

POTENTIAL OF CANE MOLASSES AS QUENCHING MEDIUM FOR (0.61%C) HIGH CARBON STEEL

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Declaration

I declare that this dissertation titled 'Potential of cane molasses as quenching medium for high carbon (0.61%C) steels' was carried out by me in the Department of Metallurgical and Materials Engineering under the supervision of Dr. T. Ause and Dr. E. T. Dauda. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at any university.

Mamuda, Rayyan Dodo _____ _____

(Signature) **Date**

Certification

The dissertation titled 'POTENTIAL OF CANE MOLASSES AS QUENCHING MEDIUM FOR HIGH CARBON (0.61%C) STEELS' by Mamuda Rayyan Dodo meets the regulations governing the award of Master of Science Degree of the Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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Dedication

This project is dedicated to my Father, Alh. Mamuda Abdullahi Dodo, for cherishing me and giving me the right upbringing.

Acknowledgement

All praise be to Allah for making it possible for me to successfully complete this work.

My profound and deepest gratitude goes to my supervisor, Dr. T. Ause for guiding and standing by me despite his tight schedules. I will also like to express my gratitude to my minor Supervisor, Dr. E. T. Dauda, for his guidance and support. May the Almighty God continue to guide, protect and grant you good health.

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Abstract

The effect of cane molasses as quenching medium for high carbon steel was investigated. Samples of high carbon steel were spheroidized annealed and then machined prior to the hardening process. Molasses of eleven different viscosities were prepared by adding varying amounts of water; such that the ratios of molasses to water were 1:1, 2.5:1, 3:1, 3.5:1, 4:1, 4.5:1, 5:1, 5.5:1, 6:1, 6.5:1 and 1:0. The samples were normalized and then austenitised at 800^{o}C. They were then soaked for 40 minutes and then quenched in water, engine oil, raw molasses and molasses solutions (in the ratio mentioned above). Half of quenched samples (ninety one) were further tempered at 350^{o}C, held for 40 minutes and then air-cooled. Cooling curves of all the quenching media used were developed. Specific heat capacities of the various media used were determined. Mechanical properties (tensile strength, percent elongation, hardness and impact energy) of the test samples were evaluated. The test results obtained showed that for the quenched specimens, the highest value of tensile strength (1360 N/mm^2) and hardness (679 HVN) was obtained in 1:1 molasses to water solution. Minimum impact strength was also obtained from sample quenched in 1:1 molasses to water solution. Microstructures of the various samples were analyzed using optical microscopy (OM) and scanning electron microscopy (SEM). In all the tests samples martensite structure was observed. Quench cracks were observed in specimen quenched in water and 1:1 molasses to water solution. It was also observed that molasses solutions with mixture ratio 1:1, 2.5:1, 3:1, 3.5:1, 4:1, 4.5:1, and 5:1 had quenching severity higher than that of engine oil but lower than that of water while molasses solution (5.5:1) gives cooling rate close to that of engine oil. The research showed that molasses solution with mixture ratio 3:1 gave good combination of mechanical properties (4.2% percent elongation, 905N/mm^2 tensile strength, 602HVN hardness and 158KJ/mm^2 impact strength); and is hereby recommended to be used as quenching medium for high carbon steels.

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ABBREVIATIONS

%	-	Percentage
EDS	-	Energy Dispersion Spectrometry
J/KgK	-	Joules per Kilogram per Kelvin
M	-	Mass
Mn	-	Manganese
Fe	-	Iron
P	-	Phosphorous
C	-	Carbon
SEM	-	Scanning Electron Microscopy
OM	-	Optical microscopy
Ti	-	Titanium
V	-	Vanadium
SHC	-	Specific heat capacity
m-w (n:1)	-	molasses to water mixture with mixture ratio n:1
r-m	-	Raw Molasses
Cp	-	Centipoises
x100	-	Magnification at 100 times
Si	-	Silicon
SAE	-	Society for Automotive Engineers
ARD, NLD & ANLD	-	As-reduced, normalized and annealed

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the study

Quenching; as an ancient art, originated from man's attempt to improve the performance of his working tools and weapons (sword, spears, etc). The main development in quenching came in the half of the 20^{th} century in conjunction with the establishment of transformation diagrams, which has made quenching less of an art and more of a science (Olson, 2001).

Quenching is a crucial process within the broader field of heat treatment. It constitutes an important process in nearly every manufacturing sector, such as railway, automotive, aerospace and others. Quenching is used to induce hardness and strength in steel so as to improve its performance in service. It involves heating steel to some temperature above the upper critical temperature, in order to convert it partially or completely to austenite, holding it long enough to ensure the desired austenitization, after which cooling is carried out at a rate equal to or faster than the critical cooling rate (Thelning, 1984). A medium that is used for quenching is called a quenchant. The primary function of a quenchant is to facilitate the hardening of steel by controlling heat transfer during quenching and also to minimize the formation of undesirable thermal and transformation stresses which may lead to increase in distortion and cracking (Totten, 1997).

The commonly used quenchants are water, oil, brine, and synthetic solutions (such as polymer solutions). Water, though abundant and low in cost, has a drawback of inducing crack or dimensional changes on quenched components due to its high cooling rate. Polymer quenchants have no definite pattern/trend of property improvement with varying concentrations and they are also more expensive relative to water. Brine produces more quenching severity than water and it

also corrodes the component and the equipment used for the quenching. Low alloy and carbon steels can be quenched in brine solution; however, the rapid cooling rate of brine can cause cracking or distortion in high carbon and low alloy steels (Olson, 2001).

Molasses is a honey-like substance. It is a waste emanating from sugar processing (Solomon *et al.,* 1991). Molasses is produced in large quantities in Nigeria. The production level as at early nineties stands at over 10 million gallons per annum. This stock constitutes fiscal menace to the sugar industries in terms of inventory and disposal cost. Furthermore, its disposal leads to pollution of streams and rivers. Even though molasses finds applications in the production of alcohol and single cell protein, there is a need to take advantage of the availability of this by-product (Solomon *et al.,* 1991).

The technical challenge of quenching has been the choice of a quenching medium that will yield the desired as-quenched properties, such as hardness, with a minimum induced distortion. There is a need, therefore, for the development of a quenching medium that is of low-cost like water, but having less severity and yet produce appreciable hardening.

1.2 Statement of the problem

Water and brine could be used to quench some grades of steels but do not produce good results with high carbon steels; the reason being that the rate of cooling is high in the temperature range of martensite formation. This exposes steels to simultaneous influences of transformational and thermal stresses. The combined effects of these stresses increase the risk of crack formation (Olson, 2001).

Over the years, engine oil has been found to be a suitable quenchant for high carbon steel (Hassan *et al.,* 2010; Joseph *et al.,* 2015). When quenched in engine oil, high carbon steels could be hardened without cracking. However, two of the major problems associated with quenching

in engine oil are; at times engine oil is combustible and could only be used under controlled atmospheres (either reducing or neutral) as the oxidation of the oil results in the formation of carboxylic acids and sludge which affects the induced hardness and colour of the work piece (Jensen, 2004). On the safety side, engine oil is hazardous to operate. Hence, there is need to develop a quenchant that is of low cost like water, environmental-friendly, non-corrosive, and effective in inducing the required hardness without the problems of distortion and residual stresses.

Based on the above aforementioned reasons, this research focuses on the use of molasses as a quenching medium for high carbon steels.

1.3 Justification

Quench cracking during water quenching has been a problem to the metallurgical industries especially with high carbon steel (Olson, 2001). Any high carbon steel that cracks due to quench hardening operations is being rendered scrap and this eventually leads to economic losses. It has been established that engine oil is a suitable quenchant for high carbon steel as it provides moderate and uniform cooling rate (Hassan *et al.*, 2010; Joseph *et al.*, 2015). However engine oil is associated with several environmental liabilities such as oil fumes, smoke emissions, fire hazard, oil spills, leaking underground storage tanks, ground water contamination and waste oil disposal (Yanet, 2012). Hence, the focus of this research is the development of a quenching medium that is eco-friendly, which will serve as an alternative to oil quenching.

1.4 Aim and Objectives

This work is aimed at investigating the suitability of sugarcane molasses as quenching medium for high carbon steels. The specific objectives targeted in this work are to:

i. investigate the effect of viscosity on the cooling rate of cane molasses.

ii. harden high carbon steel using cane molasses as a quenchant.

iii. examine the microstructures of the quenched, tempered, normalized and as-received samples using optical microscopy (OM) and scanning electron microscopy (SEM).

iv. develop the cooling curves of the prepared molasses solutions, raw molasses, water and engine oil; using high carbon steel probe.

v. determine specific heat capacity of the cane molasses, its solutions, water and engine oil using copper calorimeter.

1.5 Scope of the Work

The carbon content of the high carbon steel samples used in this research work is 0.61%C. Mechanical properties, cooling rates and viscosity were the parameters used to measure the effectiveness of the molasses as quenching medium for the high carbon steels.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Steel is a very versatile engineering material with a wide range of attractive properties and a very competitive production cost. It has diverse range of applications and is second only to concrete in its annual production tonnage (Westwood, 1996). The properties of steels are related to the structure. The desired mechanical properties can be achieved by altering the size, shape and distribution of various constituent phases by heat treatment. Heat treatment can affect the properties of most metals and alloys, but ferrous alloys, principally steels; undergo the most dramatic increase in properties. In general, the most stable steel structures are produced when steel is heated to the high temperature austenitic state and air cooled under near-equilibrium conditions. This type of heat treatment, often referred to as normalizing, produces a structure that has low level of residual stresses locked within the part and the structures can be predicted from an equilibrium diagram (Alexey *et al.,* 2006). Martensite and bainite are metastable structures produced by non-equilibrium cooling or quenching from austenitic state (Alexey *et al.*, 2006).

2.2 Classification of Steels

Steels can be classified by different systems depending on:

1. Compositions, such as plain carbon (or non alloy), low-alloy, and alloy steels
2. Microstructure, such as ferritic, pearlitic, martensitic, and austenitic steels.
3. Application or main characteristic, such as structural, tool, stainless steel, or heat resistant steels
4. Oxidation practice employed, such as rimmed, killed, semikilled, and capped steels

5. Manufacturing methods, such as converter, electric furnace, or electroslag remelting methods (Totten, 2006).

2.3 Effect of Heat on the Structure of Steels

When steel is heated to certain temperature called austenitizing temperature and held there long enough, the room temperature structure is converted into fcc solid solution called austenite. In the case of alloy steels, austenite may also have other elements dissolved in it in addition to carbon (Raghavan, 1989). This step, is the first and foremost step in the majority of heat-treating processes and the nature of the austenite that is obtained is important because it has a direct effect upon the microstructure produced during subsequent treatments in which the austenite is transformed into other phases. Thus, the array of microstructures (and thus mechanical properties) that are obtainable in steel by various heat treatments depends on the manner in which austenite transforms when it is cooled to room temperature (Sinha, 1989). The process of austenite formation on heating proceeds by nucleation and growth process. Therefore, the factors, which can vary either the rate of nucleation or the rate of growth or both, will change the kinetics of austenite formation. Two such parameters are transformation temperature and holding time at transformation temperature.

2.4 Heat Treatment of Steels

Metals and alloys develop requisite properties by heat treatment, which plays a critical role in achieving appropriate microstructure that impact the desired mechanical properties in a given metal. Thus the study of heat treatment is of great significance (Rajan *et al.*, 1988).

Heat treatment can be defined as heating, holding and controlled cooling operations applied to metals/alloys in solid state, so as to obtain the desired properties. The heating and cooling sequence may involve temperature above, below and at the ambient. Controlled heating and

cooling rates and a variety of furnace atmospheres and heating media may be used. Plastic deformation may be included in the sequence of heating and cooling steps (Rajan *et al.,* 1988). There are various types of heat treatment processes in practice some of which are discussed in the subsequent section.

2.4.1 Annealing Heat Treatment

Annealing is carried out to obtain a homogeneous structure, to produce softening or refine the grain size. The temperatures used vary widely with the material being treated and the specific properties required (Figure 2.1) (Davies and Oelmann, 1983). For these reasons, annealing heat treatment could be stress-relief, process, spheroidising or full annealing**.**

