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A Compilation of Conventional Fuel Additives

A literature review of chemical additives in diesel and biodiesel fuels for improved combustion

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***Abstract*— With the rise of carbon emissions into the atmosphere on a worldly scale, there exists a need to improve the efficiency of the internal combustion engine. This research review seeks to answer that need through the use of chemical additives. Not only has published research shown that chemical additives can decrease carbon emissions and other particulates, but that they can also improve conductivity, modify friction, demulsify, dehaze, and other types of efficiency. Furthermore, research has also been conducted on mixtures of chemical additives with diesel and biodiesel fuel that will be discussed in this report to show even more possibilities of efficiency through the use of chemical additives. Therefore, the purpose of this research is to study the efficiency of chemical additives on internal combustion engines, as well as the plausibility of such a product to exist, in the hope of developing a device that can be brought to market in the near future.**

Keywords*— *additives; diesel; biodiesel; combustion; flame temperature; emissions; power; torque; climate change

I. Introduction

Internal combustion engines (ICE) produce an average of 4.6 metric tons of carbon dioxide per year, according to the EPA. In turn, this grandiose amount of carbon dioxide has escalated to the point where the average temperature of the world is rising. This rise of temperature has devastating effects on not only health and ecosystems, but also the economy, as weather keeps getting more extreme to cause frequent destruction. Though the solution to stop using internal combustion engines seems simple, it is not easy to implement, as many individuals do not have the means to change their routines. That being said, a need exists to improve the efficiency of the internal combustion engine so that this climate crisis can be resolved.

It is believed that an engine utilizing chemical additives could be a solution to improving engine efficiency, as it would have the ability to handle the extreme conditions of heat, pressure, and possibly abrasion that combustion creates inside of a cylinder. Although this may seem like an easy improvement to the production of engines, the manufacturing of such a product can be quite difficult and expensive.

Research findings have been conclusive that various additives could indeed be utilized in diesel and biodiesel fuels to improve environmental emissions and engine performance. However, there has yet to be a standardized fuel substitute on the market. This indicates that further research and ultimately production still needs to be done. Therefore, this paper seeks to limit the potential additives that could be brought to market into a comprehensive list, while questioning other additives that have yet to be tested, in the hopes of bringing a product to market sooner to help the internal combustion engine, and ultimately the climate crisis.

II. Background

Because combustion is the driving force of engines, there exists a need to better the process, while limiting the amount of fuel required and byproducts emitted. One way to do this is to decrease the ignition delay in the engine. Ignition delay is the amount of time between the injection of fuel and the beginning of combustion, consisting of a physical and chemical delay of the system. The time of the fuel to be ready for combustion via injection is the physical delay, while the chemical delay is due to the temperature of the system and the properties of the fuel. Therefore, if the physical delay is improved by bettering the combustion chamber, injector, and injection pressure, then the ignition delay could be improved. Likewise, the chemical delay could be improved by bettering the fuel properties to have a higher cetane number, perhaps lighter weight, lower viscosity, higher exhaust gas temperature, greater fuel atomization, lower heating value, etc. Therefore, if an additive were added to the fuel to enhance these types of properties, better combustion will occur (1).

The physical amount of fuel consumed also influences the amount of byproducts. The brake specific fuel consumption describes this parameter and is defined as the quantity of fuel used by an engine for each power output unit. By decreasing the amount of fuel required, there will be less harmful waste products emitted such as oxides of nitrogen (NO_x), oxides of carbon (CO_x), and hydrocarbons (HC). Furthermore, by decreasing the amount of fuel required, the natural resource can be conserved. It should be noted that a concern by many researchers is that biodiesel may in fact increase fuel consumption due to its low energy content, in turn having a negative environmental effect in the long run (2). That being said, an additive that reduces the specific fuel consumption of the engine would be favorable in society.

Smoke emissions, a mixture of fog and smoke (SMOG) is also of concern for society that is a major product of internal combustion engines. A fuel with a higher viscosity, as well as density, potentially causes a greater likelihood of SMOG, due to its effect on the mixture's atomization and the evaporation in the engine's cylinder. Therefore, if an additive were used to decrease the viscosity and density of the fuel, as well as decrease the oxidation temperature and increase atomization, then the SMOG will likely decrease, and the negative emissions will decrease.

Likewise, viscosity is an important factor when looking into fuel alternatives. For example, many researchers realized that one of the largest drawbacks of biodiesel is its high viscosity. With a higher viscosity, fuel injectors often struggle, and a higher temperature is often required for combustion, causing incorrect atomization and thus incomplete combustion. Note that atomization is the action of the liquid fuel being broken into smaller pieces, like a spray, before undergoing a phase change to a vapor. If the droplets are smaller, there is greater surface area, and thus there is more ability to be exposed to heat to make the phase change quicker and easier. If there is inefficient atomization, the fuel stays as a liquid, likely making its way out of the system as waste byproducts impacting climate change. It also can ruin the engine performance and cause the engine to require more fuel consumption. That being said, an additive that decreases the viscosity of the fuel, and thus potentially increasing atomization, would be beneficial for the environment and engine performance (3,4).

Overall, there are many factors that improve internal combustion engines that additives can provide, which will be discussed in section 3. The types of chemical additives that have proven to exhibit these characteristics, and those that have not, will be discussed in section 4. Then, the combination of chemical additives in biofuel will be discussed in section 5.

III. Additive Effects on Diesel Fuel

A. *Reduction of Emissions*

Many studies have been conducted that study the effect of fuel additives on pollutants such as oxides of carbon, hydrocarbons, and oxides of nitrogen. A recent study by Celik et al. found that an organic based manganese fuel additive could decrease carbon emissions created by internal combustion engines while still improving the torque and power of the system (1).

Another study by Vigneswaran et al. found that an aqueous plus 1,4-dioxane and Triton X-100 additive also reduces carbon emissions up to a certain concentration, as seen in Fig. 1. At lower loads, the DWSA15 had the fewest CO emissions by volume, as seen in Fig. 1, which is 15% 1,4-dioxane and 85% DWS. DWS is 89% diesel, 10% water, and 0.2% Triton X-100 (a surfactant). However, at the peak load, the team found that carbon monoxide emissions were reduced by almost 20% compared to diesel for a solution of DWSA5, which is comprised of 5% 1,4-dioxane and 95% DWS. This shows instability if the product were brought to market. However, hydrocarbon emissions decreased by almost 40% compared to diesel fuel for DWSA5, as seen in Fig. 2. Unfortunately, oxides of nitrogen actually increase for DWSA5 in comparison to diesel, as seen in Fig. 3 (5). This finding has also been supported in other literatures using other chemical additives which will be further discussed in section 4.

