International Journal of Science Academic Research
Vol. 02, Issue 02, pp.1093-1106, February, 2021
Available online at http://www.scienceijsar.com

ISSN: 2582-6425

Research Article

COMPARATIVE ANALYSIS OF `HOT VEGETABLE OILS USED AS QUENCHANTS FOR AUSTEMPERING OF NODULAR (DUCTILE) AND GREY CAST IRONS

***Sani, A.S. and Aminu, E.I.**

Department of Mechanical Engineering, Faculty of Engineering, Kebbi State University of Science and Technology, Aliero, Kebbi State, Nigeria

Received 15th December 2020; **Accepted** 17th January 2021; **Published online** 28th February 2021

Abstract

Although salt bath continues to be the dominant type of basestock for the formulation of austempering quenchants, there in increasing pressure to identify an alternative basestock to address the limitations to their continues use because they are not a renewable basestock and they possess poor toxicity and biodegradability properties. Currently the most often cited alternative basestocks are those based on seed oils that are renewable, biodegradable and non-toxic. In this study, the comparative analysis of four vegetable oilsproduced in Nigeria as alternative quenching media to a salt bath for industrial austempering heat treatment of nodular and grey cast ironswere investigated.The study involved the characterization of physicochemical properties and fatty acid profile of marula seed oil, cotton seed oil, peanut oil and shea butter oil. Samples were austenitized at 9000C, soaked for 1hr followed by austempering: quenching them separately in a hot marula oil, shea butter oil, peanut oil, and cottonseed oil bath maintained at 2500C, 2600C and 2700C for periods of 1, 2, 3, and 4 hrs. The microstructure of austempered samples were examined using optical microscopy. The mechanical properties of the untreated and treated samples (tensile strength, impact strength, hardness, and percent elongation) of the samples were evaluated. Results obtained show the diverse effect on the microstructure and mechanical properties austempered samples in hot shea butter, peanut and marula oil developed to form bainite (ausferrite) structure at different austempering time and temperature. The results obtained show that the oil viscosity-temperature behaviour just as their molecular structures were different. The austempered ductile iron (ADI) had the highest tensile strength of 1140MPa, 1120MPa and 1075MPa using marula, shea butter, and peanut oils respectively, while austempered grey iron (AGI) recorded lower values compared to austempered ductile iron (ADI). Specimens austempered in marula, shea butter, and peanut oils showed a continuous increase in total elongation and impact energy with increase of austempering time while the hardness decreases. The increase in total elongation and impact energy is attributed to the progression of stage 1 austempering reaction which caused austenite to transform to ausferrite. The results show that better properties can be achieve by using hot marula, shea butter, and peanut oils as austempering quenching medium at 2700C austempering temperature for 4hrs.

Keywords: Austempering, Mechanical properties, Vegetable oils, Microstructure.

INTRODUCTION

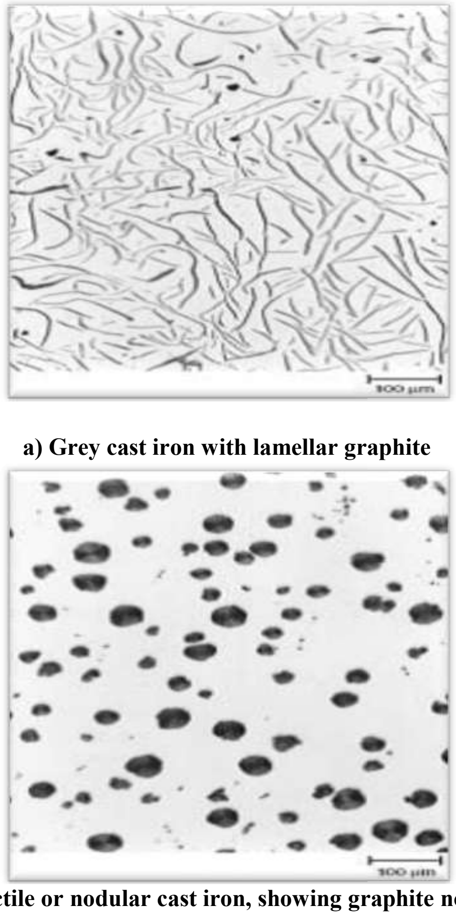
Cast irons, especially ductile cast iron and grey cast iron have been used as some of the important engineering materials in the past 70 years. Most of the engineering parts in machines, automotive, planes, etc. such as shafts, gears, precious parts, bearings, tools, disks, etc. produced today are heat treated before being put into service. These parts are being heat treated for the enhancement of certain properties. In the last forty years, heat treating technology has witnessed a lot of advances as explained by Hassan et al.(2009) and Bash (2009).Therefore, heat treatment represents crucial elements in the design and manufacture of strategic components in a wide range of market sectors and industries which include air, sea and land transportation, energy production, mining, defence and agriculture. According to Tarafder (2018), introduction of new alloys, like duplex stainless steel, micro-alloyed steel, HSLA steels, low-cobalt maraging steels, austempered ductile iron, directionally solidified and single crystal super alloys, aluminium-lithium alloys, various metal matrix composite etc., have called for new heat treatments based on structure-property correlation. Parts are heat treated to enhance particular properties, such as hardness, strength, toughness, corrosion resistance, wear-resistance, and to improve uniformity in properties. Its ultimate purpose is to increase service life of a product by increasing strength and hardness, or prepare the material for enhanced manufacturability.

Corresponding Author:** ***Sani, A.S.
Department of Mechanical Engineering, Faculty of Engineering, Kebbi State University of Science and Technology, Aliero, Kebbi State, Nigeria.

Frank (2012), explained that at a technical level, heat treatment is a technological process which is conducted in furnaces and involves thermal phenomena, phase transformations and mechanical phenomena, mainly stresses. The most pronounced beneficial effect of heat treatment in altering microstructure and modifying properties is to a range of ferrous alloys and nonferrous alloys of aluminium, copper, nickel, magnesium or titanium. Of all materials, steels and cast Irons as the most common and the most important structural material, is particularly suitable for heat treatment. The exact heat treatment applied depends on both the types of alloy and the intended service conditions (Frank, 2012 and Adeyemi and Adedayo, 2009). Cast iron typically contain 2-4% of carbon with a high silicon concentration and a greater concentration of impurities than steel. the carbon equivalent (CE) of a cast iron helps to distinguish grey cast ironswhich cool into a microstructure containing graphite and the white irons where the carbon is present mainly as cementite (Miguel and Bhadeshia, 2015). The carbon equivalent is defined as:

$$CE(wt\%) = C + \frac{SI+P}{3} \qquad (1)$$

A high cooling rate and a low carbon equivalent favours the formation of white cast iron whereas a low cooling rate or a high carbon equivalent promotes grey cast iron. It is a class of Fe-C-Si alloys with high carbon and silicon contents than steel and, depending on the alloying elements and microstructure formed during solidification, it is classified as grey cast iron, spheroidal or nodular cast iron, white cast iron, compacted graphite iron and alloy cast iron. Rajan and Sharma, (1988) explained that some of these cast irons when subjected to heat treatments give rise to classes of cast irons, such as malleable or austempered ductile cast iron. Austempering is an isothermal heat treatment mostly applied to ferrous alloys, notably steels and cast irons in order to enhance the mechanical properties. Grey cast iron (GI) is one of the conventional iron-carbon alloys with a carbon content of 2.5-4% and a silicon content of 1-3%. It's typical microstructure contains graphite flakes surrounded by pearlite or ferrite as shown in Fig. 1.Because of its excellent mach inability and damping capacity with low production cost, grey cast iron has been used in the manufacturing of clutch discs, cylinder liners, brake rotors, and tool mounts (Bingxu et al 2019 and Sani, 2008). As explained by John and Kathy, (2000) and Bingxu et al, (2019)that most of the grey cast iron require superior resistance to retard wear loss on contact surfaces and therefore, heat treatment processes such as austempering, martempering, and quenching and tempering treatment are expected to provide benefits for the tribological properties of grey cast iron.



a) Grey cast iron with lamellar graphite

b) Ductile or nodular cast iron, showing graphite nodules

(Source: Lawrence H. V. V, 1985).

