Effect of Sodium Dodecylbenzene Sulfonate as Anionic Surfactant on Water based Carbon Nanofluid Performance as Quench Medium in Heat Treatment

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Abstract. Quenching is performed as part of steel heat-treatment to enhance mechanical properties, by rapid cooling. Factors that affect the selection of quench medium are hardenability of material, geometry, and dimensions of the component. In recent developments, nanofluids are used to improve heat transfer capacity. In this research, nanofluids were synthesized using the two-step method. Milling of particles was done using a high energy ball mill for 15 hours at 500 rpm. Observation of particle size, material composition, and morphology of particle, and surface changes of the particle were measured by Field-Emission Scanning Electron Microscope (FE-SEM), and Energy Dispersive X-Ray Spectroscopy (EDX). Water-based nanofluids with a volume of 100ml were produced using the two-step method, with carbon concentrations of 0.1%, and 0.5% and Sodium Dodecylbenzene Sulfonate concentrations of 0%, 1%, 3%, and 5%. Samples of S45C steels were austenitized at 1000ºC for 60 minutes. Hardness testing results correspond to the severity of the quenching mediums, with peak hardness of 845 HV for 0.1% Carbon with 1% SDBS, and 878 HV for 0.5% carbon with 3% SDBS. Hardness testing results show a significant improvement over results without SDBS addition. Excess surfactant addition yields a lower hardness due to the re-agglomeration of particles.

1. Introduction
Quenching is the cooling process in heat treatment that hardens the treated component[1]. Hardening of steels done by quenching involves the transformation of the martensitic phase from the austenitized steel component. The component is first heated above the austenitization temperature (>723ºC) which then it is put into contact with a heat transfer medium. Upon contact, the quenchant will facilitate heat transfer within the component-quenchant interface. Selection of heat transfer medium will affect the final physical properties, residual stresses and mechanical properties of the component after the heat treatment process. Nanofluids are enhanced heat transfer fluids that are commonly used to improve cooling performance in heat exchangers, solar collectors and, radiators. Nanofluids are obtained by adding nanoparticles into a base fluid. [2] Yang et.al.[3] reviewed that the addition of nanoparticles into a base fluid showed a significant increase in thermal conductivity. However, nanoparticle dispersion in the base fluid is showed to have an effect in the heat transfer capacity of the nanofluid. Azadeh et.al. [4] revealed that the stability of nanofluids is significantly improved with the addition of surfactants and ultrasonic processing. Sodium
Dodecylbenzene Sulfonate (SDBS) is an anionic surfactant, commonly used in household products such as laundry detergent, dish soap, and floor cleaner [5]. The addition of the surfactant is done to reduce the surface tension between carbon nanoparticles and the base fluid, water. This study aims to observe the properties of quenched S45C steel using carbon nanoparticles suspended in water. Sodium Dodecylbenzene Sulfonate (SDBS) is added to assist the dispersion of the carbon nanoparticles. Ultrasonication is done to further stabilize the mixture. S45C steel samples were heated to 1000ºC and held for 60 minutes followed by immersion quenching into the nanofluid.

2. Materials and Methods

Lab-grade carbon particles procured from Sigma-Aldrich were used to prepare nanofluids by using the standard two-step method. The two-step method was selected due to it being more cost and energy efficient. Nanofluids with concentrations of 0.1% and 0.5% carbon were prepared with varying SDBS concentrations of 0%, 1%, 3% and 5%. First, carbon particles were subject to High Energy Ball Mill (HEBM) at 500 rpm for 15 hours. Then, carbon particles were weighed accordingly and dispersed with SDBS to distilled water. Ultrasonication was done for 280 seconds to ensure the stability of the mixture and prevent agglomeration.

S45C steel rods were cut to a dimension of 15mm x 10mm x 10mm. The samples were then pre-heated in a furnace to 600ºC and then left to austenize at 1000ºC for an hour. After exactly an hour, the S45C steel samples were immersed into the nanofluids. Microstructural observation was done using a Light Optical Microscope (LOM). The quenched S45C samples were then prepared for microstructural observation by using standard metallographic preparation procedures, which includes surface grinding of the S45C samples from 100 grit to 1500 grit sandpaper with 100 grit increments. Followed by polishing using velvet cloth and etching using 2% Nital.

Characterization of the carbon steel rod was done by Optical Emission Spectroscopy (OES) to determine its chemical composition. Field Emission Scanning Electron Microscope (FESEM) imaging was conducted to observe the average particle size of the lab-grade carbon powder. Microstructure analysis was carried out using a Light Optical Microscope (LOM) to observe phases formed after quenching. Preparation for metallographic analysis was done by using standard metallographic preparation procedure. The samples were etched using 3% nital solution which consists of 3 ml nitric acid and 97 ml ethyl alcohol on the polished surface of the sample. Etching of the samples was done by immersion into the etching solution for three seconds. Microstructure images were taken using an optical microscope at 100X.

