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Critical Processes Involved in Formulation of Water-in-Oil Fuel Emulsions, Combustion Efficiency of the Emulsified Fuels and Their Possible Environmental Impacts

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Abstract: The aim of this study is to highlight some problems encountered during the formulation of water-in-oil (w/o) emulsions of diesel fuel. The combustion efficiency of the resultant emulsions and some pollutant gas emissions were determined. The paper also discussed possible environmental impacts of these emissions. Internal Combustion Engines (ICE) find application in many modes of transportation including marine, land and air transportation. Economic and environmental considerations have led to the quest for improved combustion efficiency of the various fossil fuels used for these modes of transportation. The possibility of combustion of emulsified fuels has been the centre of some research efforts in the search for improved combustion efficiency. Diesel is mixed with water to form fuel-oil emulsions for combustion in some internal combustion engines. Depending on certain factors, two possible types of fuel-oil emulsions can be obtained: Oil in water and water in oil emulsions. Combustibility of the resulting emulsions was investigated. In this study, neat diesel was emulsified using polyethylene glycol as the emulsifying agent to produce water in oil emulsions. The water in oil emulsion was found to be combustible within certain limits of percentage content of water and air/fuel ratios. Problems encountered in the attempts to burn the emulsions include the nature and type of emulsifying agent, the method and means of mixing, as well as stability of the emulsions. This study shows that the emulsion containing 5% water had the highest combustion efficiency. Combustion of fuels, whether neat or emulsified, has some environmental impacts. Different noxious substances as exhaust products of combustion when emitted into the atmosphere could be injurious to human health, plants and animals within or close to the operating environments. In this study, the exhaust gases were analysed and their possible environmental impacts were discussed. The emulsion containing 7.5% water produced the least percentage of carbon monoxide (CO), a highly pollutant gas. Generally, emulsified fuels produce better combustion efficiency and less negative environmental emissions than neat fuels.

Key words: Combustion rig, emulsifying agent, emulsions, fossil fuels

INTRODUCTION

Man's quest to travel faster, improve comfort, eradicate diseases, improve and increase agricultural production, alleviate poverty as well as increasing life expectancy etc., has led to the execution of several projects that in the short and long run are not environmentally friendly (Orji-Dibofori, 2004). One of such projects is the Internal Combustion Engines (ICE) used for transportation and other engineering and industrial services today (Edward and Nicholas, 1988).

ICE finds application in many modes of transportation including marine, automobile and aviation transportation. Transport accounts for nearly one-third of the total global energy consumption, and contributes about 25% of the world carbon dioxide (CO_2) output, as well as Chlorofloro-Carbons (CFCs), Methane (CH_4) and Nitrous Oxide (NO_x) emissions (Boyle and Ardill, 1989).

In the European Union (EU), 26 percent of the total anthropogenic CO_2 emissions come from transport. The threat on global climatic changes has evolved into politics of climate change (Riordan and Jager, 1995). The political, moral and legal responses to climatic changes in the midst of significant socio-economic policy shifts have been critically analysed. Climate change has been put on policy agenda of the EU and the United Nations (UN) framework conventions and subsequent conference of parties.

In the wake of the global awareness on climate change, several efforts and technologies are emerging to cut down on emission of green house gases as well as sustaining world economy for the present and future generations. Recently, bio-diesel and ethanol-petrol have been formulated as alternative fuels for automobiles and the marine industry (NNPC, 2007). Prior to this, researches had been undertaken into combustion of emulsified fuels to reduce emission of pollutant gasses (CO_2, CO, NO_X CH_3, SO_x etc.) into the environment.

The aim of this study is to highlight some problems encountered in formulating water-in-oil (w/o) emulsions of diesel fuel: the nature and type of emulsifying agent, the method and means of mixing as well as the stability of the w/o emulsions. The combustion efficiency and some pollutant gas emissions analysed in the study are also discussed. The study also discusses the environmental impacts of burning neat fuel and fuel emulsions. The benefits of using bio-fuels are also enumerated in this study.

MATERIALS AND METHODS

Emulsion formation and stability: An emulsion is a mixture of two liquids: the droplet phase referred to as the dispersed or internal phase, and the surrounding liquid, the continuous or external phase (Becher, 1965). Such systems possess a minimal stability which may be increased by the addition of various surface-active materials or finely divided solids. These surfactants are known as emulsifying agents or emulsifiers.