Fig.1. Microstructure of cast irons

The austempering heat treatment was first proposed by Edgar C. Bain in the 1930s (Bain 1939 and ASTM, 2017). In this process, GI is austenitized above the A_{cm} critical temperature to convert the ferrite or pearlite into unstable austenite. Then, the full austenitized GI is transferred and soaked in the in a salt bath furnace at a constant temperature for a specific period. The isothermal temperatures should be between the pearlite formation temperature and martensite formation temperature, which are similar to the bainite formation temperatures of steel. The final microstructure of austempered grey cast iron (AGI) consists of acicular ferrite and carbon saturated austenite. In the austempering process, a salt bath furnace is typically used in order to eliminate or minimize surface oxidation and carburization (Bingxu *et al.,* 2019). Ductile cast iron, according to Karl, 1990, Hassan *et al.* 2008, Bashi, 2009, and Morrough, 1987, are of five types: ferritic, pearlitic, austenitic, martensitic, and ferritic-pearlitic ductile cast irons. It is not known how long oils have been used in the hardening of ferrous alloys. Many types of oils including vegetable, fish, and animal oils, and particular sperm while oil, have been used for quenching operations. The first petroleum-based quenching oils were developed around 1880 by E.F. Houghton in Philadelphia, USA. Since that time, many advancements have been made in the development of quenching oils (Scott, 2009 and Gabor *et al.,* 2016).The stability of vegetable oils depends not only on the degree of unsaturation but also on the degree of double bond conjugation as observed by Nikolai *et al.* (2010). The following approximate relative oxidation rates were reported by Schneider (200): stearic (1) > oleic (10) > linoleic (100) > linolenic (200). Similar results have been reported by Totten *et al.* (1999). There have been many investigations on the use of vegetable oils as quenchants. One of the earliest studies involving cooling curve and heat transfer analysis of quenching properties was conducted by Rose in 1940 with rapeseed oil. The cooling curve results obtained showed that the heat transfer coefficients for rapeseed oil were 1744 to 2092 W/m^2K. In 1953, Tagaya ang Tamura compared the quench severity of different vegetable oils which includes soybean, rapeseed and castor oils with mineral oils and fish/animal oils with respect to fluid source, viscosity and oxidative stability for various naturally derived fluids (Nikolai et al, 2010). These data showed that although the Grossmann quench severity factors were comparable for both castor oil (H= 0.199) and soybean oil (H= 0.2), the cooling times from 700 to 300^0C were faster for castor oil (1.8 seconds) than for soybean oil (1.42 seconds). Currently, the most commonly cite vegetable oil basestocks used for quenchant formulation in the USA are based on canola oil and soybean oil (Nikolai *et al.,* 2010 and Kobasko *et al.,* 2011). Recently, a cramble oil-based fluid has been reported as a potential quenchant.

Austempering is one of the methods used for hardening ferrous metals. According to Keough, (1998) and Adewuyi and Afonja, (2000), it is an isothermal heat treatment that produce a structure that is stronger and tougher than conventional heat treatment methods. Austempering process consist of austenitizing a ferrous component to a temperature between 825- 950^0C, soaking at this temperature for 1 to 2 hours, depending on the component thickness, quenching from this temperature into a hot liquid medium, maintained at pre-selected temperature between 250 -450^0C then removed and cooled to room temperature (Keoughand Kathy (2000), and Rimmer,(1997). Austempering cycle is shown systematically on the isothermal transformation diagram Fig. 2. During the ustempering process, ADI and AGI undergoes a two-stage transformation process (Adewuyi, 2000, and Rimmer, 1997). In the first stage, the austenite (γ) decomposes into bainitic ferrite (α) and carbon enriched austenite (γ_{hc}), a product known as ausferrite. The reaction can be expressed as

$$\gamma \rightarrow \alpha + \gamma_{hc} \quad (2)$$

On the other hand, if the austempering temperature is held for too long a second reaction occurs and must be avoided during this reaction, the high carbon austenite (γ_{hc}) is decomposed into ferrite (α) and carbide (ε), causing the embrittlement of the material (Voight, and Loper, 1984 and Darwish, 1993). This reaction can be represented by Equation 3:

$$\gamma_{hc} \rightarrow \alpha + \varepsilon \quad (3)$$

Thus, the best combination of mechanical properties and microstructure are obtained in ADI and AGI, after completion of the first stage but before the onset of the second stage. The period between the completion of the first stage and the onset of the second stage is termed as the process window (Keough, 1998, Drauglates, 1986 and Morrogh, 1987). The austempering time and temperature determine the final microstructure and properties of ADI and AGI. At lower temperatures, it has high yield strength and hardness, due to the presence of a very thin ferrite and austenite. At higher austempering temperatures, the ferrite becomes coarser with increased volume fraction of retained austenite, resulting in a significantly increase in ductility with lower values if yield strength (Kim *et al.,* 2008, Keough, 1998, Charles, 1998 and Rimmer, 1997). The objective of this research is to explore the suitability of marula seed oil, shea butter oil, peanut oil and cotton seed oil as alternative quenching media to salt bath for austempering heat treatment of ductile cast iron and grey cast iron by studying the effect of the physicochemical properties of the oils on the austempering performance. Previous works done by Larry (2001), Okwonna *et al.* (2017), Gabor *et al.* (2016), Lauralice *et al.* (2005), Dauda *et al.* (2015), Joseph *et al.* (2015), Shehu *et al.* (2015), Niall (2003), showed that vegetable oils were used for heat treatment of ferrous alloys. Joseph *et al.* (2015) reported on the performance assessment of selected Nigerian vegetables (cotton seed, palm kernel oil, neem oil, palm oil and SAE40 as quenching media in hardening process for medium carbon steel showed that different vegetable oils have viscosity and viscosity-temperature just as their molecular structures were different. It has been established in their work that palm oil has the highest viscosity value followed by cotton seed oil, neem seed oil, palm kernel oil and then SAE40 engine oil and palm kernel and cotton seed oils exhibited fast cooling during quenching period. Okwonna *et al.* (2017), on exploring the potentials of using palm kernel oil esters (palm kernel oil plus bitumen) for austempering process of medium and high carbon steel concluded that the palm kernel oil plus bitumen can be used as quenching media in austempering process.

Dauda *et al.* (2015) in their work on the effects of various quenching media (olive oil, palm kernel oil, and cotton seed oil) on mechanical properties of medium carbon steel observed that these oils can be used where cooling severity less than that water and SAE 40 engine oil is required for hardening of plain carbon steel, while for the palm kernel oil and olive, it was found that the hardness was lower than that of as-received after quenching. The toughness of the steel was improved after using these oils as compared to water and SAE40 oil. Larry (2001), on his work reported that addition of antioxidants to the vegetable oils improved the chemical stability of the oils. Lauralice *et al.* (2005) studied the oxidation of vegetable oils and its impact on quenching performance of castor oil, soybean oil and MCI petroleum oil. The results obtained indicate that vegetable oils are promising alternatives to petroleum oils as quenchants but that to be commercially feasible, appropriate antioxidants must be used. Shehu *et al.* (2015) reported that with the used of sesame oil as quenchant for austempering of ductile cast iron at 300^{0}C and held for 4 hours was able to cause the formation of ausferrite, hence could be used as an austempering quenching medium for ductile cast iron.

The traditional molten salts used as quenching bath for austempering process have many disadvantages which include: safety and environmental problems, high cost, non-availability, hazardous during cleaning and in maintaining at high temperatures and toxicity justify the search for alternative austempering quenching media (Nuhu, 2015 and Niall, 2003). Nigeria is richly endowed with different variety of these oils and is cheaper than molten salts. The advantages of using vegetable oils as alternative to molten salts bath includes: i) biodegradable ii) environmentally friendly, iii) less costly, iv) can manufactured from renewable plant source. The main objective of this research work is to assess and compare the potentials of using four types of vegetable oils (peanut, cottonseed, marula, and shea butter oils) as quenchants for austempering ductile iron and grey cast iron. To accomplish this, microstructure, tensile and yield strength, hardness, and impact strength were used as criteria to evaluate the effectiveness of these fatty based oils.

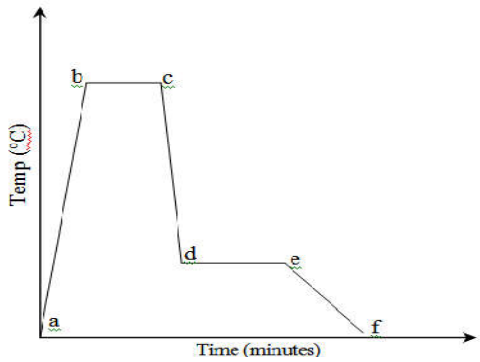


Fig. 2. Systematic diagram of austempering heat treatment

EXPERIMENTAL PROCEDURES

Materials and Equipment

The materials used for this investigation werelow alloyed nodular cast iron and low alloyed grey cast iron. The chemical compositions of these materials in weight percentage is by optical spectroscopy and is given in Table 1. These materials were individually cast in the form of KEEL blocks and from these cast cylindrical tensile and impact samples were prepared as per ASTM standard E-8 (ASTM-E8, (2013)). In addition, small cylindrical shape was also machined out of the solid cylindrical shape for heat treatment and micro structural investigation. The oils under investigation (peanut oil, marula oil, shea butter oil and cottonseed oil) are typical vegetable oils produced in Nigeria. Property analysis are however based on established parameters as used for known quenching mineral oils and solution of organic polymers. These oils were used to evaluate and compare their performance as quench ants for austempering ductile cast iron and grey cast iron as alternative to salt bath. The physicochemical properties and percentage fatty acids of the four local oils used are shown in Tables 2 and 3 respectively. The equipment used include: Optical emission spectrometer (OES) model EP 980, muffle furnace model BALTCHYIC, stove and pots for pre-heating the oils,oil baths, thermocouple, optical pyrometer, optical metallurgical microscope model METALLUXY in an in-built camera, lathe machine, grinding and polishing machines, Rockwell hardness testing machine, Avery Denison impact tester, Instron Universal machine Model-3369 for tensile test, polishing powder, grinding papers, polishing cloth, cotton wool, copper piece, nitric acid and ethanol.

