure-component octane number. In addition, the method has the potential advantage of synthesis of additional hydrocarbons with knock measurements as a major objective). Online measurements of the octane number can be done using direct octane number analyzers, that it is too expensive so we have to find feasible analyzer, Like ANFIS

estimators. ANFIS are the systems that neural network incorporated in fuzzy systems, with using data automatically by learning algorithms of NNs. ANFIS constructs an input-output mapping based both on human knowledge and on generated input-output data pairs.

Celik, B.M. (2008) studied experimental determination of suitable ethanol–gasoline blend rate at high compression ratio for gasoline engine. In this study, ethanol was used as fuel at high compression ratio to improve performance and to reduce emissions in a small gasoline engine with low efficiency. Initially, the engine whose compression ratio was 6/1 was tested with gasoline, E25 (75% gasoline + 25% ethanol), E50, E75 and E100 fuels at a constant load and speed. It was determined from the experimental results that the most suitable fuel in terms of performance and emissions was E50. Then, the compression ratio was raised from 6/1 to 10/1. The experimental results showed that engine power increased by about 29% when running with E50 fuel compared to the running with E0 fuel. Moreover, the specific fuel consumption, and CO, CO₂, HC and NO_x emissions were reduced by about 3%, 53%, 10%, 12% and 19%, respectively.

G. Najafi, et al. (2009) researched on Performance and exhaust emissions of a gasoline engine with ethanol blended gasoline fuels using artificial neural network. The purpose of this study is to experimentally analyse the performance and the pollutant emissions of a four-stroke SI engine operating on ethanol–gasoline blends of 0%, 5%, 10%, 15% and 20% with the aid of artificial neural network (ANN). The experimental results revealed that using ethanol–gasoline blended fuels increased the power and torque output of the engine marginally. This study demonstrates that ANN approach can be used to accurately predict the SI engine performance and emissions .dioxide (CO₂) and unburned hydrocarbons (HC), using unleaded gasoline–ethanol blends with different percentages of fuel at three-fourth throttle opening position and variable engine speed ranging from 1000 to 4000 rpm. The

results showed that blending unleaded gasoline with ethanol increases the brake power, torque, volumetric and brake thermal efficiencies and fuel consumption, while it decreases the brake specific fuel consumption and equivalence air–fuel ratio. The CO and HC emissions concentrations in the engine exhaust decrease, while the CO₂ concentration increases. The 20 vol.% ethanol in fuelblend gave the best results for all measured parameters at all engine speeds .

K. Venkateswarlu, et al (2009) tested the effect of methanol-gasoline blends. Their work described the improved engine efficiency with higher compression ratios by using methanol-gasoline blends (mixing-methanol in small proportions with gasoline) as methanol had high anti-knock characteristics. Existing engines were not 30 (number denotes the percentage of methanol in gasoline) as alternative fuel for four stroke variable compression ratio spark ignition (S I) engine. Experimental results demonstrated that anin brake thermal efficiency had been observed compared to gasoline operation. An increase of 8% in volumetric efficiency was found and a reduction of 24% in BSFC was observed.

H. Wei-Dong, et al (2002) did the research on effect of blending gasoline ethanol on engine performance and emissions of the engine. The purpose of the study was to experimentally investigate the engine performance and pollutant emission of a commercial SI engine using ethanol–gasoline blended fuels with various blended rates (0%, 5%, 10%, 20%, 30%). Results showed that with increasing the ethanol content, the heating value of the blended fuels is decreased, while the octane number of the blended fuels increases. Results of the engine test indicated that using ethanol–gasoline blended fuels, torque output and fuel consumption of the engine slightly increase; CO and HC emissions decrease dramatically as a result of the leaning effect caused by the ethanol addition; and CO₂ emission increases because of the improved combustion.

M. Wayne, et al (2011) presented the techniques for engine performance enhancement using ethanol fuel blends. In this paper results are presented from a flexible fuel engine capable of operating with blends from E0-E85. The increased geometric compression ratio, (from 9.2 to 11.85) can be reduced to a lower effective compression ratio using advanced valve train operating on an Early Intake Valve Closing (EIVC) or Late Intake Valve Closing (LIVC) strategy. DICP with a high authority intake phases is used to enable compression ratio management. The advanced valve train also provides significantly reduced throttling losses by efficient control of intake air and residuals. Increased ethanol blends provide improvements in power density due to knock resistance.

N. Sessaiah (2010) studied the effect of biofuel on performance of engine and its emissions. In their research work, the variable compression ratio spark ignition engine designed to run on gasoline has been tested with pure gasoline, LPG (Isobutene), and gasoline blended with ethanol 10%, 15%, 25% and 35% by volume. Also, the gasoline mixed with kerosene at 15%, 25% and 35% by volume without any engine modifications has been tested and presented the result. Brake thermal and volumetric efficiency variation with brake load is compared and presented. CO and CO₂ emissions have been also compared for all tested fuels.

S. Curtis, et al (2008) did the investigation of effect of ethanol blends on SI engine. The objective of this research was to determine the effect of ethanol blending on the performance and emissions of internal combustion engines that are calibrated to run on 100% gasoline. Experimental tests were performed on an engine using pure gasoline, 10% ethanol and 20% ethanol blends. The results of the study show that 10% ethanol blends can be used in internal combustion engines without any negative drawbacks. The fuel conversion efficiency remains the same, while CO emissions are greatly reduced. 20% ethanol blends decrease the fuel conversion efficiency and brake power of an engine, but still reduces CO emissions.

R. Scott Frazier (2011) investigated the effects of ethanol gasoline blend in small engines. In many parts of the United States, the use of ethanol/gasoline fuel blends is very common. The state of Oklahoma only recently began using 10 percent blended fuels (E10) in many service stations. Along with this new fuel availability are customer concerns regarding compatibility with small engines such as lawn mowers and trimmers.

The following presents information so consumers can decide if using ethanol blended fuels is appropriate for them. Also included are some basic suggestions to mitigate some possible problems that might exist for the blending stage. The formulation is used to address realistic case studies where feasible solutions are obtained. The problem involves the optimal operation of gasoline blending, the transfer to product stock tanks and the delivering schedule to satisfy all of the orders.

ZhenyaJia (2003) and MarianthiIerapetritou (2003) developed an efficient mixed-integer linear programming formulation based on continuous representation of the time domain. The assumption of constant recipes is used, new restrictions on vaporization loss on petroleum products give added emphasis to the measurement of vapor pressure for petroleum fractions and their blends. The common method for measuring vapor pressure is the Reid vapor pressure (RVP) test. Now an algorithm is available to calculate RVP without performing the actual test. The algorithm, based on air-and-water free model, uses the Gas Processors Association.

J. Javier, etal. (2006) stated Soave-Redlich-Kwong (2008) equation of state assumes liquid and gas volumes are additive. Since the calculations are iterative, they are incorporated into a general purpose process simulator to compare predicted values with experimental data. Good agreement is found between predicted and experimental values. Furthermore, the algorithm is fast and can be used to predict RVP of any hydrocarbon mixture of known composition.

The volatility characteristics of petroleum fuels are very important especially for gasoline's. Motor and aviation gasoline's are manufactured as liquids but they are consumed in the vapour phase. Consequently, gasoline volatility must be high enough to assure acceptable engine start-up, warm-up, acceleration and throttle response under normal driving (or flying) conditions. On the other hand, the maximum volatility of a gasoline must be restricted to avoid vapor lock, vaporization losses, air pollution, and unsafe storage and handling.

M. R. Riazi, etal (2003) Indicated the Reid vapor pressure test is widely used as a criterion for blending gasoline and other petroleum products. Once RVP of a fuel is known the methods provided in the API-TDB can be used to estimate true vapor pressure of a fuel or a crude oil at any desired temperature. True vapor pressure is an important thermo dynamic property related to volatility and phase equilibrium calculations. There are a number of methods for estimating the vapor pressure of petroleum fractions but very few for Reid vapor pressure. The method presented in the API-TDB for estimation of RVP is based on rigorous vapor-liquid equilibrium calculations.

Prasenjeet Ghosh etal (2006) presented a model that predicts the octane numbers of a wide variety of gasoline process streams and their blends including oxygenates based on detailed composition. The octane number is correlated to a total of 57 hydrocarbon lumps measured by gas chromatography. The model is applicable to any gasoline fuel regardless of the refining process it originates from. It is based on the analysis of 1471 gasoline fuels from different naphtha process streams such as reformates, cat-naphthas, alkylates, isomerates, straight runs, and various hydroprocessed naphthas. Blends of these individual process streams are also considered in this work. The model predicts the octane number within a standard error of 1 number for both the research and motor octane numbers.

CHAPTER 3

THE MODEL

The idea of material balance, mixing and linear blending is used to generate three systems of first order ordinary differential equations. Fourth Order Runge –Kutta numerical method is used to solve the problem.

3.1 Material Balance

A mass balance, also called a material balance, is an application of conservation of mass to the analysis of physical systems. By accounting for material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique. The exact conservation law used in the analysis of the system depends on the context of the problem but all revolve around mass conservation, i.e. that matter cannot disappear or be created spontaneously.

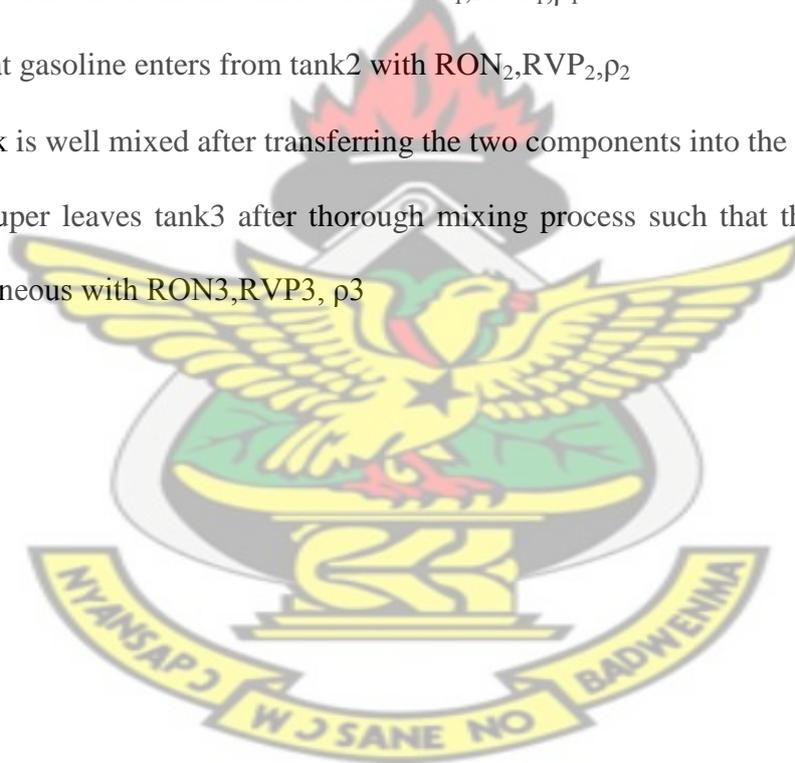
Mathematically the general material balance equation can be written as

$$\text{Input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation} \quad (3.0)$$

- Accumulation is 0, if nothing is accumulated after the blending process
- Generation is 0, if nothing is generated. No chemical reaction
- Consumption is 0, nothing is consumed
- Therefore the general material balance equation thus;
- $\text{input} \pm \text{output} \pm \text{accumulation} \pm \text{generation} \pm \text{consumption} = 0 \quad (3.0)$
 - At time zero the dependent variables (RON, RVP, ρ) are zero(0)
 - *equation (3.0) reduces to ; $\text{input} = \text{output} \quad (3.1) \text{ for our model}$*

3. 2 MODEL DEVELOPMENT

- Consider an empty cylindrical tank (tank3) in which super/petrol is to be prepared (blended) by using two different components of gasoline.
- The two components are light gasoline(low octane) and MOGAS (high octane)
- The percentage volume of the cylindrical tank is 100% by volume.
- The sum of the percentage volume of the two components flowing in, is equal to the volume flowing out
- The MOGAS enters from tank 1 with RON_1, RVP_1, ρ_1
- The light gasoline enters from tank2 with RON_2, RVP_2, ρ_2
- The tank is well mixed after transferring the two components into the cylindrical tank
- Petrol/super leaves tank3 after thorough mixing process such that the final blend is homogeneous with RON_3, RVP_3, ρ_3