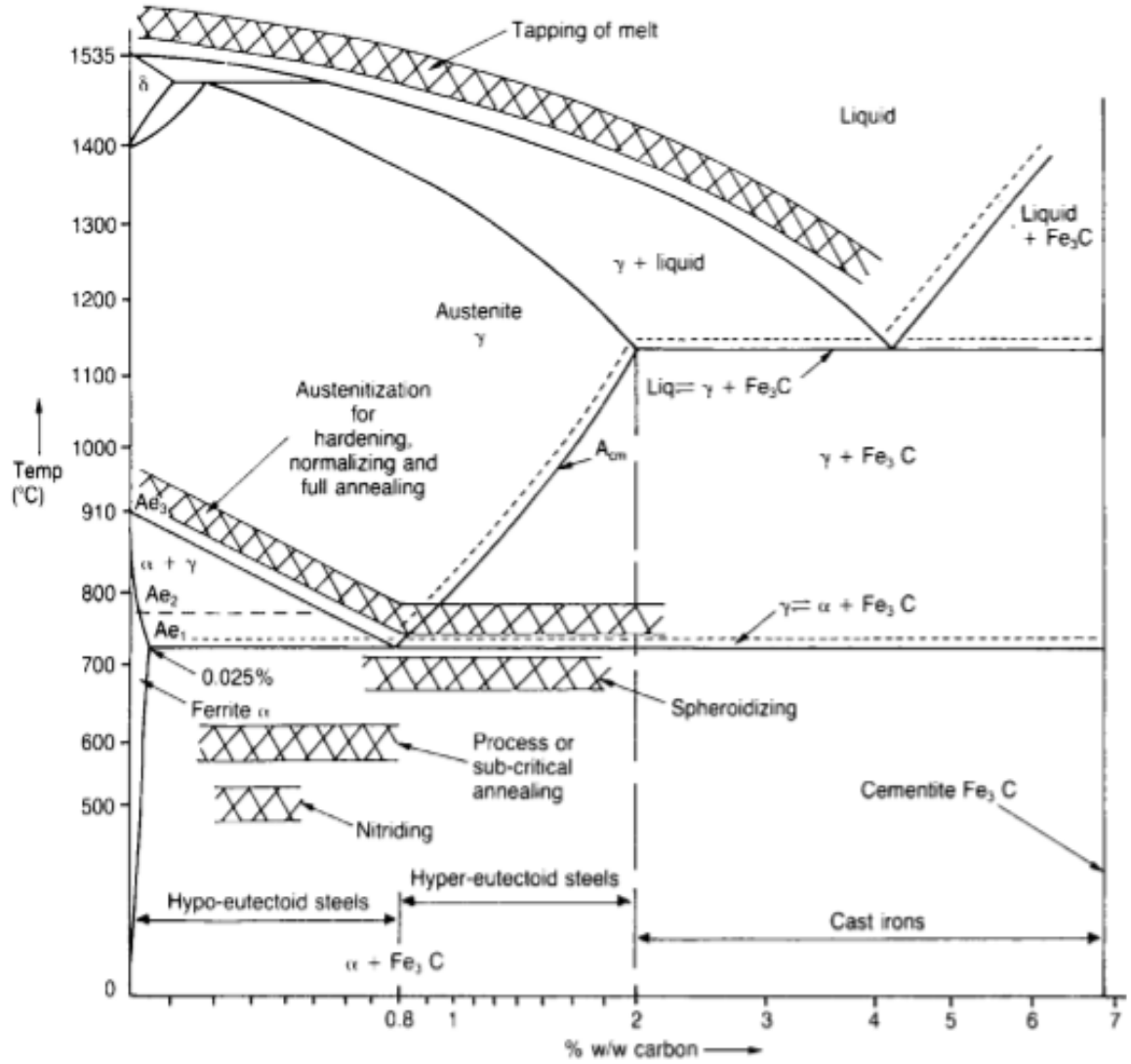


Figure 2.1: Iron-Carbon Equilibrium Diagram.
(Source: Smallman and Bishop, 1999).
Note: Dotted lines represent iron-graphite equilibrium diagram

2.4.2 Normalizing

This is the heat treatment process whereby a steel or cast iron is heated to a temperature of about $30^{O}C$ above its upper critical temperature, soaked at this temperature for the necessary homogenization to occur and then cooled in still air (Figure 2.1) (Davies and Oelmann, 1983). Fine pearlite and proeutectoid ferrites result from this treatment.

Normalizing is applied to casting and machined samples. In casting, normalizing is essential to eliminate the dendritic structure. The microstructure of the hot rolled product, cooled in air is approximate to the normalized condition. Furthermore steel that have been plastically deformed by machining operation consist of grains of pearlite which are irregularly shaped and relatively large, but varying substantially in size. In such situation, normalizing is used to refine the grains (i.e to decrease the average grain size) and produce more uniform and desirable size distribution. Fine grained pealitic steels are tougher than coarse grained ones.

Technically, the hardness and strength obtained after normalizing is higher than those obtained after annealing, but hardening processes are also available and include hardening and tempering (Taylor, 1979).

2.4.3 Hardening

High hardness can be obtained by a process known as hardening. Hardening treatment consists of heating to a sufficiently high temperature, holding at that temperature, followed by rapid cooling such as quenching in water, oil, or salt baths. The high hardness developed by this process is due to the phase transformation accompanying rapid cooling. The rapid cooling means cooling rate equal to or more than that of the upper critical cooling rate (Rajan *et al., 1988*).

The product of the hardening transformation of austenite is martensite and this is a hard micro-constituent of steel and cast iron. Hardening is not confined to only ferrous alloys but also applies to almost all non-ferrous alloys (Hassan *et al.,* 2009).

2.4.4 Tempering

According to Hassan (2009), tempering heat treatment is a process of heating martesitic steel at a temperature below the eutectoid transformation temperature in order to make the steel softer and ductile. It is a process whereby quench hardened steel and cast iron in the martesitic condition

are heated to some predetermine temperature between room temperature and lower critical temperature, holding for an hour and then followed by air or oil cooling. During tempering, hardness is reduced while toughness is increased, since the essence is to increase toughness (Alexey *et al.*, 2006).

Tempering of quenched steels occurs continuously by a gradual rejection of carbon from the matrix. On reheating as-quenched martensite, tempering takes place in four distinct, but overlapping stages.

(a) Tempering stage I

In the first stage of tempering (150 to 250^{o}C), precipitation of a carbon-rich phase called ε-carbide occurs. As a consequence, the carbon in the martensite is reduced to approximately 0.3%. In the stage, martensite formed in plain carbon steel, is heated to a temperature of approximately 100^{O}C, the tetragonal martensitic structure is said to begin to decompose into low carbon martensite,and a transition carbide called epsilon(ε) carbide with a hexagonal crystal structure. The composition of this carbide is close to $Fe_{2.4}C$. It contains approximately 8.4% carbon instead of the 6.7% C of Fe_3C and is slightly harder. This first stage of tempering is accomplished by a slight reduction in the volume of the metal reaching an apparent maximum shrinkage (Totten, 2006).

(b) Tempering stage II

In the temperature range of 200 to 350^{o}C, the retained austenite in the steel decomposes into ferrite and cementite. This decomposition was detected successfully by x-ray diffraction and dilatometric and specific volume measurements. The kinetics of this decomposition are related to carbon diffusion in austenite. The untransformed austenite may undergo transformation on application of strain and thus affect the toughness of the steel. However, the fraction of retailed

austenite is usually low in steels containing less than 0.2 wt% C. The formation of stable carbides that is typical to third stage of tempering may overlap in the second stage of tempering. (Alexey *et al.*, 2006).

(c) Tempering stage III

In the third stage of tempering (350 to 450^{o}C), which occurs rapidly, the low carbon martensite loses its carbon and tetragonality as its carbon diffuses to combine with epsilon carbide forming very fine cementite particles. There is an overall increase in toughness with some loss in strength and hardness. The tempered structure obtained in this stage is tempered martensite which is the precipitation of stable cementite in extremely fine super-saturated plates of ferrite structure (not the traditional ferrite) and lower bainite (Hassan, 2009).

(d) Tempering stage IV

Tempering in this stage (450 to 600^{o}C), causes full recovery of dislocation in the substructure. The lath like cementite agglomerates to form spheroids above 400^{o}C resulting in an appreciable loss in strength and hardness as well as improve ductility and toughness (Hassan, 2009).

2.5 Quenching

Quenching, by directly immersing hot component (heat treatable alloy) into the quenching medium, is the simplest and most widely used hardening method. Quenching is performed by cooling rapidly from the austenitizing temperature to room temperature to obtain martensite structure, hence, preventing ferrite and pearlite formation (Rajan *et al.*, 1988). The main requirement of the quenching medium is to cool the component fast enough to produce the required structure. After quenching, the steel in the as-quenched condition is often tempered to obtain an optimal combination of strength, hardness and toughness.

During quenching, heat is extracted at a very fast rate from the material. The rate should be equal or faster than the critical cooling rate. For specific steel composition and heat treatment, there is a cooling rate known as the critical cooling rate for the full hardening of steel, at which most of the high temperature austenite is transformed into martensite, preventing the formation of bainite, pearlite or ferrite. It is important to understand the mechanism of quenching and the factors that affect the process, since this can influence quenchant selection and the performance obtained from the process. The rate of cooling in the hot component depends on the heat removal characteristic of the cooling medium, the thermal characteristics of the alloy, and the section thickness of the component (Rajan *et al.*, 1988).

2.5.1 Stages of Quenching

A useful way of accurately describing the complex mechanism of quenching is to develop a cooling curve for the fluid under a controlled condition. The heat energy absorbed by the steel part is dissipated by the quenching medium in the quenching process. The temperature-time curve indicates the heat transfer characteristics of the fluid. The shape of cooling curve is a representative of the various stages of the cooling mechanism that occur during the quenching process. Removal of heat from a steel component during quenching is classified into three stages; the film boiling stage, nucleate boiling and convention stage. These are referred to as the first, second and third stage (ASM, 1978). Figure 2.2 shows a typical cooling curve during a quenching process with the stages of the process indicated.

(a) First stage

As soon as the metal component makes contact with the quenching medium, the surrounding quenching fluid is instantaneously heated up and vapour is enveloped around the

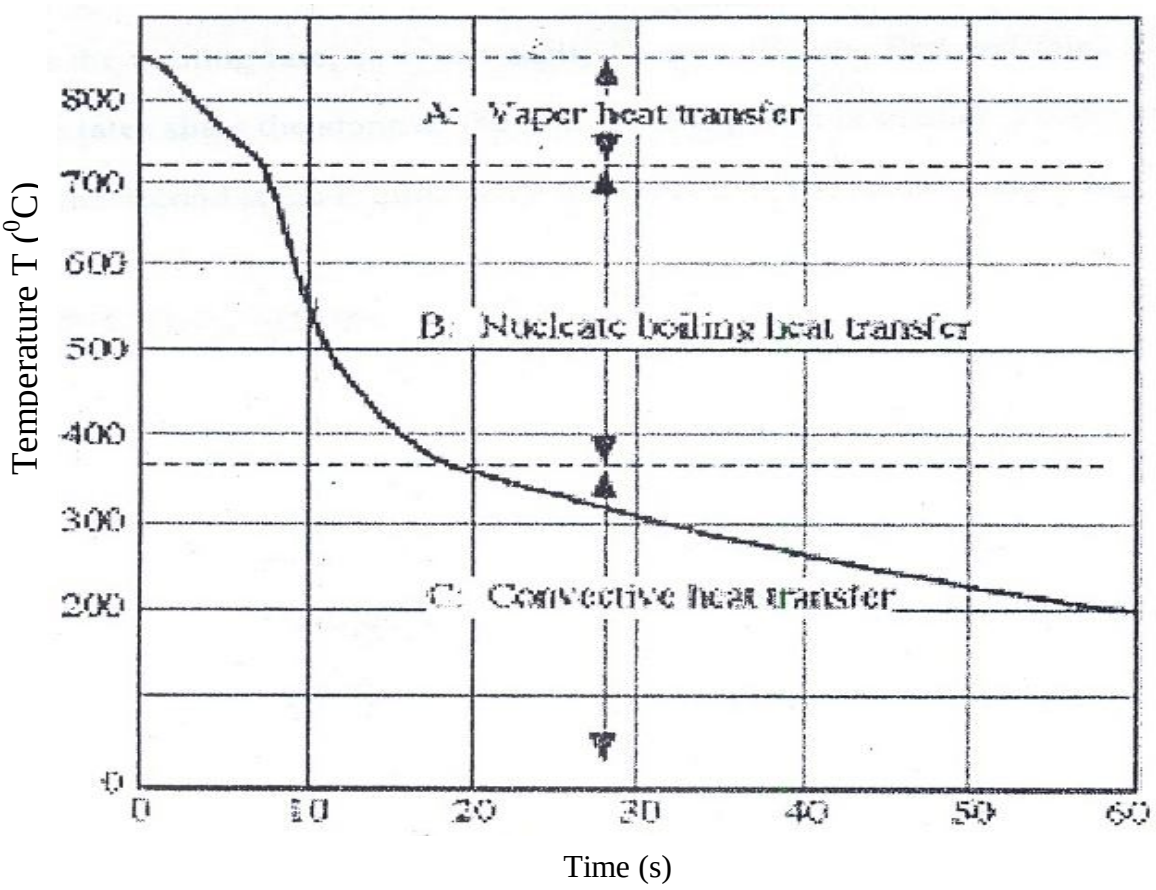


Figure 2.2: Cooling curve showing various stages of cooling
(*Source*: John, 2005).

metal piece reducing further cooling of the metal component. This stage is characterized by a relatively slow cooling rate since the vapour of the quenching medium film that surrounds the part has relatively poor heat conduction property.

In this particular stage, heat is removed from the part by radiation and some conduction through the vapour layer (ASM, 1978). This stage is shown in the B region in Figure 2.2.

(b) Second stage

The second stage starts when vapour film envelope begins to break down as the temperature of the component reduces. Fresh liquid quenchant now comes in direct contact with the metal component; the process is repeated, resulting to violent boiling of the liquid. Boiling continues till the temperature of the surface of the work piece comes down below the boiling point of the

liquid. This stage is characterized by rapid cooling through the heat of vapourazation. Size and shape of the vapour bubbles are important in controlling the duration of this stage as well as its corresponding cooling rate (Rajan *et al*., 1988).

(c) Third Stage

As the temperature of the component continues to reduce below the boiling point of the medium; the boiling stage breaks down giving way to the liquid cooling stage. The stage, much like the vapor blanket stage, is also characterized by slow cooling rates. Heat dissipated from the part takes place by both conduction and convection process. The difference in temperature between the boiling point of the quenching medium and actual temperature of the medium is the major factor influencing the rate of heat transfer in liquid quenchants (ASM, 1995).

Figure 2.2 above, illustrates the stages of quenching and cooling rate seen on a typical cooling curve as the quench is being monitored. The slope of the curve between the stages is the cooling rate, so it can easily be seen that the first and third stages have slow cooling rates since the slope of the line at those points is smaller. On the other hand, the slope of the second stage is quite big and therefore, the cooling rate is high.

2.5.2 Quenching media

Some of the widely used quenching media for steels are water, oil, aqueous solution, molten salts and air. And more recently polymers and gas are used.

The media differ in the rate at which they dissipate heat out of quenched part. Brine and water, by far, have the fastest cooling rate, followed by polymer solutions and finally oil.