Method

Determination of physicochemical properties of the vegetable Oils: The investigation of the oil's properties in this work, that were purchased from local market in Birnin/Kebbi, we considered those properties that are directly affecting the use of oil as quenching medium. The properties are: 1) Viscosity, 2) Iodine value, 3) Flash point, 4) Acid value, 5) Pour point, 6) Saponification value, 7) Specific heat, 8) Fire point, 9) kinematic viscosity. The viscosity of each sample of the oils was measured according to ASTM D445-06 and viscosity index was determined from kinematic viscosities at 40 and 100^{0}C according to ASTM D2270-04. Pour point was tested according to ASTM D97. Iodine number of each oil was determined according to ASTM D5554-95 and the Flash point of oil was measured using the Pensky-Martens closed Tester (PMC) procedure. The flash is the reduced point in that a substance can momentarily take fire. The fatty acid composition of the four vegetable oils were determined by a gas chromatographic analysis procedure using a Model GCMS-OP2010 PLUS Shimadzu, Japan gas chromatograph equipped with a flame ionization detector set to 300^{0}C and a "split" injection system ratio of 1:30 at 280^{0}C.Specific heat was determined with a differential scanning calorimeter –DSC and was calibrated with indium before use. About 8 to 10 mg of oil was placed in hermetically sealed aluminium pans. An empty aluminium pan was use as reference. The Acid number (AN) was determined using titration procedure with potassium hydroxide (KOH) and was reported as milligrams of KOH per gram of sample (mgKOH/g). Acid number (AN) is given by the expression:

$$AN = \frac{56.1 \text{ x NV}}{\text{W}}\left[\frac{mgKOH}{g}\right] \quad (4)$$

Where 56.1 = molar mass of the KOH;
Volume of KOH solution in ml; = V
Normality of KOH solution; = N
Weight of sample in g. = W

$$\text{Iodine value (IV)} = \frac{(\text{mL Blank} - \text{mL Sample})(\text{N})(12.69)}{\text{Sample wt.}} \quad (5)$$

The physic-chemical properties and percentage fatty acids of these oils were analysed at National Research Institute for Chemical Technology Zaria, using gas chromatography and resultsare shown in Tables 2 and 3 respectively.

Heat treatment operations

Annealing: Annealing of as-received nodular cast iron and grey cast iron samples were carried out at austenitizing temperature of 900^{0}C, soaked for 1 hour followed by cooling in the furnace to room temperature. The objective of austenitising is to produce an austenitic matrix with uniform carbon content prior to thermal processing.

Normalising: Normalising heat treatment was carried for all nodular cast iron and grey cast iron specimens to be austempered as pre-austempering treatment. This was done by heating the samples to austenitizing temperature of 900^{0}C, holding at that temperature for 1 hour followed by cooling in air.

Austenitizing procedure: The objective of austenitizing is to produce an austenitic matrix with uniform carbon content prior to thermal processing. Austenitizing temperature has a direct effect on the austempering kinetics through its effect on the carbon content of the austenitized matrix.

Austempering procedures: The austempering process was carried out by packing specimens of nodular cast iron and grey cast iron into metallic container and charged into the furnace in batches. Each batch contains grey cast iron and nodular cast iron specimens and was austenitized at 900^{0}C, soaked for 1 hour followed by quenching in the various hot vegetable oil baths at variable temperatures of 250^{0}C, 260^{0}C and 270^{0}C and held isothermally for 1 to 4 hours, at 1-hour intervals and thereafter cooled in air prior to austempering, oils were pre-heated with stove before being transferred to an electric oven.

Table 1. Chemical composition of ductile and grey cast irons (wt. %)

Element	C	Si	Mn	P	S	Cr	Cu	Ni	Fe
Ductile cast iron	3.65	2.55	0. 28	0.015	0.012	0.061	0.424	0.010	Bal.
Grey cast iron	3.35	2.35	0.45	0.04	0.025	0.003	0.950	0.001	Bal.

Table 2. Properties of vegetable oils under investigation

Oil	Free fatty acid, %	Iodine value, g/100g	Viscosity at 40^{0}C, mm^2/sec	Flash point, ^{0}C	Viscosity at 100^{0}C, mm^2/sec	Viscosity index	Saponification value, mgKOH/g	Specific heat, kJ/kg K)	Acid value (mgKOH/g)
Marula	0.70	68.92	23.4	278	9.50	162.10	190. 8	2.176	6. 02
Cottonseed	0.16	110.35	33.5	264	7.75	211. 00	205. 2	2.158	5.80
Shea butter	0.60	70.40	28.9	284	9.20	148.204	170. 5	2.214	14.81,
Peanut	0.21	90.53	33.65	271	8.43	174.098	223. 3	2.045	5.60

Table 3. Percentage fatty acids of selected vegetable oils (w%)

Oil	Saturated	Saturated	Saturated	Saturated	Monounsaturated	Polyunsaturated	Others	Total unsaturated	Total saturated	Uns/ saturated
Oil	Lauric acid (i)	Myristic acid (ii)	Palmitic acid (iii)	Stearic acid (iv)	Oleic acid (v)	Linoleic acid (vi)		(v +vi)	(i+ii +iii +iv	
	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_{12}COOH$	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$	$CH_3(CH_2)_7CH\text{-}CH(CH_2)_7COOH$	$CH_3(CH_2)_4CH\text{-}CH(CH_2)CH\text{-}CH(CH_2)_7COOH$				
	12:0^x	14:0^x	16: 0^x	18:0^x	18:1^{xx}	18:2^{xx}				
Maruula	-	-	11.0	7.1	71.8	8.5	2.6	80.3	18.1	4.45
Shea butter	-		9.0	25.0	45	0. 96	20.04	45.96	34	1.35
Cotton seed	-	-	32.46	9.07	19.06	37.33	2.07	56.37	41.57	1.34
Peanut	-	-	11	2	48	32	7.0	80	13	6.15

There were four austempering oil baths (cottonseed oil, marula oil, peanut oil, shea butter oil) on all the specimens. The heat treatment conditions and the total number of samples used are shown in Table 4.

Table 4. Heat Treatment conditions for the nodular cast iron and grey cast iron

Material	Condition	Heat treatment temperature,(^{0}C)	Austempering time (hrs.)	N0 of sample
	As-received	-	-	1
	Annealed	900	-	1
	Normalized	900	-	1
Nodular	Austempered in:			
cast iron	-Marula oil	250, 260, 270	1, 2, 3, 4	12
	-Peanut oil	250, 260, 270	1,2, 3, 4	12
	-Shea butter oil	250, 260, 270	1, 2, 3, 4	12
	-Cottonseed oil	250, 260, 270	1, 2, 3, 4	12
	As-received	-	-	1
	Annealed	900	-	1
	Normalized	900	-	1
Grey	Austempered in:			
cast iron	-Marula oil	250, 260, 270	1, 2, 3, 4	12
	-Peanut oil	250, 260, 270	1, 2, 3, 4	12
	-Shea butter oil	250, 260, 270	1, 2, 3, 4	12
	-Cottonseed oil	250, 260, 270	1, 2, 3, 4	12

After machining, the samples of both ductile cast and grey cast iron were austenitized at 900^{0}C for 60 minutes for proper homogenization and followed by instantaneous transfer to hot oils baths(marula, cottonseed, peanut, and shea butter) for austempering at 250^{0}C, 260^{0}C, 270^{0}C and 280^{0}C, and held for different periods of 1 hr, 2 hrs, 3 hrs and 4hrs. Following austempering, the test pieces were withdrawn from hot oils bath (marula, cottonseed, peanut, and shea butter) and air cooled to room temperature, after which they were washed with kerosene. Figure 2. Shows schematically the summary of heat treatments.

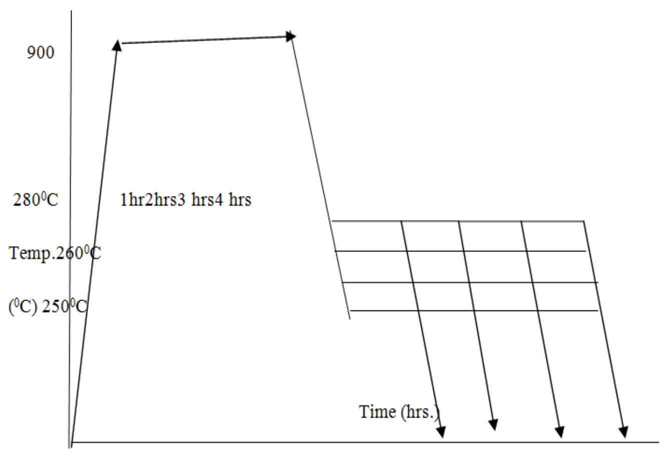


Fig. 2. Systematic diagram of austempering heat treatment of ductile and grey cast irons

Determination of Mechanical Properties

The mechanical properties of heat specimens of austempered nodular cast iron and grey cast iron were determined by tensile, hardness and impact tests.

Tensile test: The tensile strength determinations were carried out on test pieces on an Instron Universal machine Model-3369 by using standard tensile test specimens that have been subjected to the under listed heat treatment as indicated in Table 4. Figure 3 shows the standard tensile sample used for this as specified in BS 2789:2002.The values were recorded in Tables 5, 6, and 7.