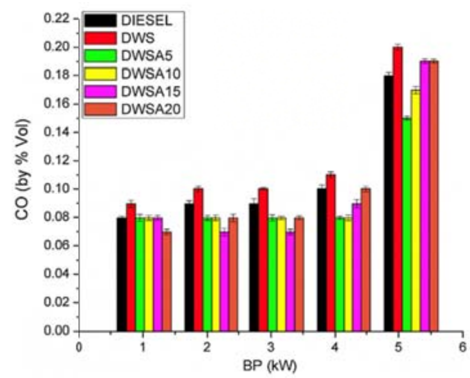

Fig. 1 CO Produced with Variable Brake Power

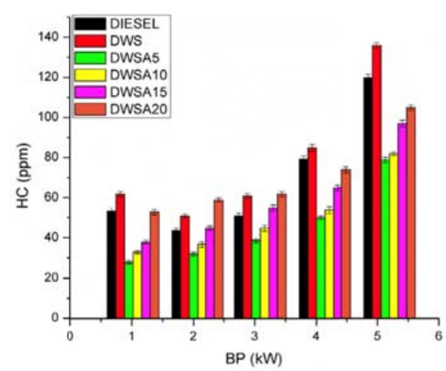

Fig. 2 HC Produced with Variable Brake Power

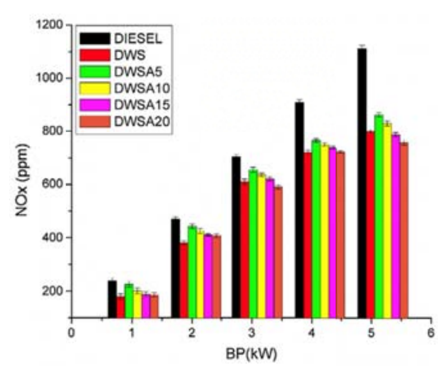

Fig. 3 NO_x Produced with Variable Brake Power

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B. Reduction of Specific Fuel Consumption

A reduction of specific fuel consumption is vital when the goal is to reduce carbon emissions and conserve resources. Brake specific fuel consumption is a better comparison of fuel consumption quantity, as it is the rate of fuel consumed by the power produced. The primary method to decreasing fuel consumption is to improve combustion. That being said, additives that accelerate combustion, decrease ignition delay, boost calorific values, decrease the time of burning, and allow for faster oxidation, could ultimately improve combustion and thereby improve specific fuel consumption. Metal additives, which will be discussed later in section 4.1, have been reported by multiple sources to exhibit these traits and more, including decrease friction on the engine parts, which also decreases the specific fuel consumption (1, 6, 7, 8). Other additives such as antioxidants have also shown to decrease specific fuel consumption, but unfortunately no justifications have been stated as to why aside from their oxidation properties and chain reactions (9,10). That being said, as previously noted, using solely biodiesel as a fuel alternative has shown to increase fuel consumption rates in multiple case studies, but when used in conjunction with additives may prove to be a sustainable option, which will be discussed in section 5 further (11,12).

C. Increasing Power and Torque

A recent study by Celik et al. found that an organic based manganese fuel additive could decrease carbon emissions created by internal combustion engines while still improving the torque and power of a single-cylinder diesel engine. Because of the higher rate of combustion due to the lower viscosity and density created by the metal additive, in conjunction with the lower heating value, more power and torque in the engine are created. In the study, four different dosages of manganese (Mn) were added to conventional diesel fuel: 4ppm (D0Mn4), 8ppm (D0Mn8), 12 ppm(D0Mn12), and 16ppm (D0Mn16). The properties of these fuels can be seen in Table 1 (1).

TABLE I. PROPERTIES OF MN ADDITIVE DIESEL FUEL

Parameter	Diesel	D0Mn4	D0Mn8	D0Mn12	D0Mn16
Viscosity (mm^2/s, 40℃)	2.5	2.4	2.34	2.25	2.18
Density (kg/m^3, 15℃)	0.84	0.833	0.830	0.828	0.827
Flash Point (℃)	64	62	59	58	57
Lower heating value (MJ/kg)	41.13	41.19	41.22	41.24	41.25

1) Test Set Up for Mn Additive Diesel Fuel by Celik et al.

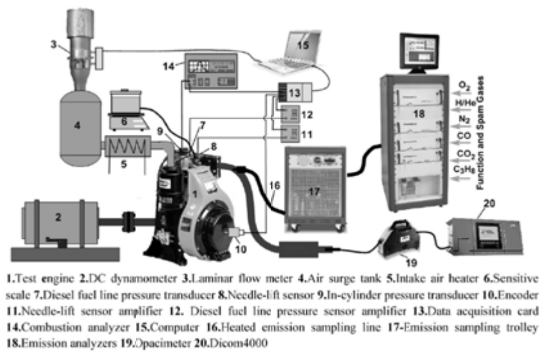

Fig. 4 Schematic Representation of Engine Test Bed (1)

2) Results

It was found that an increasing amount of manganese, up to a certain threshold, increased the power and torque of a single- cylinder diesel fueled engine. Thus, the proper concentration of additives is vital and using too much can cause detrimental effects. That being said, the optimal concentration of manganese in this test was found to be 12ppm, producing a maximum torque of 24.52Nm at 2200 rpm. Past this dosage, at 16ppm, the torque and power decreases. The data of each dosage is located in Fig. 5 and Fig. 6 (1).