Vickers hardness testing was done to observe the hardness value of each sample. Testing was done by applying a force of 300 gf using a diamond indenter on the samples' surface, and the load is given for 10 seconds. The resulting indent on the sample's surface is then examined using a microscope to be measured for its size and to be calculated for its hardness value. The testing was done on five different points on the samples' surface to obtain the mean hardness value of each point.

3. Results and discussion

3.1. Carbon powder characterization

Characterization of the carbon nanoparticles was done using a Field Emission Scanning Electron Microscope (FE-SEM) as observed in Figure 1. The FE-SEM imaging was conducted to observe the average particle size of the lab-grade carbon powder at magnifications of 500X and 1000X. From the result, it was determined that the average size of the carbon particle used in this study was 15.08 µm. Furthermore, the lab-grade carbon powder was also tested for impurities by using an Energy Dispersive X-Ray (EDX). The EDX result presented in Table 1 showed that the lab-grade carbon powder used in this research was free from any impurities.
Figure 1. FE-SEM image of lab-grade carbon powder at magnification of (a) 500X and (b) 1000X.

Table 1. The result of EDX for chemical composition (wt%) of laboratory-grade carbon powder

| Laboratory-grade carbon powder | C   | O   |
|-------------------------------|-----|-----|
|                               | 94.63% | 5.37% |

It is seen in Table 1 that the EDS shows the carbon powder used in this study has a purity of 94.63%. It is observed that an oxygen content of 4.45% is present as an impurity. This confirms that the carbon used in this study consist of >90% carbon.

3.2. S45C steel characterization

Table 2. The chemical composition of S45C carbon steel (%) [6]

|   | Fe  | C   | Si  | Mn  | P   | S   | Cr  | Mo  |
|---|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 98.3 | 0.47 | 0.287 | 0.718 | 0.0261 | 0.005 | 0.028 | 0.005 |
| Ni | 0.005 | 0.02 | 0.003 | 0.018 | <0.002 | 0.035 | <0.002 | <0.01 |
| Pb | 0.025 | <0.002 | 0.0013 | 0.0005 | <0.002 | 0.008 | <0.03 |

The OES results shown in Table 2 of the S45C sample show that the steel used is in accordance with the AISI 1045 steel standard. S45C steel was chosen because medium carbon steel is heat treatable and changes in properties by heat treatment process can be observed.

3.3. Microstructure analysis

It is observed in Figure 2, the microstructure of S45C after being quenched in water-based carbon nanofluid with varying surfactant concentration, the structure mainly consists of pearlite, which is represented in the brighter regions, while martensite structure appears in the darker regions. In figure 2a, for S45C quenched in pure distilled water, shows mostly pearlite regions, with few martensite regions. In
figure 2b, it is observed that the contrast between the darker and the lighter regions are more apparent, this shows the addition of carbon particles increase the cooling rate of the S45C sample. In figure 2c, the martensite structure that occurs is quite apparent, as seen in the dark areas. As in figure 2d and 2e, martensite structures were not as heavily shown as previously. Figure 2f was quenched in 0.5% carbon without surfactant, very few martensite structures that appeared, this may happen due to the agglomeration of carbon particles in the fluid [7]. In figure 2g and 2h, quite significant numbers of martensite regions were observed, while figure 2i shows few martensite structures are observed.

![Images of microstructures](image1.png)

Figure 2. Microstructure of S45C after quenching in water based laboratory grade nanofluid (a) 0% vol. carbon, pure distilled water, (b) 0.1% vol. carbon, (c) 0.1% vol. carbon, 1% SDBS, (d) 0.1% vol. carbon, 3% SDBS, (e) 0.1% vol. carbon, 5% SDBS, (f) 0.5% vol. carbon, (g) 0.5% vol. carbon, 1% SDBS, (h) 0.5% vol. carbon, 3% SDBS, and (i) 0.5% vol. carbon, 5% SDBS. Magnification 100X.

Figure 3 compiled the hardness result for the S45C sample in all experiment variables. The sample quenched in pure distilled water has an average hardness of 667 HV. For a small increase in found in the sample quenched with 0.1% carbon nanofluid with no surfactant, which results in 712 HV. The hardness result for nanofluid without any added surfactant was similar to our previous result, whereas the 0.5% carbon was lower than 0.1% carbon nanofluid [8]. A significant increase in hardness found with the addition of 1% SDBS in the 0.1% carbon nanofluid, this results in a hardness value of 845 HV. However,
after further addition of SDBS of 3% and 5% respectively, the hardness value was observed to be decreasing.