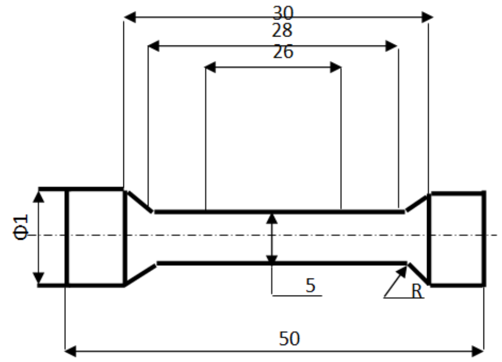


Figure 3. Tensile test specimen used (BS 2789:2002)

Impact test: The impact tests were carried out on the austempered ductile cast iron (ADI) and austempered grey cast iron (AGI) specimens that were subjected to Table 4 conditions. A 150 Joules capacity Avery Denison machine with a sticking velocity of 5.24 m/sec was used for these tests. Figure 4 shows the standard test bar used the tests. Specimen is fixed on horizontal position and the hammer strikes the impact specimen on the notched face. The energy absorbed is a measure of the impact strength of the material. The values were recorded in Tables 5, 6, and 7.

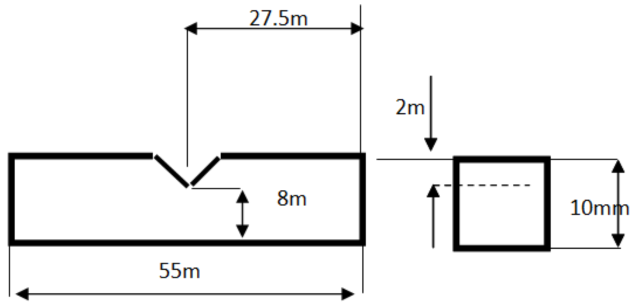


Figure 4. Charpy test specimen

Hardness test: Hardness tests samples in as-cast, annealed, normalized and austempered conditions were carried out at room temperature using Rockwell Hardness testing machine with a diamond indenter, in the form of square pyramid with an apex angle of 136^0,by applying a load of 150 kg. The hardness values obtained were converted to Vickers hardness number. This was necessary because Vickers hardness measurement is not suitable for hardened materials like cast irons. The values of hardness test are shown in Table 5, 6, and 7.

Metallography

Metallographic examination was carried out on ductile and grey cast irons specimens that have been subjected to the various heat treatment conditions as indicated in Tables 6 & 7. All the specimens were prepared of optical examination. Samples of as-cast, annealed, normalized and austempered ductile and grey cast irons were cut and prepared for metallographic investigation using standard techniques of specimens' preparation for the microstructure observation. Following polishing of samples on a rotating disc and subsequent surface cleaning, specimens were etched using 2% natal solution for 15-30 seconds to develop the structure. The structures obtained were photograph and are shown in plate A (micrographs 1 to 21).

RESULTS

Comparative mechanical properties

The mechanical properties obtained for ductile cast iron and grey cast iron in as-received, normalised, annealed and austempered conditions are show in Tables 5 to 7. The average chemical composition of the ductile and grey cast irons used is given in Table 1. The physicochemical and percentage fatty acids of the quenching media areshown in Tables 2 and 3 respectively. The fee fatty acid, viscosity values, iodine values, flash points, acid values, and specific heat are in Table 2. The results of the mechanical properties of the as-received, annealed, normalized and austempered ductile cast iron and grey cast iron are given in Tables 5, 6, and 7.

The effect of selected austempering oils and austempering time on the mechanical properties of austempered ductile cast iron (ADI) and austempered grey cast iron (AGI) using the selected vegetable oils are shown in Figs. 10-20. The oils used as austempering bath had effect on the mechanical properties, with hot marula, peanut, and shea butter oils obtaining high mechanical properties as compared with hot cotton seed oil. This was because of the substantial variation in the compositions of these vegetable oils. In addition to oxidative stability, the most important physical property of any potential quenchant, including vegetable oils, is the viscosity. For vegetable oils, viscosity increases with fatty acid ester chain length and decreases with the amount of unsaturation in the fatty acid ester alkyl chain.

Table 4. Results of Hardness, Tensile and Impact Tests for As-Received, Normalized, and Annealed

Cast iron	Hardness (HV)			Tensile (MPa)			Impact, (J)		
	As-received	Normalized	Annealed	As-received	Normalized	Annealed	As-received	Normalized	Annealed
Ductile cast iron	206	272	185	590	682	810	46	58	66
Grey cast iron	241	252	228	455	397	286	32	35	49

Table 5. Mechanical properties of austempered ductile cast iron samples austenitized at 900^{0}C

Medium	Austenitizing temperature,	Austempering temperature (^{0}C)	Austempering time (hr)	Tensile strength, MPa	Yield strength, MPa	Hardness (HV)	Elongation (%)	Impact strength, (J)
Marula oil	900	250	1	752	550	396	1.5	65
			2	798	592	384	3.0	50
			3	850	621	321	4.2	35
			4	1047	844	358	8.0	25
		260	1	670	424	320	3.0	64
			2	842	638	332	4.5	47
			3	984	730	349	7.5	32
			4	1120	921	346	8.0	24
		270	1	690	443	380	3.5	70
			2	785	556	375	4.5	55
			3	896	632	346	7.0	46
			4	1140	935	338	8.5	32
Peanut oil	900	250	1	620	424	312	1.5	56
			2	659	402	320	3.0	40
			3	780	528	448	4.0	35
			4	958	743	340	4.5	30
		260	1	689	428	370	1.6	64
			2	790	590	375	3.0	50
			3	865	612	346	4.0	42
			4	1032	820	321	7.5	28
		270	1	683	430	338	1.5	68
			2	779	521	386	3.0	50
			3	885	670	349	4.2	42
			4	1075	892	332	7.5	32
Shea butter oil	900	250	1	650	401	382	1.5	65
			2	685	426	364	3.0	45
			3	800	650	351	4.5	32
			4	1055	882	340	8.0	28
		260	1	710	501	392	1.5	65
			2	824	624	375	3.0	40
			3	884	689	349	4.5	32
			4	1045	878	335	8.0	26
		270	1	734	514	382	1.5	70
			2	842	652	358	3.5	42
			3	902	743	364	4.5	34
			4	1120	956	378	8.5	25
Cotton-seed oil	900	250	1	483	232	398	1.0	55
			2	509	260	410	1.5	42
			3	660	392	289	1.5	40
			4	744	523	247	1.5	39
		260	1	498	246	482	1.0	59
			2	585	306	391	1.5	42
			3	669	403	282	2.0	34
			4	787	543	263	2.2	32
	900	270	1	521	368	438	1.0	59
			2	597	394	395	1.5.	48
			3	700	525	284	2.0	37
			4	820	625	254	2.0	30

Table 6. Mechanical Properties of ustempered grey cast iron samples austenitized at 9000C

Medium	Austenitizing temperature, ^{0}C	Austempering temperature (^{0}C)	Austempering time (hr)	Tensile strength, MPa	Yield strength, MPa	Hardness (HV)	Elongation (%)	Impact strength, (J)
		250	1	540	353	316	0.1	62
			2	582	384	293	0.1	52
			3	637	482	272	0.1	48
			4	778	564	236	0.1	45
		260	1	550	361	321	0.1	60
Marula oil			2	625	419	325	0.1	50
			3	785	584	330	0.1	38
			4	895	649	335	0.15	30
	900	270	1	638	428	338	0.1	58
			2	784	594	340	0.1	50
			3	849	636	341	015	40
			4	957	721	344	0.2	55
		250	1	529	386	285	0.1	46
			2	552	390	285	0.1	42
			3	621	415	290	0.1	40
			4	732	558	300	0.1	30
		260	1	584	389	260	0.1	56
			2	628	464	290	0.1	48
			3	710	576	310	0.1	40
Peanut oil	900		4	790	588	320	0.15	30
		270	1	615	431	265	0.1	57
			2	712	548	320	0.1	45
			3	785	594	340	0.1	40
			4	864	650	345	0.15	30
		250	1	530	376	268	0.1	58
			2	560	388	275	0.1	45
			3	632	470	290	0.1	38
			4	743	565	329	0.15	29
		260	1	550	390	260	0.1	57
Shea butter oil			2	635	429	280	0.1	52
			3	749	564	317	0.15	40
	900		4	884	658	386	0.2	30
		270	1	630	498	269	0.1	55
			2	776	587	298	0.15	45
			3	845	645	350	0.15	42
			4	954	792	398	0.2	30
		250	1	510	316	210	0.1	56
			2	522	332	220	0.1	50
			3	549	375	249	0.1	40
Cotton-seed oil	900		4	622	416	280	0.1	35
		260	1	528	330	211	0.1	56
			2	548	380	239	0.1	51
			3	597	420	239	0.1	40
			4	621	442	298	0.1	38
		270	1	549	368	289	0.1	55
Cotton-seed oil	900		2	596	398	295	0.1	45
			3	690	401	299	0.1	34
			4	795	586	312	0.1	30