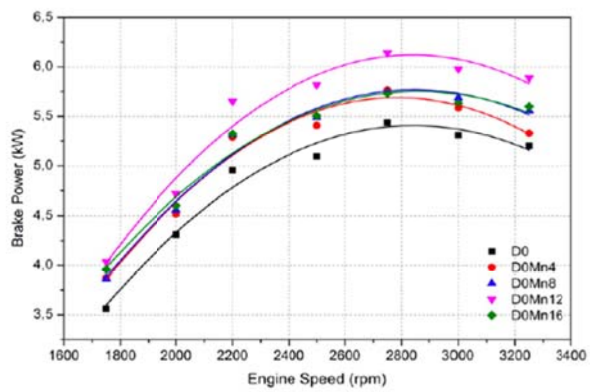

Fig. 5 Engine Power Produced with Variable Mn Additive (1)

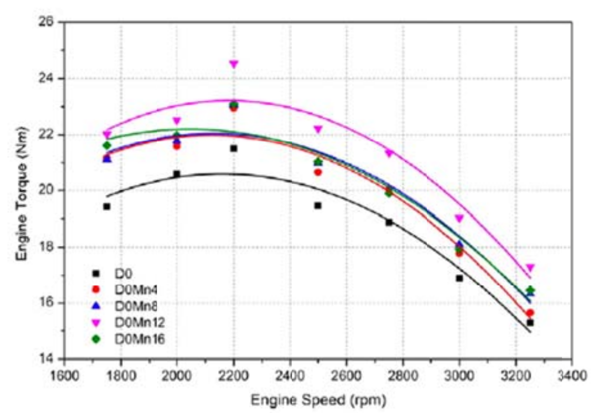

Fig. 6 Engine Torque Produced with Variable Mn Additive (1)

From Fig. 6, the 12ppm dosage of Mn appears to be an optimal outlier, producing the greatest maximum torque by far. It is unfortunate that the 16 ppm dosage decreased the torque and power, however it raises the question of what the optimal dosage actually is if it is brought to market, as it could potentially be in between 12ppm and 16ppm. The improvements in the torque and power are expected to be because of the improved combustion and better mixing with air due to the catalyzing properties of manganese. Furthermore, the greatest indicated mean effective pressure and the maximum heat dissipation was found in the 12ppm dosage. This is due to the high cetane number, effectively decreasing the ignition delay, and therefore increasing combustion faster and allowing for greater power to be achieved. Overall, it can be concluded that manganese as an additive can increase engine performance by improving the fuel viscosity, heating value, flashpoint, and density, thanks to the study conducted by Celik et al (1).

D. Noise and Vibrational Effects

Metal additives with conventional diesel fuel have shown promising results amongst a plethora of research studies. However, the optimal concentration or ratio of additives to fuel has not been discovered yet, as many other factors aside from chemical emissions play a major role in the commercialization of internal combustion engines such as noise and vibration. One case study at Cukurova University tested two different blends of Titanium (IV) Dioxide (TiO_2), Copper (II) Nitrate ($Cu(NO_3)_2$), and Cerium (III) Acetate Hydrate ($Ce(CH_3CO_2)_3H_2O$) in a single cylinder diesel engine. Although only two different blends and dosages were used, the purpose of the test was not to study emissions, but rather the physical effects of the engine, primarily the vibration. In each variable blend, the primary additive component was Titanium (IV) Dioxide (TiO_2). The first 50 ppm blend, deemed DTiCuN50 was composed of 25 ppm TiO_2 and 25 ppm $Cu(NO_3)_2$ with diesel fuel. The first 100 ppm blend, deemed DTiCuN100, was composed of 100 ppm TiO_2 and 100 ppm $Cu(NO_3)_2$ with diesel fuel. The second 50 ppm blend, deemed DTiCeA50 was composed of 25 ppm TiO_2 and 25 ppm $Ce(CH_3CO_2)_3H_2O$ with diesel fuel. The second 100 ppm blend, deemed DTiCeA100 was composed of 50 ppm TiO_2 and 50 ppm $Ce(CH_3CO_2)_3H_2O$ with diesel fuel (13). The properties can be seen in Table 2.

TABLE II. PROPERTIES OF THE FUEL BLENDS (13)

Fuel	Cetane Number	Density (kg/m^3)	Viscosity (mm^2/s)	Heating Value (MJ/kg)
EN590	Min 51	820-840	2-4.5	-
Diesel	56.86	835.3	2.699	44.63
DTiCuN50	57.17	836.3	2.759	45.18
DTiCuN100	57.51	837.4	2.799	45.22
DTiCeA50	57.21	836.1	2.719	45.19
DTiCeA100	57.53	837.2	2.739	45.23

1) Test Set Up for Vibration and Noise Analysis of Blends

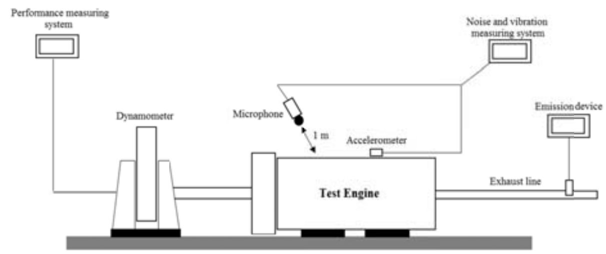

Fig. 7 Schematic Representation of Test-Rig (13)

The exhaust, vibration, and noise emission effects were all examined on a single cylinder VCR diesel engine with two variable loads of 4Nm and 8Nm at a constant 1500 rpm and two variable compression ratios of 17:1 and 18:1. The calculations are as follows:

$$a_w = \sqrt{\frac{1}{T}\int_0^T a_w^t(t)dt} \quad (1)$$

Where;
a_{total} is total acceleration
T is a measurement time

$$a_w = \sqrt{a_{vertical}^2 + a_{lateral}^2 + a_{longitudinal}^2} \quad (2)$$

Where;
$a_{vertical}$ is the vertical axis acceleration
$a_{lateral}$ is the lateral axis acceleration
$a_{kongitudinal}$ is the longitudinal axis acceleration

2) Results

It should be noted that the CO and HC emissions were lowest using the DTiCeA100 blend at the higher compression ratio, and the lowest NOx emissions were with DTiCeA50. It was also found that the brake specific fuel consumption decreased when using metal chemical additives. This was not the focal of this piece, however, as the concept of using a metal chemical additive with fuel to better fuel consumption and emissions is not new, which will be discussed in section 4. Nevertheless, it is good that this research supported prior research findings.

Again, the focus of this article was to examine the effects of nanoparticles on the vibration and noise of the engine, as without proper mechanical efficiency then additives are not a plausible solution. It was found that addition of various metal additives decreased the vibration experienced by the engine block. Again, this also is in agreement with case studies performed by other researchers. That being said, in this study, the greatest decrease in vibration was found using DTiCuN100 and DTiCeA100. The results can be seen in Fig. 8 and Fig. 9. It should be noted that vibration can be influenced by other parameters such as engine fittings, cooling conditions, burning pressure, and many more (13).

