ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Investigation on Biodiesel Nanoemulsion Preparation and Performance.

Nbila H Hussien, HH Shaarawy*, and SI Hawash.

Chemical Engineering & Pilot Plant Dept., National Research Centre, Giza, Egypt.

ABSTRACT

In this study, water in biodiesel fuel nanoemulsion was prepared by mixing with nonionic surfactant. Biodiesel nanoemulsion was prepared by blending different percentages of water along with nonylphenol and oleic acid to improve the combustion of the fuel. Droplet size of the optimum prepared nanoemulsion was determined by atomic transmission microscope (ATM) and it was ranged from 18nm to 124nm. The histogram shows that 8.5% of our sample was of 124nm size, while 18nm represents 73% of our sample. Experimental results confirmed that: blends of 1.82%, nonylphenol +0.98% oleic acid ,24.5% H_2O and 72.7 biodiesel was thermodynamically stable for more than 6 months and gave higher performance regarding longer ignition time with higher flame length and calorific value of 35.94 KJ/Kg.

Keywords: Nanoemulsions, emulsion fuel, water in diesel fuel nanoemulsion.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

The resulted rising fuel costs and more and more stringed emission standards have driven researchers to look into new solutions for increased engine efficiency and reduced emissions for future transportation system.

Diesel engines are obtaining more and more attention in transportation, industrial and agricultural applications due to their high efficiency and reliability [1,2]. Also transportation has seen growth in recent decades due to new demand for personal- use vehicles powered by internal combustion engine [3]. Diesel engines also face the major disadvantage of increased NO_x emissions. Future legislation to control vehicle exhaust emissions will restrict NO_x emissions to very low levels [4]. As the formation of NO_x emissions highly depends on the operating temperature [5, 6], various methods including exhaust gas recirculation technology [7], and retarding fuel injection timing [8] have been developed to bring down the peak temperature, thereby reducing NO_x emissions. Water injection is also an effective method to reduce NO_x emissions. The use of water into diesel engines has a number of possible benefits. For example water can effectively reduce the peak flame temperature and thereby reducing NO_x emissions [9-14].

Methods of introducing water into the engine , most of them are : water injection into the cylinder using a separate injector[11,12],spraying water into the intake manifold[15,16], and water/diesel emulsions[10,17-21]. The first two methods are accompanied by a significant increase of HC and CO emissions. Meanwhile the presence of liquid water in the combustion chamber results in oil contamination and an increase in engine wear. To overcome these disadvantages resulted from direct water injection on the engine performance, water/diesel emulsion fuels have been developed , which is the addition of surfactants to reduce the oil and water surface tension, activate their surface, and maximize their superfacial contact areas to form finely dispersed droplets phase[22].

Emulsion droplets are normally stabilized by surfactants or amphiphilic polymers. The adsorbed surfactant causes lowering in interfacial tension between water molecules and biodiesel which further promotes easier emulsification and stabilizes the droplet against coalescence by static or electrostatic repulsion. Amount of emulsifier added to stabilize the blends also plays an important role in keeping the suspensions in single phase. But higher than required concentration (Critical Micelle concentration), may lead to crowding effect of micelles which eventually increase the viscosity of surfactants added in the biodiesel–water emulsions in order to effectively formulation of nanoemulsion fuels in order to keep the water droplets and nano-particles in uniform suspension, both physical and chemical stabilization were provided [23].

The aim of this study is to introduce nanobiodiesel using nonylphenol as surfactant with oleic acid and water. The prepared emulsion fuel (nanobiodiesel) was evaluated by measuring its pore size, testing ignition time and measuring its calorific value.

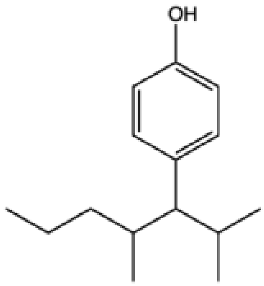
In our study we use magnetic stirring for the formation of the biodiesel nanoemulsion fuel via the selected surfactants (nonylphenol and oleic acid).