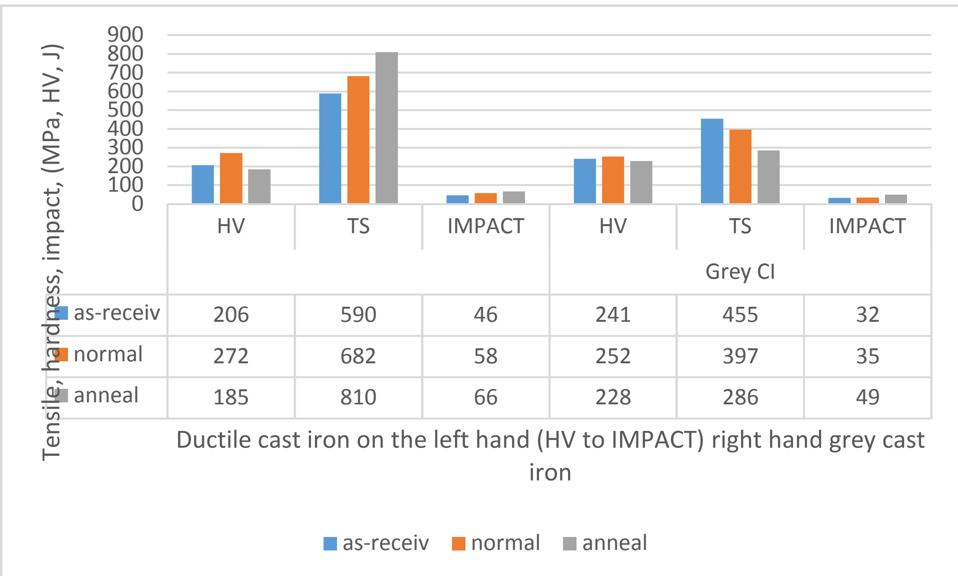


Figure 5. Variation of hardness, tensile strength, and impact strength of as-received, normalised, and annealed samples of ductile and grey cast irons

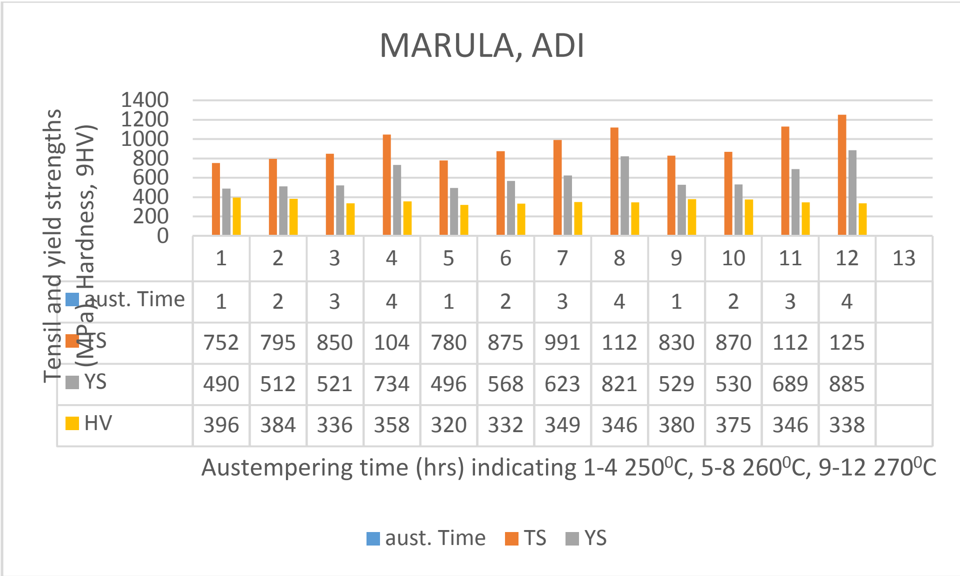


Figure 6. Effect of Austempering time on the tensile and yield strengths of ADI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Marula oil)

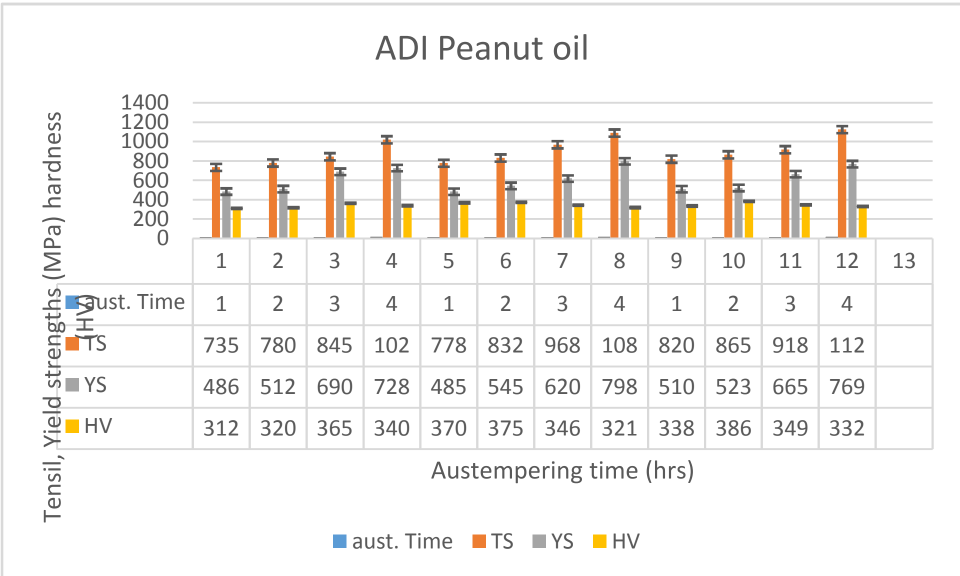


Figure 7. Effect of Austempering time on the tensile and yield strengths of ADI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Peanut oil)

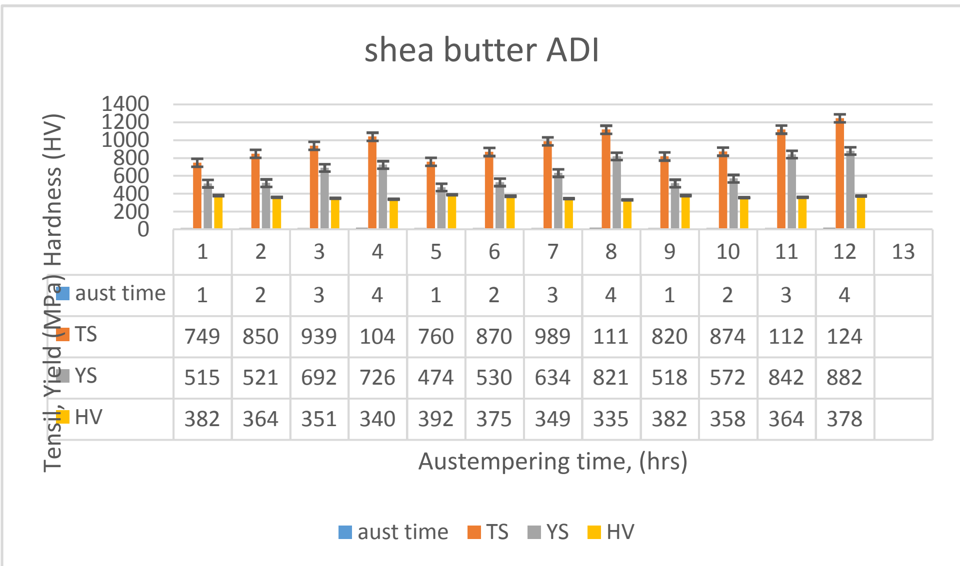


Figure 8. Effect of Austempering time on the tensile and yield strengths of ADI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Shea butter oil)

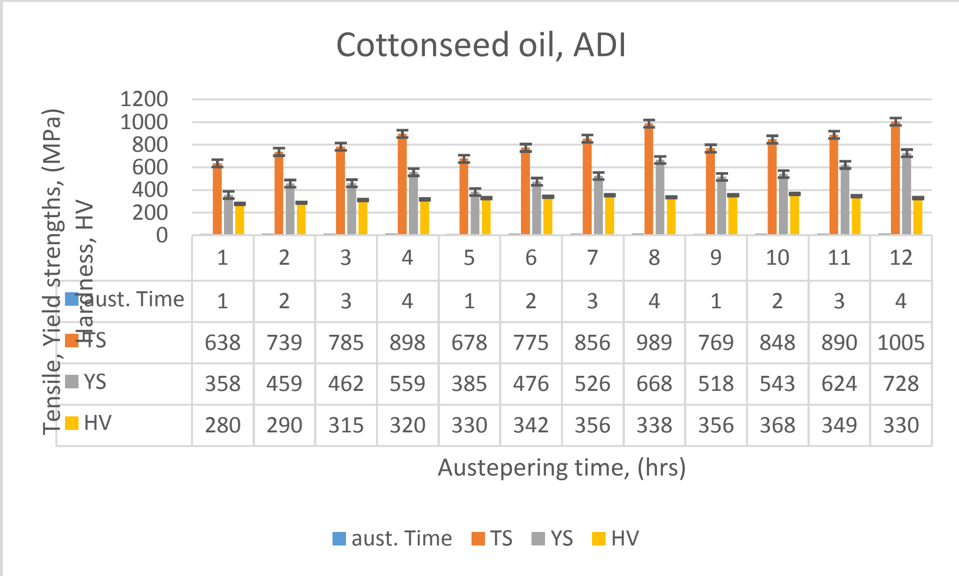


Figure 9. Effect of Austempering time on the tensile and yield strengths of ADI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Cottonseed oil)