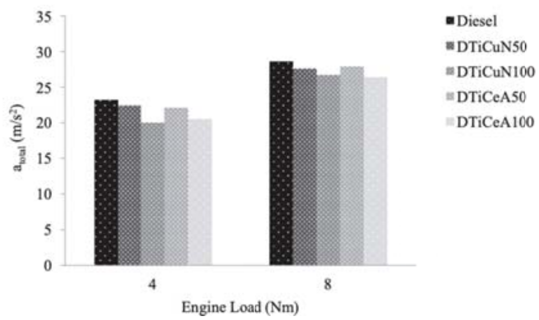

Fig. 8 Vibration with Various Test Fuels at 17:1 Com. Ratio (13)

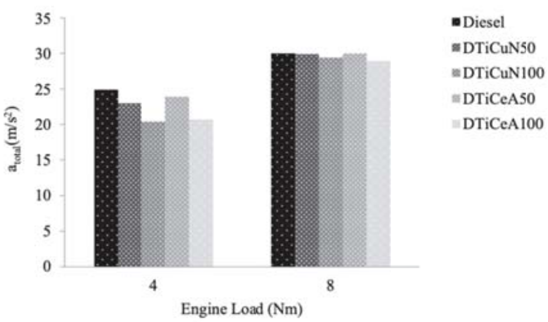

Fig. 9 Vibration with Various Test Fuels at 18:1 Com. Ratio (13)

Although minimal, there was also a decrease in the sound pressure of the engine when using metal chemical additives in comparison to just using diesel fuel. The results of this can be seen in Fig. 10.

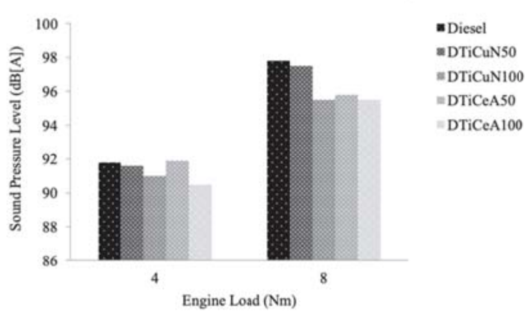

Fig. 10 Sound Pressure Results using Various Test Fuels (13)

Thus based on this particular case study and other current work, it can be seen that a Cerium (III) Acetate Hydrate ($Ce(CH_3CO_2)_3H_2O$) additive could be used to decrease noise, vibration, CO emissions, and HC emissions in conjunction with diesel fuel.

E. *Reduction of Ignition Delay*

Ignition delay is the time between the fuel injection and the start of combustion inside of the engine. This delay consists of both chemical and physical attributes. Physically, the atomization of the fuel, best visualized with a spray injector, is where the vaporization of the air and fuel mixes. Chemically, it is the time attributed to giving chemicals of performing pre-combustion reactions. That being said, in order to maximize combustion, it is best to minimize the time given to the chemicals to do other additional reactions. Thus, unnecessarily long ignition delays can cause detrimental reactions to occur in the premixed phase of combustion inside the engine. Furthermore, by decreasing the ignition delay, other parameters such as brake specific fuel consumption, as mentioned prior, could also decrease due to the reduction of capable fuel burning (14, 15). Contributing factors, besides physical parameters such as bettering the injector, to decreasing ignition delay include increasing the cetane number of the fuel, adding esthers to the fuel, using fuel with a lower temperature reactivity and heating values, lower viscosity, and more. Therefore, if additives were used to apply these factors and ultimately decrease ignition delay, then better combustion would result. Types of additives that have shown to decrease ignition delay will be discussed in section 4.

F. *Reduction of Smoke Emissions and Opacity*

Smoke emissions are another necessary factor that should be decreased in the future of this industry. Comparable smoke emission levels in various brake powers can be seen in Fig. 11. A few researchers, such as Vigneswaran et al. who were mentioned in section 3.1, found that their DWS mixtures have substantially lower smoke at various brake powers, when compared to diesel fuel (5). This was due to the improved atomization of the lower viscosity fuels. Because this mixture contained water, when passing the 100 °F temperature, more evaporation takes place, acting almost as a secondary atomization. In turn, a lower smoke emission was experienced, by approximately 25% when compared to the pure diesel. This finding of water as an additive was also conclusive in a study conducted by Yilmaz (16). Therefore, a reduction of smoke emissions is a possibility due to fuel additives.

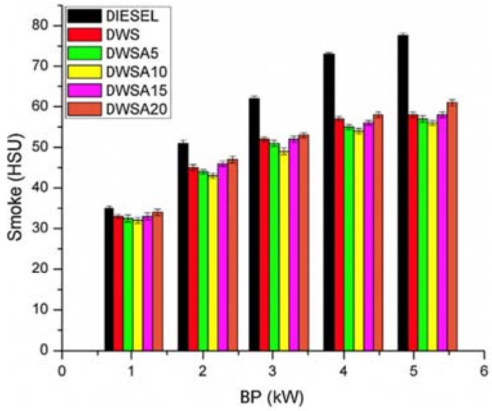

Fig. 11 Smoke Emissions of Various Brake Powers (5)

IV. Chemical Additive Types

There are many types of additives that have proven to induce the qualities and characteristics discussed in section 3. They will be discussed in the section herein, along with one definitive additive that is counterproductive in section 4.4. This is in hopes of narrowing down potential candidates that can be brought to market.

A. *Metallic Nanoparticle Additives*

Common metallic additives that have been studied for diesel engine performance and environmental emissions include zinc, zirconium, aluminum, platinum-cerium, titanium, nickel, manganese, copper, and more. Most metallic nanoparticle additives are either bimetallic or organic metallic. Organic metallic additives, such as MgO which was discussed earlier, readily dissolves homogenously into diesel fuel while the bimetallic are not easy to blend but could be combined with another material to overcome this challenge. For example, Ganesh et al. understood that Al-Mg additives could improve engine performance and emissions but knew that blending was a challenge, and therefore coated their additives with cetyl trimethyl ammonium bromide (17).

Multiple researchers have made claims the reason that metallic additives reduce emissions is due to their high cetane number, lower soot oxidation temperature, and secondary atomization properties (18, 19, 20, 21).