3.3 DIAGRAMATIC REPRESENTATION OF PROCESS

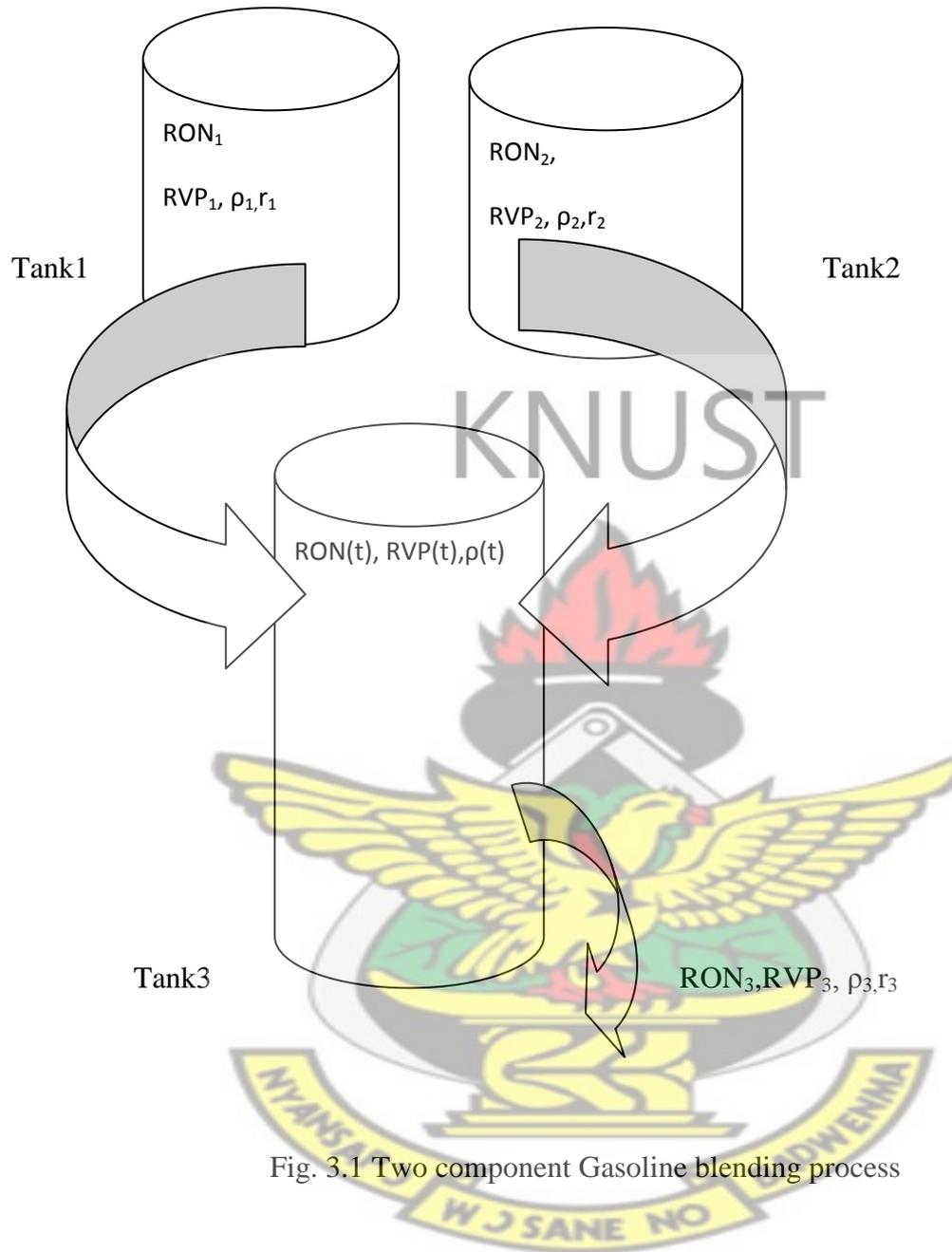


Fig. 3.1 Two component Gasoline blending process

3.4 VARIABLES

- RON_i is the Research Octane Number at points $i=1,2,3$. For simplification it will be called a_i
- RVP_i is the Reid Vapour Pressure at points $i=1,2,3$. For simplification it will be called b_i
- ρ_i is the density at points $i=1,2,3$
- t is the independent variable.
- The dependent variables are $a(t), b(t)$ and $\rho(t)$
- $RON(t) = RON_3$
- $RVP(t) = RVP_3$
- $\rho(t) = \rho_3$

3.5 ASSUMPTIONS:

- The $r_i (i=1,2,3)$ are determined using linear blending model

$$RON = \sum_{i=1}^2 (RON_i) \quad (3.2)$$

- $r_3 = r_1 + r_2 \quad (3.3)$

- Product in the tank 3 is homogenous after the transfer and mixing process
- The rate of change of the individual dependent variable is equal to the rate of input minus the rate of output;

3.6 MODEL EQUATIONS

Rate of change of the dependent variables is equal to the rate of flow from tank1 plus the rate of flow from tank2 minus the rate of flow from tank3

$$\text{Considering } RON = a(t) \quad (3.4)$$

$$\frac{da(t)}{dt} = (r_1a_1 + r_2a_2) - r_3a(t) \quad (3.5)$$

$$\text{Considering } RVP = b(t) \quad (3.6)$$

$$\frac{db(t)}{dt} = (r_1b_1 + r_2b_2) - r_3b(t) \quad (3.7)$$

$$\text{Considering } \rho(t) = c(t) \quad (3.8)$$

$$\frac{dc(t)}{dt} = r_1c_1 + r_2c_2 - r_3c(t) \quad (3.9)$$

The r_1 and r_2 is determined using a general simultaneous equation of the form;

$$100r_1 + 100r_2 = 100 \quad (3.10)$$

$$A_1r_1 + A_2r_2 = 91 \quad (3.11)$$

A_1 and A_2 are the mogas and light gasoline for the blend respectively.

And r_1 and r_2 are the fractions or percentage of the mogas and light gasoline to be blended .

Equation (3.10) is ideal equation. Where 100 RON of higher octane gasoline plus 100 RON of lower octane gasoline equals 100 .And equation (3.11) is the problem equation where A_1 represents the RON for the higher gasoline and A_2 is that of the lower gasoline and is equal to the target octane (RON) of 91

The three differential equations from the model can be written as;

$$\frac{da(t)}{dt} = -a(t) + k_1 \quad (3.12)$$

$$\frac{db(t)}{dt} = -b(t) + k_2 \quad (3.13)$$

$$\frac{dc(t)}{dt} = -c(t) + k_3 \quad (3.14)$$

k_1, k_2 and k_3 are constants

Equations (3.12), (3.13) and 3.14 can be written as (3.15)

$$\frac{dx}{dt} = AX + f(t) \quad (3.15)$$

From equation (3.15)

$$\frac{dx}{dt} = \begin{pmatrix} \frac{da}{dt} \\ \frac{db}{dt} \\ \frac{dc}{dt} \end{pmatrix}$$

$$A = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$f(t) = \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix} \quad \text{and} \quad X = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Linearizing equation (3.15) by finding the Jacobian

$$\text{Jacobian (J)} = \begin{pmatrix} \frac{df1}{da} & \frac{df1}{db} & \frac{df1}{dc} \\ \frac{df2}{da} & \frac{df2}{db} & \frac{df2}{dc} \\ \frac{df3}{da} & \frac{df3}{db} & \frac{df3}{dc} \end{pmatrix} \quad (3.16)$$

$$\text{Jacobian (J)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (3.17)$$

The characteristic equation from the Jacobian Matrix is given as

$$(J - \lambda I) = 0 \quad (3.18)$$

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Now substituting appropriate terms into equation (3.18) yields equation (3.19)

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 0 \quad (3.19)$$

Simplifying equation (3.19) yields (3.20)

$$\begin{vmatrix} -1 - \lambda & 0 & 0 \\ 0 & -1 - \lambda & 0 \\ 0 & 0 & -1 - \lambda \end{vmatrix} = 0 \quad (3.20)$$

$$(-1 - \lambda)(-1 - \lambda)(-1 - \lambda) = 0 \quad 3.21$$

Evaluating equation (3.21) yields $\lambda = -1$ and is repeated thrice.

Since the Eigen value (λ) is repeated real number, it means there are three linearly independent solutions to the model. Because the Eigen value λ is negative it means the system is stable around the origin.

3.7 ANALYTICAL SOLUTION OF THE MODEL

Below is the generic analytical solution for the model. The method used is separation of variables

KNUST

$$RON(t) = a(t)$$

$$\frac{da(t)}{dt} = -a + k_1 \quad (3.22)$$

$$\int \frac{da(t)}{-a+k_1} = \int dt$$

$$-\ln(k_1 - a) = t + c$$

$$\ln(k_1 - a) = -t - c$$

$$k_1 - a = e^{(-t-c)}$$

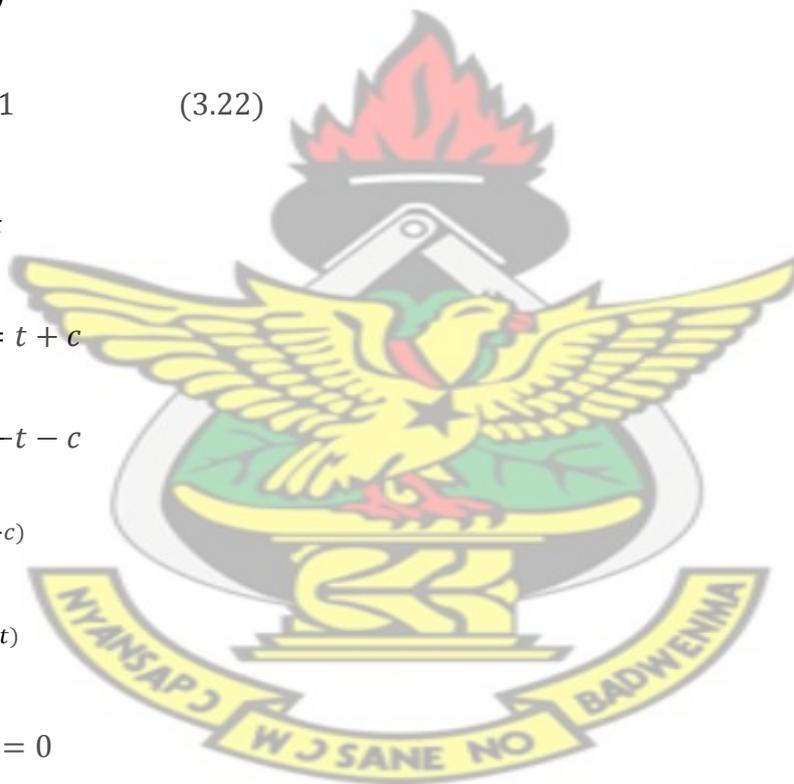
$$a = k_1 - Ue^{(-t)}$$

$$\text{At } t = 0 \text{ } RON = 0$$

$$\text{At } t = +\infty \text{ } RON = k_1$$

U is a constant, $k_1 = r_1 a_1 + r_2 a_2$; $a = a r_3$

Where r_1 and r_2 are the fractions of MOGAS and Light gasoline to be blended a_1 and a_2 are the RON for the MOGAS and Light gasoline.



The r_1 and r_2 is determined using a general simultaneous equation of the form;

$$100r_1 + 100r_2 = 100 \quad (3.10)$$

$$A_1r_1 + A_2r_2 = 91 \quad (3.11)$$

$$RVP(t) = b(t)$$

$$\frac{db(t)}{dt} = -b + k_2 \dots \dots \dots 3.55$$

$$\int \frac{db(t)}{-b+k_2} = \int dt$$

$$-\ln(k_2 - b) = t + c$$

$$\ln(k_2 - b) = -t - c$$

$$k_2 - b = e^{(-t-c)}$$

$$b = k_2 - V e^{(-t)}$$

$$\text{At } t = 0 \text{ } RVP = 0$$

$$\text{At } t = +\infty \text{ } RVP = k_2$$

V is a constant, $k_2 = r_1b_1 + r_2b_2$; $b = br_3$

Where r_1 and r_2 are the fractions of MOGAS and Light gasoline to be blended b_1 and b_2 are the RVP for the MOGAS and Light gasoline. r_3 is the sum of r_1 and r_2

$$\frac{d\rho(t)}{dt} = -\rho + k_3 \dots \dots \dots 3.55 \setminus$$

$$\int \frac{d\rho(t)}{-\rho+k_3} = \int dt$$



$$-\ln(k_3 - \rho) = t + c$$

$$\ln(k_3 - \rho) = -t - c$$

$$k_3 - \rho = e^{(-t-c)}$$

$$\rho = k_3 - We^{(-t)}$$

W is a constant, $k_3 = r_1\rho_1 + r_2\rho_2$; $\rho = \rho_3$

Where r_1 and r_2 are the fractions of MOGAS and Light gasoline to be blended ρ_1 and ρ_2 are the densities for the MOGAS and Light gasoline

3.8 FOURTH ORDER RUNGE-KUTTA-NUMERICAL SOLUTION

The Runge-Kutta method, discovered by German mathematicians Carl Runge and Martin Kutta around 1900, is a powerful fourth order method (i.e. the error is at most a fixed constant times the fourth power of the step size, h), thus a great improvement over the Improved Euler's method. In contrast to the multistep methods of the previous section, Runge-Kutta methods are single-step methods with multiple stages per step. They are motivated by the dependence of the Taylor methods on the specific IVP. These new methods do not require derivatives of the right-hand side function f in the code, and are therefore general-purpose initial value problem solvers. Runge-Kutta methods are among the most popular ODE solver.