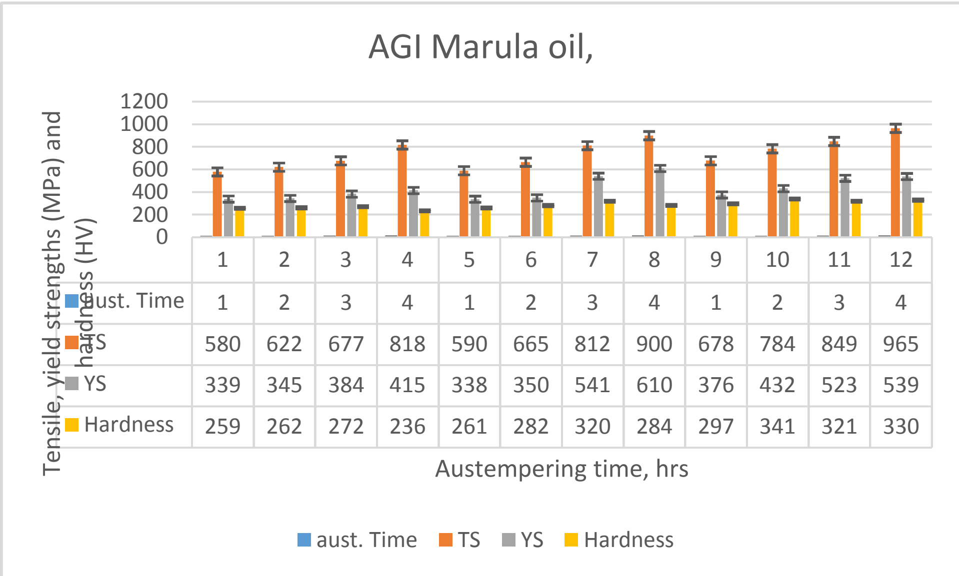


Figure 10. .Effect of Austempering time on the tensile and yield strengths of AGI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Marula oil)

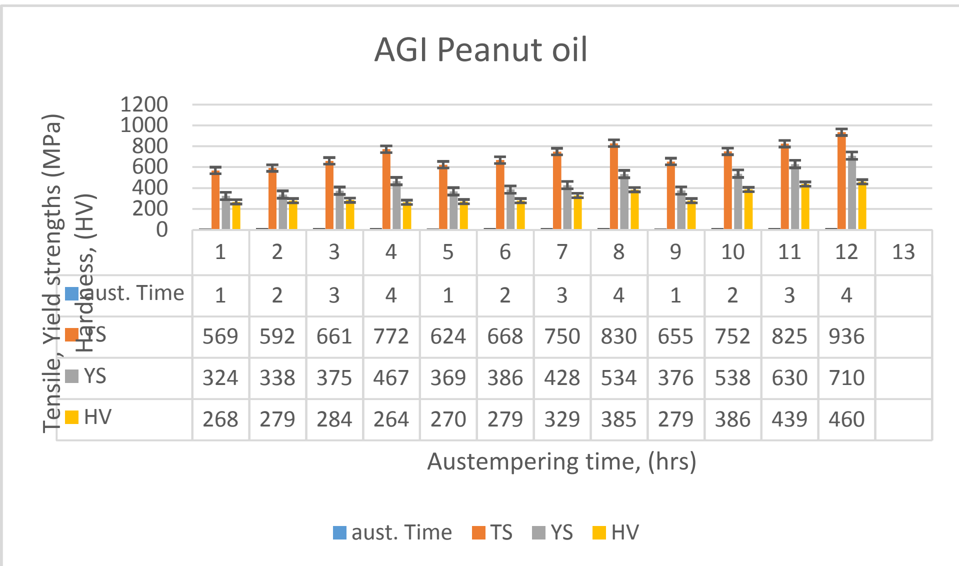


Figure 11. Effect of Austempering time on the tensile and yield strengths of AGI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Peanut oil)

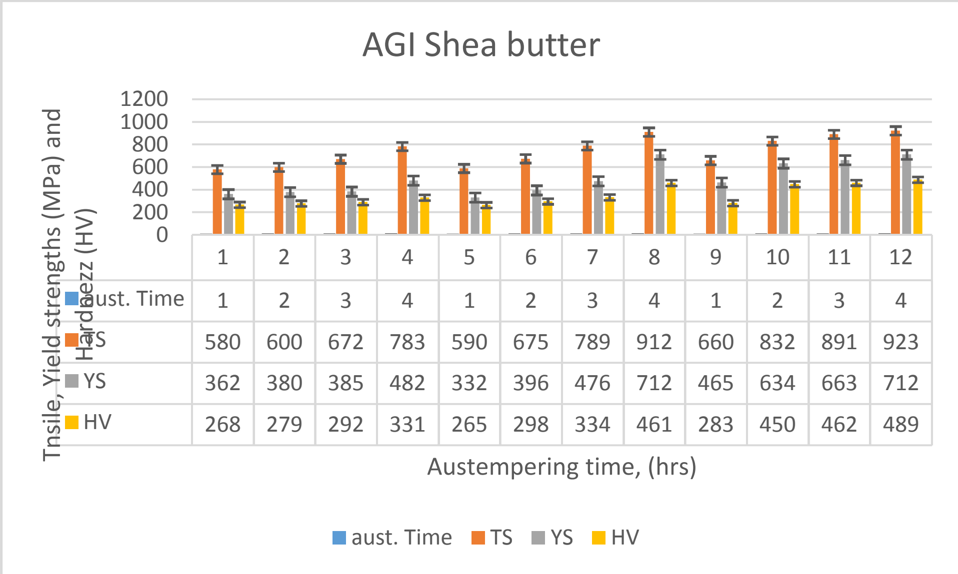


Figure 12. Effect of Austempering time on the hardness and impact strength of AGI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Shea butter oil)

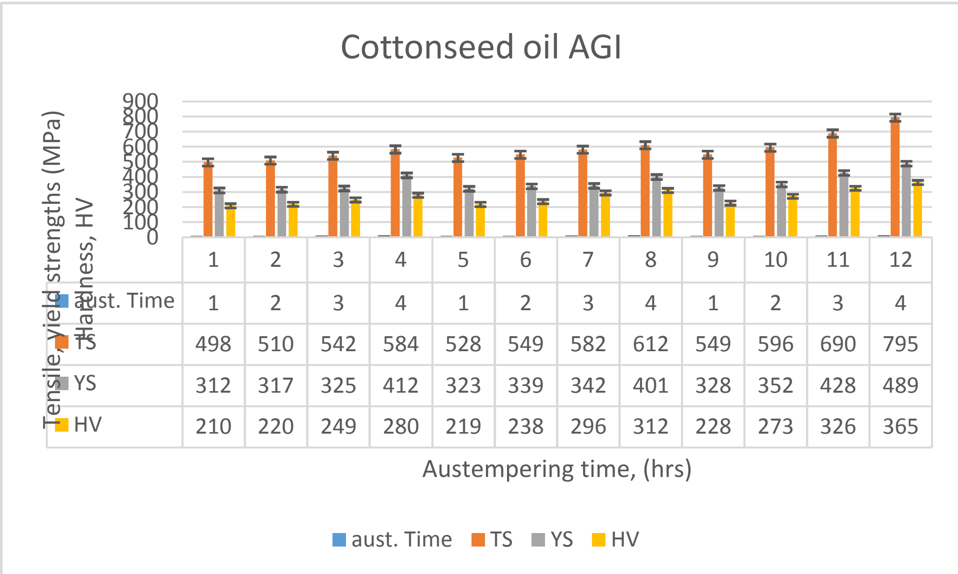


Figure 13. Effect of Austempering time on the hardness and impact strength of AGI (Austempering temperature 260^{0}C, 260^{0}C, 270^{0}C -Cottonseed oil)

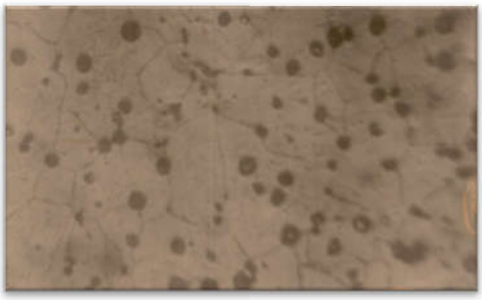
In this work, viscosity-temperature properties were determined from kinematic viscosity measurements (ASTM D445) and calculation of the viscosity index according to ASTM D2270.The viscosity index of each vegetable oil used is shown in Table 2 and from the Table, it has been established from this work that cottonseed oil has the highest viscosity value and followed by peanut, marula and then shea butter oil. As indicated by Addison, (2004) and Ajala, (1982) that iodine value is a measurement of the total unsaturation of vegetable oils, as well as indicator of their susceptibility to oxidation. It has shown that marula oil has least iodine value followed by shea butter and therefore the most stable at high temperature. The unsaturated /saturated ratio of peanut oil, marula oil, shea butter oil, cotton seed oil is in the order of: cottonseed oil > peanut oil > shea butter oil > marula oil > peanut oil. From this investigation, it shows that cotton seed is the most unsaturated and most unstable with respect to quenching bath treatment only. However, the present research work is focusing on austemperingof ductile and grey cast irons and not on quenching but quenching bath, and therefore in austempering process, the most stable austempering hot oils is in the order of > marula oil > shea butter oil >peanut oil >cotton seed oil as observed from the microstructures and experimental results.