1) *Metallic Nanoparticle Emission Effects*

Many types of metallic additives have proven to decrease emission rates. Manganese (Mn) has shown to decrease various types of emissions in multiple case studies. One in particular by Lenin et al. showed that using 100 mg/L of MnO could decrease CO emissions by 37% in comparison to neat diesel during full load. It was also found that CuO additive could decrease CO emissions. Results can be seen in Fig 12.

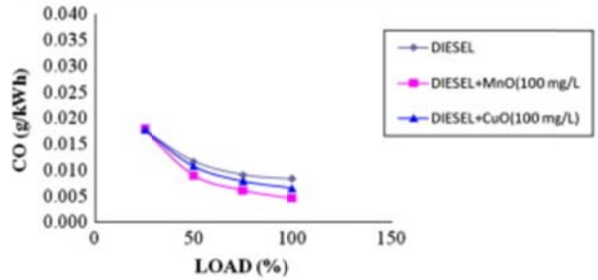

Fig. 12 CO Emissions of Various Loads (22)

Likewise, both MnO and CuO were also found to decrease NO_x emissions by about 4% at full load conditions. Results can be seen in Figure 13.

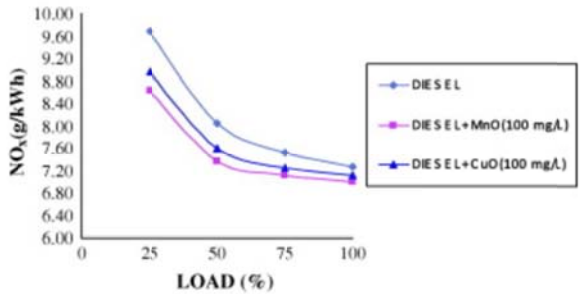

Fig. 13 NOx Emissions of Various Loads (22)

Again, the addition of MnO and CuO has shown to decrease HC emissions as well, though not as much as NO_x or CO. The results can be seen in Figure 14 (22).

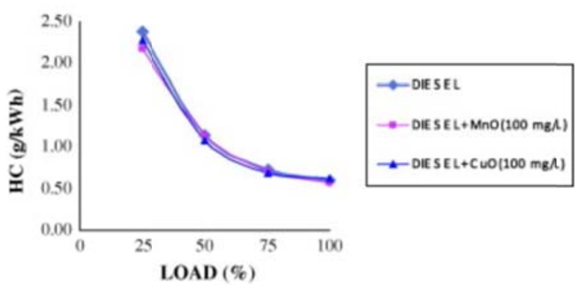

Fig. 14 HC Emissions of Various Loads (22)

Manganese has proven to be one of the most beneficial metallic additives thus far in reducing the hydrocarbon, oxides of nitrogen, particulate matter, and carbon monoxide emissions into the atmosphere in comparison to conventional neat diesel fuel. Many researchers have supported these findings and their trends, but as shown previously, the highest decrease in emissions was found through the study by Lenin et al. (18, 22, 23, 24, 25). As previously stated, there are many different types of metallic additives that have been studied such as Cu, Mg, Fe, Ce, etc.; however, based on current research, Mn seems to provide the best results over multiple studies that have been conducted thus far.

That being said, it is imperative that other metallic additives be researched. Though Mn seems to be a successful additive based on multiple case studies, other additives also seem promising and just need more verification by researchers. For example, although not researched as much as Mn, other metallic additives, $FeCl_3$ and Co_3O_4 reduced CO emissions by 50%. This shows that an increase in oxygen, which will be discussed further in section 4.2, also influences the emission effects of fuel. Likewise, Jelles et al. found that NO_x could be reduced by as much as 20% when platinum/cerium additive is used, which is five times greater reduction than the results by manganese. That being said, these findings should be validated by other researchers as much as the manganese additives.

Most metallic nanoparticles investigated thus far have all shown to decrease HC emissions, but not all investigations have shown to decrease other emissions such as NO_x. However, although this may seem detrimental, it can be rationalized by considering the various different concentrations that researchers from all over the world have tested. Too much oxygen is detrimental for NO_x emissions, which is discussed further in section 4.2.1 for oxygenated additives. Therefore, the ratio of metallic catalysis to fuel should always be considered, as too much can influence parameters such as flame temperature and cylinder pressure, causing more NO_x production (26). This is even more true for biodiesel mixtures which will be discussed further in section 5.

2) Metallic Nanoparticle Engine Efficiency

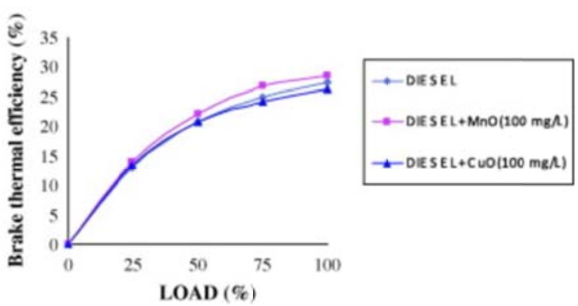

Fig. 15 BTE of Various Loads (22)

In conjunction with the lower emissions, metal additives can also have positive effects on the brake thermal efficiency. Results from the same study by Lenin et al. can be seen in Figure 15. This is important to note because it is hard to compromise efficiency and power in a commercial enterprise. Thus, metal additives should definitely be considered for commercial use in the near future.

B. Oxygenated Additives

When there is not enough oxygen in the system, incomplete combustion occurs. Thus, adding more oxygen to the systems may seem like an optimal solution to overcome this problem. This concept was thought of, and mass produced, decades ago with tertiary butyl ether or methyl tert-butyl ether (MTBE) but was soon outlawed due to the carcinogenic effects that occurred as a result. Common oxygenated additives that are regularly seen are alcohols such as methanol and ethanol due to their hydroxide (OH) chemical attachment. Other oxygenated additives include acetone, dimethoxyethane, ethylene glycol monoacetate, polythoxy-ester, n-butanol, and many more. However, another oxygenated additive that will be discussed further in section 5 is in fact biodiesel.

Although the presence of more oxygen allows for more complete combustion to occur, the physical and kinetic chemistry properties between oxygen atoms and fuel could actually hinder combustion. This could be seen in the research by Coniglio et al. where biodiesel decreased the combustion temperature and ultimately weakened the oxidation reaction. To solve this oxidation problem, various oxygenated compounds were tested with different amounts of molecules. Interestingly, it was concluded that the amount of compounds in the fuel influences the reactivity. Given a low reactivity temperature amongst the tested compounds, it was found that the greater amount of compounds, the higher the cetane number, and thus the greater rate of combustion (27). This is interesting as simpler is often better, but not in this case. Although, this was only one test case so this should be studied further. Often, studies are conducted to test ethanol, and methanol, which are rather simpler compounds. This definitely raises the question of why more studies with greater molecular compounds have not been investigated.