(a) Water

Water as a quenchant is one of the most commonly used, this is because is abundant (easily available), inexpensive and easy to handle. It also has little disposal consideration and is

one of the fastest quenching media being second only to aqueous solution. (Rajan *et al.*, 1988). Therefore water can be used successfully for certain carbon steels, some alloy steels and non ferrous alloys. However, water does have a number of limitations that makes it less desirable a choice in certain application. For steels with high hardenability water quenching generally results to cooling rates that are higher than the critical cooling rate. It is generally admitted, as expressed by De Oliveira *et al*. (2002), that oil quenching and water quenching lead to the development of high residual stresses resulting to distortion or cracks in a component. In practice, the applicability of water as a quenching medium is restricted to plain carbon steels and some low alloy steels. The high cooling rate offered by water also puts limitations on the shape of the object to be heat treated. Thus, only articles with simple geometry can be water-quenched.

Water quenched objects are also prone to corrosion. Studies have shown that the best results are obtained using water at the temperature range of 20 – 40^{o}C (Thelning, 1984).

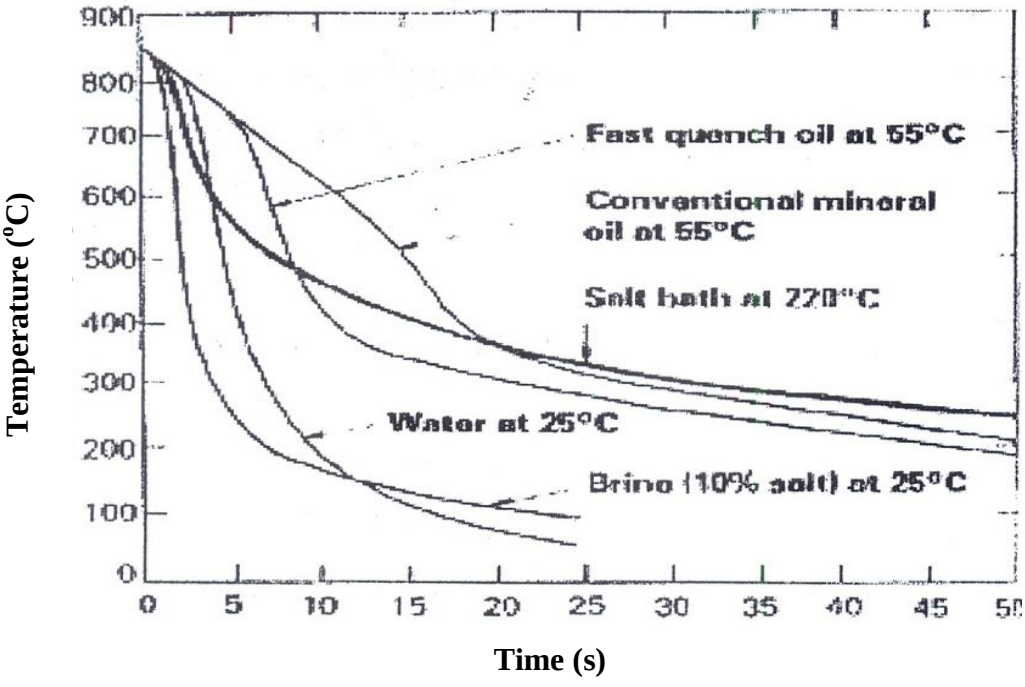


Figure 2.3: Cooling curve of various common quenching media, using a stainless steel probe (*Source*: Skidmore, 1986).

(b) Oil

Use of oil as quenching medium has been investigated and used during the past years. Oil quenchants can be categorized into normal, accelerated and marquench oil (Totten, 1993). For accelerated oil, additives are included to produce increased quenching speed. The normal or conventional oil does not include additive.

Although mineral oil traditionally has been commonly used as quenching medium, for example engine oil, SAE40, spindle oil, and industrial lubrication oil, various vegetable oils have been used as well (Zhou, 1987). Hassan and Yusuf (2005) experimentally investigated the use of various vegetable oils and showed that palm kernel oil will induced a higher hardness value. Generally, oil quenching has a number of advantages in comparison with water. Quenching oils provide slower cooling rate as compared to water quenchant. The slower cooling rate reduces the possibility of inducing cracks or distortion in the quenched piece. The duration of the first stage is longer than that achieved by water as a quenching medium.

The cooling rate and the duration in the second stage are also considerably lower. Therefore, oils are used where severe quenching is not required and so result to less distortion. Also, oil of viscosity value as low as 50 SUS at 40^{o}C gives higher cooling rate (Rajan *et al.*,1988). A problem with oil quenchant is ageing of the bath. Immersion of very hot steel can lead to oxidation of the oil and removal of the quenched component can lead to lose of some of the liquid quenchant. Oil also has a limitation of low flash point and hence danger of explosion and fuming.

(c) Polymer

This quenchant consists of water with a polymer dissolved in it at some specific concentration level. There are numerous polymers that may be dissolved in aqueous solution to

produce polymer quenchant. The most commonly encountered polymers are; polysodium acrylate (PSAs), polyethyl oxazoline, polyalkylene glycol (PGA) and polyvinyl pyrrolidone (PVPs). Polymer quenchants can be formulated to provide quenching speed ranging from that similar to fast quenching oil to that greater than water (Edens, 2006).

Polymer quenchants degrades or ages slowly on usage and affects the quenching power, so it is necessary to provide process control by periodic monitoring of the quench bath by routine maintenance (Totten, 2006). The quench severity is dependent on the polymer concentration. Muhammad (2007) reported that the highest cooling rate of glycerol solution is obtained with 5 to 25% concentration. Polymer quenchants can be used to reduce the cooling rate of water by forming an insulating film on the work piece surface, and distortion problem can be effectively reduced (Zhoa and Yi, 1996). Two different principles explain the formation of the insulating film.

The first principle is referred to as “reverse insolubility or inverse solubility” (Beitz, 1998). This means that polymer which is soluble at room temperature becomes insoluble when certain temperature is reached. So, during quenching, at high temperature, the polymer condenses at the surface of the work piece forming an insulation film. However when the temperature drops below the point of inverse solubility the polymer dissolves back into the water.

The second principle is referred to as “film forming by up-concentration”. The polymer forms an insulating film resulting to evaporation of water from the work piece surface, hence higher concentration of polymer is left on the metal surface (Beitz, 1998 and Zhoa *et al.*, 1996). The quenching rate is reduced, thus minimizing the potential of crack and distortion in the quenched components.

2.5.3 Metallurgical Effect of Quenching

Quenching of steel is done to control the transformation of austenite to desired microconstituents (pearlite, banite, and/or martensite). Martensite is the as–quench microstructure usually desired when hardening by quenching is done. If the cooling curve is superimposed on the Temperature–Time–Transformation (TTT) diagram for the particular steel quenched, it is possible to make a reasonable estimate of the product of austenite transformation, whether ferrite, pearlite, banite or martensite will be formed during the quenching process.

For specific steels composition and heat treatment condition, there is a critical cooling rate for full hardening at which most of the high temperature austenite is transformed into martensite without the formation of either pearlite or banite. To obtain the maximum amount of martensite, the cooling rate must be fast enough to miss the nose of the TTT curve. If the cooling rate is lower than the critical cooling rate, formation of bainite, pearlite or ferrite would occur. Thus, full hardening will not be attained.

2.5.4 Factor Affecting Quenching

Heat transfer during quenching is influence by many factors. These include the following:

i. Effect of temperature

The rate at which heat is extracted from a quenched metal depends on the temperature of the quenching medium; nevertheless, lowering the bath temperature does not necessarily increase the performance of the quenching medium (Totten *et al*., 2006). Ause, (1997) showed that the initial temperature of the component as well as the temperature of the medium has an effect on the quenching process. In general, higher quenching temperature lowers the temperature at which a total vapour blanket is maintained in the medium. As a result, the duration of the first stage of

quenching is increased as the time at which the part is cooled at slower cooling rates (Totten, 2006).

ii. Effect of Agitation

Agitation plays an important role in the effectiveness of a medium to quench a part. The effect of agitation on the performance of various quenching media has been studied. Agitation of a quenching medium is necessary to destabilize the vapour blanket and nucleate boiling if uniform heat transfer throughout the quenching is to be achieved (Totten, 2006). In addition, it will also produce smaller, more frequent bubbles during the boiling stage, which in turn, creates faster rates of heat transfer throughout the part (Mackenzie and Totten, 1989).

iii. Mass Effect

Mass of the component affects quenching in that as the mass increases, the time required for complete cooling also increases (Olson, 2001). The volume of the quenching medium depends on the weight of the component to be quenched. As more metals/alloys are quenched, the liquid absorbs the heat and this temperature rise causes a decrease in the cooling rate. Thus the volume of the quenchant should be large enough to absorb all the heat during a normal quenching operation without additional cooling (Olson, 2001).

iv. Surface Oxidation and Roughness Effects

The surface roughness of the body and surface layers, such as oxides or organic substances, also strongly influence the cooling process. Chromium-alloy steels are oxidation-resistant due to concentration of chromium oxide at the surface. Oxide layers have greater surface roughness and a lower thermal conductivity (Totten, 2006).

v. Effect of Cross- Section Size on Cooling

With large cross- sections, the cooling rate in the specimen center is limited by the rate of heat conduction from the interior to the surface.

vi. Geometry (design)

As the initial rupture of the vapor blanket is always related to the decrease of surface temperatures below the wetting temperature (Leidenfrost temperature), wetting behavior is strongly influenced by the radius of the lower edge of a cylindrical steel sample.

A sharp edge will cause high heat removal rates across the surface and a premature breakdown of the vapor blanket. Increasingly, the lower surface radius from a rounded edge to a radius of 2.5 mm reduces the initial wetting temperature and the influence of bath temperature is diminished due to the greater thickness of the vapor blanket (Totten, 2006).

2.5.5 Evaluation of quenching media

Various methods have been developed to ensure the effectiveness or cooling power of a quenchant. These include magnetic test (General motor, GM, quenchometer) method, the hot wire test, the cooling curve test, and measuring the hardness of the quenched part.

The cooling curve has been generally accepted as the most accurate means of determining the cooling power of a quenchant, cooling curves are particularly sensitive to all the factors that affect the ability of a quenching medium to extract heat from hot metal. These include quenchant type, physical properties, bath temperature and bath agitation (ASM, 1978).

2.6 Microstructure of Martensite

Of the various microstructures that may be produced for a given steel alloy, martensite is the hardest, the most brittle with most negligible ductility. These properties are attributed to the effectiveness of the interstitial carbon atom in hindering dislocation motion and to the relatively

few slip systems (along which dislocation moves) for body centered tetragonal (BCT) structure (Callister, 2007). Successful heat treating of steels to produce a predominantly martensitic microstructure throughout the cross section depends largely on the grade of steel, the conditions of austenitizing treatment, and the rate of cooling on quenching for hardening. Based on the appropriateness of application manipulation of these parameters, one can come up with the following possible martensitic microstructures (Kenneth, 2002).

(a) 100% martensitic structure (M): ideal parameter selection.

(b) Martensite + intermediate phase: inadequate quenching rate.

(c) Martensite + retained austenite: existence of alloying elements such as chromium.

(d) Martensite + segregates of carbon atoms: martensitic transformation atom with subsequent natural ageing.

(e) Martensite + pearlite structures: incomplete austenitization before quenching.

(f) Martensite + pearlite + iron carbide: by hypereutectoid steels and insufficient austenitization time.

Krauss & Marder (1971) studied the structure of martensite and found two different types depending on the composition and temperature at which they are formed. These are lath (massive) and acicular (plate) martensite. The lath martensite consists of packets of parallel lath with carbon contents up to 0.6% in carbon steel.

2.7 Molasses

The term molasses refers specifically to the final effluent obtained in the preparation of sucrose by repeated evaporation, crystallization and centrifugation of juices from sugar cane and sugar beets. Today, several types of molasses are recognized and in general, any liquid feed ingredient that contains excess of 43% sugars is termed molasses (Leo, 1983).

2.7.1 Types of Molasses

The Association of American Feed Control officials (AAFCO, 1982) describes the following types of molasses.

i. Cane molasses is a by-product of the manufacture or refining of sucrose from sugar cane. It must not contain less than 46% total sugars expressed as invert. If its moisture content exceeds 27%, its density determined by double dilution must not be less than 79.50 Brix.

ii. Beet molasses is a by-product of the manufacture of sucrose from sugar beets. It must contain not less than 48% total sugars expressed as invert and its density determined by double dilution must not be less than 79.50 Brix.

iii. Citrus molasses is the partially dehydrated juices obtained from the manufacture of dried citrus pulp. It must contain not less than 45% total sugars expressed as invert and its density determined by double dilution must not be less than 71.00 Brix.

iv. Hemicellulose extract is a by-product of the manufacture of pressed wood. It is the concentrated soluble material obtained from the treatment of wood at elevated temperature and pressure without use of acids, alkalis, or salts. It contains pentose and hexose sugars, and has a total carbohydrate content of not less than 55%.

v. Starch molasses is a by-product of dextrose manufacture from starch derived from corn or grain sorghums where the starch is hydrolyzed by enzymes and/or acid. It must contain not less than 43% reducing sugars expressed as dextrose and not less than 50% total sugars expressed as dextrose. It shall contain not less than 73% total solids.

2.8 Review of Previous Works

Because of the limitations of water and engine oil as quenching medium, researchers over the years have been searching for alternatives to water and engine oil. Among others are:

Balogun (2008) worked on the possibility of using cassava extracts as a quenching medium for plain carbon and low alloy steels. It was concluded that cassava liquid extract could be used as a quenching medium which gives mechanical properties better than that given by SAE40 engine oil.

Ause (2007) studied hot bitumen bath as a quenching medium for austempering of steel and ductile cast iron. The finding showed that hot bitumen can be used as quenching medium in austempering process.

Hassan *et al.* (2010) also studied the hardening characteristics of plain carbon steel and ductile cast iron using neem oil as a quenchant. It was revealed that neem oil could be used as a quenching medium.

Muhammad (2007) investigated the use of polymer (glycerol) quenchants for hardening process of steels and cast irons. It was found that aqueous solutions of polymer (glycerol) had quenching severity higher than that of oil but lower than that of water.

Saska (2005) studied the relationship between boiling rate, heat transfer and viscosity of cane molasses. The finding showed that thermal property (Heat Transfer Coefficient) of cane molasses is inversely proportional to its viscosity.