Let an initial value problem be specified as

$$\frac{dy(t)}{dt} = f(t, y)$$

$$a \leq t \leq b \quad ; \quad y(t = a) = y_a$$

The fourth order Runge-Kutta is given as below;

$$k1 = hf(ti, yi)$$

$$k2 = hf(ti + h/2, yi + k1/2)$$

$$k3 = hf(ti + h/2, yi + k2/2)$$

$$k4 = hf(ti + h, yi + k3)$$

$$y(i + 1) = yi + 1/6(k1 + 2k2 + 2k3 + k4)$$

$k1$ is the slope at the beginning of the interval;

$k2$ is the slope at the midpoint of the interval, using slope $k1$ to determine the value of y at the point ;

$k3$ is again the slope at the midpoint, but now using the slope $k2$ to determine the y -value;

$k4$ is the slope at the end of the interval, with its y -value determined using $k3$.

3.8 MATLAB CODE TO SOLVE MODEL NUMERICALLY

THIS PROGRAM SEEKS TO DETERMINE THE RON, RVP AND DENSITY !OF TWO COMPONENT GASOLINE BLEND.

THE PROGRAM ACCEPTS A1 (RON OF THE MOGAS) AND THE A2(RON !OF THE LIGHT GASOLINE AS INPUTS INORDER TO COMPUTE R1 AND !R2 THUS THE FRACTIONS OF THE COMPONENTS TO BE BLENDED !TOGETHER

```
A1=input('Enter the value of A1 for RON \n ');
```

```
A2=input('Enter the value of A2 for RON \n ');
```

```
r2=((91-A1)/(-A1+A2));
```

```
r1= (1-r2);
```

```
r3=r1+r2;
```

! HERE AN ANONYMOUS FUNCTION IS DEFINED FOR THE MODEL AND A STEP SIZE OF HOURS USED FOR DIFFERENT HOURS DEPENDING ON OPTIMUM BLEND TIME

```
f= @(A) -r3*A +r1*A1+r2*A2;
```

```
h=1;
```

```
ta= 0:h:t;
```

```
ma= length(ta)-1;
```

```
A=zeros (size (ta));
```

```
A(1)=0;
```

```
for j=1:ma
```

```
    ka1=h*f(A(j));
```

```
    ka2=h*f(A(j)+0.5*ka1);
```

```
    ka3=h*f(A(j) + 0.5*ka2);
```

```
    ka4=h*f(A(j) + ka3);
```

```
A(j+1)=A(j)+(ka1+2*ka2+2*ka3+ka4)/6;
```

```
end
```

! DISPLAYING THE OUTPUT OF THE PROGRAM

```
disp('')
```

```
fprintf(' ANSWERS \n')
```

```
fprintf('-----\n');
```

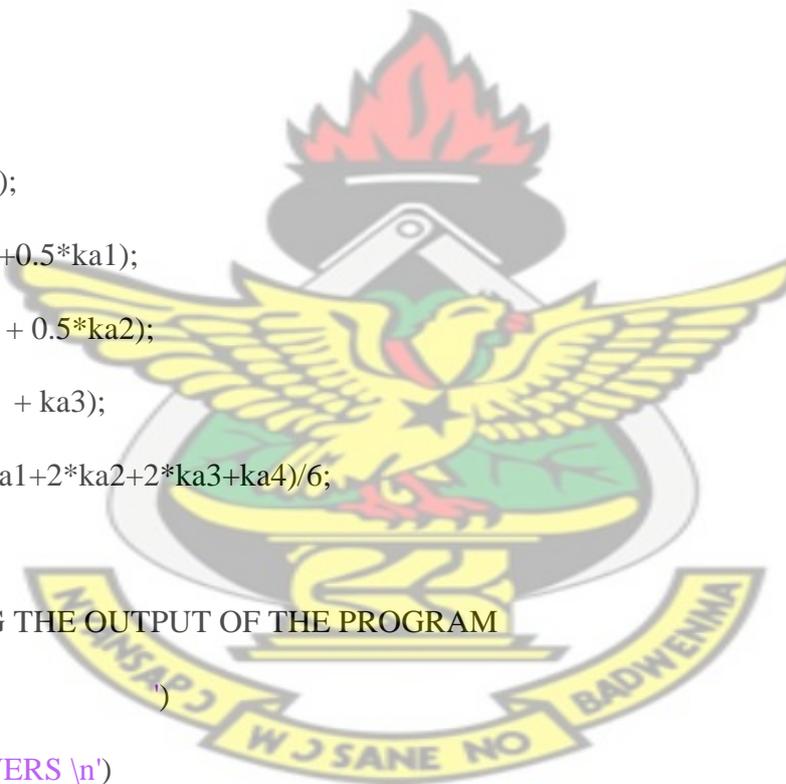
```
fprintf('The R1 is : %6.4f \n', r1 )
```

```
fprintf('The R2 is : %6.4f \n', r2 )
```

```
fprintf('The RON is : %6.1f \n', A(j+1) )
```

```
Option=1;
```

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```

while Option ~= 0

disp(' ')
disp(' ')
disp(' ')
disp(' CONTINUE BY SELECTING ONE OF THE OPTIONS ')

disp(' ')
disp(' ')
disp(' ')
disp('***** MENU***** ')
disp(' ')
disp(' 1. RVP ')
disp(' 2. DENSITY')
disp(' 3. QUIT ')

Option=input('Select option: 1 , 2 OR 3\n ');

if Option == 1

B1=input ('Enter the Reid Vapour Pressure of MOGAS \n ');
B2=input ('Enter the Reid Vapour Pressure of Light Gasoline \n ');

disp(' ')

f= @(B) -r3*B +r1*B1+r2*B2 ;

h=1;

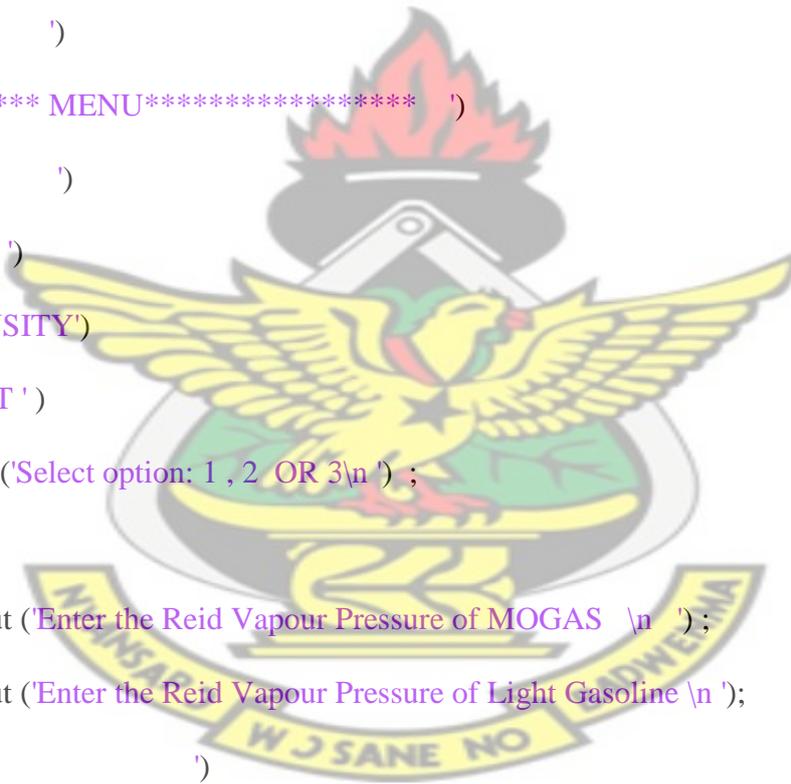
tb=0:h:t ;

mb=length(tb)-1;

B=zeros(size(tb));

```

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```
B(1)=0;
```

```
for w=1:mb
```

```
    kb1=h*f(B(w));
```

```
    kb2=h*f(B(w)+0.5*kb1);
```

```
    kb3=h*f(B(w) + 0.5*kb2);
```

```
    kb4=h*f(B(w) + kb3);
```

```
B(w+1)=B(w)+(kb1+2*kb2+2*kb3+kb4)/6;
```

```
end
```

```
disp('')
```

```
fprintf('The answer is : %6.2f \n', B(w+1) )
```

```
disp('')
```

```
disp('')
```

```
elseif Option == 2
```

```
    C1=input('Enter the density of MOGAS \n ');
```

```
    C2=input('Enter the density of Light Gasoline \n ');
```

```
disp('')
```

```
f= @(C) -r3*C +r1*C1+r2*C2 ;
```

```
h=1;
```

```
tc=0:h:t;
```

```
mc=length(tc)-1;
```

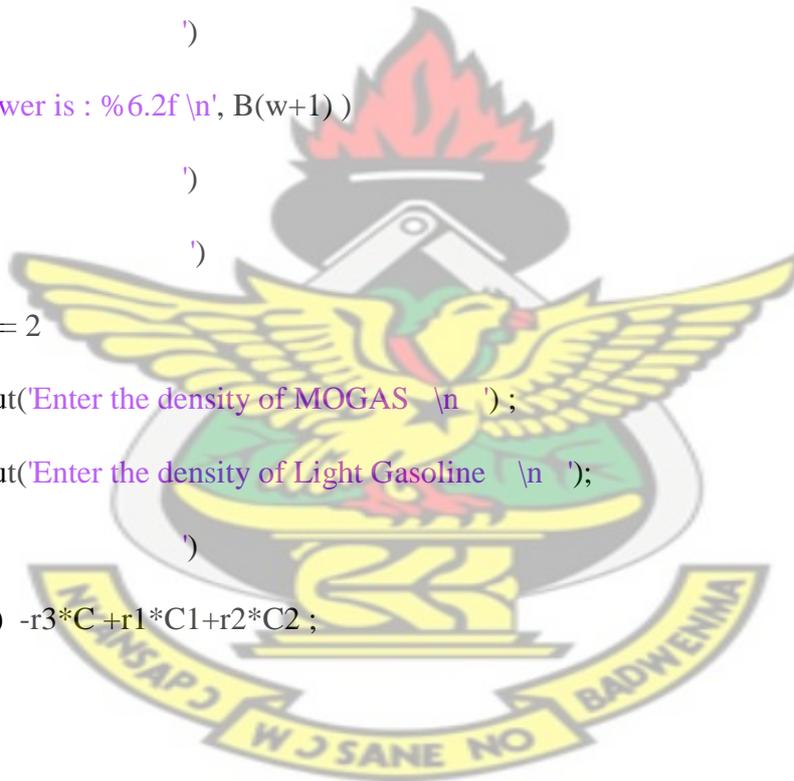
```
C=zeros(size(tc));
```

```
C(1)=0;
```

```
for i=1:mc
```

```
    kc1=h*f(C(i));
```

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```
kc2=h*f(C(i)+0.5*kc1);
```

```
kc3=h*f(C(i) + 0.5*kc2);
```

```
kc4=h*f(C(i) + kc3);
```

```
C(i+1)=C(i)+(kc1+2*kc2+2*kc3+kc4)/6;
```

```
end
```

```
disp('          ')
```

```
fprintf('The answer is : %6.2f \n', C(i+1))
```

```
disp('          ')
```

```
disp('          ')
```

```
elseif Option==3
```

```
disp('Program is exiting.....')
```

```
disp('Press any key to continue')
```

```
pause
```

```
break
```

```
else
```

```
disp('THE OPTION YOU HAVE ENTERED IS NOT VALID.PLEASE SELECT THE  
RIGHT OPTION')
```

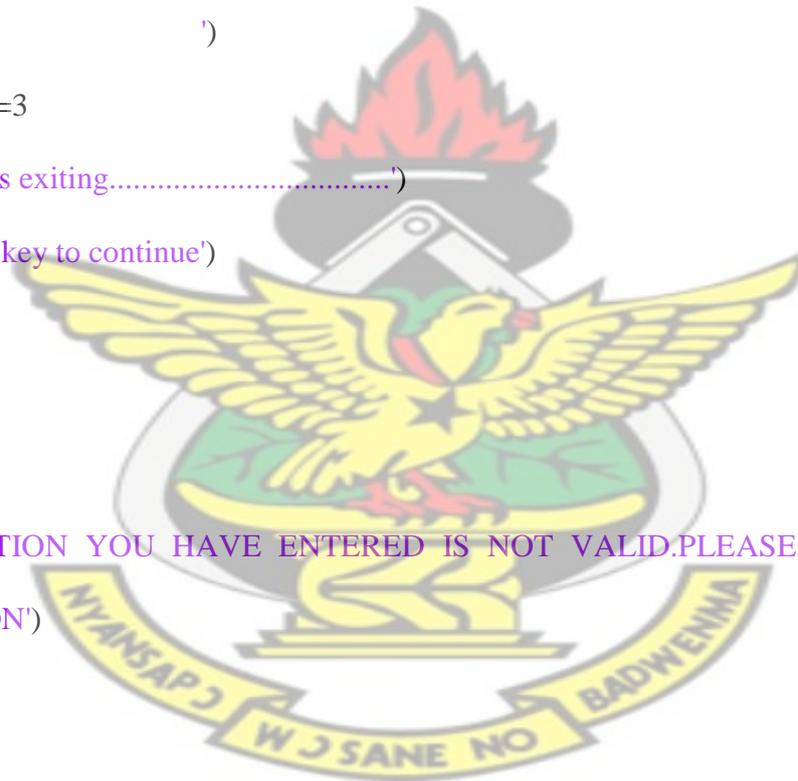
```
end
```