The duration of physical mixing was gradually increased in the intervals of 5 up to 30 minutes along with a constant stirring slow mixing for 5mintues at 100rpm followed by fast stirring (500rpm) for dispersion characteristics of the emulsion.

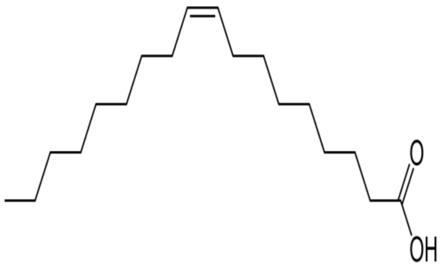
MATERIALS AND METHOD

Raw Materials

In this study, technical grade biodiesel was used as the continuous emulsion phase. This biodiesel was prepared by conventional trans-esertification of a mixture of soybean and sunflower oil using methanol and potassium hydroxide as catalyst. Biodiesel produced is of over 95% purity. The technical grade emulsifying agent used throughout the current investigation namely; 4-(2,4-dimethylheptan-3-yl)phenol (Nonylphenol) (Aldrich) and oleic acid (Aldrich). The water in all experiments was demineralized and doubly distilled. Chemical structures of the used surfactants were presented by the following structure.



4-(2,4-dimethylheptan-3-yl)phenol $C_{15}H_{24}O$ Density 0.953g/mL.



Cis-9-Octadecenoic acid $C_{18}H_{34}O_2$ Density 0.895 g/mL.

Preparation of nano emulsion fuel

In our study we use magnetic stirring for the formation of the biodiesel nanoemulsion via the selected surfactants (nonylphenol and oleic acid). The duration of physical mixing was gradually increased in the intervals of 5 up to 30 min along with a constant stirring (500rpm) for dispersion characteristics of the emulsion. Preparing pre-emulsion by addition of water with different percentages (10%, to 35%) to a surfactant of nonylphenol and 0.5mL of oleic acid and biodiesel fuel. The rate of addition was kept approximately constant with slow constant stirring at 100 rpm for 5min., and then followed by faster stirring for another 5minutes at 500rpm. After complete stirring milky emulsion fuel is obtained.

Analytical measurement

Droplet size measurement

Atomic transmission microscope ATM model JEM-1230 is used for nano emulsion fuel particle size measurement. It is also used for measuring the histogram of the obtained nano emulsion blend. Max magnification of the used ATM is 600Kx with max resolving power about 0.3nm per line. Energy intensity was in the range from 40kv up to 120kv on steps.

Calorific value determination

The calorific value of the sample was measured in the Egyptian Petroleum Research Institute using Parr 6200 calorific value tester.

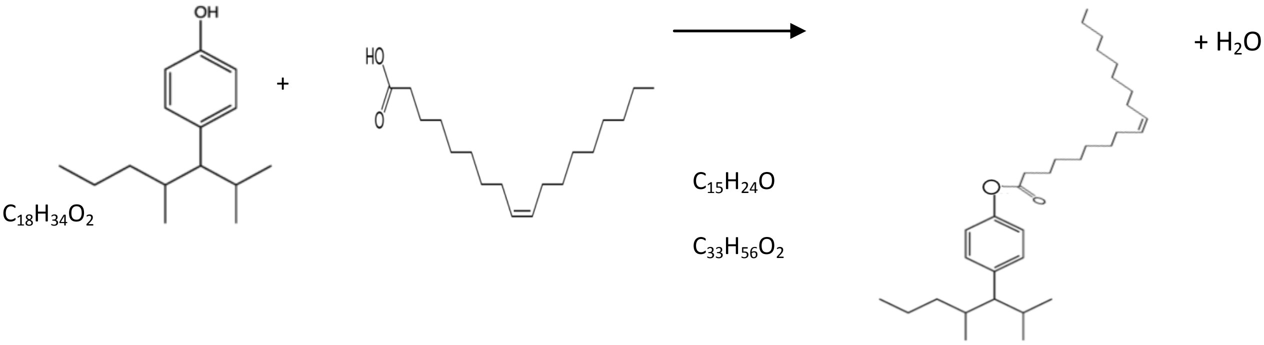
Determination of viscosity

Brook filed model DV-II**+** viscometer was used to determine the viscosity and sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 18°C. After reaching the equilibrium temperature, the viscometer tip was inserted to the sample and the reading was taken from the controller.