An emulsion consisting of water and oil can take two forms: an oil-in-water emulsion designated (o/w), in which the oil assumes the role of the internal phase; and a water-in-oil emulsion (w/o) in which the oil is the external phase. The form a particular emulsion system assumes is determined by the chemical nature of the emulsifying agent.

The stability of the emulsions especially with respect to this study is of prime importance. The emulsion has to pass through a length of tube from the mixing tank before it is admitted into the combustion chamber. An unstable emulsion would begin to separate before it enters the combustion chamber.

Means of mixing: There are several types of emulsification equipment available. These may include ultrasonic devices, colloid mills, high pressure homogenizers and mechanical mixers. In this study, the Silverson Mechanical Mixer or emulsifier was used. It is an adequate mixer that shears molecules of the liquid phases and mixes then up. This mode of operation is referred to as using "brute force" to break up the interface between the liquid phases.

Choice of emulsifying agent: The real importance of the emulsifier lies in the profound changes, especially of the electric double layers near the interfaces.

The electric double layers, controls the stability of the emulsion by hindering the coagulation of the particles. The emulsifier effects dispersion because it is a molecule with one water - loving (hydrophilic) tail and one oil-loving (hydrophobic or lipophilic) tail. It therefore makes it possible for water and oil to become finely dispersed in each other, creating a stable homogeneous, smooth emulsion.

Table 1: Hydrophile--Lipophile Balance (HLB) ranges and their applications

Range	Application
3-6	W/O emulsifiers
7-9	Wetting agents
8-12	O/W emulsifiers
12-15	Detergents
15-20	Solubilizers (or Hydrotrope)

Elshafie and Khalid (2008)

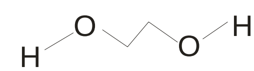

Fig. 1: Ethylene oxide

For this purpose, an emulsifier can be characterized by a number specifying its hydrophile-lipophile Balance (HLB), (Becher, 1965).

HLB for emulsifiers is still a subject of practical interest. Bancroft's rules state that the type of emulsion is dictated by the emulsifier that should be soluble in the continuous phase (Elshafie and Khalid, 2008). HLB is based on the concept that some molecules have hydrophilic groups, other molecules have lipophilic groups and some both. Weight of each group on a molecule predicts what behavior the molecular structure will exhibit. HLB values of emulsifying agents can be determined experimentally through laborious determination of emulsion stability. Griftin's method for non ionic surfactants is described as follows:

$$HLB = (20 \times M_{EO})/M_W$$

where M_{EO} = Molecular Mass of the hydrophilic moiety
M_W = Molecular Mass of the whole molecule

A HLB value of 0 corresponds to a completely hydrophobic molecule and a value of 20 corresponds to a molecule made up completely of hydrophilic components. Surfactants with low HLB values typically around 4 are more oil soluble and thus tend to make w/o emulsions, while those with high HLB values are more hydrophilic and tend to make o/w emulsions.

Table 1 gives the range of HLB numbers of emulsifiers and their applications.

The emulsifier used in this study was polyethylene glycol, a polymer of ethylene oxide, water and their esters. A single unit of ethylene oxide has a molecular weight of 2.06784 g/mol, the molecular formula: $C_2H_6O_2$ and a chemical structure as shown in Fig. 1.

Polyethylene emulsifiers vary in consistency from liquid to solid, depending on the molecular weight indicated by a number following the name. They are lipophiles used as surfactants, dispersing agents, solvents, ointments and suppository bases, vehicles, and tabletsexcipients. Some other specific groups are lauromagrogols, nonoxynols, octoxynol and poloxamers.

Mode of adding the emulsifier: In emulsion formulation, either of these methods could be used to achieve the desired objective:

- **Agent-in-water method:** The emulsifier is dissolved in the water phase and the oil added with suitable agitation. This yields o/w emulsion. However, if a w/o emulsion is desired, the oil addition must be continued until phase inversion takes place.
- **Agent-in-oil method:** This is the reverse of (i). It produces w/o emulsion directly.
- **Nascent soap method:** This is used for emulsions stabilized by soaps.
- **Alternate addition method:** Water and oil are added alternatively.

In this study, the agent-in-oil method was used to produce the w/o emulsions used.