```
end
```

```
clear
```

```
clc
```

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CHAPTER 4

4. DATA COLLECTION AND ANALYSIS

The quality control department of Tema Oil Refinery Ltd were requested to sample five(5) different gasoline tanks (namely tanks 1,2,3,4 and 40).The octane(Research Octane Number),reid vapour pressure and the density of the five tanks were determined by the quality control department using standard analytical methods.

After the octanes, Reid vapour pressure and densities were determined, four blends of gasoline were prepared in the laboratory using the highest octane gasoline as a pivot and analysis done to determine the results.

The results determined from the blends were the densities, Reid vapour pressure and research octane number.

Table 4.1 Results from Laboratory Analysis

Tank	Octane number	Density Kg/m ³	Reid vapour pressure Kg/cm ²
1	71.1	723.0	0.35
2	90.4	760.0	0.18
3	92.3	742.4	0.21
4	62.8	768.5	0
40	68.7	738.2	0.28

Table 4.2 Blend result from laboratory Analysis.

Blend	Octane number	Density Kg/m ³	Reid vapour pressure Kg/cm ²
3/1	88.8	735.4	0.42
3/40	90.0	737.5	0.35
3/2	90.8	751.7	0.32
3/4	90.0	738.1	0.34

After the Quality Control Department finished analyzing the four(4) different blends, The MATLAB code(MODEL) developed was used to solve the three systems of first order ordinary differential equation. Analytical method was also used to solve. The table below is the results produced from the two methods.

Table 4.3 MATLAB Code (MODEL) and Analytical Solution with varying time

BLEND	Tank 3 and 1		Tank 3 and 2		Tank 3 and 40		Tank 3 and 4		
	MODEL	Analytical	MODEL	Analytical	MODEL	Analytical	MODEL	Analytical	
4HRS	Density	726.55	727.8	739.52	740.5	728.85	728.5	728.85	730.5
	RON	89.2	89.3	89.2	89.3	89.2	89.3	89.2	89.3
	RVP	0.22	0.206	0.18	0.185	0.2	0.21	.20	0.186

5HRS	Density	735.71	736.4	739.52	749.3	738.04	737.1	738	739.1
	RON	90.3	90.4	90.3	90.4	90.3	90.4	90.3	90.3
	RVP	0.22	0.208	0.19	0.187	0.21	0.208	0.20	0.188
6HRS	Density	739.13	739.5	752.34	752.5	740.1	740.2	741.48	742.3
	RON	90.7	90.7	90.7	90.7	90.7	90.7	90.7	90.7
	RVP	0.22	0.209	0.19	0.189	0.21	0.209	0.20	0.189
7HRS	Density	740.44	740.7	753.66	753.7	741.39	741.4	742.77	743.5
	RON	90.9	90.9	90.9	90.9	90.9	90.9	90.9	90.9
	RVP	.22	0.21	0.19	0.189	0.21	0.209	0.20	0.19
8HRS	Density	740.92	741.1	754.15	754.1	741.88	741.85	743.26	743.9
	RON	91	91	91	91	91	91	91	91
	RVP	0.22	0.21	0.19	0.189	0.20	0.21	0.2	0.19

9HRS	Density	741.1	741.1	754.33	754.3	742.06	742.01	743.44	744.1
	RON	91	91	91	91	91	91	91	91
	RVP	0.22	0.21	0.19	0.189	0.20	0.21	0.2	0.19
10HRS	Density	741.1	741.4	754.4	754.4	742.06	742.06	743.5	744.1
	RON	91	91	91	91	91	91	91	91
	RVP	0.22	0.21	0.19	0.189	0.20	0.21	0.20	0.19