At 0.5% carbon concentration with no surfactant added, the hardness value was found to be quite low, which is due to the particle agglomeration [9]. However, with increasing surfactant addition at 1% and 3% SDBS addition, the hardness value increased and peak hardness value in this study was observed to be at 0.5% carbon with 3% SDBS. Further addition of 5% SDBS in 0.5% carbon nanofluid, caused the hardness value to decrease. The peak hardness for water-based nanofluid with SDBS addition was obtained at 0.5% vol. carbon nanofluid with 3% SDBS addition at 878 HV. The hardness value is in line with the microstructural observation, as the 0.5% carbon nanofluid with 5% SDBS shows a quite large martensite region.

Figure 3. Graph displaying result of Vickers Hardness Testing vs. Concentration of respective variation

From the result, it is found that carbon nanofluid can be enhanced further by adding a surfactant to increase carbon stability in the fluid. An optimum amount of surfactant addition may enhance the quench severity of the nanofluid. The addition of surfactant helps the carbon reduce its surface tension with water, as carbon is hydrophobic in nature. The anionic surfactant, SDBS, physically adsorb to the carbon nanoparticle's surface, while its tail is in direct contact with water, causes the carbon to be able to be stably dispersed in water [10]. While the excess addition of the surfactant may cause the carbon to re-agglomerate, this is observed as the decreasing in hardness as excess surfactant concentration is added [11].

Conclusion
The effect of SDBS surfactant additions in various concentration for use as quenching medium in a carbon nanofluid is investigated in this study by using S45C medium carbon steel samples. The surfactant was added to carbon-distilled water nanofluid. Synthesis of the nanofluid was done by the two-step process. The variation of surfactant concentration is 0.1%, 0.3% and 0.5% volume and the variation of carbon concentration is 0%, 0.1% and 0.3% volume. The microstructure and hardness obtained in this study show that the concentration of surfactant added in the carbon nanofluids quite affected the quenching results. The quenched product by using a carbon nanofluid will result in a martensite structure, however, with the added surfactant an increase in the martensite structure is observed. At excess surfactant concentrations, the structure mainly consists of pearlite, with very few martensites. Hardness testing results also correspond to the severity of the quenching mediums, with peak hardness of 845 HV for 0.1% Carbon
with 1% SDBS, and 878 HV for 0.5% carbon with 3% SDBS. The hardness value shows a significant improvement over hardness results without SDBS addition. Excess surfactant addition will also yield a lower hardness due to the re-agglomeration of particles. Overall, the hardness value was still improved compared to cooling without the addition of surfactant. This study concluded that surfactant addition into the nanofluid will enhance its heat transfer capability, which in turn will also improve the severity of the quench, at the appropriate concentration.

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References
[1] Babu K and Prasanna Kumar T 2011 Effect of CNT concentration and agitation on surface heat flux during quenching in CNT nanofluids International Journal of Heat and Mass Transfer 54 106-117
[2] Vignesh Nayak U and Prabhu K 2015 Heat Transfer during Immersion Quenching in MWCNT Nanofluids Materials Science Forum 830-831 172-176
[3] Yang L, Xu J, Du K and Zhang X 2017 Recent developments on viscosity and thermal conductivity of nanofluids Powder Technology 317 348-369
[4] Azadeh G, Ibrahim H M 2013 The influence of surfactant and ultrasonic processsing on improvement of stability, thermal conductivity, and viscosity of titania nanofluid Experimental Thermal and Fluid Science 51 1-9
[5] Wusiman K, Jeong H, Tulugan K, Afrianto H and Chung H 2013 Thermal performance of multi-walled carbon nanotubes (MWCNTs) in aqueous suspensions with surfactants SDBS and SDS International Communications in Heat and Mass Transfer 41 28-33
[6] Kresnodrianto, Harjanto S, Putra W, Ramahdita G, Yahya S and Mahiswara E 2018 Characterization of water based nanofluid for quench medium IOP Conference Series: Materials Science and Engineering 348 012009
[7] Sadri R, Ahmadi G, Togun H, Dahari M, Kazi S, Sadeghinezhad E and Zubir N 2014 An experimental study on thermal conductivity and viscosity of nanofluids containing carbon nanotubes Nanoscale Research Letters 9
[8] Akhyyar I and Sayuti M 2015 Effect of Heat Treatment on Hardness and Microstructures of AISI 1045 Advanced Materials Research 1119 575-579
[9] Yu W and Xie H 2012 A Review on Nanofluids: Preparation, Stability Mechanisms, and Applications Journal of Nanomaterials 2012 1-17
[10] Farbod M, Ahangarpour A and Etemad S 2015 Stability and thermal conductivity of water-based carbon nanotube nanofluids Particuology 22 59-65
[11] Yang K, Yi Z, Jing Q and Lin D 2014 Dispersion and aggregation of single-walled carbon nanotubes in aqueous solutions of anionic surfactants Journal of Zhejiang University Science A 15 624-633