Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 11, pp.22496-22500, November, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

INVESTIGATION ON THE ROLE OF EMULSIFIER AND WATER CONTENT IN WATER IN DIESEL NANOEMULSION

Shaarawy, H. H., Nabila H. Hussien, Abdel Kader, E., *El – Araby, R. and Hawash, S. I.

Chemical Engineering and Pilot Plant Department, National Research Centre, Cairo, Egypt

ARTICLE INFO

Article History:
Received 23rd August, 2015
Received in revised form
06th September, 2015
Accepted 09th October, 2015
Published online 30th November, 2015

Key words:

Diesel, emulsion,
Nano-fuels,
Emulsification,
Nanoparticles.

ABSTRACT

The formation of nanoemulsions water – in – diesel using nonionic surfactant, nonionic emulsifier and different water content from 14 to 40% (v/v) was investigated. The effect of water content on the emulsion stability was studied. The efficiency of the formed water- in- diesel was studied by measuring open burning time, calorific value, viscosity and mean droplet sizes using atomic transmission microscope (ATM). It was found that the optimum water content was 30% at which longer burning time is obtained and the mean sizes of the formed droplets between 20 and 27 nm depending on the water content. Measuring the viscosity it was 8 cP while its calorific value was 35.9 KJ/kg while ignition time was 15.5 minutes with flame length 15 cm.

Citation: Shaarawy, H. H., Nabila H. Hussien, Abdel Kader, E., *El – Araby, R. and Hawash, S. I. 2015. "Investigation on the Role of Emulsifier and water content in Water in Diesel Nanoemulsion", *International Journal of Current Research*, 7, (11), 22496-22500.

INTRODUCTION

The main advantages of the diesel engine over the gasoline spark ignition engine are its durability, reduced fuel consumption and lower emission of carbon monoxide and unburned hydrocarbon. (Ajay Kumar and Sumeet Sharma, 2014) Diesel engine plays an important role in power generation, transportation, industrial activities and it is high interest in light duty vehicles. The transport sector solely ingests more than 50% of oil consumption. (Sood, 2012) Increasing fuel prices and impending emission regulations have sharped the automotive industries to focus on efficiency. Emission of dieselfueled vehicle have high concentration of NO_x and particulate matter so in order to reduce the vehicle emissions it needs to improve fuel quality as to minimize the pollutants. Thus, alternative energy sources based on sustainable, regenerative and ecologically friendly processes are urgently needed. Nano particles are generally having higher surface area and hence surface energy will be high and it will tend to agglomerate to form a micro molecule and starts to sediment in order to make nano particle to be stable in a base fluid. (Yanan Gan and Li Qiao, 2010) Micro –emulsions are thermodynamically stable, but nano – emulsions are only kinetically stable. (Wang *et al*., 2007; Ruckenstein and Chi, 1960; Sole *et al*., 2003) Nano –emulsions can be transparent or translucent (droplet size range 50-200 nm or milky (up to 500 nm). (Lee and Tadros, 1982; Sagitani *et al*., 1992; Forgiarini *et al*., 2001; Nabila *et al*., 2015) The use of water into diesel engines has a number of possible benefits such as it can effectively reduce the peak flame temperature (Mello *et al*., 1999; Hountalas *et al*., 2006; Psota *et al*., 1997; Bedford *et al*., 2000; Nishijima *et al*., 2002; Kegl and Pehan, 2001) and reducing NO_x emissions. The formation of emulsions with droplet size in the nanometer range (50-200nm) [Sole *et al*., 2003] can be achieved either by high – energy emulsification methods (e.g.by high – shear stirring, high pressure homogenizers or ultrasound generators) (Izquierdo *et al*., 2004; Nbila *et al*., 2015) or by low – energy emulsification [Sole *et al*., 2003] methods (e.g. phase inversion temperature). (Fernandez *et al*., 2004; Lamdfester *et al*., 2000; Wu *et al*., 2001; Uson *et al*., 2004; Tadros *et al*., 2004; Shinod and Kunieda,1983; Kentish *et al*., 2008; Lin and Wang, 2004) The objective of our present study is to maximize the role of oleic acid as an emulsifier for the conversion of dieselto nano-emulsion fuel using water.