From the table above it can be seen clearly that, the MODEL solution produces almost the same result as the analytical. The RON results for different blending time for both solution is the same at any particular time. The RVP is also approximately the same at any particular time for the two type of solution. The densities for the two solutions varies slightly at the beginning of the blend but approximate to be the same later.

The following graphs below represent the behaviour of the dependent variables RON,RVP and RON from four hours to ten hours.

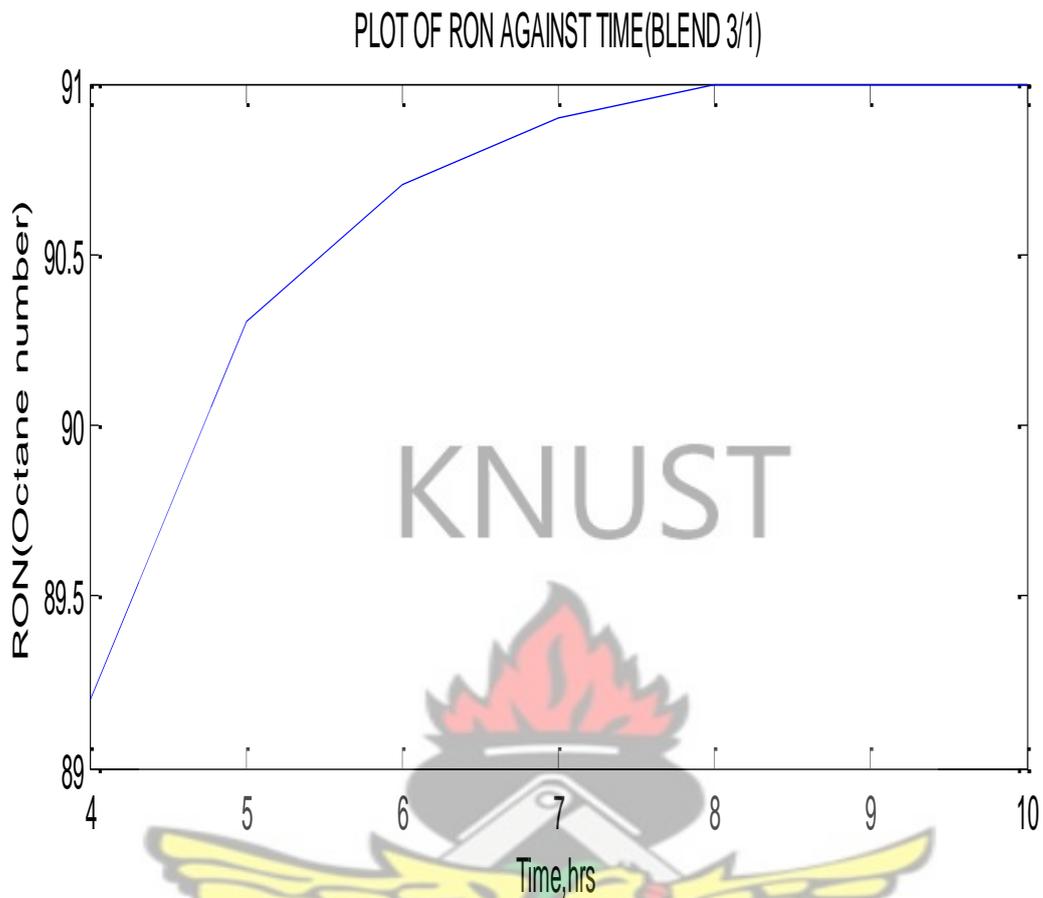


Fig. 4.1 Plot of RON against Time

The fig. 4.1 above is a blend of tank 3 against 1 and it displays a plot of RON against time in hours. The RON is 89.2 after 4 hours of mixing. At 5 hours of mixing the RON is 90.3, at 6 hours 90.7 and 7 hours 90.9. After 8 hours of mixing the RON is 91 and stays constant at 91 till 10 hours of mixing.

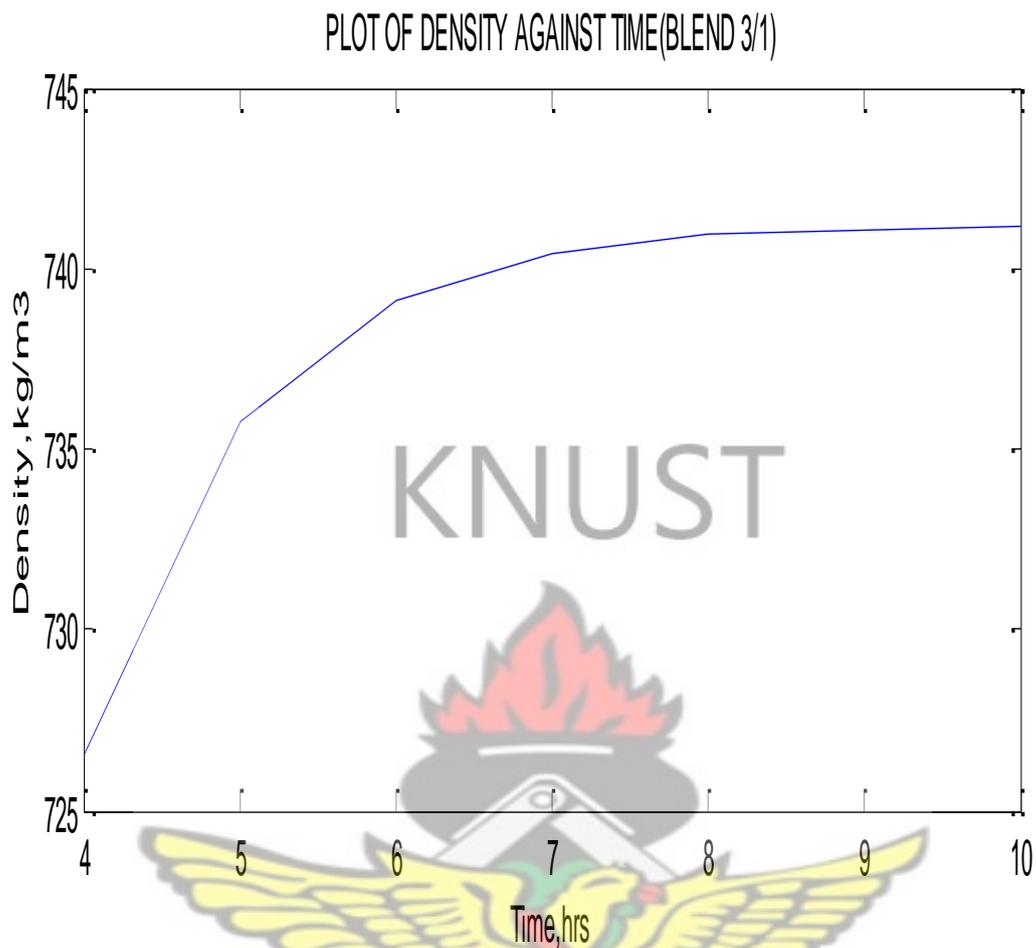


Fig 4.2 Plot of Density against Time

The Fig 4.2 is a plot of density against time as a result of a blend of 3 and 1. The density increase gradually from 726.55 at 4 hours to 741.1 at 8 hours and remains constant till 10 hours.

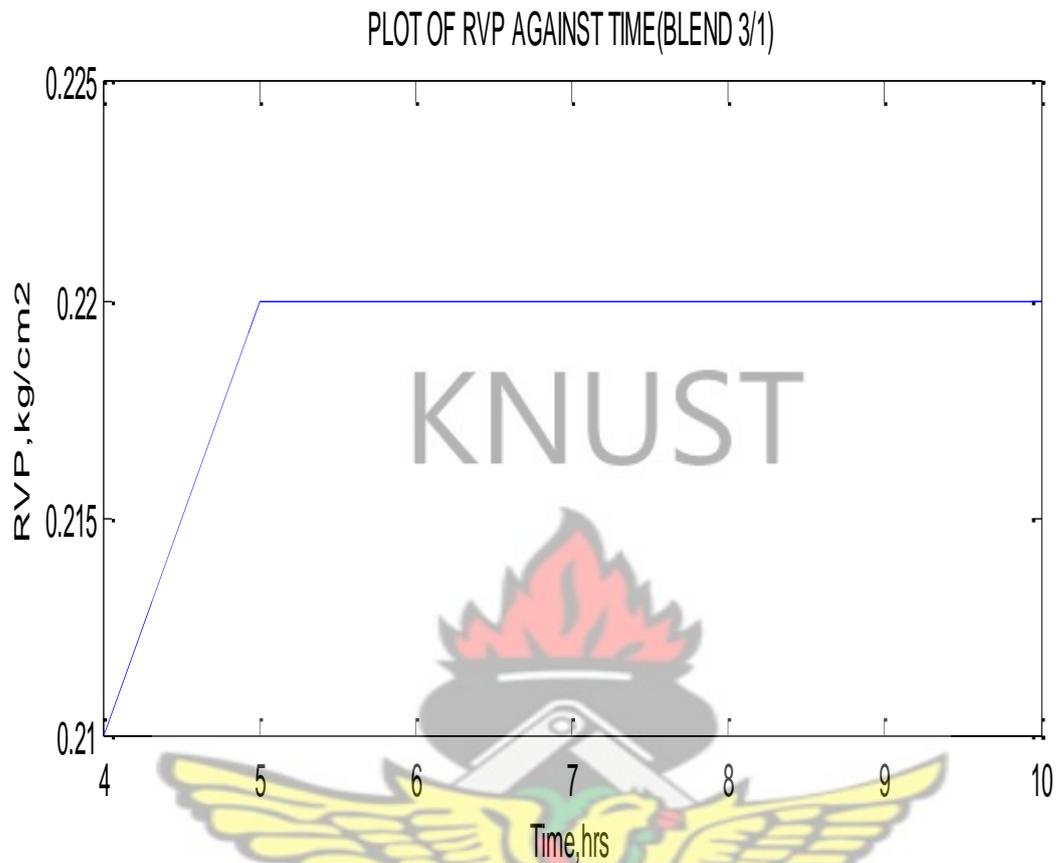


Fig. 4.3 Plot of RVP against Time

The fig. 4.3 is a representation of RVP versus time for a blend of tank 3 and 1. At 4 hours the RVP is 0.21 but level after 5 hours of mixing and it remains constant till 10 hours of mixing.

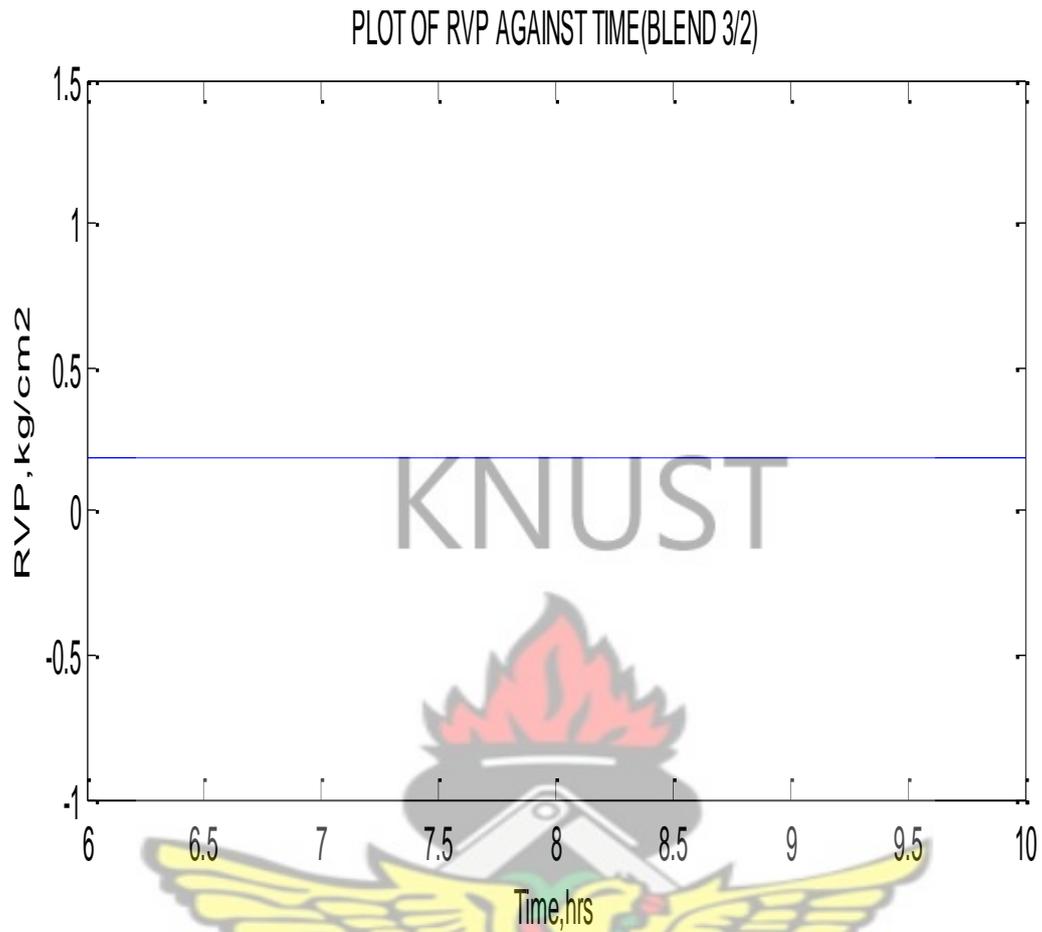


Fig 4.4 Plot of RVP against Time

The fig. 4.4 gives the results for RVP against time for a blend of tank 3 versus 1. At 6 hours the RVP is 0.19 and it maintains till 10 hours of mixing.

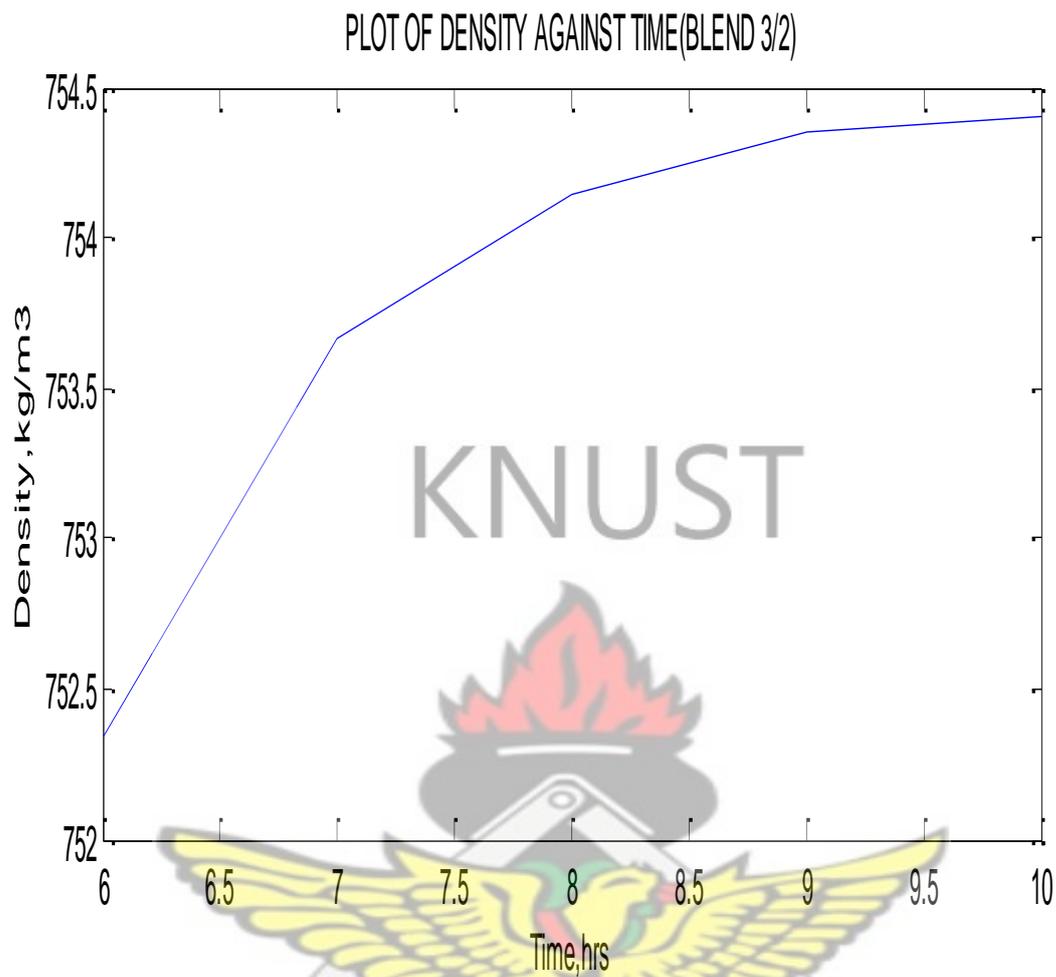


Fig 4.5 Plot of Density against Time

Fig4.5 represent density –time graph for a blend of tank 3 and 2. At 6 hours of mixing the density is 752.34 and it approach 754 at 8 hours and it maintained fairly till 10 hours.

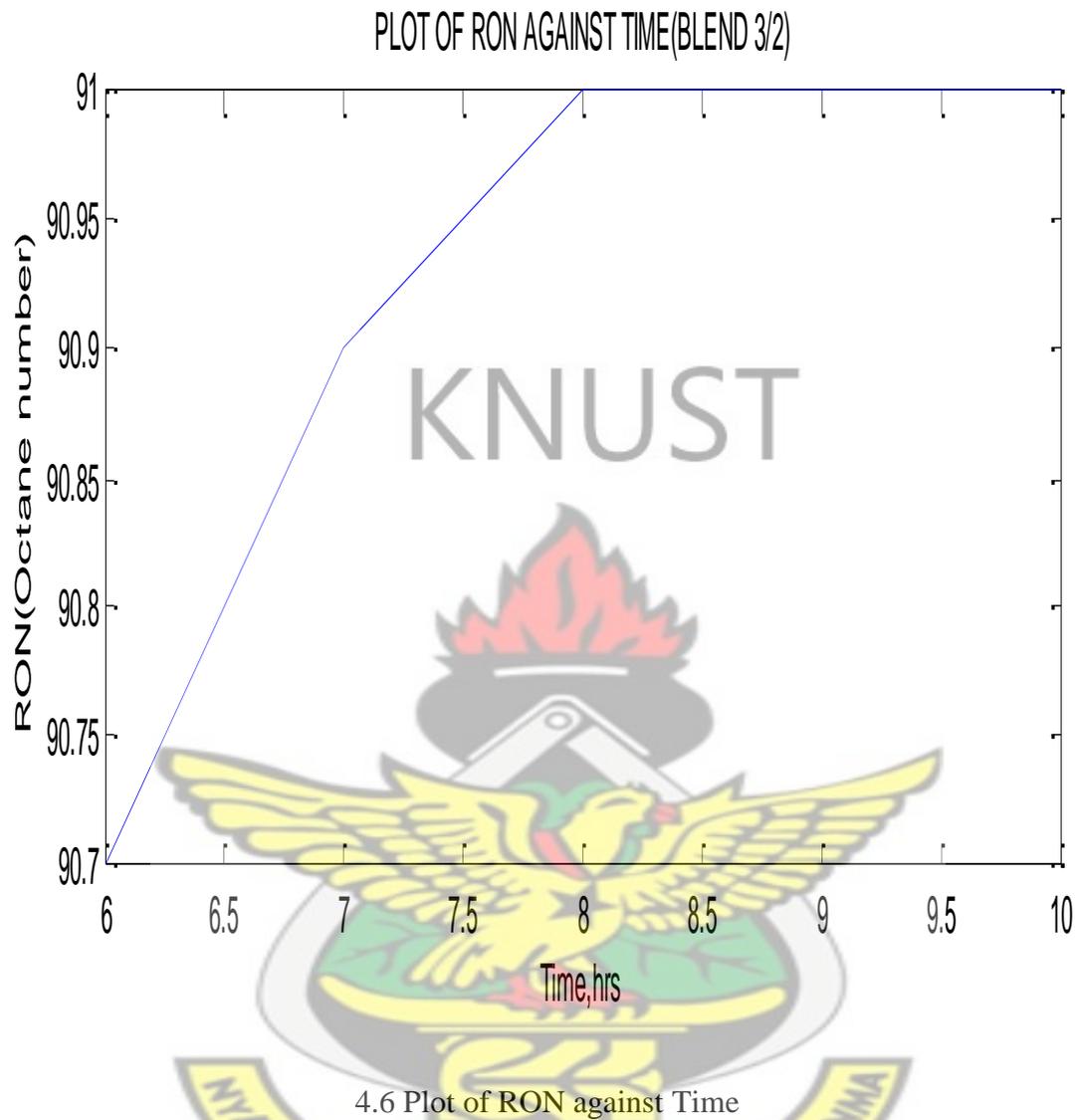


Fig. 4.6 represents a plot of RON against time for a blend of tank3 and 2. At 6 hours the RON is 90.7, 7 hours 90.9 and between 8 and 10 hours maintains RON 91 .

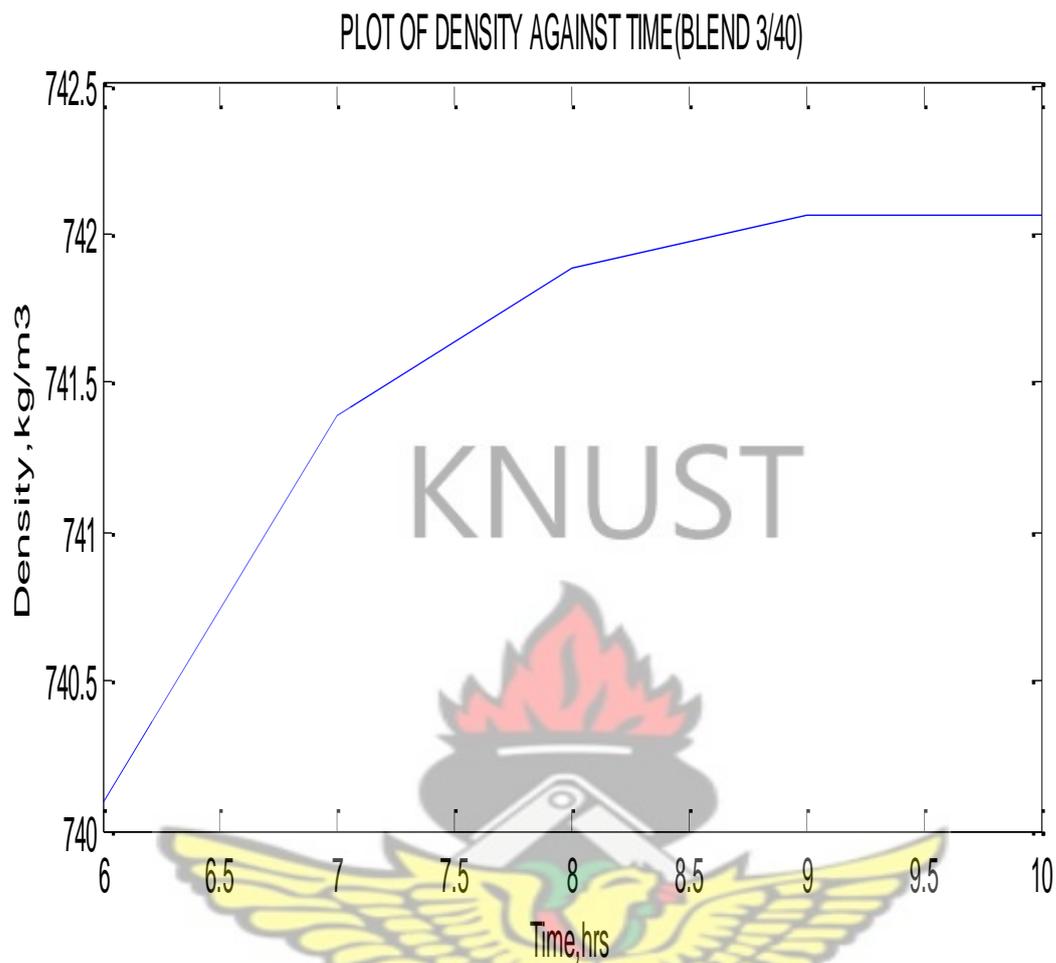


Fig. 4.7 Plot of Density against Time

Fig. 4.7 is a graph of density against time for a blend of 3 and 40. At 6 hours the density is 740.10 and approaches 742 gradually between 8 and 10 hours.

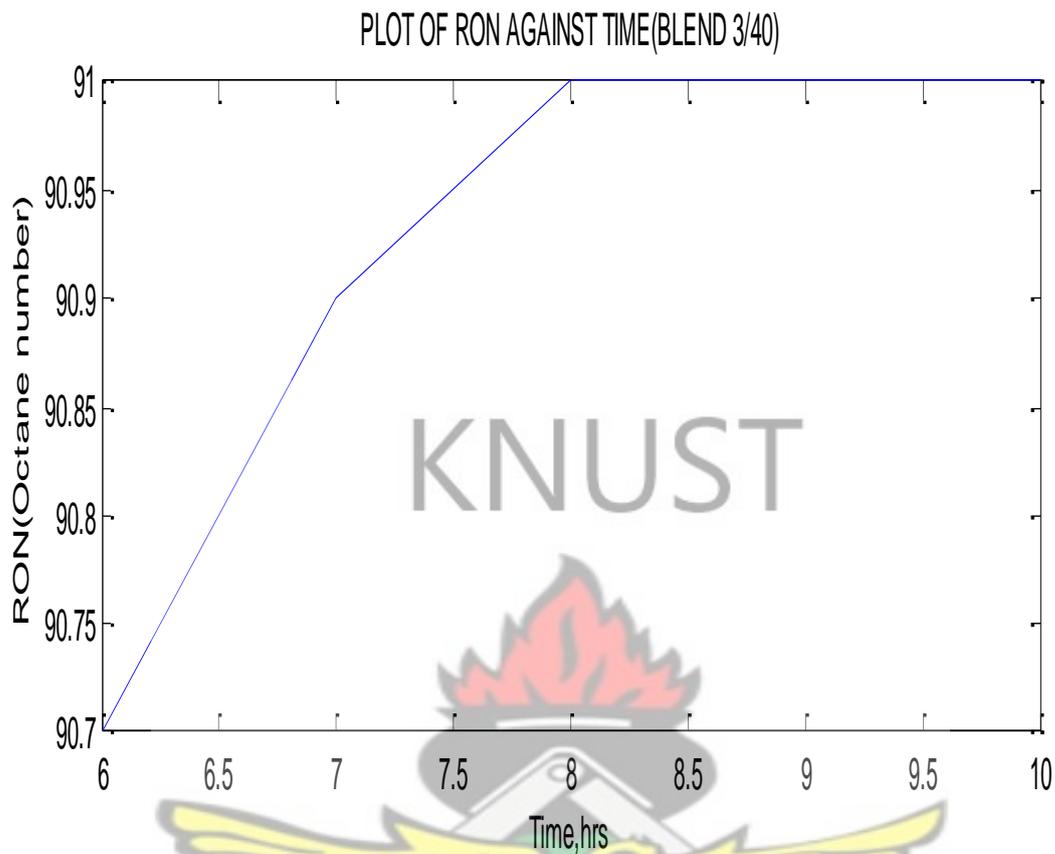


Fig 4.8 Plot of RON against Time

Fig 4.8 represents a blend of tank 3 and 40 specifically a plot of RON against time. The blend approaches 91 from 90.7 RON at 6 hours .Until 91 RON was reached at 8 hours and it maintained till 10 hours.

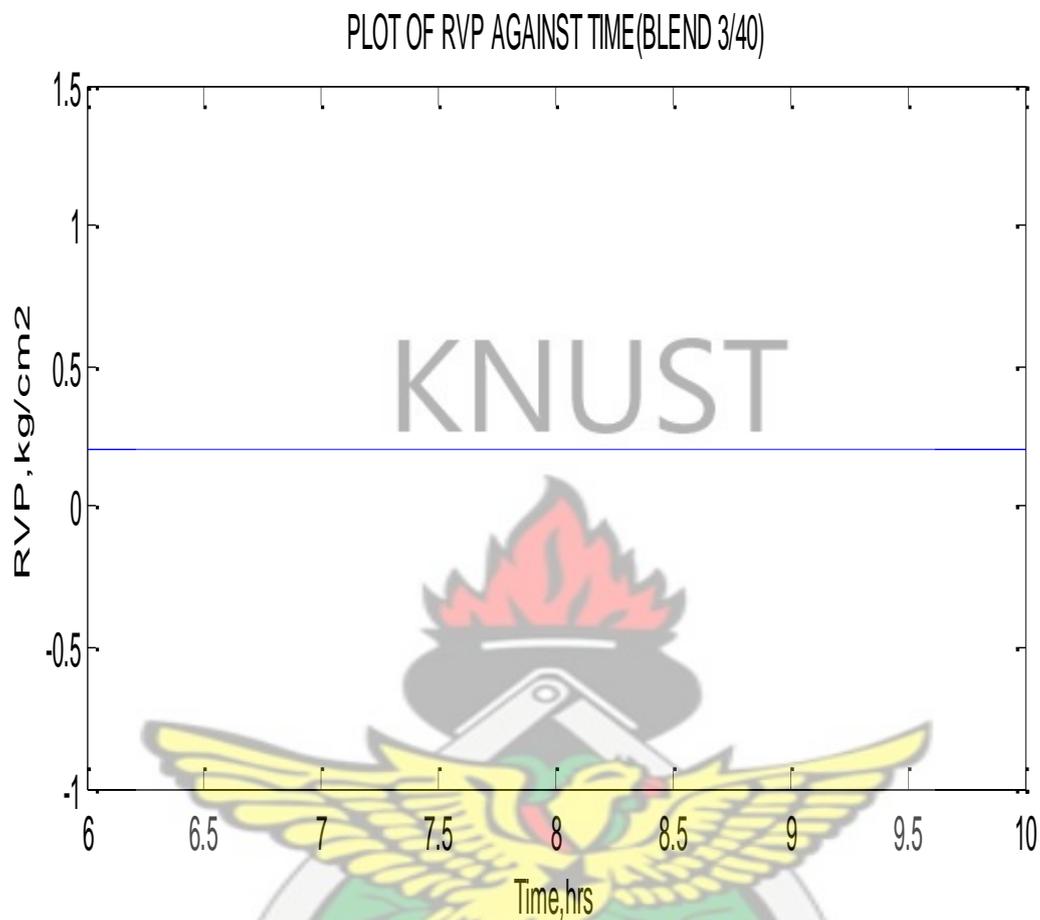


Fig 4.9 Plot of RVP against Time

Fig. 4.9 above represents a plot of RVP against time for a blend of tank 3 and 40. The RVP remains constant at 0.21 after 6 to 10 hours of mixing.

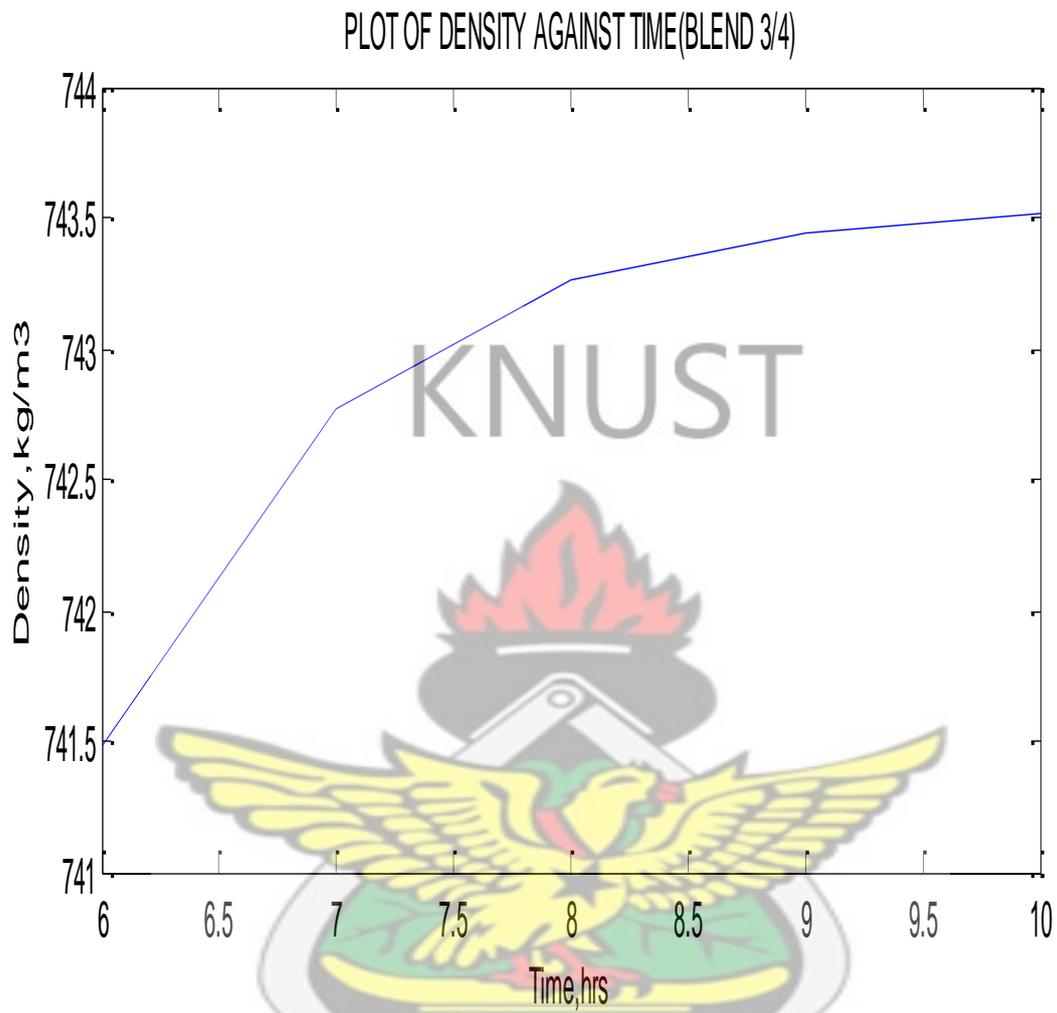