ISSN: 0975-8585

RESULTS AND DISCUSSION

Reaction Mechanism



The above equation presents the estimated slow reaction mechanism of nonylphenol and oleic acid in which neutralization reaction was obtained showing the formation of one molecule of water and condensation of nonylphenol and oleic acid resulting viscous dispersing agent of water in biodiesel. Also this high viscosity may be is the reason for the long stability of the obtained biodiesel nanoemulsion fuel.

Effect of nonylphenol concentration

Fig.1 shows the effect of nonylphenol surfactant concentration on the ignition time at biodiesel concentration 80%, and 1% oleic acid. The results show that as the nonylphenol concentration increases from 1.82% to 6% no significant change in ignition time is observed and the ignition times were 15.33, 15, and 15mins., respectively, while at 8% dose nonylphenol no ignition is obtained. Also the observations showed that as the nonylphenol concentration increases the flame length decreases and no flame at all was obtained at 8% nonylphenol concentration. Based on the above results 1.82% nonylphenol surfactant was selected as the optimum surfactant concentration.

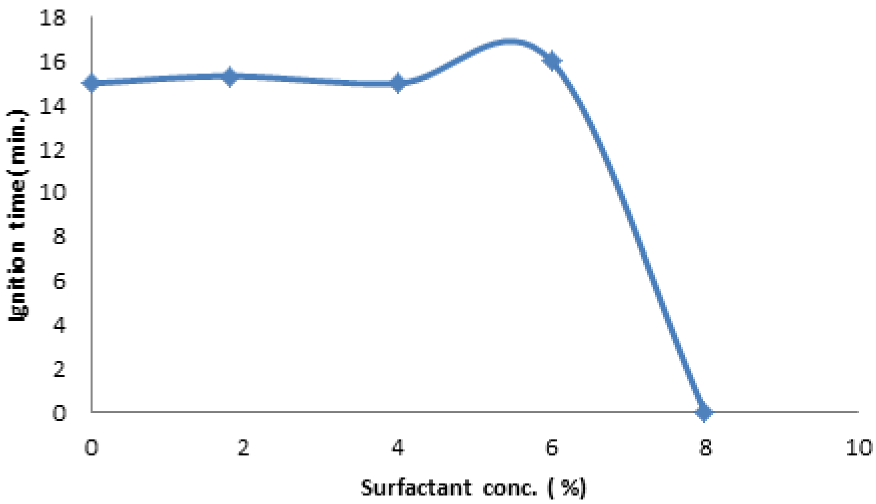


Figure 1: Effect of nonylphenol concentration on Ignition time

Effect of Water content

The effect of water content on the ignition time of the obtained biodiesel nanoemulsion fuel at nonylphenol concentration of 1.82% was illustrated in Fig.2. Biodiesel percentage normally changed with the variation of water content at 0.5ml oleic acid was added for each sample. The results showed that as the water percentage increases the ignition time decreases where it was 18minutes for 5ml raw biodiesel and decreases to 15min., 15min, and 10min. at water content 15%, 24.5% and 35% respectively. The observation shows that the flame length was the highest at raw biodiesel and slightly decreases at the rest of the sample at different water percentages. Based on the above obtained results water content of 24.5% which is balanced with 72.7% biodiesel was selected as the optimum water concentration.