Bodede *et al.* (2011) evaluated as-quenched hardness of high carbon steels in different quenching media. It was reported that quenching in more severe media, such as water and brine, resulted in adequate hardening

In summary, it could be seen from the literature survey that several attempted have been made to developed quenching medium that is cheaper, eco-friendly and non-corrosive. Among others were use of vegetable oils (e.g neem oil, cottonseed, soybean oil, palm oil and so on) and starchy liquids (horney, cassava liquid extract…). Vegetable oils encounter problems of oxidation when used at ordinary atmospheric condition. Some starchy liquids (e.g horney) are costly. Modern research techniques in evaluating of quenching media include the cooling curve test, measuring the hardness of the quenched component, measuring the specific heat capacities of the quenching medium and OM and SEM/EDS analyses. This research considers these techniques in developing and evaluating quenching medium that is of low cost, environmental-friendly, non-corrosive, and effective in inducing the required hardness without problems of distortion and residual stresses.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials, Equipment/apparatuses and machines

3.1.1 Materials and reagents

The materials used in this research include: high carbon steel samples (which were obtained from Dana Steel Ltd, Katsina), Cane Molasses, water and used SAE 40 Engine oil. Other materials includes: polishing powder, water, grinding papers, polishing cloth, cotton wool, copper piece, nitric acid, and ethanol.

Table 3.1: Chemical composition of the as-received high carbon steel

Element	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**	**Sn**
Content(%)	0.61	0.254	0.754	0.0132	0.0172	0.108	0.0278	0.130	0.0054

As	**Ca**	**B**	**Pb**	**Sb**	**Al**	**Co**	**Cu**	**Fe**
0.0233	0.0016	0.0010	0.0109	0.0130	0.0103	0.0153	0.196	balance

Table 3.2: Total solid content of the cane molasses used

constituents	**(%)**	**Viscosity(cp)**
sugar content	34	1041
Water content	26	
Non-sugar materials	40	
Brix No.	74	

(*Source:* Savannah Sugar Company, Yola)

3.1.2 Equipment/apparatuses and machines

The equipment used include: viscometer, copper calorimeter, weighing balance, , muffle furnance (electric resistance furnace), Optical Metallurgical microscope (OM), Scanning

Electron Microscope (SEM),Vickers hardness tester, Honsfield tensometer, Izod impact testing machine, lathe machine and polishing machine.

3.2 Methods

Molasses of eleven different viscosities were prepared by adding varying amount of water; such that the ratio of molasses to water were 1:1, 2.5:1, 3:1, 3.5:1, 4:1, 4.5:1, 5:1, 5.5:1, 6:1, 6.5:1 and 1:0. The viscosity of molasses solution [m-w (4.5:1)] were equal to that of engine oil. While for the other prepared molasses solutions; five had lower and the other five had higher viscosities than engine oil. Viscometer was used to measure the respective viscosities. Engine oil served as control.

The machined samples were initially normalized. They were austenitized at 800^{o} C, soaked for 40 minutes and then quenching in all the prepared molasses solutions, water and SAE 40 engine oil. Half of the quenched samples (ninety one) were further tempered at 350^{o}C for 40 minutes. Mechanical property tests (tensile strength, percent elongation, hardness and impact energy) were carried out on the as-quenched samples to determine the severity of the molasses as quenchant and compared with that of water and engine oil. Mechanical property tests were also carried out on the as-received, normalized and tempered samples. Microstructural analyses using OM and SEM were carried out. Cooling curves for all the prepared molasses solutions, raw molasses, water and engine oil were plotted using high carbon steel probes.

3.2.1 Heat Treatment Operations

Test samples were given the following treatments:

- As-received condition (untreated).
- Normalized condition.
- Quenched condition.

- Quenched and Tempered condition

The distribution of samples for the various tests and analyses is presented on table 3.3.

Table 3.3: Number of the samples used for various heat treatment operations.

Sample condition	No. of samples required for mechanical property tests and metallographic analysis			Total
	Tensile test	Impact test	Hardness and metallographic analysis	
As-received	3	3	1	196
Normalized	3	3	1	
Quenched	3x13	3x13	13	
Quenched and Tempered	3x13	3x13	13	
Cooling curves (no. of samples used)		13		209

(a) Spheroidize annealing

Spheroidize annealing was conducted purposely to improve machinability of the high carbon steel used. Samples were heated to 730^{o}C and soaked for four hours for the transformation of cementite lamella to spheroids; after which the samples were furnace-cooled.

(b) Normalizing

202 samples were heated to 800^{o}C and soaked for 75 min for the necessary transformation to occur and the attainment of homogenization after which the samples were air-cooled. This normalizing heat treatment was conducted purposely to remove the effects of undesirable structures due to machining and also to restore original condition of the structure and induce homogeneity.

(c) Hardening by quenching

182 samples were austenitized at 800^{o}C, soaked for 40 min and then quickly quenched in the raw molasses, prepared molasses solutions, water and SAE 40 engine oil. There were

fourteen samples for each of the thirteen containers (eleven containers for the raw and prepared molasses solutions, one for water and the other one for engine oil). All the quenching media were maintained at room temperature of 27^{o}C.

(d) Tempering

91 samples in the as-quenched conditions from all the quenching media were tempered. This involved heating the samples to 350^{o}C and holding for 40 minutes after which the samples were air cooled.

3.3 Mechanical Tests

3.3.1 Tensile Test

Samples were machined to the standard dimensions prior to the heat treatment operations. The tensile test samples were machined to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E8. The test sample was mounted at its ends onto the holding grips of the testing apparatus. The maximum loads were recorded directly from the Hounsfield tensometer. Following the fracture, the two broken ends of the specimens were fitted together and final gauge length was measured. The readings obtained were used in the calculation of tensile strength and percentage elongation. The dimension of the tensile test sample used is shown below.

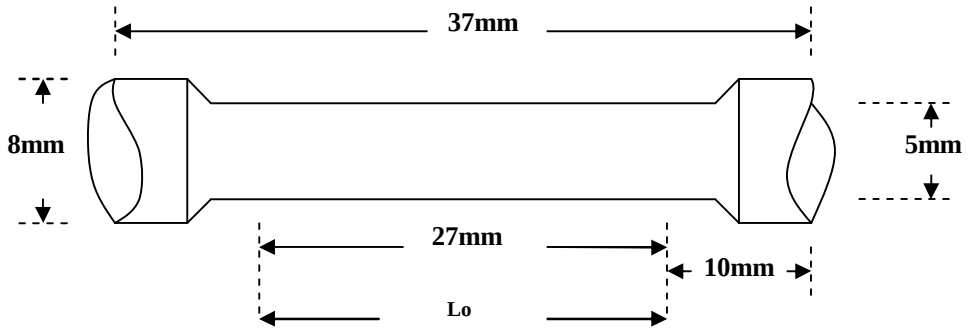


Figure 3.1: Standard tensile test piece
(*Source:* ASTM, 2007a).

3.3.2 Hardness Test Measurement

Vickers hardness tester was used for hardness measurement. The hardness test samples were prepared to standard dimensions as specified in ASTM A370 (Figure 3.2). The test method adopted was ASTM E18. The samples were prepared with flat surface. A diamond indenter was used to indent the surface of the test specimen by the application of static load of 30kgf, which was maintained for fifteen minutes. Both diagonals of the impression were measured using a lower power graduated microscope. The mean value of the diagonal length was used in the determination of the hardness number as shown in formula 3.3.

$$H_D = \frac{1.8544F}{D^2} \qquad (3.3)$$

Where F is the applied load in kg, and D is the mean diagonal length in mm.

The procedure was repeated at 2 different points on the test piece and the average was recorded.

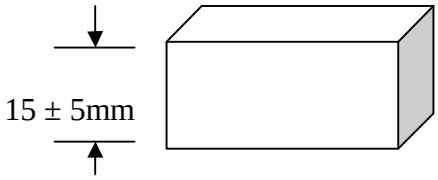


Figure 3.2: Standard hardness test piece.
(*Source:* ASTM, 2007a).

3.3.3 Izod Impact Test

The impact test samples were machined to standard dimensions as specified in ASTM A370. The test method adopted was ASTM E23. The samples were machined to 8 mm diameter and 45 mm length with a 1 mm deep V-notch. Before the test, the pendulum was set to a potential energy position of 162.75 J. The test specimen was then gripped vertically in a vice, the trigger was released and the registering pointer of the quadrant scale indicated the energy absorbed in Joule to break the specimen. The energy absorbed in breaking the sample was recorded and the same was repeated for other test pieces.

3.4 Microstructural examinations

All the specimens (both untreated and heat-treated) were prepared for optical microscopic examination. The specimens were ground on a water lubricated silicon carbide abrasive papers of 180, 240, 320, 400 and 600 grit sizes. Polishing was carried out on 15cm rotating discs of a METASERV universal polishing machine with synthetic velvet polishing clothes impregnated with 1 µm Alumina paste. The specimens were then etched with 2% Nital solution using the swabbing method with cotton wool soaked in the etchant.

The microscopic examinations were carried out on M100 optical metallurgical microscope and the microstructures obtained were captured with the aid of in built camera.

SEM/EDS were also carried out on some of the quenched samples. The surface of the specimens to be examined were polished and then etched (as described above). They were then scanned with an electron beam, and the reflected (or back-scattered) beam of electrons was collected, displayed at the same scanning rate on a cathode ray tube (similar to a TV screen). The images on the screen were photographed. Analysis of the elemental composition of very localized surface areas were carried out.

3.5 Determination of Cooling Curve

Cooling curves were obtained under unagitated conditions according to ASTM D6200-01 (the test method is based on the 12.5 mm diameter x 60 mm length of high carbon steel sample). A K-type thermocouple was fitted in a hole drilled at the geometric centre of the test piece. The test piece was heated in the furnace to 800^{o}C, held for 40 minutes, and then quenched in [m-w (1:1)] solution. On cooling, the temperature dropped and the corresponding times were recorded. The data obtained were used to plot the cooling curve for the medium. The same procedure was repeated for the other twelve quenching media.

3.6 Determination of specific heat capacity

Raw molasses sample was poured into a beaker; a copper piece was placed in boiling water. The calorimeter and stirrer were weighed and then filled half-way with the sample and weighed again. Initial temperatures of the sample (θ_1) and that of the hot copper piece (θ_3) were recorded. The hot copper piece was then transferred quickly into the sample. The mixture was stirred and the temperature attained by the mixture was recorded (θ_2). The mixture was weighed again to determine the mass of the copper piece. Hence the specific heat capacity S_1 of the sample was calculated using the equation below.

If M, M_1 and M_2 are the respective masses of calorimeter and stirrer, sample and copper piece,

S_1 and S_2 the specific heat capacities of sample and copper respectively, then:

$$(MS_1 + M_1S_1)(\theta_2 - \theta_1) = M_2S_2(\theta_3 - \theta_2) \quad (3.1)$$

$$S_1 = \frac{M_2S_2(\theta_3 - \theta_2)}{M_1(\theta_2 - \theta_1)} - \frac{MS_2}{M_1} \quad (3.2)$$

The same procedure was repeated for all the prepared molasses solutions, water and engine oil.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the mechanical properties tests result, optical micrographs, SEM/EDS results, cooling curves of the quenching media used and physical and thermal properties test results; alongside with the discussion of such results.

4.2 Mechanical Properties

Figures 4.1, 4.2, 4.3 and 4.4 are results obtained from mechanical tests of the quenched and quenched-tempered samples in the various media.

4.2.1 Tensile Properties

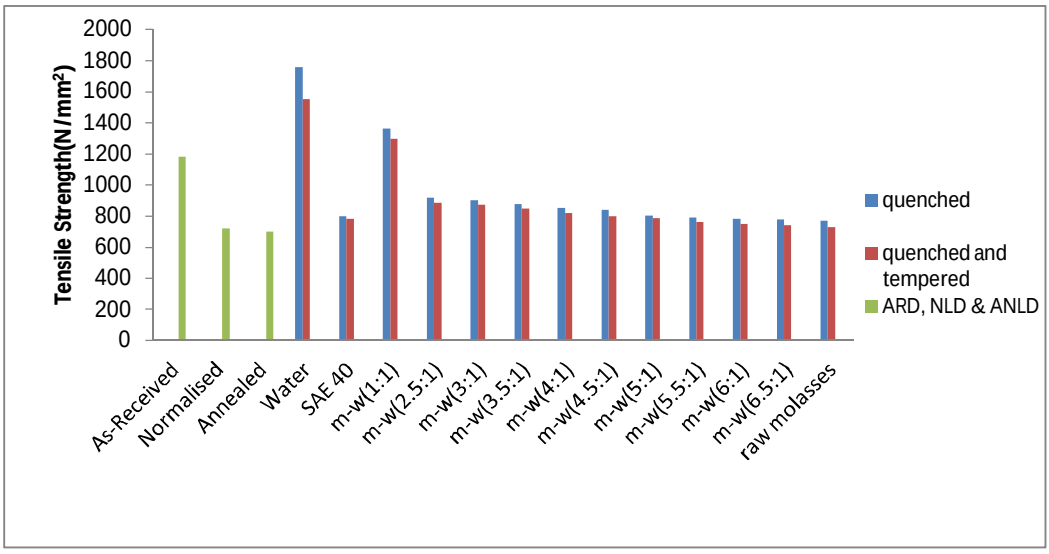


Figure 4.1: Profile of Tensile Strength of the high carbon steel samples quenched in different Quenching media (in quenched and quenched-tempered conditions).