Time of agitation: Under normal conditions of emulsification, the mean size of the particles decreases very rapidly in the first few seconds and then gradually attains the limiting value in 1-5 min. Thereafter, there would not be any appreciable reduction in size. This was the case during the formulation and stabilization of the w/o emulsion in this study.

Intensity of agitation: The principal parameter which can be varied to give different emulsions is the intensity of agitation. More efficient agitation produces a better emulsion.

The combustion RIG: The Hilton Continuous Combustion Unit used in this study is designed for research in combustion and fuel technology and for demonstration of handling and operation of typical furnace equipment. It is a constant pressure unit with a medium pressure liquid-gas burner which fires into a stainless steel water-cooled combustion chamber. The combustion unit has provision for sight glasses and tapping points.

Instruments and controls are incorporated to enable the selection of a wide range of air/fuel ratios. The burner and combustion chamber are sealed against air leakages so that the air flow measured is the total amount used in the combustion process. Exhaust gas analysis can be carried out from any point within the combustion chamber or zone. The equipment is designed to accommodate any of the standard methods for gas analysis e.g., the Orsat apparatus or Gas chromatograph. With accurate measurement of the heat absorbed by the cooling water and measurement of the exhaust gas temperature, a clear picture of the effects of the major variables which contribute towards the efficient use of liquid and gaseous fuels is obtained.

Experimental procedure:

Emulsion preparation: Different percentages of water-in-fuel (diesel) mixtures, adequately stabilized with 1% polyethylene glycol were prepared (2.5, 5.0, 7.5 and 10.0%) in stainless steel containers. By means of the Siliverson Mechanical Mixer, the mixtures were respectively mixed and agitated thoroughly for a period of 5 minutes. It is worthy of note that the emulsifying agent (1% polyethylene glycol) was dissolved in the diesel and then the required percentage of water was added with suitable agitation. The result is an emergence of different w/o emulsions. To ascertain the strength or stability of the emulsions, they were made to pass through a long tube into the combustion chamber. A stable emulsion would not coagulate or separate into the different component parts. The study recorded some failed trial runs before stable emulsions were obtained. Also, higher percentages of w/o emulsions (i.e., >10% water) were prepared, but attempt to burn them proved unsuccessful.

Combustion procedure: The combustion chamber was ignited using propane gas. When the chamber was hot enough and a steady flame created, a gradual change from the gaseous fuel (propane) to liquid fuel (neat diesel or emulsified diesel) was made. A steady mass flow rate of the fuel was achieved and the corresponding air flow rate to give the desired air/fuel ratio was calculated.

The combustion was allowed to proceed at the set conditions until steady state conditions were attained. The following readings were then taken: Exhaust temperature (T_E), cooling water outlet temperature (T_2), cooling water inlet temperature (T_1), Air inlet temperature (Ti_a), and Fuel inlet temperature (Ti_f)

Samples of the exhaust gases were taken for analysis in the Orsat Apparatus and the air, fuel and cooling water mass flow rates were also noted. The Stoichiometric air/fuel ratio of plain diesel was calculated to be 14.7:1.

RESULTS AND DISCUSSION

Effect of the emulsifying agent: The choice of an emulsifying agent is very important as it determines whether the resulting emulsion will be of the o/w or the w/o type. Emulsions for combustion processes must be of the w/o type. If any o/w emulsion is formed, its combustion will be very difficult, if not impossible, as experienced in the early experiments of this investigation.

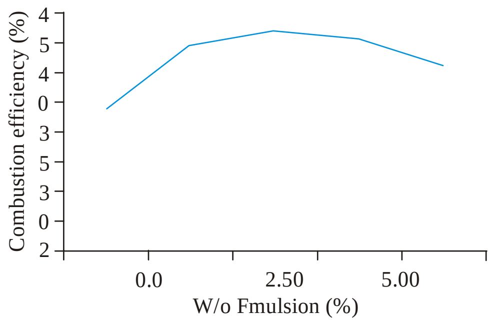

Fig. 2: Combustion efficiency v. W/O emulsion

In such an emulsion, the flame in the combustion chamber cannot be sustained by the water surrounding the oil droplets and will be rapidly extinguished. The emulsifying agent used in this study is polyethylene glycol, a polymer of ethylene oxide, water and their esters (Fig. 1).