Fig 10 Plot of Density against Time

Fig. 10 represents a plot of density against time for a blend of 3 and 4. The density increases gradually from 741.1 to fairly constant value of 743 between 6 to 10 hours.

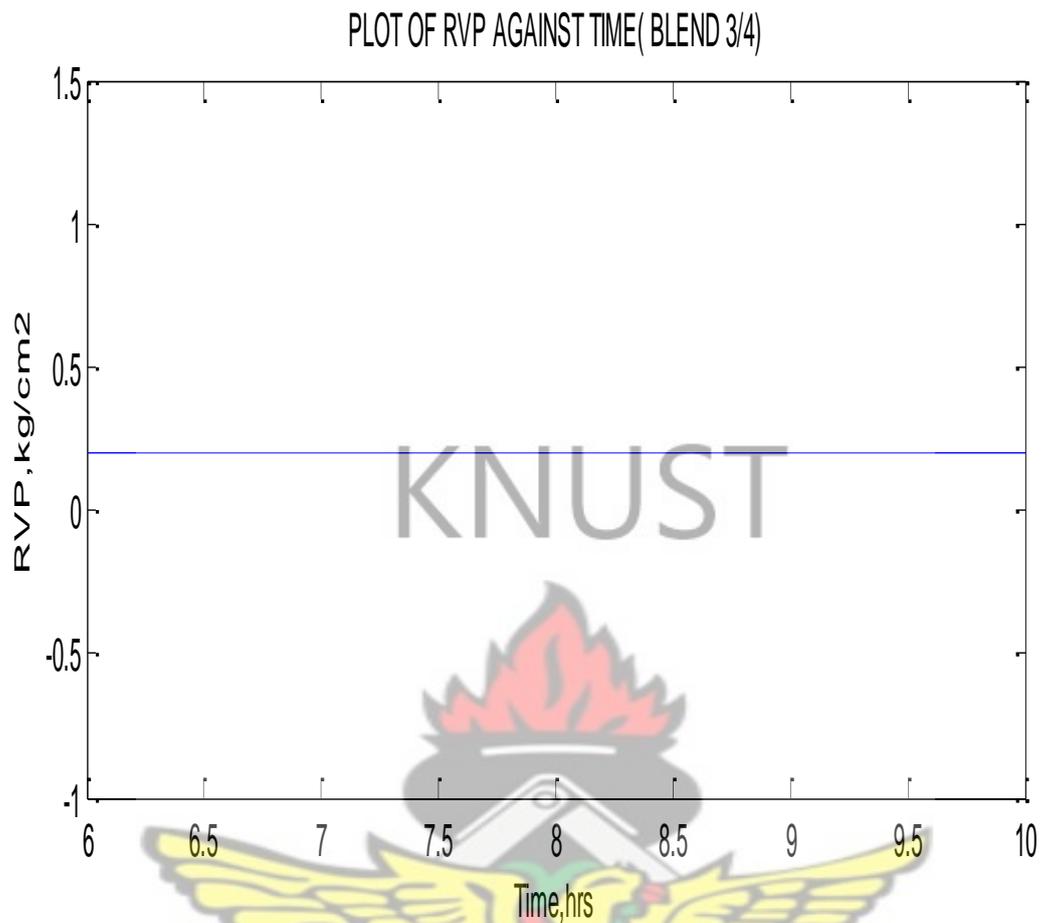


Fig. 11 Plot of RVP against Time

The Fig 11 represent a plot of RVP versus time for a blend of tank 3 and 4. The value of the RVP remains constant between 6 to 10 hours.

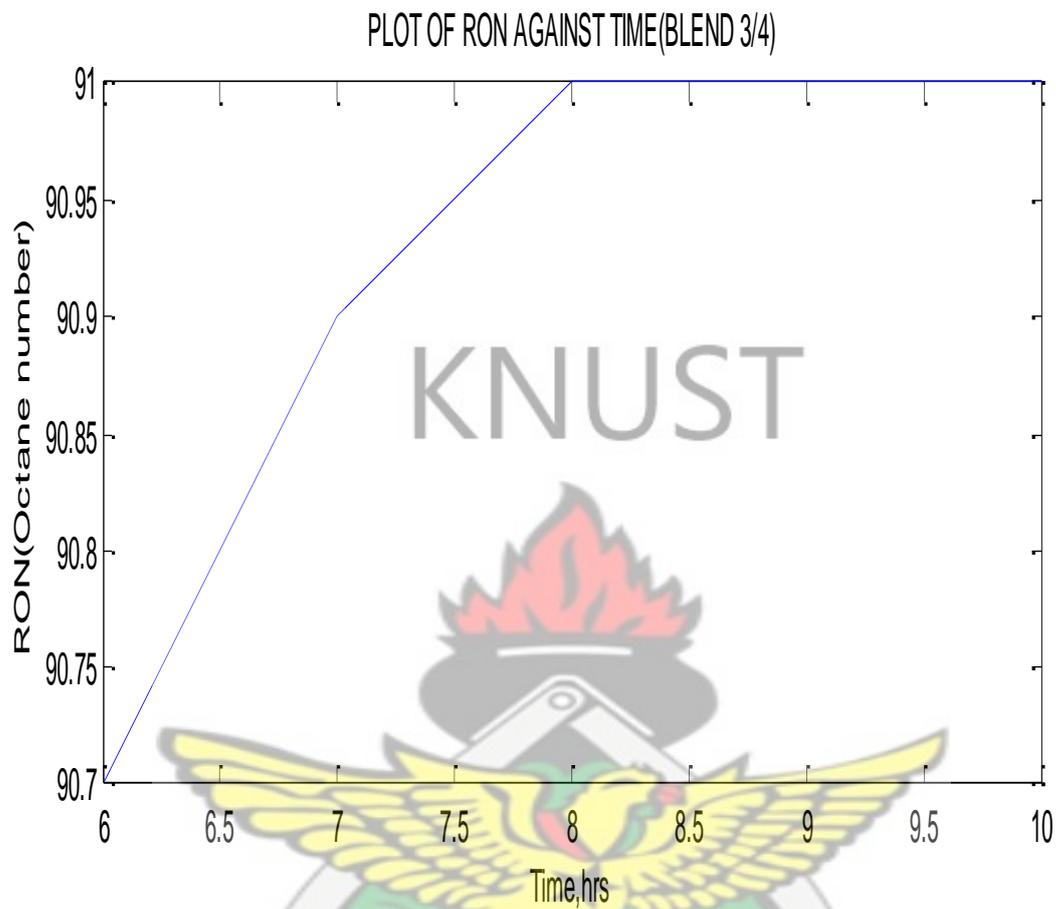


Fig.12 Plot of RON against Time

Fig 12 is a plot of RON against time for blend of tank 3 and 1. After 6 hours of mixing the RON is 90.7 and rises to 90.9 at 7 hours and 91 at 8 hours and maintains till 10 hours.

CHAPTER 5

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

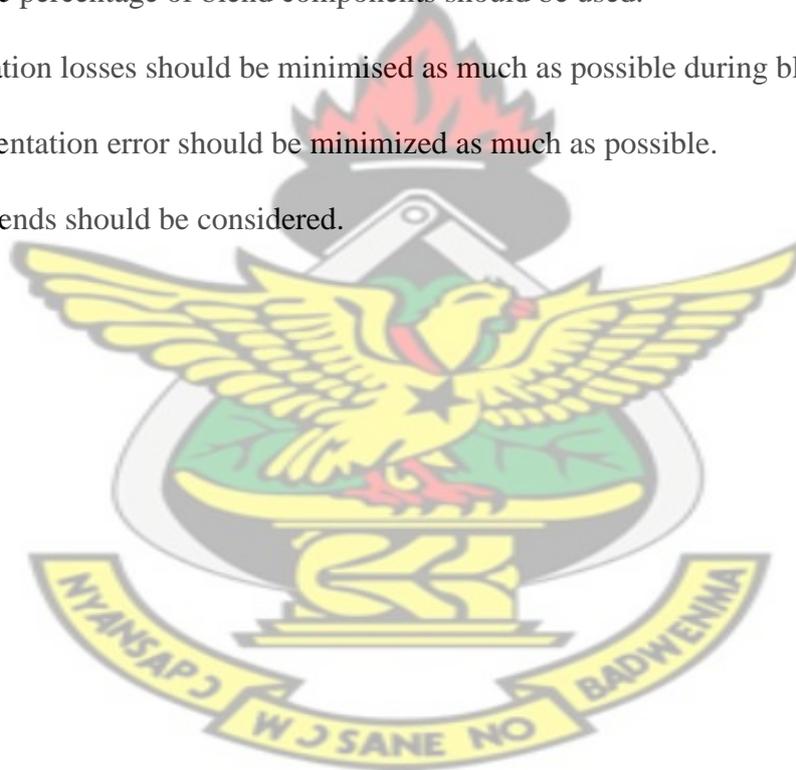
The objective of the project was to come out with a model for blending motor gasoline which can predict the RON (Research Octane Number), RVP (Reid Vapour Pressure) and Density of the gasoline blend. The study was successful .Three first order differential equations were derived from first principles .Generic analytical solution was deduce and MATLAB code (MODEL) was written to solve the equations using Runge-Kutta numerical Method of solution.

The quality control department of Tema Oil Refinery were consulted and they sampled five different gasoline tanks namely; tank 1,2,3,4 and 40.The highest octane gasoline tank was tank 3.The tank 3 was used as a pivot and five different blends were prepared .The model was used to predict the RON,RVP and Density of the blends by varying the mixing or blending time from 4 hours to 10hours. Analytical solution was determined and compared to the model solution.

From the results of the model it was evident that the blend improved with time. The higher the mixing time the better the blend .However at an optimum time the blend remains stable. When a particular blending process starts the dependent variables thus RVP,RON and density keep changing with time until they reach their optimum and they remain constant irrespective of the mixing time.

5.2 Recommendation

- It is recommended that the optimum blending time is established for each of the dependent variables before blending begins. The dependent variable with the highest mixing time becomes the rate determining step. The optimum time helps to save energy and time since exact mixing time will be adhered to.
- It is recommended a lot of caution and pain is taken to determine accurately the inputs to the model. Since the blend result is dependent on the inputs.
- Accurate percentage of blend components should be used.
- Evaporation losses should be minimised as much as possible during blending
- Instrumentation error should be minimized as much as possible.
- More blends should be considered.



REFERENCE.