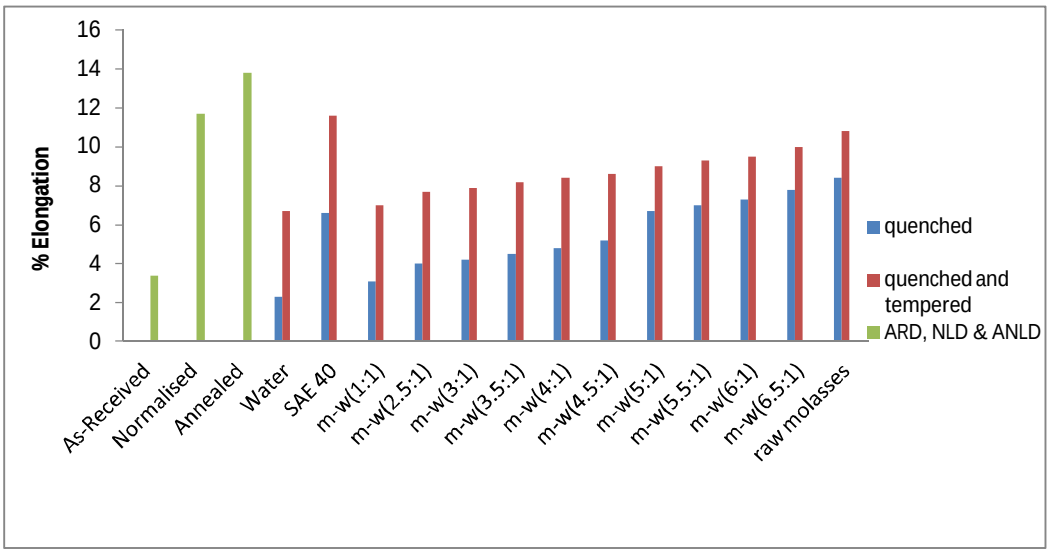


Figure 4.2: Profile of Percent elongation of the high carbon steel samples quenched in different quenching media (in quenched and quenched-tempered conditions).

Figures 4.1 and 4.2 above show tensile strength and percent elongation respectively for samples quenched in different media. The tensile strength increased whereas percent elongation decreased after quenching in all the media. Samples quenched in raw molasses and its solutions showed lower tensile strength and higher percent elongation compared to water; this could be attributed to the fact that water has higher specific heat capacity (Table A4) than molasses and its solutions. This is in line with the earlier observation by Hassan *et al.* (2009). Samples quenched in less viscous molasses solutions gave higher tensile strength and lower percent elongation than those quenched in higher viscous molasses solutions. The reason could be attributed to the fact that the lower the viscosity of cane molasses the better the heat extraction ability of the molasses. This is in line with the earlier observation by Saska, (2005). The tensile strength and percent elongation results showed that molasses solutions with mixture ratios 1:1, 2.5:1, 3:1, 3.5:1, 4:1,4.5:1 and 5:1 had better heat extraction ability than SAE 40 engine oil, while solutions 6:1,

6.5:1 and raw molasses had lower heat extraction ability than SAE 40 engine oil. Solution 5.5:1 was found to have similar severity to that of SAE 40 engine oil.

4.2.2 Hardness

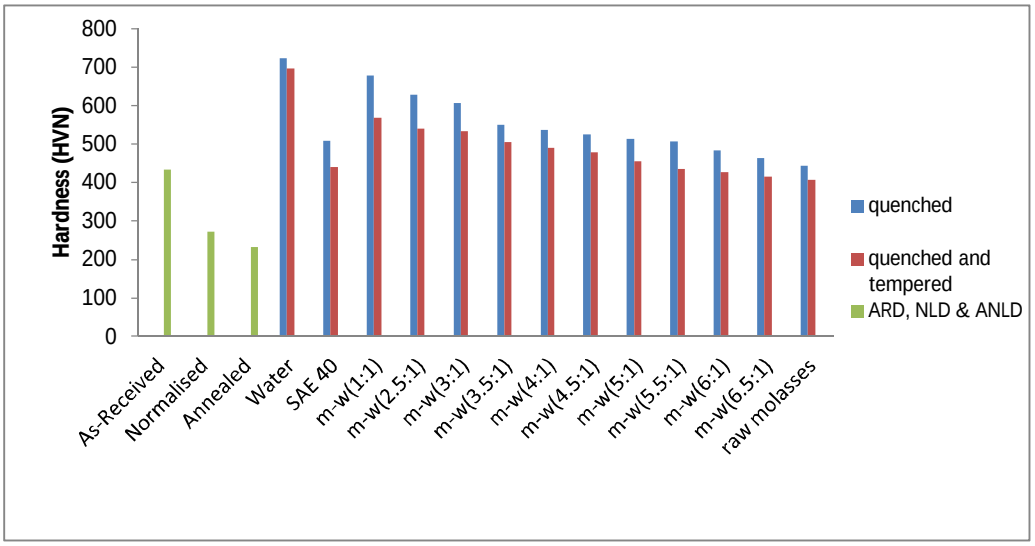


Figure 4.3: Hardness profile of the high carbon steel samples quenched in different quenching media (in quenched and quenched-tempered conditions).

Figure 4.3 above shows hardness results for samples quenched in different media (of different viscosities). The hardness values of 723 HVN was obtained for the water-quenched sample compared to 434 HVN for the as-received sample. From the chart, it is clear that decrease in viscosity of the cane molasses caused increase in hardness value. Molasses solution with mixture ratio 1:1 produced highest hardness of 679 HVN while raw molasses produced the least value of 444 HVN. The high hardness values obtained for sample quenched in less viscous molasses could be explained by the fact that high density of dislocations were induced into the samples due to the higher cooling rate than those quenched in high viscous molasses solution. Molasses solution 5.5:1 developed hardness close to that obtained from SAE engine oil. This might be due to the fact that m-w (5.5:1) and engine oil have similar cooling rate. The trend showed by the

hardness values in relation to the cooling rate of molasses solutions is similar to that observed in vegetable oils by Joseph *et al*. (2015).

4.2.3 Impact Strength

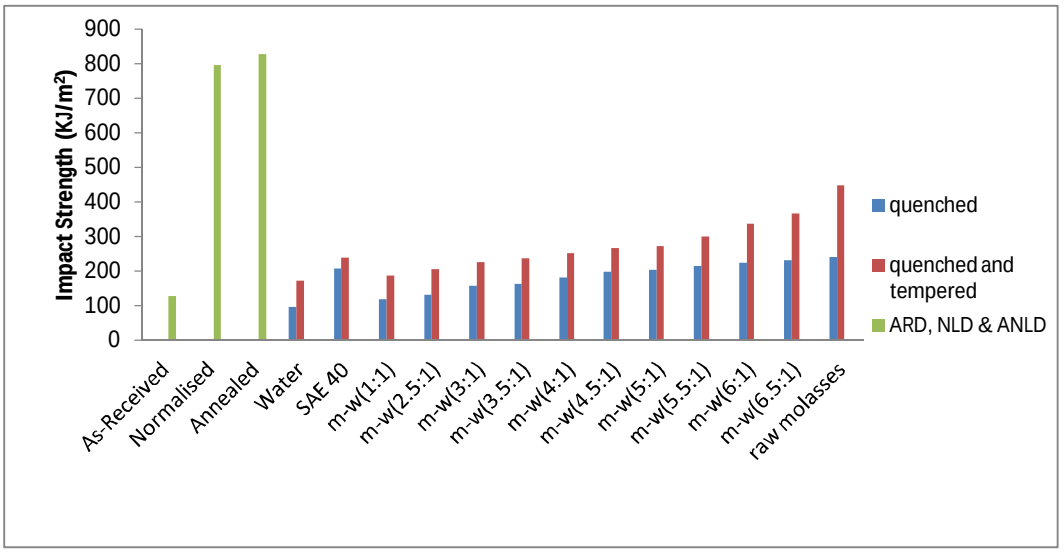


Figure 4.4: profile of Impact Strength of the high carbon steel samples quenched in different Quenching media (in quenched and quenched-tempered conditions).

Figure 4.4 shows the impact strength (energy absorbed per unit area under the notch) for samples quenched in different media. The least impact energy absorbed before fracture (98 KJ/m^2) was obtained from the water quenched specimen. Also, impact strength of 208 KJ/m^2 was obtained for oil quenched specimen while the highest impact energy absorbed was obtained for the sample quenched in raw molasses. Samples quenched in less viscous molasses solutions absorbed lower impact energy than those quenched in high viscous molasses; this could be as a result of the fact that the brittleness of the samples quenched in less viscous molasses is higher compared to those quenched in high viscous molasses solutions. However, 215 KJ/m^2 was obtained for the sample quenched in solution m-w (5.5:1) which fell to the range obtained from the samples quenched in oil (208 KJ/m^2). The trend showed by the impact strength values in relation to the quenching

severity of the raw molasses and its solutions was similar to that observed in polymer solutions (Muhammad, 2007).

4.3 Mechanical Properties of quenched and tempered high carbon steel samples

The tensile strength and hardness values of the quenched samples decreased slightly (Figure 4.2 and 4.3) after tempering. However, the percent elongation and impact strengths improved significantly (Figure 4.1 and 4.4). This trend obtained after tempering could be attributed to the various microstructures obtained which revealed an increased in precipitation of cementite in fine supersaturated ferrite and lower bainite, due to decomposition of martensite and retained austenite [Plate 2(b, d), 3(b, d), 4(b, d), 5(b, d), 6(b, d), 7(b, d), 8(b)]. These observations are in line with what Hassan *et al*. (2009) established.

4.4 Microstructures

The microstructures of the as-received, annealed, normalized, quenched and quenched-tempered samples are shown in plates 1 to 12. The as-received structure of the test sample is shown in plate 1(a); the structure consists of fine pearlite oriented in one direction. The normalized structure of the high carbon steels used is shown in plate 1(b); the structure reveals proeutectoid ferrite in pearlite matrix. The structure of the spheroidized annealed test sample is shown in plate 1(c); it consists of spheroids (sphere-like structure) of carbide in ferrite matrix. The microstructures of the test samples quenched in water and engine oil are shown in plates 2a and 2c respectively. Water quenched samples showed high proportions of martensite (because of the high hardness value obtained from the sample). Oil quenched samples showed martensite proportion lower than that of water quenched sample. Both microstructures are associated with retained austenite. This is in line with the findings of Vivek *et al.* (2014).

The microstructures of the samples quenched in molasses solutions (1:1, 2.5:1, 3:1, 3.5:1 4:1, 4.5:1, 5:1, 5.5:1, 6:1, 6.5:1) and raw molasses are shown in plate 3(a, c), 4(a, c), 5(a, c), (a, c),

7(a, c) and 8(a) respectively. All the microstructures of the samples quenched in molasses and its solutions revealed the formation of martensite and retained austenite in varying proportions. The microstructures of samples quenched in molasses solutions (1:1, 2.5:1, 3:1, 3.5:1, 4:1, 4.5:1) showed more of the austenite transforming to martensite compared to those quenched in molasses solutions (5:1, 5.5:1, 6:1, 6.5:1) and this might have accounted for the high hardness induced in the samples. This is in agreement with what was reported by Balogun (2008).

The SEM images (plate 9, 10, 11 and 12) showed that the martensite grains got coarser with increase in viscosity of molasses solutions. The reason could be attributed to fact that the cooling rate decreased as the viscosity was increased. This trend explains clearly the high strength and hardness obtained for samples quenched in less viscous molasses solutions.

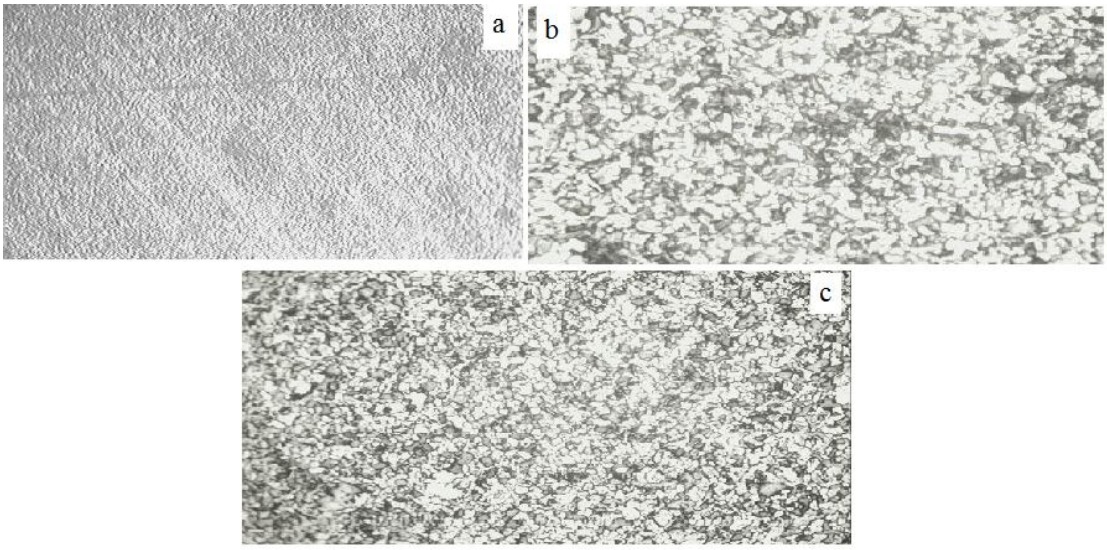


Plate 1: Optical micrograph of high carbon steel (a) as-received; the structure consists of fine pearlite oriented in one direction (b) after normalizing; showing regions of ferrite (white) and pearlite (black) structure (c) after spheroidize annealing; it consists of spheroids of carbides in ferrite matrix. 2% Nital etch. (x100)