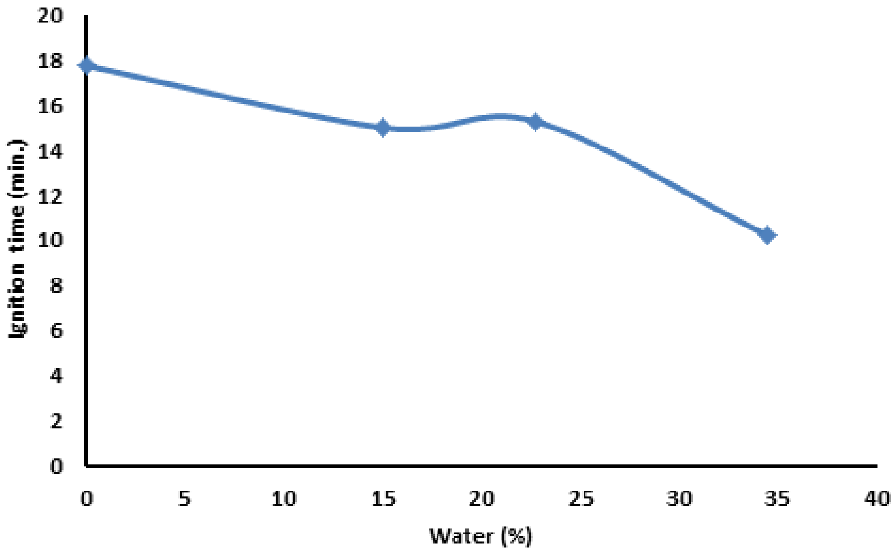


Figure 2: Effect of water content on Ignition time

Nanoemulsion stability

Fig. 3 shows the effect of water content on the observed viscosity of the obtained biodiesel nanoemulsion. It was found that as the water content increases the viscosity of the obtained biodiesel nanoemulsion increases too. Fig. 4 shows the change of the viscosity of the optimum selected composition with storage time. Biodiesel nanoemulsion prepared in this work exhibited good stability without phase separation for more than 6 months but with dramatic decrease in the viscosity. The results show that the raw biodiesel has a viscosity of 6.81MP at 18°C, while the obtained viscosity of prepared nanoemulsion at the beginning of preparation was decreased to 18 MP at 18°C then after 4 months the viscosity of the same nano emulsion reached 3.5 MP at 18°C. The decrement of the nano emulsion fuel viscosity with regard to storage time may be attributed to the continuous slow decomposition of the reaction product of nonylphenol and oleic acid.

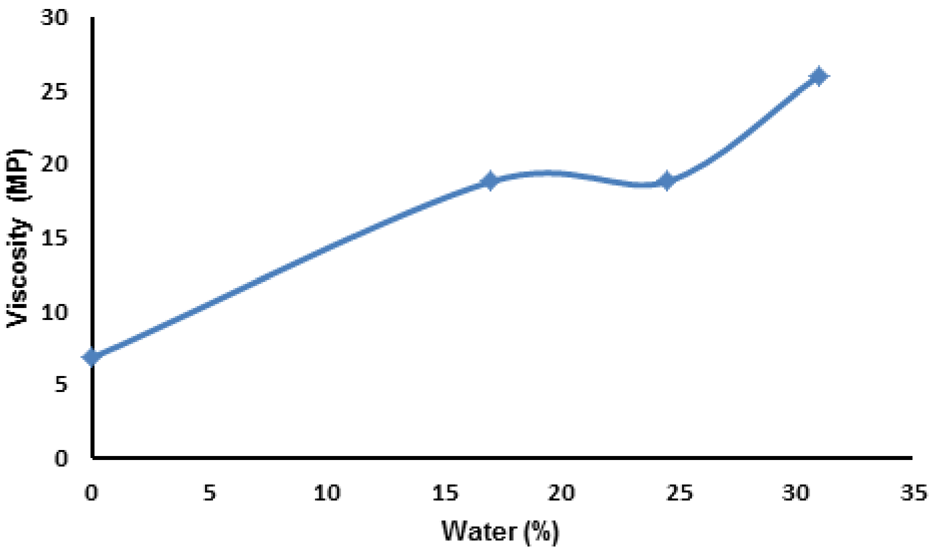


Figure 3: Effect of Water content on obtained nano emulsion Viscosity

ISSN: 0975-8585

From the above obtained data and according to the emulsion satiability, ignition time, and flame length, the following composition was selected as the optimum biodiesel nanoemulsion fuel. This composition was water percentage 24.5%, biodiesel 72.7%, nonylphenol 1.82%, and oleic acid 0.98%. This sample has a density of 0.92g/mL, viscosity of 3.5MP at 18°C at the beginning of preparation.