- Auckland, M.H.T. and Charnock, D.J., (1969). “The Development of Linear Blending Indices for Petroleum Properties”, *J. of the Inst. of Petroleum*, 55(545), 322- (1969).
- Celik, M. B. (2008) Experimental determination of suitable ethanol-gasoline blend rate at high compression ratio for gasoline engine.
- Chevron (2001). “Petrol and Driving Performance” Accessed on 2nd March, 2012 [[http://www.chevron.com/ Petrol and Driving Performance, 2001](http://www.chevron.com/Petrol and Driving Performance, 2001)]
- Chromatography Online (2008). “[Gasoline components](#)”. Retrieved September 9, 2008.
- Downs, D. and Walsh, A.D. (1949) “Knock in Internal Combustion Engines”. *Nature*, vol 163, p 370, 1949.
- Moore, W., Foster, M., and Hoyer, K (2011) "Engine Efficiency Improvements Enabled by Ethanol Fuel Blends in a GDi VVA Flex Fuel Engine," SAE Technical Paper 2011-01-0900 doi:10.4271/2011-01-0900.
- Morris, W.E (1975). “Interaction Approach to Gasoline Blending”, NPRA Paper AM-75-30, National Petroleum Refiners Association annual meeting
- Najafi,G.,Ghodadiam,B.,Tavakoli,T.,Buttsworth,D.R.,Yusaf,T.F.,Faizollahnejad,M (2009) Performance and exhaust emissions of a gasoline engine with ethanol blended gasoline fuels using artificial neural network”Volume 86, Issue 5, Pages 630–639.
- OSHA (2008). OSHA Technical Manuel. Accessed on 18th March, 2012 [<http://www.osha.gov>]

- Redlich, O. and Kister, A.T (1948). “Thermodynamics of Non electrolytic Solution. Algebraic Representation of Thermodynamic Properties and Classification of Solutions”, Ind. Eng. Chem. 40, 345-348 (1948).
- Rusin, M.H., Chung, H.S., and Marshall, J.F (1981). “A Transformation Method for Calculating the Research and Motor Octane Numbers of Gasoline Blends”, Ind. Eng. Chem. Fundam., 20(3), 195-204 .
- Schoen, W.F. and Mrstik, A.V (1955). “Calculating Gasoline Blend Octane Ratings”, Ind. and Engr. Chem., 47(9), 1740-1742 (1955).
- Seddon, D (2000). “Octane Enhancing Petrol Additive/Products”
- Stewart, D.W., & Kamins, M.A. (1993). “Secondary research”. Information sources and methods (2nd ed.). London: Sage.
- Stewart, W.E (1959). “Predict Octanes for Gasoline Blend”, Petroleum Refiner, 38(12), 135-139 .
- Taylor C.F (1985). “The Internal Combustion Engine in Theory and Practice”. Volume 1 and 2, MT Press., Second editions 1985.
- Tema Oil Refinery (2008). Accessed on 5th March, 2012 <http://www.torghana.com>
- Tema Oil Refinery (2007). “Distillation process”. *Operational Manual for CDU*, Tema, Ghana 2007.
- Tema Oil Refinery (2008). “Blending and Tank Farm Operations”. *Operational Manual for MOP*.
- Tema Oil Refinery (2008). “Catalytic cracking”. *Operational Manual for RFCC*,
- Tema Oil Refinery online, (2008). Accessed on 5th March, 2012 [<http://www.torghana.com>]

APPENDIX

FLOW CHART

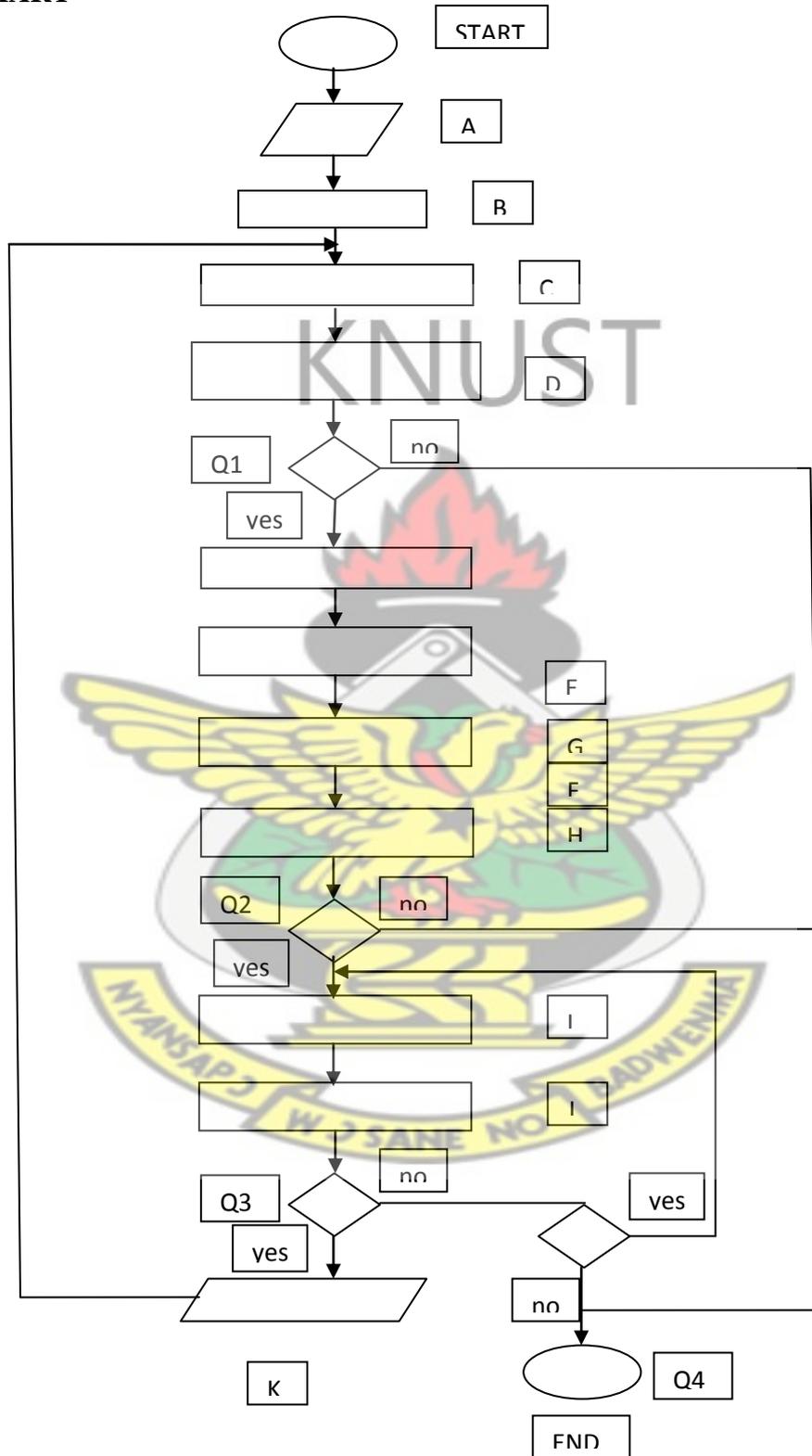