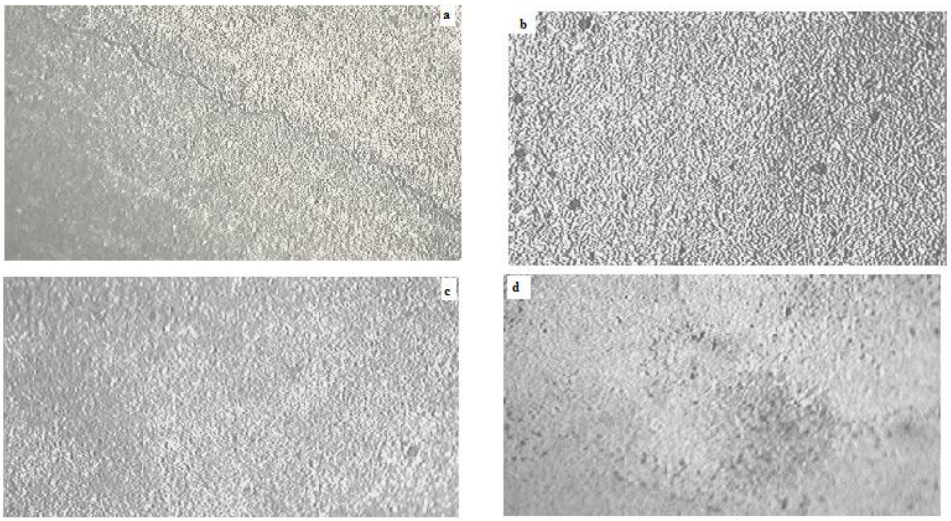


Plate 2: Optical micrograph of the high carbon steel quenched (a) in water; a structure of martensite (dark) and retained austenite (light-colored areas), with crack due to thermal and transformational stress (b) in water and tempered at 350^{o}C; the structure consists of tempered martensite (c) in SAE 40 Engine oil; a structure of martensite (dark) and retained austenite (light-colored areas) (d) in SAE 40 engine oil and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

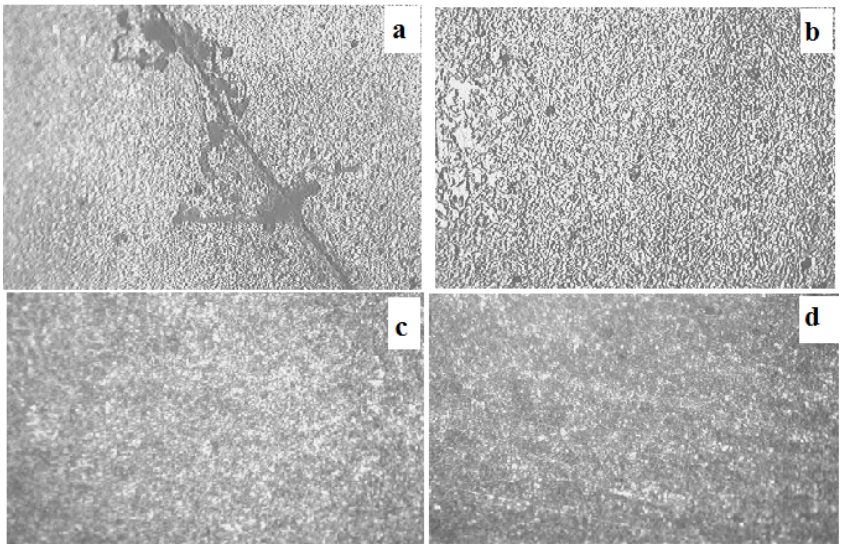


Plate 3: Optical micrograph of the high carbon steel quenched (a) in molasses solution (1:1); a structure of martensite (dark) and retained austenite (light-colored areas) with crack due to thermal and transformational stress (b) in molasses solution (1:1) and tempered at 350^{o}C; the structure consists of tempered martensite (c) in molasses solution (2.5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (d) in molasses solution (2.5:1) and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

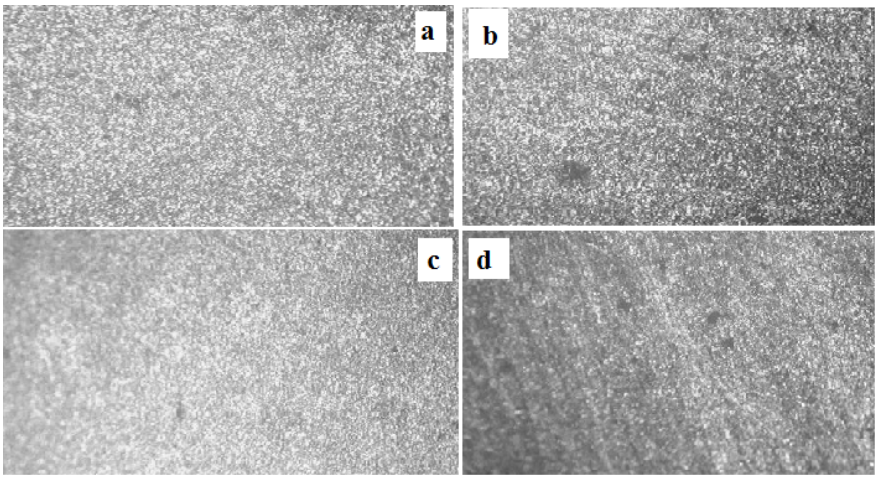


Plate 4: Optical micrograph of the high carbon steel quenched (a) in molasses solution (3:1); a structure of martensite (dark) and retained austenite (light-colored areas) (b) in molasses solution (3:1) and tempered at 350^{o}C; the structure consists of tempered martensite (c) in molasses solution (3.5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (d) in molasses solution (3.5:1) and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

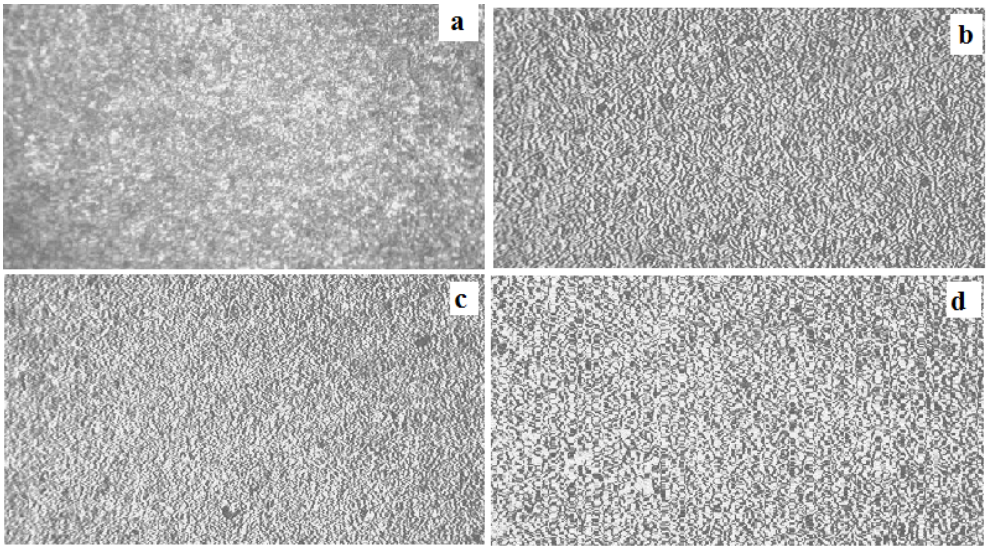


Plate 5: Optical micrograph of the high carbon steel quenched (a) in molasses solution (4:1); a structure of martensite (dark) and retained austenite (light-colored areas) (b) in molasses solution (4:1) and tempered at 350^{o}C; the structure consists of tempered martensite (c) in molasses solution (4.5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (d) in molasses solution (4.5:1) and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

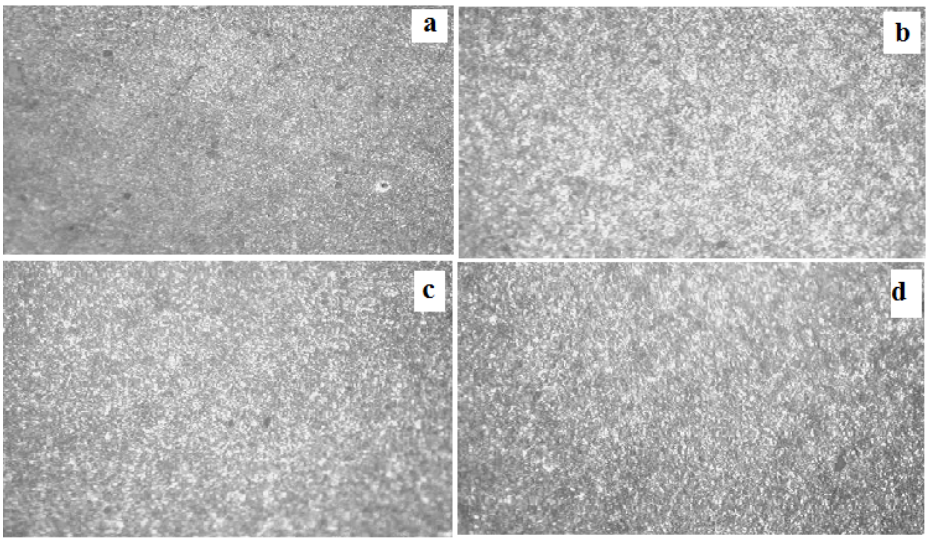


Plate 6: Optical micrograph of the high carbon steel quenched (a) in molasses solution (5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (b) in molasses solution (5:1) and tempered at 350^{o}C; the structure consists of tempered martensite (c) in molasses solution (5.5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (d) in molasses solution (5.5:1) and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

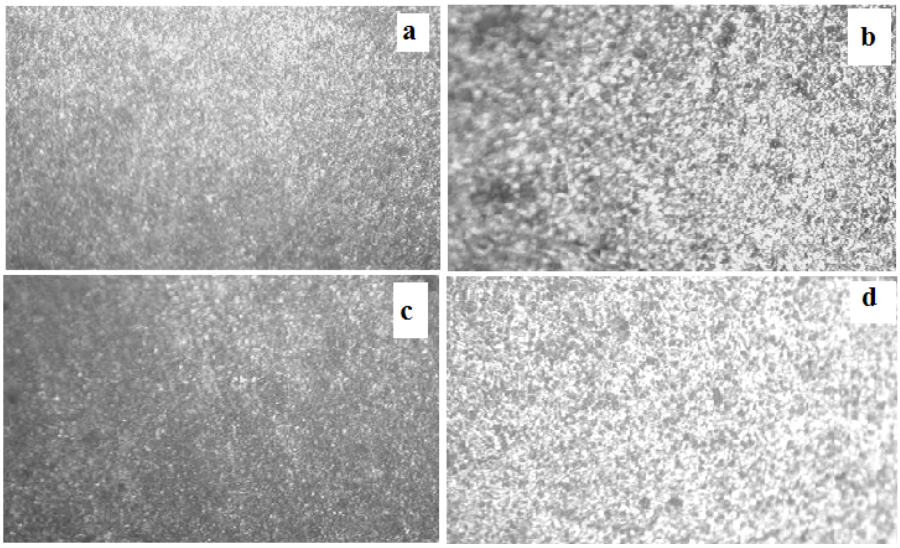


Plate 7: Optical micrograph of the high carbon steel quenched (a) in molasses solution (6:1); a structure of martensite (dark) and retained austenite (light-colored areas) (b) in molasses solution (6:1) and tempered at 350^{o}C; the structure consists of tempered martensite (c) in molasses solution (6.5:1); a structure of martensite (dark) and retained austenite (light-colored areas) (d) in molasses solution (6.5:1) and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

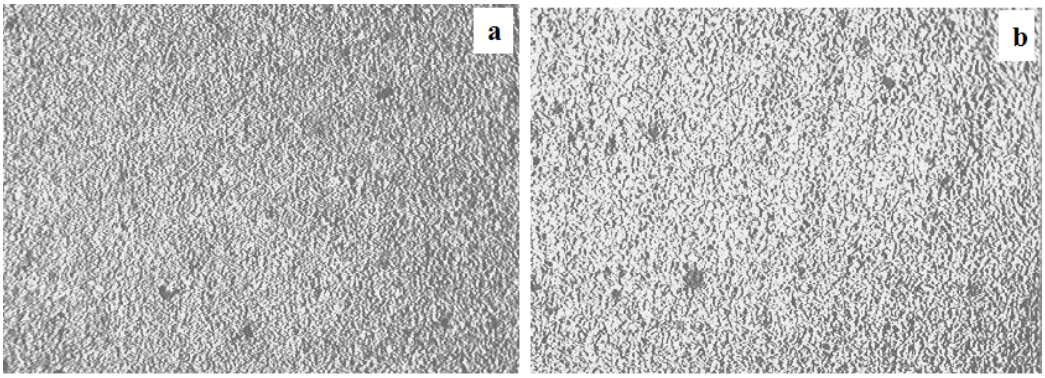


Plate 8: Optical micrograph of the high carbon steel quenched (a) in raw molasses; a structure of martensite (dark) and retained austenite (light-colored areas) (b) in raw molasses and tempered at 350^{o}C; the structure consists of tempered martensite. 2% Nital etch. (x100)