Having obtained the appropriate agent, it is necessary to determine experimentally the suitable quantity of it to be added to the oil or water phase. In this study, the former was the case. Too small a quantity will not provide good emulsion stability, such that no sooner does the mixture leave the mixing tank than it starts to separate out. Such a situation will extinguish the flame when the separated water portion enters the combustion chamber. On the other hand, too large a quantity will cause creaming of the resulting emulsion, that can hardly burn, or would clog the pump blades, and thus impairing their movements and action. Both effects of the quantity of the emulsifying agents were experienced in the course of the experiments for this investigation. After several trials, the quantity of polytethylene glycol used was 1% by volume of the total diesel (oil) content for each composition.

Combustion efficiency: There are many ways of defining combustion efficiency based on various criteria. The criterion for the choice of the definition given by the equation:

$$\eta = [iCpi/R(Ti - To) - iCpi/P(T_E - To) - Cp_w(T_2 - T_1)]/(\Delta h_R)_F$$

where

h_R = Enthalpy of reaction of fuel
To = Reference temperature (usually 298K)
Ti = Inlet temperature of reactants
T_1, T_2 = Cooling water inlet and outlet temperatures, respectively
= Mass flow rate of Combustion Unit cooling water
η = Combustion efficiency

Subscripts F, R, P, E, W designate fuel, reactants, products, exhaust and cooling water respectively; is that the principle of the Hilton Continuous Combustion Unit is based on the exchange of enthalpies (Mayhew and Rogers, 1978).

Using the equation, the combustion efficiencies for the various emulsions were calculated and depicted in a graphical form (Fig. 2). The curves show a consistent increase in combustion efficiency compared with neat diesel: However, the efficiency decreased with increasing water content beyond 5% water content.

A lower combustion efficiency of neat fuel compared to the w/o emulsions could be attributed to the physical property of water. Water has a lower boiling point (100ºC) than diesel fuel (200-400ºC). Thus when the emulsion with water droplet dispersed in the oil undergoes combustion; the water will be surrounded by a diffusion flame from which heat is transferred into the drop (Jarvis, 1975).

The water will begin to vaporize before the bulk of the oil. Super heated boiling or spontaneous nucleation occurs "explosively". This results in vaporization of the water in part and impart of kinetic energy of the oil. The overall effect is the breaking into smaller molecules or atomization of the diesel oil resulting in higher combustion efficiency compared with the neat fuel.

Pollutant gas emissions and their environmental impacts: Four exhaust gases were measured and quantified using the Orsat Apparatus. These are: CO_2, CO, O_2, and N_2. The 5% w/o emulsion yielded 13.0% CO_2 with <0% CO, while neat fuel (diesel) yielded 9.5% CO_2 and 0.2% CO. The higher CO_2 emission from 5% emulsion could explain its greater combustion efficiency (41.6%).

Table 2 gives a summary of percentages of the exhaust gases emitted from neat fuel and the emulsions with their respective combustion efficiencies.From this study, emulsification of diesel (w/o) improved combustion efficiency of the fuel, as shown in Fig. 2.

However, the amount of CO_2 emission from the emulsions was high enough to be of environmental concern. At high temperatures as are obtained in furnaces and automobile engines, nitrogen combines with oxygen to produce oxides of nitrogen (NO_X). Ordinarily, at normal atmospheric temperatures, nitrogen and oxygen in air may not pose pollution problems. The volumes of nitrogen (73.4-75.9%) and oxygen (8.2-15.8%) measured at the exhaust are high enough to produce nitrous oxides considering the high exhaust temperatures. CO emission was not produced at an appreciable level. Obviously, the formulation of emulsions from water and diesel could be used to drive diesel engines, to cut down on the use of neat fuel.