Microstructure

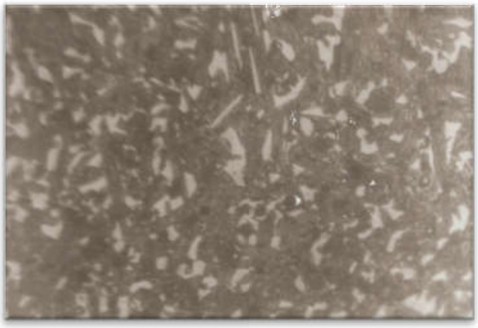
The optical microstructure of the as-cast ductile cast iron and grey cast iron are reported in the plate 1 and 2 respectively. The microstructure of ductile cast iron consisted of matrix of fine ferrite and pearlite along with dispersed graphite nodules, while grey cast iron structure consisted of matrix of ferrite and pearlite in lamellar form with graphite distributed as flakes. The graphite in the as-cast structure of ductile iron appears well rounded with about70% nodality. The microstructures of annealed, and normalized samples are shown in plates3 and 4. The annealed structure of ductile cast iron is shown in plate 3, with the structure consists of graphite nodule in pearlite matrix. The optical micrographs in plates 6, and 7 show structure of ADI austempered at 250^{0}C, 260^{0}C, and 270^{0}C in marula oil for 1,2,3, and 4 hours respectively. At the initial period of austempering 250^{0}C, (1hr), there was little or no ausferrite, but more retained austenite was observed. However, with increased of austempering time and temperature progressively, ausferrite structure was formed with less quantity of retained austenite as observed in plate. At austempering time of 4 hours there was decrease in the amount of retained austenite and fine precipitates of cementite was observed. The austempering time has direct impact on the amount of ausferrite and austenite produced during transformation. These observations are in line with what Alves et al, 2016, Giulliana and Glaucio, 2020 reported. Plates 3, 4, 5, 8, 9, 10, and 11 showed the effects of austempering time and temperature on the microstructure of ADI in hot oils (marula, shea butter, peanut, and cottonseed oils) at 250^{0}C, 260^{0}C, and 270^{0}C, with some indicating graphite nodules (black and grey balls) in ausferrite matrix others with the structure showing graphite nodules in ausferrite and martensite (plate 4) while plate 7 shows ADI in hot marula oil at 260^{0}C for 4 hrs, indicating graphite nodules in a matrix of ausferrite. Plate 10 shows graphite nodules in retained austenite after austempering in cottonseed oil at 250^{0}C. As observed, the original pearlitic structure was transformed into acicular ferrite and carbon saturated austenite, as shown in plates 7, 8, 9 and 10. As compared with the microstructure of as-cast grey cast iron in plate 2, there was little changes could be found related to the characteristics of graphite flakes after austempering heat treatment. Plates 12 to 22 shows the micrographs of AGI and their effects of austempering time and temperature in hot vegetables at 250^{0}C, 260^{0}C, and 270^{0}C, indicating graphite flakes in pearlite matrix. Plate 15 shows graphite (dark flakes) in network of ausferrite and martensite after austempering in marula oil for 4 hrs, while plate 14 indicate the AGI structure consisting of graphite flakes in martensite, this was after austempering in hot peanut oil for 3hrs. Plate 13 indicating annealed structure of grey cast iron consisting of graphite flakes (black) and ferrite (light colour), while plate 16 shows the micrograph of austempered grey cast iron in hot peanut oil 250^{0}C for 1 hr and it shows graphite flakes (black) and retained austenite. Plate 17 shows the AGI in hot shea butter oil for 3 hrs at 260^{0}C and reveals graphite flakes (black) transforming to ausferrite and martensite, while plate 18 shows the structure of AGI in hot marula oil at 270^{0}C for 4 hrs, consists of graphite flakes transformed to ausferrite and martensite. Plate 21 shows the structure of AGI in cottonseed oil for 4 hrs and reveals the transformation of graphite flakes to ausferrite and martensite.

1

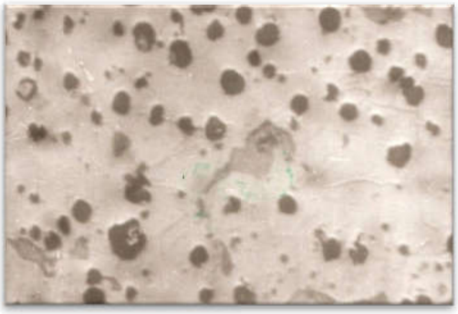
2



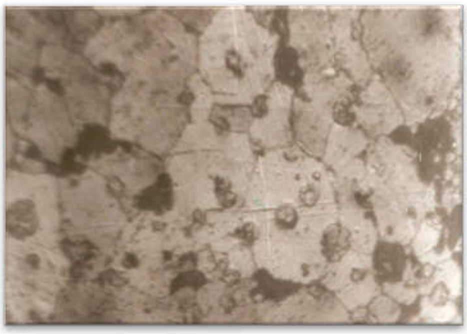
3



4

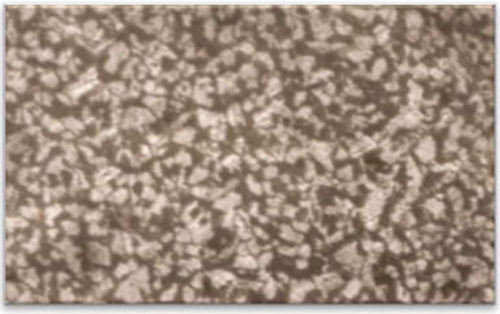


5



6

7



8

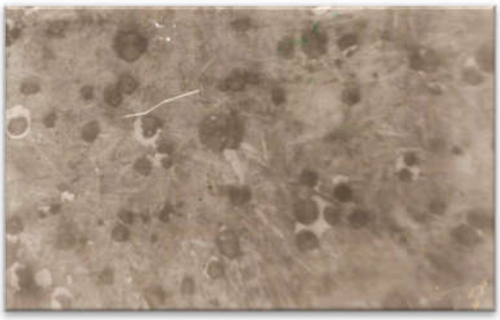
13

9

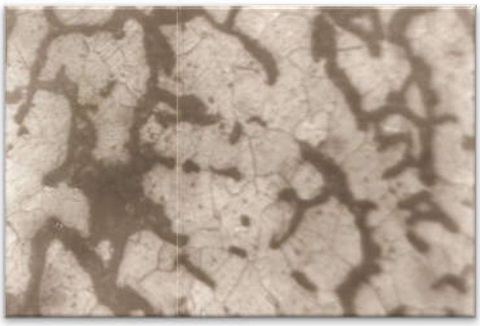
14

10

15

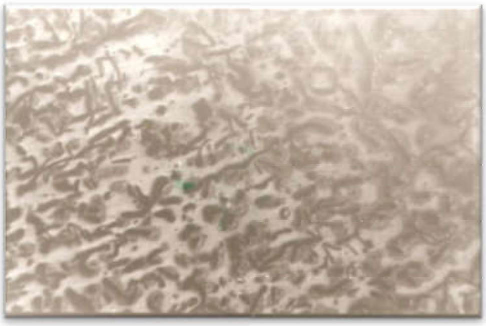


11



16

12

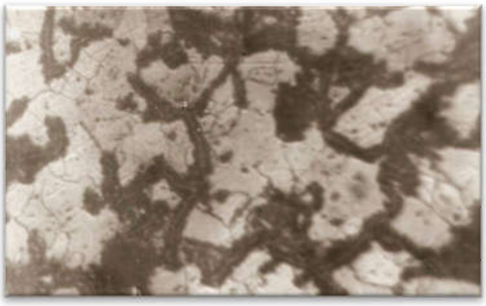


17

18

19

20



21

Conclusion

The austempering process performed on the ductile and grey cast irons with hot vegetable oils as quenchants in placed of molten salt (nitrate) bath have significantly improved the mechanical properties of these materials. From this study, both the austempering temperature and austempering time affects the iodine value is a measurement of the total unsaturation of vegetable oils, as well as an indicator of their susceptibility to oxidation ( ) viscosity and specific heat of vegetable oils

1. The as-cast sample of nodular cast iron has a graphite nodule, ferrite, and pearlite while the as-cast sample of grey cast iron has structure of ferritic-pearlitic matrix
2. The mechanical properties of ADI and AGI depend on their microstructures which in turn depend on the austempering temperature and austempering time. When ADI were austempered at lower temperatures (260- 270^{0}C) produced very fine scale microstructures with higher ferrite (α) content and lower volume fraction of austenite (γ). The strength of ADI and AGI austempered at 250^{0}C did not follow the expected trend but was found to be lower than ADI and AGI at 260^{0}C and 270^{0}C. The decrease is associated to the lower carbon content of retained austenite in ADI and AGI austempered at 250^{0}C than at 260^{0}C and 270^{0}C.
3. With an increase of austempering temperature from 250^{0}C to 270^{0}C, elongation as well as impact toughness gradually increase on both ADI and AGI. This is because of an increase amount of austenite is stabilized/enriched due to carbon dissolution at a higher temperature.
4. ADI microstructures of all samples austempered between 250-270^{0}C consist of acicular ferrite and carbon enriched austenite called ausferrite, but was more pronounce at 270^{0}C.
5. For both ADI and AGI samples, the tensile and yield strength increases with increase of austempering time, while hardness decreases with of austempering time.
6. For both samples (ADI and AGI), the oil quenchants had pronounce effect on the properties and microstructures with marula, shear butter and peanut oils were able to cause the formation of ausferrite between 260-270^{0}C for 4 hrs with ductile cast iron. The oils properties, like iodine value, free acid content, viscosity measure the stability of the oil at high temperature.
7. The best mechanical properties are achieved when austempered ductile iron samples with marula peanut, and shea butter oils for 4 hrs at 270^{0}C.
8. The experimental results show that mechanical properties of austempered ductile are more than that of austempered grey cast iron. However, the austempered properties of both ductile and grey cast irons were more than as-received samples.