1) Oxygenated Additive Emission Effects

Although carbon dioxide is a natural product of complete combustion, other carbon emissions are not and should be limited. Carbon dioxide should also be limited, because as stated previously, it is the main contributor to the climate change crisis occurring in the world. Unfortunately, the most common oxygenated additives, alcohols, has been shown to increase carbon monoxide when blended with fuel. This is due to the lower combustion temperature required when alcohols are used, and the local equivalence ratio of air to fuel, can stir up carbon monoxide more easily (28). Although testing conditions such as load intensity and injection timing can play a part in these findings, carbon monoxide emissions should still be treated as serious effect of oxygenated additives like alcohols (29). That being said, the other mechanical aspects such as injection timing and type should always be considered when proposing a new innovation to additives. For example, in one study, the CO emissions rapidly increased when the injection timing changed to 30° from 10-25° before top dead center (30). Furthermore, in another study that researched the effect of types of injection pumps on combustion of oxygenated additives, the results varied greatly depending on the type. Merritt et al. found that when using a rotary pump line nozzle, more carbon monoxide was produced, whereas in the electric injectors or high-pressure common rail, less carbon monoxide was produced in comparison to diesel (31).

Although bad, the oxide of carbon emissions is not as bad as the oxide of nitrogen emissions. The oxide of nitrogen emissions occurs at higher temperatures than those of typical carbon emissions. Because oxygenated additives increase temperature peaks, this causes the oxides of nitrogen to form more easily. This increase of NO_x has been seen in many case studies using oxygenated additives. However, there have also been case studies using oxygenated additives that have shown to decrease NO_x due to the lower adiabatic flame temperature and larger enthalpy of vaporization. This definitely begs the question of what the optimal parameters are of the engine, and no answer has been generated yet. Nevertheless, the production of NO_x depends on the ignition conditions such as temperature which influences the equilibrium time constant of NO_x in the reaction: $O_2 + N_2 \leftrightarrow NO_x$. Therefore, the increasing oxygen content in oxygenated additives allows for more opportunity for NO_x to be generated. The increase in NO_x due to the increased oxygen concentration was found in various case studies (32, 33). Yet, there were also case studies that found a decrease in NO_x with the addition of oxygenated additives, particularly with esthers in diesel or biodiesel blends (34, 35). Other oxygenated additives that have been found to decrease NO_x emissions include triacetine-biodiesel, EGM-diesel, ethanol-DEE, di methoxy ethane-diesel, and 1,4-dioxane-diesel blend (36, 37, 38). Nevertheless, it appears there are far more case studies that find an increase in NO_x when oxygenated additives are used. This poses as a problem for the biodiesel, which will be discussed further in section 5. However, as previously stated, changing other parameters such as load, injection type, and injection timing may be able to control this negative emission effect. A shorter ignition delay would also help contribute to decreasing the emissions. Furthermore, if additional subsystems were incorporated into the internal combustion engine, such as a lean NO_x trap or adsorbent materials, the emission problem may be able to be avoided for all types of compounds (39).

Likewise, to the oxides of nitrogen emissions (NO_x), hydrocarbon (HC) emissions were also generally found to increase when oxygenated additives were tested in comparison to neat diesel fuel. Specifically, alcohol oxygenated additives at low loads allow for an increased HC level as seen in various case studies. This is unfortunate but could perhaps be avoided with traps or adsorbent materials, as referenced for oxides of nitrogen. That being said, altering other parameters like speed and load can be a simple fix to decrease HC emissions, and this has already been seen for alcohols at high loads and speeds in diesel by Sayin et al. for example (40). It was found that ethanol and methanol blends had less HC emissions than neat diesel by about 40% when run at high loads and speeds (40). It should also be noted that when reducing the premix burn will also reduce the HC emissions (41). Again, the parameters that are run for each individual engine influence so many effects.

Although the oxides of nitrogen and hydrocarbon emissions have generally been found to increase in most cases of oxygenated additives, the particulate matter emissions have generally been shown to decrease. Particulate matter (PM) contributes to the SMOG effect, as discussed previously, and is considered to be unwanted solid and liquid matter such as soot. Not only does this affect the mechanical efficiency of the engine, it also is problematic for the environment. Significant reductions of particulate matter have been observed when oxygenated additives have been used in alcohol-diesel blends (42). In the case study by Imtenan et al., a definitive negative relation was found between oxygen content and PM; as oxygen concentration increased, PM decreased (43). Another significant oxygenated additive that has been shown to decrease PM is dimethyl ether due to its carbon bonds not being bonded to other carbon and just oxygen and hydrogen. Another method to be used in conjunction with oxygenated additives is alcohol fumigation, where the alcohol is premixed with the intake air. This just reiterates the fact that optimal parameters must be used in conjunction with additives to further decrease emissions and increase efficiency.

2) Oxygenated Additive Power Effects

Overall, looking at the positives of oxygenated additives, aside from decreasing the amount of carbon emissions into the atmosphere, there is also an increase in power generally when additional oxygen molecules are added to the system. When more oxygen is added to the system, the viscosity decreases. This allows for better atomization as discussed previously, allowing for better combustion as well as brake specific fuel consumption. That being said, a lower viscosity mixture increases the latent heat of vaporization, decreasing the compression stroke temperature, and perhaps increases the volumetric efficiency to decrease the work required for compression. Although the brake specific fuel consumption generally decreases when using oxygenated fuel additives, the brake thermal efficiency has not shown any general leadings. On the contrary, the brake thermal efficiency was found to be greater in some studies and less in others in comparison to diesel when used in conjunction with oxygenated fuel additives (29). Therefore, more research is needed to define a scope of advantages and disadvantages of oxygenated additives, as the term encompasses so many different chemical compounds.

One oxygenated additive that has not been researched as much in the United States is nitroparaffins. Although the name may appear misleading, it is indeed classified as an oxygenated additive. One study conducted at the Tarbiat Modarres University in Tehran by Moghaddam et al., showed promising results of increasing brake thermal efficiency while decreasing soot levels when using the nitroparaffins nitromethane (NM) and nitroethane (NE). The additives followed the same trend discussed throughout this report, decreasing viscosity with increasing cetane index and oxygen content. Specifically, the nitromethane is prone to inducing pre-ignition due to its heat sensitivity, promoting better combustion and thus brake thermal efficiency. The results can be seen in Figure 16 and their operating modes are defined in Figure 17 (44).