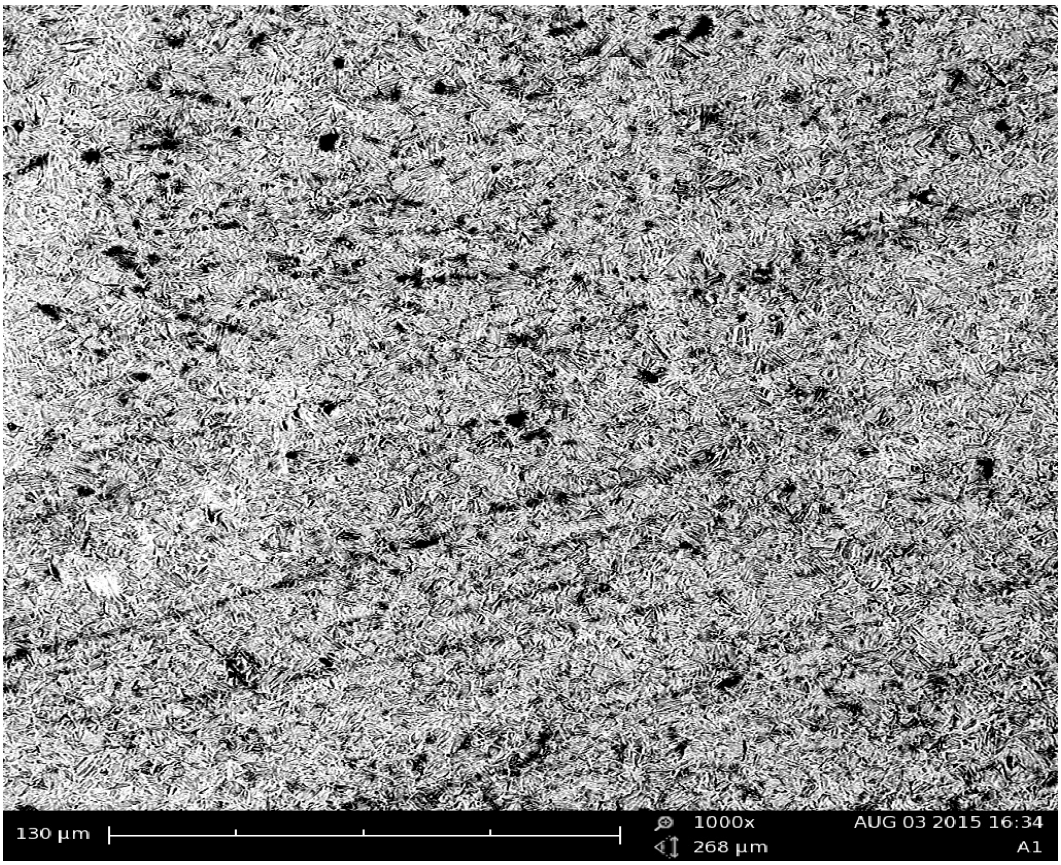
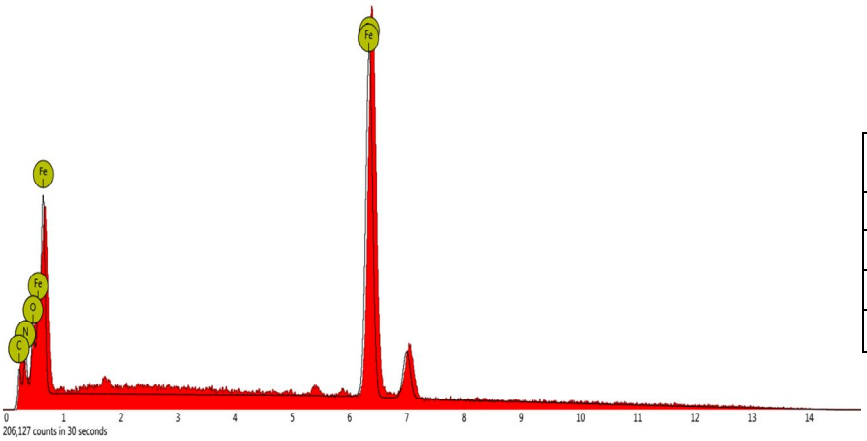


Plate 9: SEM micrograph of high carbon steel quenched in molasses solution (1:1)



Element	Conc. (%)	Error
Fe	74.5	0.6
O	18.1	2.1
N	6.1	3.1
C	1.3	4.2

Figure 4.8: ED spectrum of the major elements for sample quenched in molasses solution (1:1)

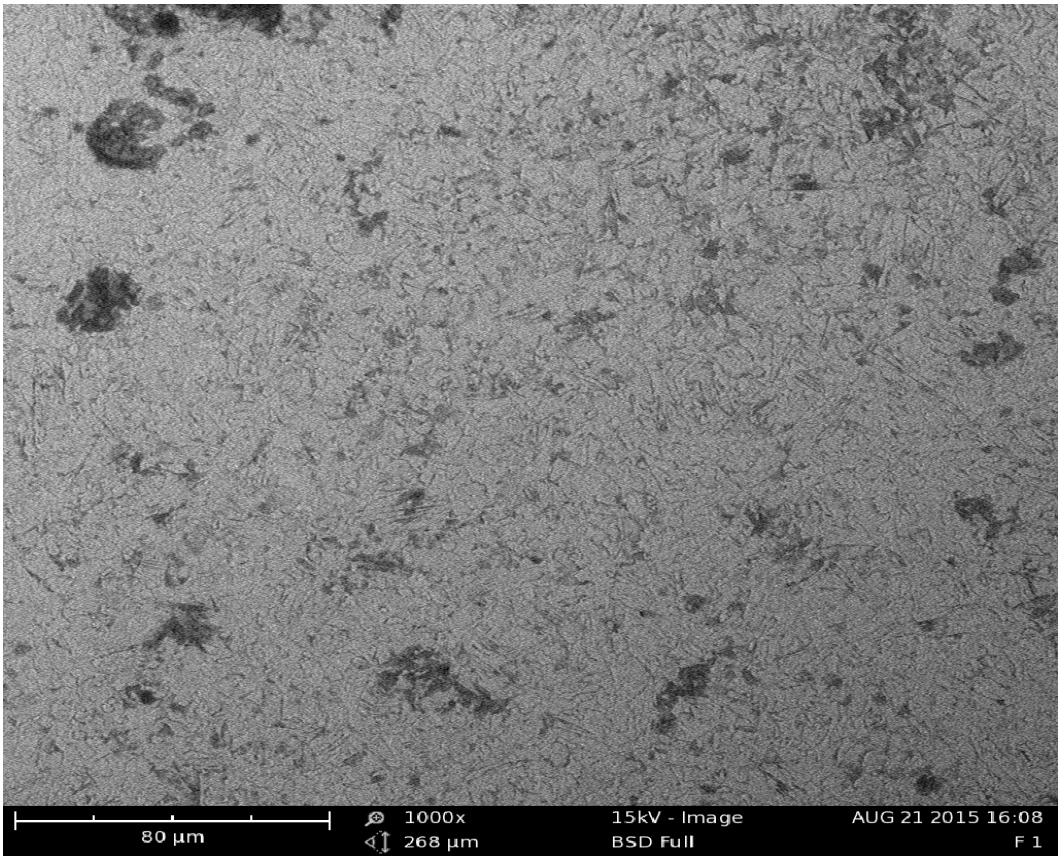
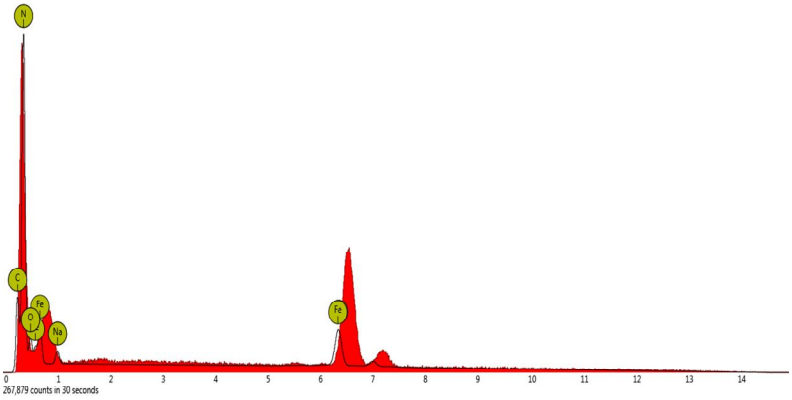


Plate 10: SEM micrograph of high carbon steel quenched in molasses solution (2.5:1)



Element	Conc. (%)	Error
N	51.5	0.6
C	3.3	1.4
Fe	11.8	1.4
O	28.3	2.3
Na	5.0	3.8

Figure 4.9: ED spectrum of the major elements for sample quenched in molasses solution (2.5:1)

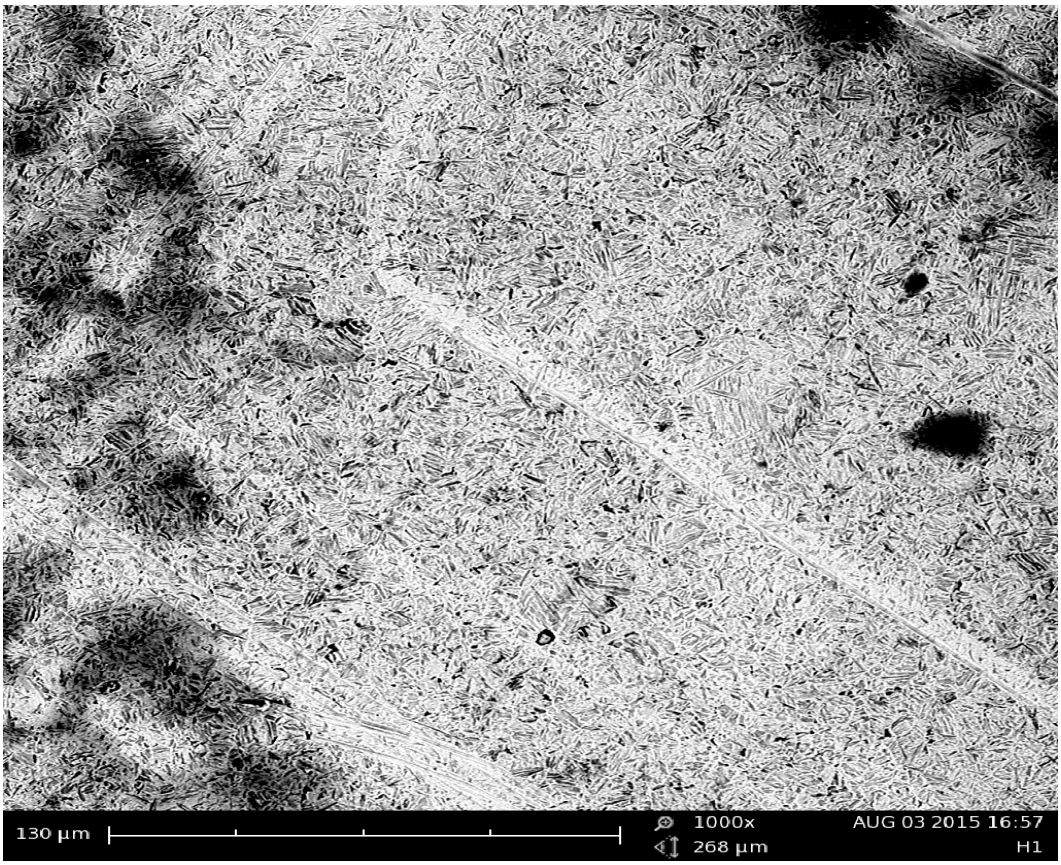
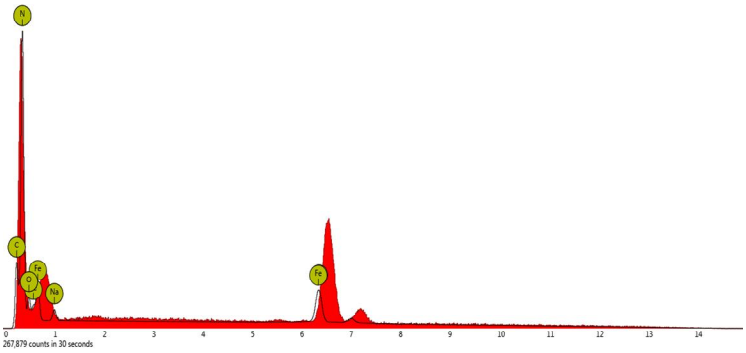


Plate 11: SEM micrograph of high carbon steel quenched in molasses solution (3:1)



Element	Conc. (%)	Error
N	51.5	0.7
C	3.0	1.4
Fe	12.1	1.8
O	28.3	2.3
Na	5.0	3.6

Figure 4.10: ED spectrum of the major elements for sample quenched in molasses solution (3:1)

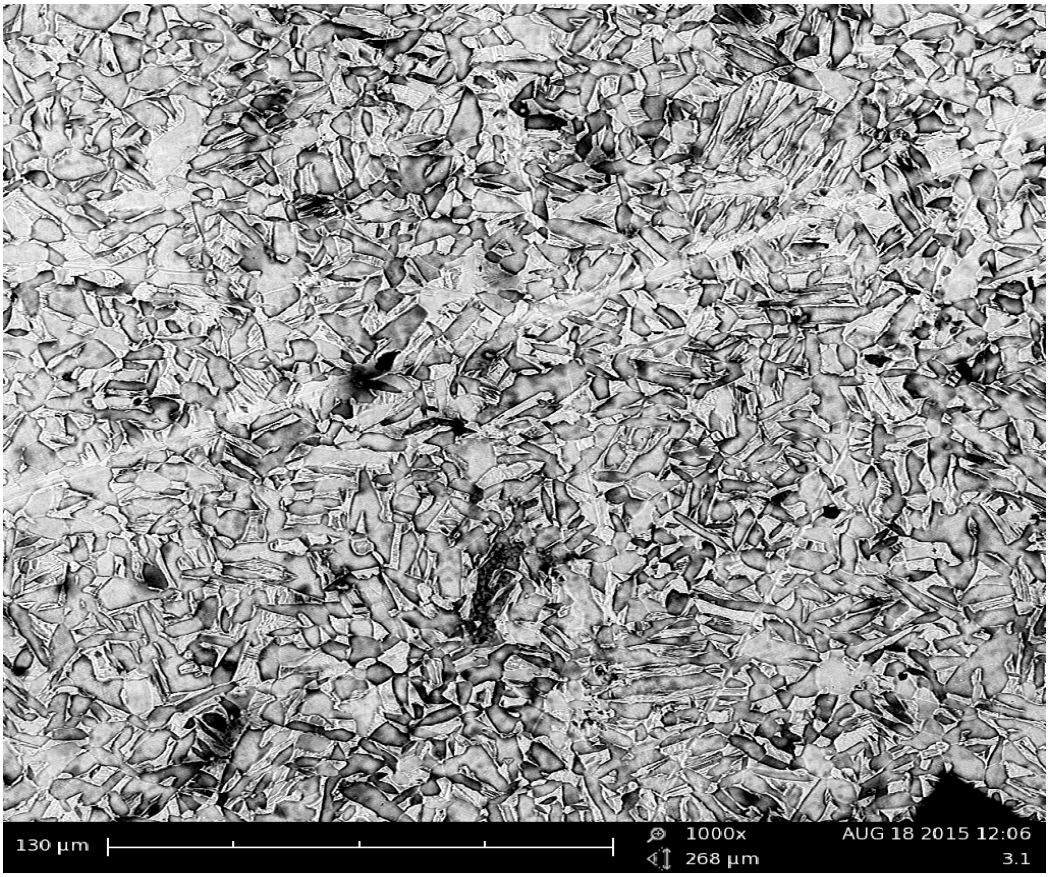
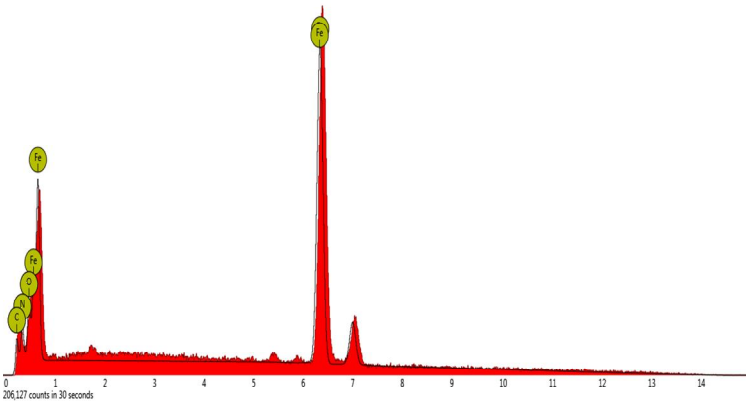


Plate 12: SEM micrograph of high carbon steel quenched in molasses solution (6:1)



Element	Conc. (%)	Error
Fe	74.9	0.6
O	18.1	2.6
N	6.1	3.1
C	0.9	4.9

Figure 4.11: ED spectrum of the major elements for sample quenched in molasses solution (6:1)

The structure of the quenched and tempered samples showed an increased in precipitation of cementite in fine supersaturated ferrite and lower bainite due to the decomposition of martensite and retained austenite [Plate 2(b, d), 3(b, d), 4(b, d), 5(b, d), 6(b, d), 7(b, d), 8(b)]. The

decomposition might have accounted for the reduction in hardness and strength after tempering. The observations are in line with what is obtained in the literature (Hassan *et al.*, 2009).