Acknowledgements

The authors express their thanks to the Kebbi State University of Science and Technology, Aliero and "TetFUND" for the Research Grand Committee for providing the funds for this project. We also acknowledge the NMDC, Jos and National Chemical and Research Centre, Zaria for the technical support rendered to us.

REFERENCES

Adewuyi, B.O. and Afonja, A.A. 2000 Austempered ductile iron available alternative to steel. *Nigerian journal of Engineering and management,* Vol.1. No 1 pg.6-13.

Adewuyi, B.O. and Afonja, A.A. 2000 Austempered ductile iron available alternative to steel. *Nigerian journal of Engineering and Management,* vol.1. No 1, pp 6-13

Akor T., Ashwe A. 2014. Investigation of the potential of jatropha seed oil as austempering quenchant for medium carbon steel. *American Journal of Engineering Research (AJER),* Vol.3, Issue 8, pp. 209-211

ASTM International, 2017. ASTM Standard A247-Standard Test Method for Evaluating the Microstructure of Graphite in Iron Castings: West Conshohocken, USA.

ASTM-E8, 2013. Standard test methods for tension testing of metallic materials. West Conshohocken, USA.

Bain, E.C. 1939. Functions of Alloying Elements in Steel; American Society for Metals: Materials park, OH, USA.

Bingxu Wang, Xue Han, Gary C. and Yuming Pan, 2019. Wear Behavior of Austempered and Quenched and Tempered Grey Cast Iron under Similar Hardness. MDPI, Basel, Switzerland.

Bingxu Wang, Xue Han, Gary C. Barber, and Yuming Pan, 2019. Wear Behaviour of Austempered and Quenched and Tempered Grey Cast Irons Under Similar Hardness, MDPI, USA.

Bish A. 2009. Effect of heat treatment procedure and microstructure and mechanical properties on Nodular Iron: Thesis Master of Technology. Rourkela.

Charles, F. Walton, 1998. Grey and Ductile Iron Casting handbook. Grey and Ductile Iron Founders Society Inc. Cleveland. pg.160-165.

Charles,F. Walton, 1998. Grey and ductile iron casting handbook. Grey and Ductile Iron Founders Society Inc. Cleveland. Pp 160-165

Dauda M., Kuburi IS, Obada DO, Mustapha RI. 2015. Effects of various quenching media on mechanical properties of annealed 0.509 Wt%Mn steel. *Nigerian Journal of Technology,* Vol 34, Number3, pp506-512.

David Moore, 2004. Safer Liquid Quenchants. Houghton plc Manchester, England.

Drauglates, U. and H.G. Boase, 1989 Second International conference on ADI, Michigan, USA.

Eder, C.A.S., Rosa, L.S.O., Lauralice, C. F.C., George E.T. 2016. "Stabilization of vegetable oil-based quenchants to thermal-oxidative degradation": Experimental strategy and effect of oxidation on quenching performance. La Metallurgin Italiana, 3. PDXScholar.

Gabor Kerekes, Maria Kocsis Baan, Imre Felde, 2016. Possibility of use Bio-Oils as Quenchant. MultiScience – XXX. MicroCAD International Multidisciplinary Scientific Conference, University of Miskolc, Hungary.

Guilliana V. T. and Glaucio S. F. 2020. Influence of austempering time and austempering temperature in microstructure and mechanical properties in austempered ductile iron, *International Journal of Research-GRANTHAALAYAH,* Vol. 8, 51-62

Hassan, SB and Aigbodian, VS. 2013. Evaluation of khaya seed oil (mahogany oil) as quenchants in the hardening process of plain carbon steel. *Pacific journal of science and technology,* Vol. 4, number 1, pp19-30.

John Nsely, 1970. Practical Metallurgy and Materials of Industry. Edward Arnold Ltd.UK.pg.70-151

Joseph B.A., Oladiran A.K., Edeki M., Michael B.A., Samuel A. A. 2015. Performance assessment of selected Nigerian vegetable oils as quenchinmg media in hardening process for medium carbon steel, *Journal of Minerals and Materials Characterization and Engineering,* 85-93

Keough, J.K. 1998. Ductile Iron data. http://www.ductile.org/ didata/section.com.

Keough, J.K. 1998. Ductile irondata. http://www.ductile.org/ didata/section.com

Kobasko NI, Carvalho de Souza E., Totten GE. 2011. Vegetable oil quenchants: Calculation and comparison of the cooling properties of a series of vegetable oils.

Larry, Olson 2001. Proper Quenching Option Yields Better Results .Modern Application News.pg.1-5

Lauralice de C.F C., Mauro R. F., George E. T., Alessandro F. F. 2005. Oxidation of vegetable oils and its impact on quenching performance, *Int. J. Materials and Product Technology,* vol. 24, Nos. 1-4

Lawrence, H.V.V. 1980. Elements of materials science and engineering, 5th Edition. Addison Wesley Publishing Comp. USA. PP 402-568.

Morrough, H. 1987 A new Engineering material. Production of Nodular Graphite structures in Grey cast irons. ASM Source book on ductile iron. Ohio, USA. PP 72-90. www.ductile.org/associatedlinks/DIMG/Ductile Iron

Niall Guerin, 2003. Vegetable oils proposed as viable fuel alternative. http://www.media52.net/archives/00085.htm

Nikolai, I.K., Lauralice, C.F.C., G.E. Totten, 2010. Vegetable Oil Quenchants: Calculation and Comparison of The Colling Properties of a Series of Vegetable Oils, Strojniski vestnik- *Journal of Mechanical Engineering,* vol. 56, No2 pp 131-142

Nuhu AA. 2015. Effect of Nigerian neem seed oil as austempering quenchant for locally recycled mild steel. *Middle-East Journal of Scientific Research,* 23 (1), pp. 110-118

Okwonna OC, Nwankwojike BN, Abam FI. 2017. Exploring the potentials of using palm kernel oil esters (palm kernel oil + bitumen) for austempering process of medium carbon and high carbon steel. European Journal of Materials Sciences, Vol.4, No. 2, pp.28-37, European Centre for Research Training and Development UK.

Rajan, T. V. And C. P. Sharma, 1988. Heat Treatment, principles and Techniques. Prentice-Hall of New Delhi, India. Pp 20-150, 236-380

Rimmer A. 1997. Austempered Ductile Iron is growing. Materials World. *Journal of the Institute of Materials,* vol.5, pp 252-256

Sani SA. 2008. Potentials of using some vegetable oils as quenchants for austempering of steels and cast irons. Unpublished PhD dissertation, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.

Scott MacKenzie D., FASM 2009. The chemistry of oil quenchants. Houghton International Inc. Valley Forge, Pa. USA.

Shehu A., Yohanna M., Rayyan D. 2015. Potential of hot sesame oil (sesanum indicum oil) bath as quenchant for austempering of ductile cast iron. vol. 6, Issue 6, www.jisr.net

Totten, G.E., Tensi, H.M., Lanier, K. 1999. "Performance of vegetable oils as a cooling media in comparison to a standard mineral oil". *J. Mat. and Perf.,* vol.8, No 4, p. 409-416.

V.C.C.Alves, L.L.A. Baracho, E.R. Slva, L.C.R. Lopes, G.S. Fonseca, F,R.F. Silva, R.H. Leal, C.T.A. Santos, 2016. Correlation between microstructure and mechanical properties of an austempered ductile iron. 22 CBECiMat. Congresso Brasileiro de Engenharia e Ciencia dos Materiais, Natal, RN, 5595-5602 Brasil

Voight, R. and C. Loper, 1984. Proceeding 1st International conference on ADI. Metal park, OH, ASM 83

Zharare, P. and Dhlamini, N. 2015. Characterization of Marula (Sclerocarya caffra) Kernal Oil and assessment of its potential use in Zimbabwe, *The Journal of Food Technology in Africa,* vol. 5 No 4, pp126-132

****