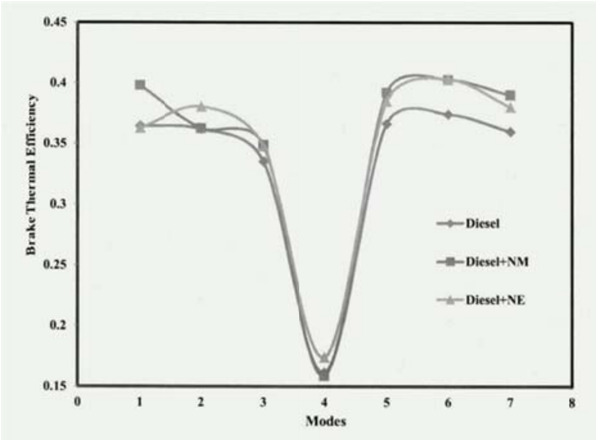

Fig. 16 BTE with Nitromethane & Nitroethane in Diesel (44)

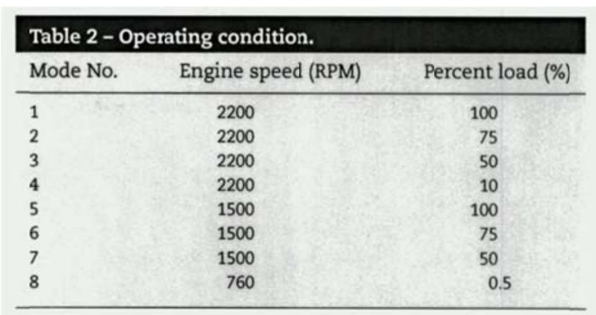

Table 2 – Operating condition.

Mode No.	Engine speed (RPM)	Percent load (%)
1	2200	100
2	2200	75
3	2200	50
4	2200	10
5	1500	100
6	1500	75
7	1500	50
8	760	0.5

Fig. 17 Operating Conditions of Nitroparaffin Study (44)

C. *Carbon Nanotube (CNT) Additives*

The benefit of carbon nanotube additives is its surface area to volume ratio, as well as settling time. It has been acknowledged that the addition of CNT additives could enhance the burning rate with the greater cetane number of the fuel that would result. This would, in turn, allow for better combustion, fuel consumption, anti-knocking, emissions, and more. Types of CNT additives include various single and multi-walled carbon nanotubes.

More efficient reactions have been observed as a result of CNT additives in fuel. This is assumed to be from the surface to volume ratio being greater than the norm, and thus improves the fuel's ignition. Furthermore, it could also be considered to be a contribution to better secondary atomization in the combustion chamber which ultimately allows for a better dispersion of fuel particles and thus more efficient combustion with lower emissions.

Unfortunately, not enough research has been conducted on CNT additives with diesel to make any definitive conclusions. However, there was a study by Balaji et al. who did a study with biodiesel that will be briefly discussed in section 5. Furthermore, there was also a study conducted by Senthilkumar et al. who mixed CNT and water with diesel and found that CO emissions decreased as CNT levels increased (45). More research needs to be conducted to make any conclusions about CNT. Thus far, they have been shown to decrease HC, PM, CO, and NOx emissions. Yet, CNT additives have also been reported to cause negative health effects such as lung inflammation. Ultimately, as with all additives and fuels, more research must be conducted to know the long-term effects for the environment and the consumer.

D. *Polymer Waste Additives*

Although polymer waste additives seem like an optimal fuel alternative or additive due to its increased quantity in a more progressive world, research thus far has shown that polymer additives increase harmful emissions such as CO. The higher viscosity of polymers is a likely reason as to why emissions increased, because as discussed previously, worse atomization results when the viscosity is too high. Therefore, worse combustion results, leading to more emissions. Furthermore, with the addition of polymers, the combustion temperature in the cylinder is higher, leading to more harmful emissions. For example, in one recent study by Venkatesan et al., every type of emission was greater in the polymer additive fuel. Although the mechanical thermal efficiency for the polymer blend was slightly higher, the brake-specific fuel consumption and emissions were very much higher. This agrees with other findings by researchers. The results can be seen in Figures 18, 19, 20, and 21 (46).

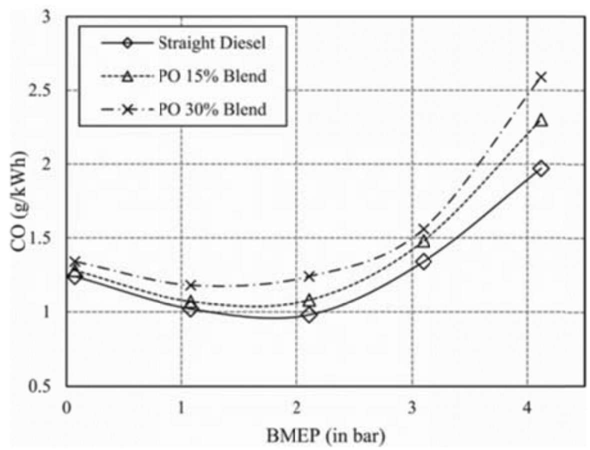

Figure 18. CO Emission Levels with Polymer Additive (46)

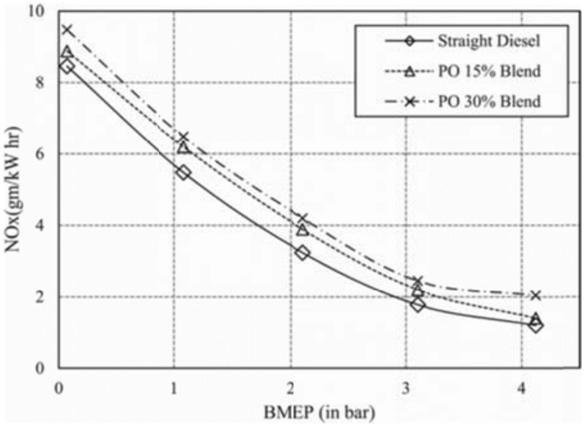

Figure 19. NOx Emission Levels with Polymer Additive (46)