4.5 Cooling Curves

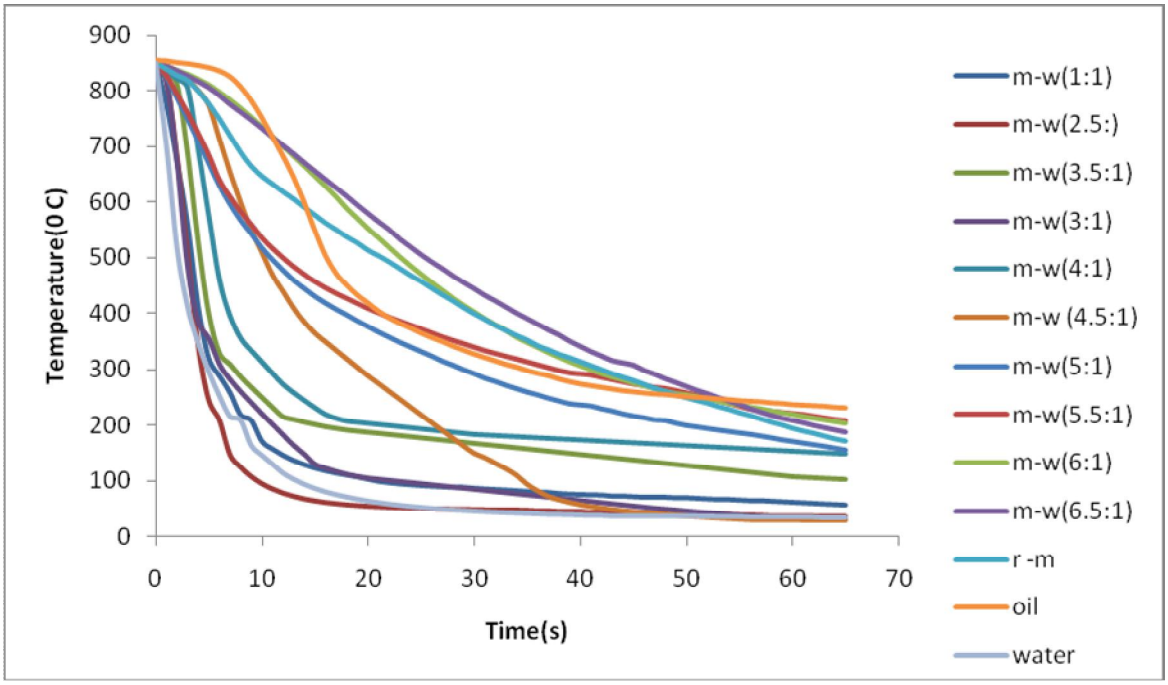


Figure 4.5: Cooling curves of the quenching media used using high carbon steel probe.

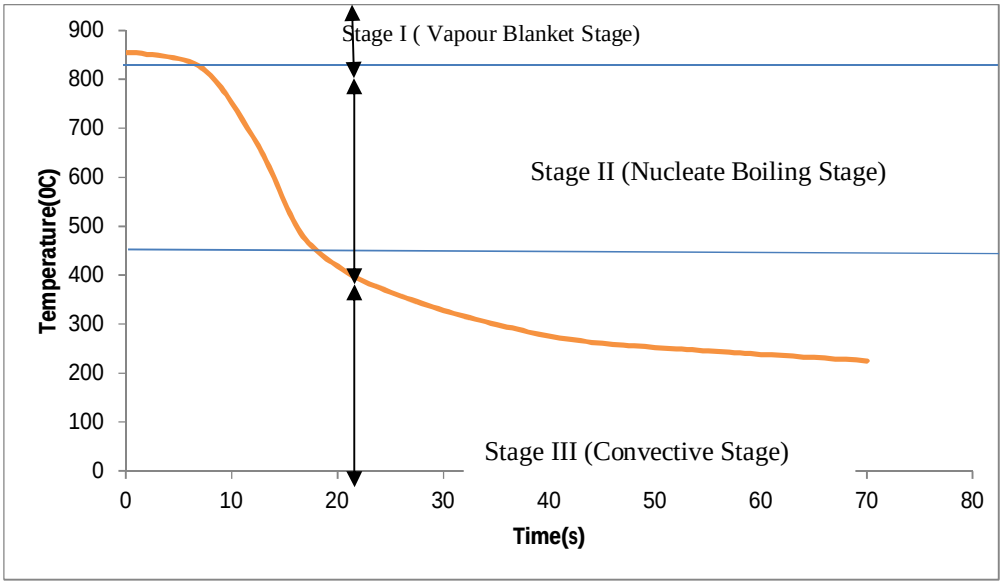


Figure 4.6: Cooling curve of the SAE Engine oil using high carbon steel probe.

4.5.1 Cooling Rate of the Various Quenching Media

Figure 4.5 shows the cooling curves of the various quenching media used. The assumption used in arriving at it was that the temperature of the medium remained constant throughout the cooling operation. Water proved to have the shortest stage I (vapour blanket stage); which is estimated to last for less than a second, whereas stage II is estimated to last for 9 seconds. This is in agreement with what is obtained in the literature (Skidmore, 1986). SAE 40 engine oil presented a prolonged vapour blanket and boiling stage enabling it to have lower cooling rate than water. This is in line with what was reported by William (1967) and Komatsu *et al.* (2009). However, solutions 1:1, 2.5:1, 3:1, 3.5:1 and 4:1 exhibited nearly the same film boiling and nucleate boiling behavior during quenching as shown in Figure 4.5. Their nucleate boiling stage was estimated to last for 12 seconds; this might be due to the fact that the heat extraction ability of these solutions was relatively high. However, solutions 4.5:1, 5:1, 5.5:1, 6:1, 6.5:1 and raw molasses exhibited evidence of full-film boiling, suggesting that the molasses solutions and raw molasses had lower quenching severity compared to solutions 1:1, 2.5:1, 3:1, 3.5:1 and 4:1. A more prolonged nucleate boiling stage was observed with molasses solutions (5.5:1); and this conferred an intermediate severity, compared to solutions 1:1, 2.5:1, 3:1, 3.5:1 4:1, 4.5:1, 5:1 and solutions 6:1, 6.5:1, 1:0.

4.6 Physical and Thermal Properties of the Cane molasses used

The relationship between viscosity and the specific heat capacity of the raw molasses and its solutions is shown in Figure 4.7.

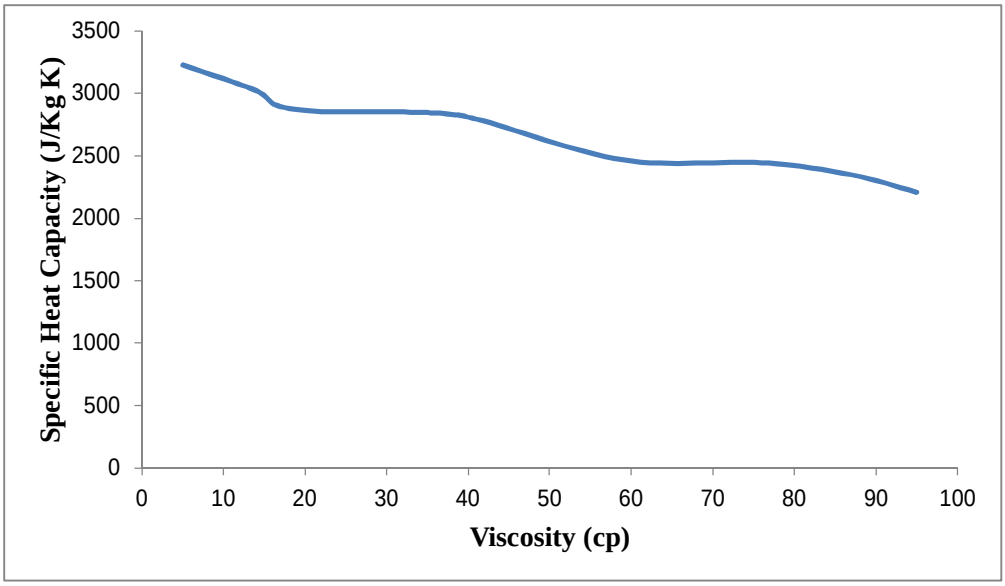


Figure 4.7: Variation of specific heat capacity of the various molasses solutions against viscosity.

It is evident from Figure 4.7 that as the viscosity of the cane molasses increased, specific heat capacity of the various molasses solutions decreased. The reason could be attributed to the fact that the lower the viscosity of cane molasses the higher the heat transfer rate of the molasses. This is in line with the earlier observation of Saska (2005).

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Potential of cane molasses and its solutions as quenching media in the hardening process of high carbon steel has been assessed using microstructure and mechanical properties. Based on the results obtained, the following conclusions were drawn;

- High carbon steel could be hardened when quenched in cane molasses.
- The optical and SEM micrograph showed that the martensite lath got coarser with increase in viscosity of molasses solutions. The reason could be attributed to fact that the cooling rate decreased as the viscosity was increased. This trend explains clearly the high strength and hardness obtained for samples quenched in less viscous molasses solutions.
- Based on the mechanical properties obtained and SEM micrographs, molasses solution [m-w (3:1)] could be recommended to be used as quenching medium for high carbon steels.
- It was also clear from the cooling curves that viscosity plays a key role in the heat extraction ability of cane molasses; the lower the viscosity the higher the heat extraction ability.
- Quenching in raw molasses and its solutions effectively caused the formation of martensite structure in the high carbon steel.
- The quench severities of the quenching media used depict the following descending order: Water>m-w(1:1)>m-w(2.5:1)>m-w(3:1)>(3.5:1)>m-w(4:1)>m-w(4.5:1)>m-w(5:1)>m-w(5.5:1)≈SAE 40 Oil>m-w(6:1)>m-w(6.5:1)> raw molasses.

1.2 Recommendations

Based on the research the following recommendations are offered:

- The effect of temperature and agitation should be investigated.

- The suitability of cane molasses for hardening of other alloys such as medium carbon steel, low alloy steel, ductile cast iron and other nonferrous alloys should be investigated.
- Quenching additives that is either increasing or decreasing cooling rate of cane molasses should be investigated.
- The effect of cross-section size on the cooling rate of cane molasses should be investigated.
- High speed camera should be used to study the cooling process distinctively for the three stages during quenching in all the media.

5.3 Contribution to Knowledge

Although information is available on several utilizations of molasses, to the best knowledge of the author, no previous work has been reported concerning the utilization of molasses for heat treatment (quenching media). Therefore the study, established that:

- Molasses can harden high carbon steel without cracking the component in the same way as engine oil, hence, molasses could be good alternative to engine oil for use as quenching medium.
- Since molasses is cheaper and environmentally friendly compared to engine oil, molasses could be added to the list of existing quenching media.

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APPENDIX A

Table A1: viscosity and specific heat capacity of the raw and molasses solutions

quenchant	Viscosity (cp)	SHC ($Jkg^{-1}K^{-1}$)
m-w(1:1)	5	3225.80
m-w(2.5:1)	14	3019.64
m-w(3:1)	16.5	2902.03
m-w(3.5:1)	22	2853.98
m-w(4:1)	35	2844.89
m-w(4.5:1)	41	2793.15
m-w(5:1)	59	2465.69
m-w(5.5:1)	76	2443.72
m-w(6:1)	87	2347.39
m-w(6.5:1)	95	2208.36
r-m	1041	2162.48

Table A2: Physicochemical and thermal properties of the engine oil used (SAE 40)

Viscosity at 25˚C (cp)	Viscosity at 100˚C (cp)	Viscosity Index	Flash Point (˚C)	Pour Point (˚C)	Specific Gravity	SHC ($Jkg^{-1}K^{-1}$)
40	5.03	105	260	9	0.868	1740.21

Table A3: Viscosity, specific gravity and specific heat capacity of water used

Viscosity at 25˚C (cp)	Specific Gravity	SHC ($Jkg^{-1}K^{-1}$)
1	1	3976.80