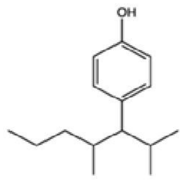
****Corresponding author: El – Arby, R.,***
Chemical Engineering and Pilot Plant Department, National Research Centre, Cairo, Egypt.

MATERIALS AND METHODS

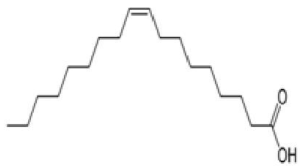
Raw Materials

In this study, commercial grade diesel, over 95% purity was used as the continuous emulsion phase.

The technical grade emulsifying agents were used throughout the current investigation namely are; 4-(2,4-dimethylheptan-3-yl)phenol (Nonylphenol)(Aldrich) and oleic acid (Aldrich). The water in all experiments was demineralized or double distilled. Chemical structures of the used surfactants were presented by the following structure in Fig. 1.



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

Figure 1. Chemical structures of the used surfactants

Preparation of nano-emulsion fuel

In our study we use magnetic stirring for the formation of the diesel nano-emulsion 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 rate of 500 rpm for dispersion characteristics of the emulsion. Preparing pre-emulsion by addition of water with different percentages (14%, to 40%) to the surfactant of nonylphenol then 0.5mL of oleic acid and diesel fuel. The rate of addition was kept approximately constant with slow constant stirring rate (100 rpm) for 5min., and then continue 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

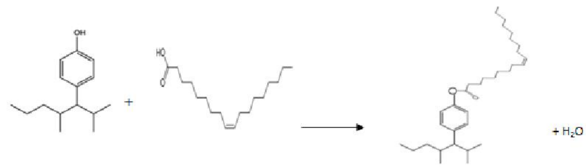
The calorific value of the samples was measured in the Egyptian Petroleum Research Institute using Parr 6200 calorific value tester.

Viscosity measurement

Brook filed model DV-II+ viscometer was used to determine the samples viscosity at room temperature 25°C, then the viscometer tip was inserted to the sample and the reading was taken from the controller.

RESULTS AND DISCUSSION

The 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 is shown by the following Equation. Also the high viscosity may be due to the long stability of the obtained diesel nano-emulsion fuel.



$C_{15}H_{24}OC_{18}H_{34}O_2$ $C_{33}H_{56}O_2$

Effect of nonylphenol concentration

Fig.2 shows the effect of nonylphenol surfactant concentration on the ignition time and flame length at diesel concentration 80%, and 3% oleic acid. The results show that increasing nonylphenol concentration from 1% to 2.8 % increases ignition time from 8 to 15.5 minutes while increasing nonylphenol from 1% to 2% increases flame length from 3 to 10 cm. More increase of nonylphenol to 3% decreases the ignition time to 14min. with very low flame length (2cm.), this may be attributed to the dramatic increment in obtained fuel composition viscosity. More addition of nonylphenol resulted viscous component without any ignition ability. Based on the above results 2% nonylphenol surfactant was selected as the optimum surfactant concentration.

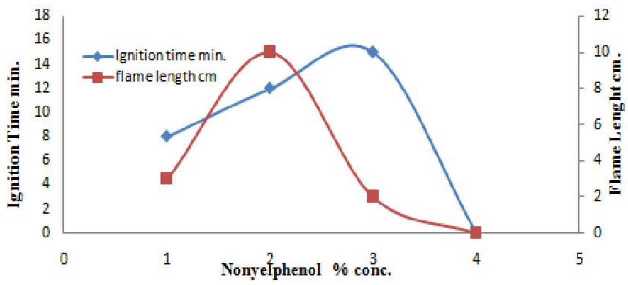


Figure 2. Effect of nonylphenol concentration on Ignition time and flame length

Effect of oleic acid concentration

From Fig.3it is clear that as the oleic acid concentration increases from 1 % to 3% both of the ignition time and flame length increases sharply from 8.5 min. and 4.5cm to 13.5minand 11cm, respectively. More increase to 4% no significant change was obtained. More increment in oleic acid concentration dramatic decrement in both ignition time and flame length was obtained reaching no ignition at oleic acid concentration 6% with very viscous liquid. Based on the above results 3 % oleic acid surfactant was selected as the optimum surfactant concentration. From the above results it is found that the optimum surfactant composition obtained for the formation of the Diesel nano emulsion fuel is 5% (containing2% nonylphenol and 3% oleic acid), at diesel concentration 80% and 15% water.