Table 2: Percent gaseous emissions and combustion efficiencies of neat diesel, and w/o emulsions

W/O emulsion (%)	CO_2	CO	N_2	O_2	H_2O	Combustion efficiency
0% (Neat fuel)	9.5	0.2	74.6	12.0	3.9	27.0
2.5%	9.0	<0	75.2	12.1	3.7	39.4
5.0%	13.0	<0	73.4	8.2	5.4	41.6
7.5%	5.9	<0	75.9	15.8	2.4	39.9
10.0%	7.5	<0	74.8	14.6	3.1	35.0

CO_2, NO_x, CH_4, and tropospheric (ground level) Ozone (O_3), with other potentially harmful chemicals including carbon tetrachloride, are gases that are released during human activities. They have an overall warming effect on the global climate (Houghton *et al.*, 1990). These gases absorb infrared radiation in the range 7-12 μm, which is part of the "window" through which more than 70% of the radiation emitted from the surface of the earth escapes into space. They cause radiative forcing, a measure of their ability to perturb the heat balance in a simplified model of the Earth-atmosphere system. According to Houghton *et al*. (1992), the contribution made by the main green house gases to global warming breaks down as follows: 72% due to CO_2, 18% due to CH_4 and 10% due to nitrous oxide.

Global awareness on world climate change is the current topical issue. Humanity is faced with the challenge of extremes of weather conditions, floods, heat waves, draughts, etc. (Kemp, 1994).

Most recently in December, 2009, United Nations (UN) climate change conference was held in Copenhagen. For the first time, the shipping industry was singled out for regulation (The Motorship, 2009).

It is certainly true that in terms of tons moved per mile, ships have lower Carbon dioxide emissions (3%) than other forms of bulk transport. But on the hand, looking at total emissions, ships are responsible for high levels of harmful substances such as Sulphur and particulate matter via emission of smoke and soot. Transport (i.e., shipping and aviation) has been excluded from previous international protocols on emissions but the general view is that this cannot last.

There is the need to formulate technologies that would keep in check the emissions of pollutants into the environment despite human activities. Improvements should continue to be gained through automobile, ship and aircraft designs and operational efficiency to guarantee overall CO_2 emissions reduction.

In addition to such designs and operational efficiency, fuels that are environmentally friendly should be encouraged for use. Bio-diesels and ethanol-fuels abound. Countries already using ethanol fuels include: USA: E10, E85; Brazil: E10, E85; Argentina; E15; Germany: E10; China: E10, and Thailand: E10. USA and Brazil have already developed Flexible Fuel Vehicles (FFV). These are Cars/Trucks that can run any blend of unleaded gasoline with ethanol i.e. engines run on E10; E85. Installed computer in the fuel system automatically compensates for the varying amount of ethanol in the fuel to assure optimum performance.

The benefits of using ethanol petrol (and bio-diesel) may therefore include:

- Higher Octane rating
- Fuel burns cleaner and produces fewer harmful emission
- Has lower auto ignition temperature
- Fuel is more environmentally friendly
- Reduces effect of global warming
- Fuel (E10) can be used in all cars
- Oxygenates can be produced from renewable sources such as corn, sugar cane, cassava etc.
- The fuel is expectedly cheaper than conventional fuels (NNPC, 2007)

CONCLUSION AND RECOMMENDATION

Preparation of stable emulsions presented a lot of problems. It requires an emulsifying agent to produce stable distillate fuel emulsions (diesel is a distillate fuel). The choice of emulsifying agent is very important as a w/o or o/w emulsion can be obtained, depending on the chemical nature of the agent.

Successful combustion of fuels emulsified with water can only be achieved if the emulsion is of the water-in-oil (w/o) type. The limit on the percentage water content of an emulsion for effective and controllable combustion depends on the chemical nature of the emulsifying agent (which must be of the w/o type or a lipophile) and the mixing device employed.

Over the range of emulsions burnt during the experiments, the emulsified fuels exhibited characteristic higher combustion efficiency than the neat diesel fuel under the same conditions. The maximum efficiency in each case, was obtained with emulsions containing 5% water.

Water-in-oil emulsions did not reduce the emission of pollutant gases per se. In the past such formulation would have been welcomed as shipping companies would have embraced a fuel with higher combustion efficiency. But with the present trend of global events, interest is directed to operations that are rather environmentally friendly in terms of low pollutant emissions.

Bio-fuels utilizing appropriate oxygenates are being formulated especially in the developed World. The developing World should also welcome this development. The use of bio-fuels for the automobile, aviation and shipping industries is highly recommended. These Sectors are known to introduce the greatest amounts of pollutants into the atmosphere through exhaust emissions. The use of bio-fuels, apart from being environmentally friendly would create more job opportunities in the agro sector of the economy. The net effect is a shift from over dependence on fossil fuel as the primary source of energy to renewable energy source (Oxygenates). The World therefore should embark on projects that would sustain the present and future generations.

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