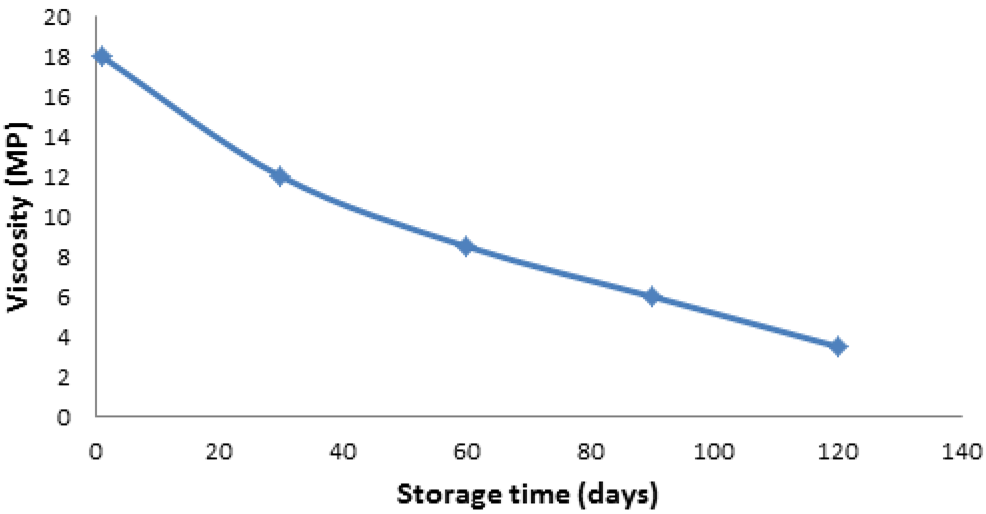


Figure 4: Effect of storage time on biodiesel nanoemulsion viscosity

ATM and Droplet size results

The optimum sample was subjected to ATM analysis for obtaining the biodiesel nanoemulsion fuel particle size and its histogram.