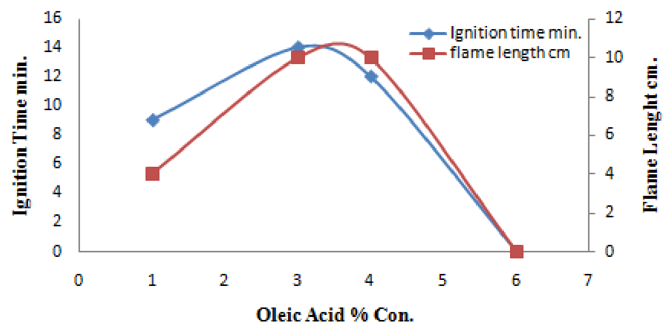


Figure 3. Effect of oleic acid concentration on Ignition time and flame length

Effect of Water content

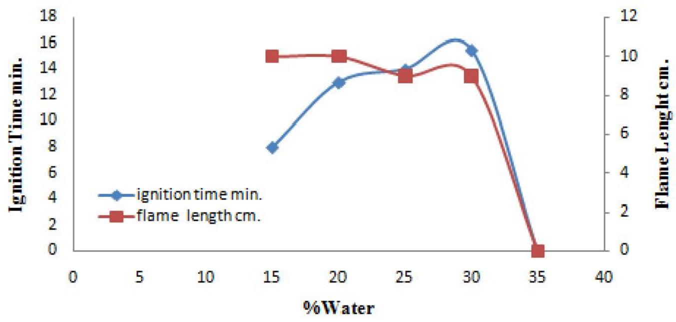


Figure 4. Effect of Water percentage on Ignition time and flame length

The effect of water content on the ignition time and flame length of the obtained diesel nano-emulsion fuel at nonylphenol concentration of 2 %, and 3% oleic acid was illustrated in Fig.4. Diesel percentage normally changed with the variation of water content. The results showed that as the water percentage increases the ignition time increases till 27.5% water percentage with low flame length. At water percentage 35% no ignition was obtained. From the above 27.5% water content was selected to be optimum composition where the ignition time was 15.5mins with flame length 10cm.

Effect of agitation method

Effect of agitation method on ignition time and flame length

It was mentioned that the method of agitation has strongly effect on the formation of diesel nano-emulsion fuel. Based on that, we use three agitation methods for preparation of the above selected optimum composition which is: nonylphenol 2%, oleic acid 3%, water percentage 27.5%, and diesel 67.5%. Those agitation methods are magnetic stirrer till 500rpm, high shear mixer (till 10000rpm), and ultrasonic apparatus of 500wt. the results obtained due to the effect of the three agitation methods is graphically presented in Fig.5. The results show that the high shear mixing gave ignition time of 17mins with flame length of 10cm, while that of magnetic stirrer was 15.5mins and 9cm,also the ignition time was 5mins with flame length 10cm and strong release of black fumes.