Fig. 3.2

LEGENDS:

A Input A_1 **R** $r_2 = (91-A_1)/(A_2-A_1)$ **C** $f = @(H) -r_3+r_1A_1+r_2A_2$

Input A_2 $r_1 = 1-r_2$

$$r_3 = r_1+r_2$$

D $h = 1$ **F** $K_1 = hf(A_{ij})$ **F** output r_1 and r_2

$t = 0:h:5$ $K_2 = hf(A(j)+0.5K_1)$

$m = \text{length}(t) - 1$ $K_3 = hf(A(j)+0.5K_2)$

$A = \text{zeros}(\text{size}(t))$ $K_4 = hf(A(j)+K_3)$

$A(1) = 0$

G output $A(j+1) = A(j)+(K_1+2K_2+2K_3+K_4)/6$ **H** option = 1

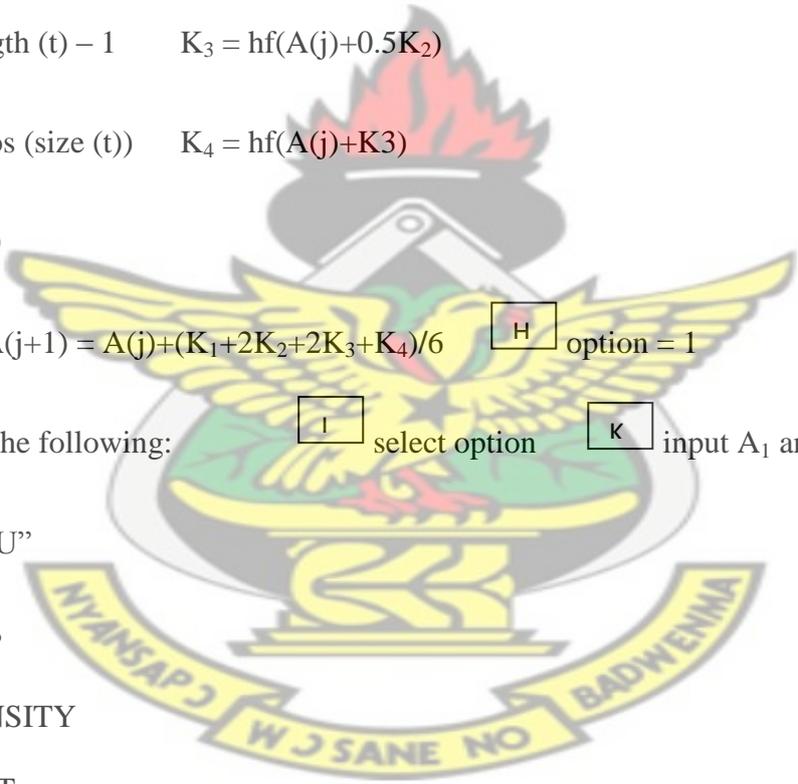
I display the following: **J** select option **K** input A_1 and A_2

“LVΨNU”

1. RVP
2. DENSITY
3. QUIT

Q1 for $j = 1$ to m **Q2** while option $\neq 0$

Q3 if option = 1 or 2 **Q4** if option > 3



SAMPLE SOLUTION DISPLAY

Enter the value of A1 for RON

92.3

Enter the value of A2 for RON

71.1

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ANSWERS

The R1 is : 0.9387

The R2 is : 0.0613

The RON is : 91.0

CONTINUE BY SELECTING ONE OF THE OPTIONS

***** MENU*****

1. RVP
2. DENSITY
3. QUIT

Select option: 1 , 2 OR 3

1

Enter the Reid Data Pressure of MOGAS

.21

Enter the Reid Data Pressure of Light Gasoline

.35

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The answer is : 0.22 kg/cm²

CONTINUE BY SELECTING ONE OF THE OPTIONS

***** MENU*****

1. RVP
2. DENSITY
3. QUIT

Select option: 1 , 2 OR 3

2

Enter the density of MOGAS

742.4

Enter the density of Light Gasoline

723

The answer is : 741.17

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CONTINUE BY SELECTING ONE OF THE OPTIONS

***** MENU*****

1. RVP
2. DENSITY
3. QUIT

Select option: 1 , 2 OR 3



SAMPLE ANALYTICAL SOLUTION DISPLAY

$$100r_1 + 100r_2 = 100 \quad (3.10)$$

$$A_1r_1 + A_2r_2 = 91 \quad (3.11)$$

$$A_1=92.3 \text{ ans } A_2= 71.1$$

Evaluating equations (3.10) ans (3.11) simultaneously yields $r_1=93.9\%$ and $r_2=6.13\%$

$$RON(t=0)=0; RVP(t=0)=0 \text{ and } \rho(t=0) = 0$$

$$RON(t) = r_1A_1 + r_2A_2 - Ue^{-t}$$

$$RON(t=4) = 91 - 91e^{-4} = 89.3$$

$$RON(t=5) = 91 - 91e^{-5} = 90.4$$

$$RON(t=6) = 91 - 91e^{-6} = 90.7$$

$$RVP(t) = r_1B_1 + r_2B_2 - Ve^{-t}$$

$$B_1=0.21 \text{ and } B_2=0.35$$

$$RVP(t=4) = 0.21 - 0.21e^{-4} = 0.206$$

$$RVP(t=5) = 0.21 - 0.21e^{-5} = 0.208$$

$$RVP(t=6) = 0.21 - 0.21e^{-6} = 0.209$$

C1=742.4 and C2=723

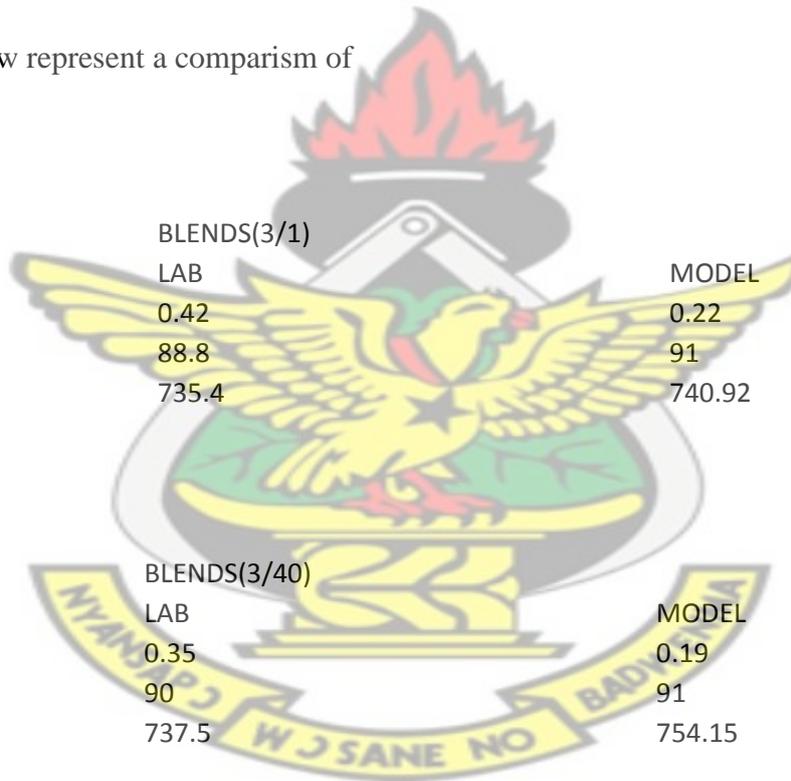
$$\rho(t = 4) = 741.4 - 741.4e^{(-4)} = 727.8$$

$$\rho(t = 5) = 0.21 - 0.21e^{(-5)} = 736.4$$

$$\rho(t = 6) = 0.21 - 0.21e^{(-6)} = 739.5$$

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The tables below represent a comparison of



	BLEND(3/1)	MODEL
RVP	0.42	0.22
RON	88.8	91
Density	735.4	740.92

	BLEND(3/40)	MODEL
RVP	0.35	0.19
RON	90	91
Density	737.5	754.15

	BLEND(3/4)	MODEL
RVP	0.34	0.2
RON	90	91
Density	738.1	743.26

	BLEND(3/2)	MODEL
RVP	0.32	0.2
RON	90.8	91
Density	751.7	741.88

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