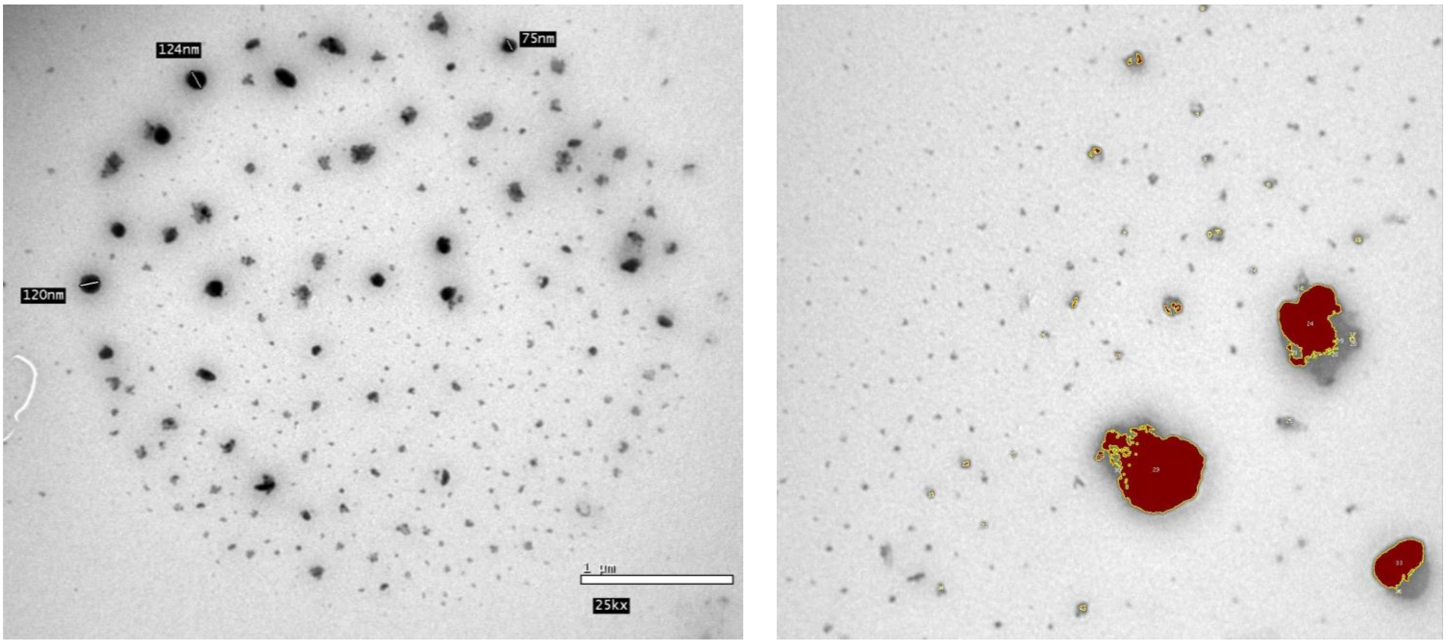


Figure 5: Photographs of ATM analysis

Fig.5 shows the ATM analysis for the measurement of selected optimum composition particle size. The analysis shows that the obtained particle sizes were ranged from 18nm to 240nm. Fig. 6 shows the histogram of the optimum sample of biodiesel nanoemulsion fuel prepared using nonylphenol and oleic acid surfactant at water percentage of 24.5%. The major particle size was 18nm (73%) and the minor particle size was 124nm (8.5%).

Calorific value

The prepared biodiesel nanoemulsion fuel under optimum conditions was subjected to calorific value tester and it is found 35.94KJ/Kg.

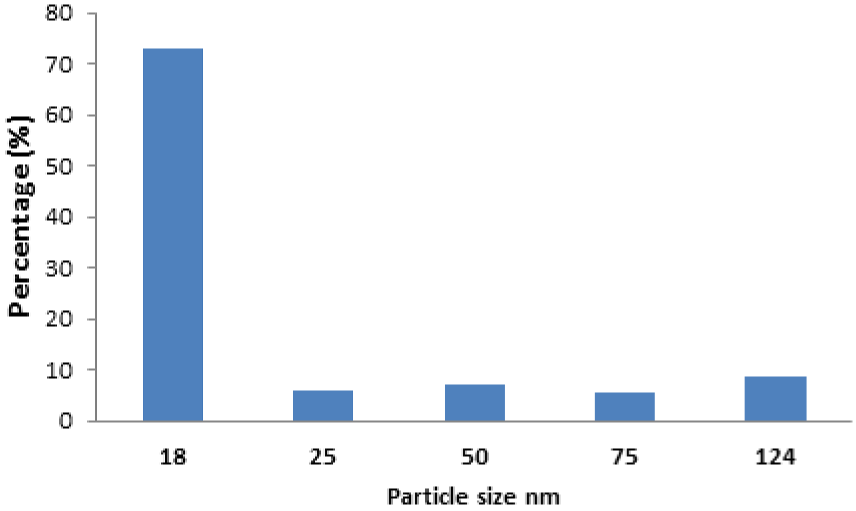


Figure 6: Histogram of the optimum composition of biodiesel nanoemulsion fuel

CONCLUSIONS

Novel formulation of water in biodiesel nanoemulsion form is successfully prepared with the composition of 72.7% biodiesel, 1.82% nonylphenol, and 0.98% oleic acid with water balance of 24.5%.