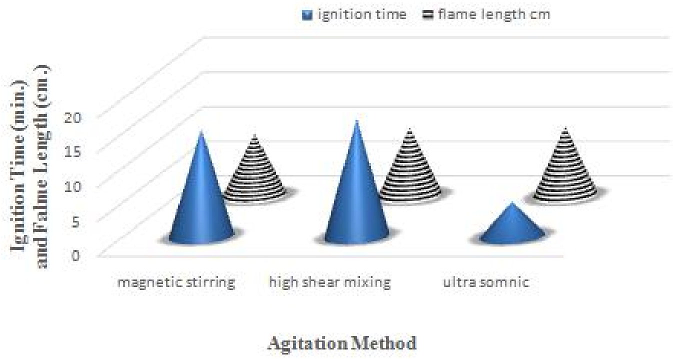


Figure 5. Effect of agitation method on Ignition time and flame length

Effect of agitation method on viscosity and emulsion stability

The viscosity obtained of the high shear mixer was 8 while that of magnetic stirrer was 21. The emulsion stability for that obtained with high shear mixing extended for more than 4 months while that of magnetic stirrer reaches to three months and start to separates to two layers. The ultrasonic sample has emulsion stability only for three hours and after that strong phase separation was obtained. Based on the above high shear mixing was selected for the preparation of the diesel nano emulsion fuel.

Effect of increasing water content using high shear mixing

In the light of the use of high shear mixing method, we try to increase the water percentage over the optimum selected before, so we try 35%, 40%, and 50%. The effect of these water percentages increments in both ignition time and flame length was graphically presented in Fig.6. The results showed that as the water percentage increases slightly decrement in the ignition time while no significant change in the flame length was obtained. So 50% percentage of water was selected as optimum.

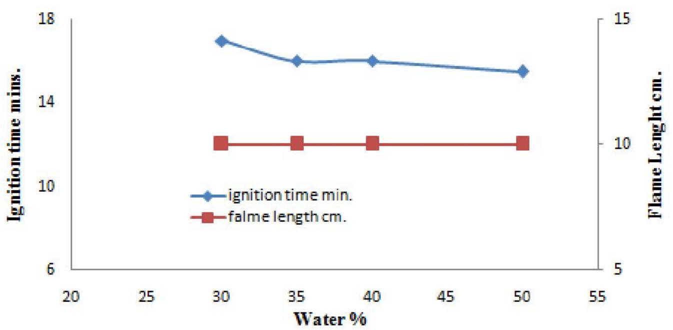


Figure 6. Effect of water percentage using high shear mixing on Ignition time and flame length

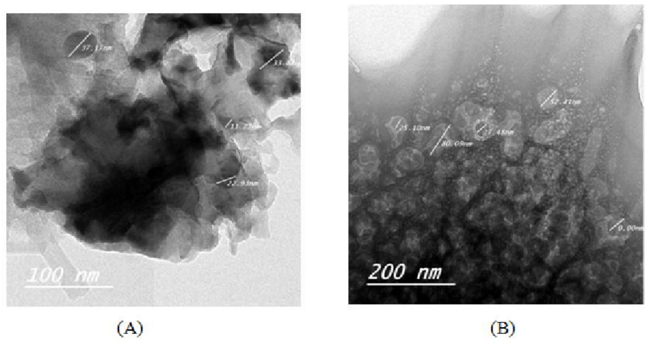


Fig.7. (A & B) the ATM analysis of the optimum selected diesel nano-emulsion fuel prepared with magnetic stirrer and high shear mixing, respectively

ATM for Droplet size results

The optimum sampleswere subjected to ATM analysis for obtaining the diesel nano-emulsion fuelparticle size and its histogram. One of these two samples was the optimum selected for the magnetic agitation and the other was the optimum selected for the high shear mixing. Fig.7 (A, and B) shows the ATM analysis for the measurement of selected optimum compositions particle size, respectively. While Fig. 8(A &B) shows the histogram of both the selected optimum samples.

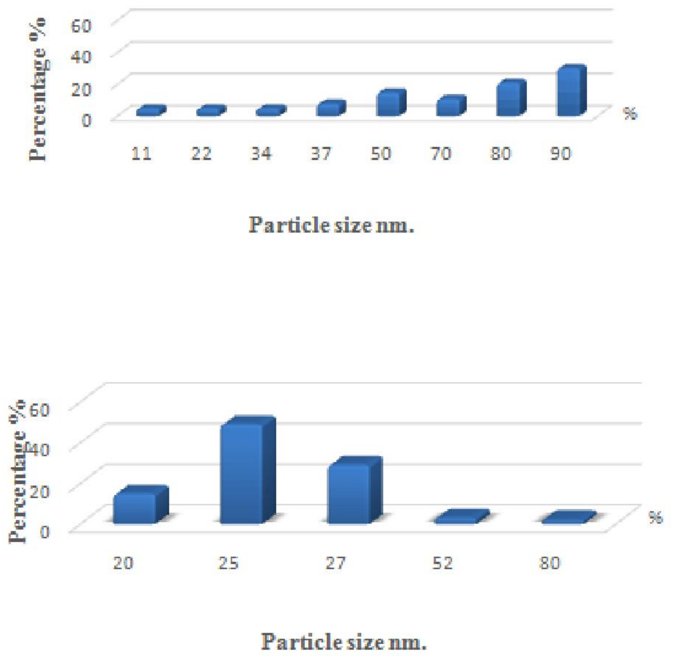


Figure 8. (A & B) the Histogram analysis of the optimum selected diesel nano-emulsion fuel prepared with magnetic stirrer and high shear mixing, respectively

It is clear that the sample prepared with magnetic stirrer gave particles size ranged with the nano size with particles overlap and the major particle size is 80nm and 90nm with 21% and 30% respectively as clear from Fig. 7A and 8A. The sample prepared with high shear mixing shows particle size ranged with the nano size with sharp particle boundaries and the major particle size are 20nm, 25nm and 27nm with 15%, 49% and 29% respectively as clear from fig. 7B and 8B.

Calorific value

The prepared diesel nano-emulsion fuel under optimum conditions was subjected to calorific value tester to measure its calorific value which was found about 40 KJ/Kg.

Conclusion

Novel formulation of water in biodiesel nano-emulsion 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 nano-emulsion, prepared under optimum conditions, has major particle size 18nmand the minor particle size was 52 nm, density of 0.92g/mL, viscosity of 8MP at 24°C and calorific value of 40 KJ/kg. Sample prepared with the high shear mixing has better performance that that prepared with magnetic stirrer. The optimum conditions for preparation of diesel nano-emulsion fuel were 2% nonylphenol, oleic acid 3%, water% 50%, and diesel of 45%. This sample prepared at agitation speed of 10000rpm for 5mins and showing viscosity of 8cP and emulsion stability of more than 4months with ignition time 15.5mins and flame length of 10cm.

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 nano-emulsion on the engine and investigate its effect on the engine performance, fuel consumption and so on.

REFERENCES

Ajay Kumar and Sumeet Sharma, 2014."Role of Emulsion and Nanotechnology in Alternative Fuel for Compression Ignition Engine: Review". *International Journal of Current Engineering and Technology,* 4(4) 2892-2897.

Bedford, F., Rutland, C., Dittrich, P., Raab, A. and Wirbeleit, F. 2000. "Effect of direct water injection on Di- diesel engine combustion". SAE Paper no. 01-2938.

Fernandez, P., Andre, V., Riegger, J. and Kuhnle, A. 2004. "Nanoemulsion formation by emulsion phase inversion." Colloids Surf", A: *Physicochem. Eng. Aspects,* 251, 53-58.

Forgiarini, A., Esquena, J., Gonzalez, C. and C.Solans, 2001. "Formation of nanoemulsions by low energy emulsification methods at constant temperature". Langmuir 17 (7), 2076-2083.

Hountalas, D.T., Mavropoulos, G.C., Zannis, T.C. and Mamalis, S.D. 2006. " Use of water emulsion and intake water injection as NOx reduction techniques for heavy –duty diesel engines". SAE paper no. 01-1414.

I.Sole, A., Maestro, C., Gonzalez, C., Solans and Jose, M. 2003. "Optimization of nanoemulsion preparation by low –energy methods in an ionic surfactant system". Langmuir, 22, 8326-8332.

Izquierdo, P., Esquena, J., Tadros, T.F., Dederen, J.C., Feng, J., Mari, J.C., Azemar, N. and Solans, C. 2004. "Phase behavior and nanoemulsion formation by the phase inversion temperature methods". Langmuir20, 6594-6598.