Resulted biodiesel nanoemulsion, prepared under optimum conditions, has major particle size 18nm and the minor particle size was 124nm, density of 0.92g/mL, viscosity of 3.5MP at 18°C and calorific value of 35.94 KJ/kg.

Recommendations

- It is recommended to decrease surfactant dose to ensure maintaining low viscosity by time and also studying the effect of oleic acid concentration.

- Also it is recommended to apply the prepared biodiesel nanoemulsion on the engine and investigate its effect on the engine performance, fuel consumption and so on.

REFERENCES

[1] Heywood JB. Internal combustion engine fundamentals. McGraw - Hill; (1988).
[2] Taylor AMKP. Energy Policy 36:4657-67; (2008).
[3] Z Fu, Liu, J Xu, Q Wang, Z Fan. Fuel 89; 2838-2843 (2010).
[4] Kokjohn SL, Hanson RM, Splitter DA, Reitz RD. Int.J Engine Res 12:209-26(2011).
[5] Raslavicius Lm Bazaras Z. Fuel Process Technol 91:1049-54(2010).
[6] Monyem A, Gerpen JHV, Canakci M. Trans Am Soc Agric Eng 44(1): 35-42(2001).
[7] Rajasekar E, Murugesan A, Subramanian R, Nedunchezhian N. Renew Sustain Energy Rev 14:2113-21(2010).
[8] Choi CY, Ritz RD. Fuel 78:1303-17(1999).
[9] Mello Jp, Mellor AM. No_x emissions from direct injection diesel engines with water/steam dilution. SAE paper 010836(1999).

ISSN: 0975-8585

[10] Hountalas DT, Mavropoulos GC, Zannis TC, Mamalis SD. Use of water emulsion and intake water injection as No_x reduction techniques for heavy – duty diesel engines. SAE paper no. 01-1414(2006).

[11] Psota MA, Easley WL, Fort TH Mellor AM. Water injection effects on No_x emissions for engines utilizing diffusion flame combustion. SAE Paper no. 971657; (1997).

[12] BedfordF, Rutland C, Dittrich P,Raab A, Wirbeleit F. Effect of direct water injection on Di diesel engine combustion. SAE Paper no. 01-2938(2000).

[13] Nishijima Y, Asaumi Y, Aoyagi Y. Impingement spray system with direct injection for premixed lean diesel combustion control. SAE Paper no.01-0109(2002).

[14] Kegl Bm Pehan S. Reduction of diesel engine emissions by water injection. SAE Paper no.01-3259 (2001).

[15] Udayakumar R, Sundaram S, Stiram R. Reduction of Nox emissions by water injection into the inlet manifold of a DI diesel engine. SAE Paper, 01-0264(2003).

[16] Xavier T, Alain M, Samiur RS. Experimental study of inlet manifold water engine. Energy; 35:3628-39(2010).

[17] Nazha MAA, Rajukaruna H, Wagstaff SA. The use of biofuel emulsions, water induction and EGR for controlling diesel engine emissions. SAE Paper no.01-1941(2001).

[18] Kumar MS, Bellettre J, Tazerout M. Proc I Mech E, part A: J Power Energy 223:729-42(2009).

[19] Anna L, Krister H. Adv Colloid Interface Sci 123-126:231-9(2006).

[20] Sheng HZ, chen L, zhang ZA, WU ck, An C Cheng CQ. The droplet group micro explosions in water – in-oil emulsion spray and their effects on diesel engine combustion in: Twenty fifth symposium (international on combustion / the combustion institute) p.175-81(1994).

[21] Kadota T, Yamasaki H. Prog Energy Combust Sci 28:385-404(2002).

[22] Kumar MS, Bellettre J,Tazerout M. The use of biofuel emulsions as fuel for diesel engines: a review. Proc I Mech E, part A: J Power Energy 223:729-742(2009).

[23] Sergio C. Trindade. Biofuels Engineering Process Technology (August 2011).

[24] G El Diwani, SI Hawash**,** and N Kamal. Int J Environ Sci Technol Vol 6, No 2, pp 219 – 224 (2009).