Kegl, B.M. and Pehan, S. 2001." Reduction of diesel engine emissions by water injection". SAE Paper no.01-3259.

Kentish, S. Wooster, T.J. Ashokkumar, M. Balachandra, S. Mawson, R. and Simons, L. 2008. "The use of ultrasonics for nanoemulsion preparation." *Innovat. Food Sci.Emerg. Technol.,* 9, 170-175.

Lamdfester, K., Willert, M. and Antonietti, M. 2000. " Preparation of polymer particles in non- aqueous direct and inversemini emulsions". *Macromolecules,*33(7),2370-2376.

Lee, G.W.J. and Tadros, T.F. 1982. "Formation and stability of emulsions produced by dilution of emulsifiable concentrates. Part 1. An investigation of the dispersion on dilution of emulsifiable concentrates containing cationic and non – ionic surfactants". Colloids Surf. A: *Physicochem. Eng. Aspects,* 5,105-115.

Lin, C.Y. and Wang, K.H. 2004. "Effects of a combustion improver on diesel engine performance and emission characteristics when using three –phase emulsions as an alternative fuel."*Energy Fuel,* 18(2),477-488.

Mello, J.P. and Mellor, A.M. 1999. " NOx emissions from direct injection diesel engines with water/steam dilution". SAE paper 010836.

Nabila H. Hussien, Shaarawy, H.H. and Hawash, S.I. 2015. "Investigation on Biodiesel Nanoemulsion Preparation and Performance". *Research Journal of Pharmaceutical, Biological and Chemical Sciences,* 6(3),1234-1241 May – June.

Nbila H. Hussien, Shaarawy, H.H. and Hawash, S.I. 2015. “Investigation on Biodiesel Nanoemulsion Preparation and Performance”. *Research Journal of Pharmaceutical ,Biological and Chemical Science,* 6(3)-1234.

Nishijima, Y., Asaumi, Y. and Aoyagi, Y. 2002. "Impingement spray system with direct injection for premixed leandiesel combustion control". SAE Paper no.01-0109.

Psota, M.A., Easley, W.L., Fort, T.H. and Mellor, A.M. 1997. "Water injection effects on NOx emissions for engines utilizing diffusion flame combustion". SAE Paper no. 971657.

Ruckenstein, E. and Chi, J. C. 1960. " Introduction to micro – and macro – emulsions". *Chem. Soc.,* 71, 2-7.

Sagitani, H. Fiberg, S. and Lindman, B. (Eds), 1992. "Emulsion and Emulsion Stabiliy". Marcel Dekker, 259-271.

Shinod, K. and Kunieda, H. 1983. in: P. Becker (Ed). Encyclopedia of Emulsion Technology, Marcel Dekker, NY.

Sood, P.R. 2012. "Air Pollution through Vehicular Emission in Urban India and Preventive Measure". *Energy and Biotechnology,* 33,45-49.

Tadros, T.F. Isquirdo, P. and Solans, J.C. 2004. "Formation and stabilityof nanoemulsions." *Adv.Colloid Interface Sci.,* 108-109,303-318.

Uson, N., Garcia, M.J. and Solans, C. 2004. "Formation of water- in – oil nano- emulsions in a water/mixed non- ionic surfactant/oil system prepared by a low- energy emulsification method."*Colloid Surf. A. Phisicochem. Eng. Aspects,* 250,415-421.

Wang, L., Li, X., Zhang, G., Dong, J. and Estoe, J. 2007. "Oil – in-water nanoemulsions for pesticide formulations". *Colloid Interface Sci.,* 314, 230-235.

Wu, H., Ramachandran, C., Weiner, N.D. and Rossler, B.J. 2001. "Topical transport of hydrophilic compounds using water in oil nano-emulsions." *Int. J. Pharm.,* 220,63-75.

Yanan Gan, and Li Qiao, 2010. "Combustion Characteristics of fuel droplets with addition of nano and micron sized aluminum particles". Combustion and Flame, 1-15.

****