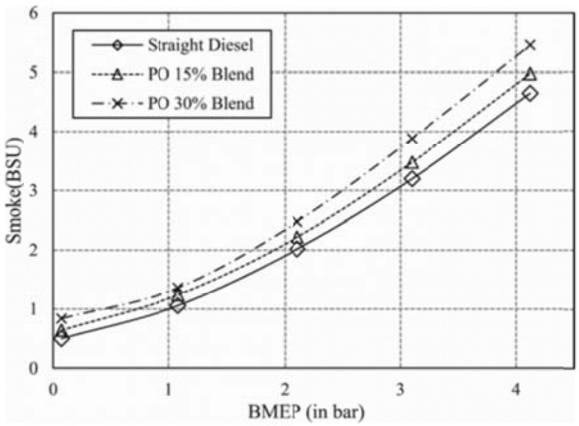

Figure 20. Smoke Emission Levels with Polymer Additive (46)

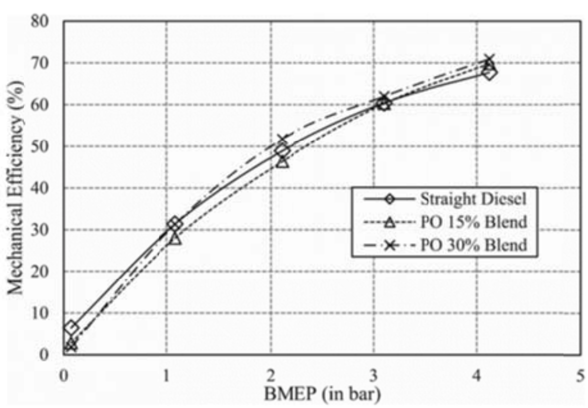

Figure 21. Mechanical Efficiency with Polymer Additive (46)

Therefore, because multiple studies aside from Venkatesan et al. have been produced that show multiple types of emissions increase with the use of polymers, with only marginal engine efficiency increase which can be seen in Figure 21, it is suggested to research other chemical additives for future progress.

E. *Water Additives*

The addition of water as a fuel additive has many potential combustion advantages such as better atomization and lower heating value. Water also has been shown to decrease NO_x emissions, as well as particular matter and soot. However, water has also been shown to increase CO_2 and HC emissions (47). The effects of water on internal combustion engines depends on the method that is used. The main methods that are known and have been researched thus far include water-diesel emulsion, direct water injection, and water fumigation.

Using a water-diesel emulsion method has its benefits, like the generally being able to lower the temperature to limit oxides of nitrogen emissions, however this in itself could lead to other negative effects. For example, lowering the temperature by too much or too soon leads to a longer ignition delay, contributes to engine noise, and thus ends up being costly for maintenance (48). However, these factors can be somewhat controlled better using the alternative method, direct water injection, as it allows for the delivery of water via an electronic injector. Therefore, the fuel to water ratio can be easily changed and allow for better conditions on ignition delay and cold start. The downside to this method is the addition of more equipment to a commercial engine. This would add more cost for the consumer in addition to other additives investigated in this report. That being said, water fumigation is another option that has noteworthily been investigated in marine diesel engines. In water fumigation, water is supplied uniformly by a variety of methods, some being a compressor, or an intake pipe close to the inlet valves.

1) *Water Additive Emission Effects*

One schematic of a water fumigation injection system can be seen in Figure 22. In this study, by Tauzia et al., NO_x emissions were reduced immensely, and when using 60-65% water mass, the NO_x was reduced by about 50%. This can be seen in Figure 23, where the operating conditions of the points shown in Figure 23 can be found in Figure 24 (49).

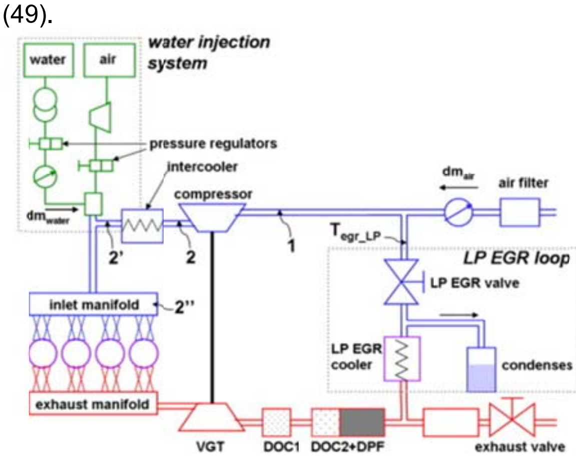

Fig. 22 Schematic of Water Fumigation System in ICE (49)

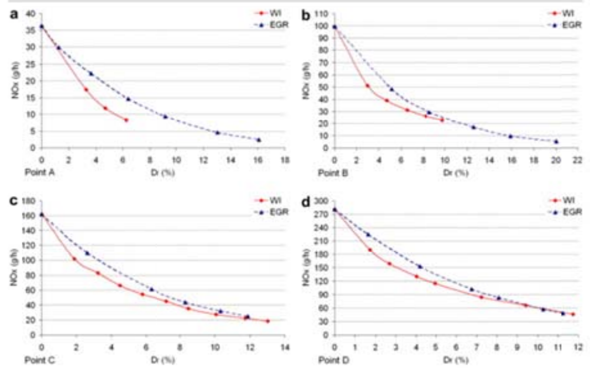

Fig. 23 Water Injection vs. Exhaust Gas Recirculation NO_x (49)

Point	A	B	C	D
Engine speed (rpm)	1500	1665	2050	2000
Torque (N m)	45	114	140	200
Pilot quantity (mg/stroke)	1.2	1.5	1.7	2.4
Principal quantity (mg/stroke)	11.2	22.8	30.7	39.7
BMEP (bar)	2.8	7.1	9.5	12.7
P_{rail} (bar)	600	865	1028	1154

Fig. 24 Operating Points of Tauzia et al. (49)

The addition of water as a fuel additive has many potential advantages, but unfortunately may be counteracted with the increase of brake specific fuel consumption that has been reported. Specifically, at lower engine speeds, which would be seen regularly in cities where carbon emissions are of greatest concern, higher fuel consumption was reported. This is most likely due to the friction and heat transfer to the combustion chamber, which is intuitively bound to increase as engine speed increases, as well. An example of this can be seen in Figure 25, as well as Figure 26 which exemplifies the tradeoff of bsfc and bte (50).

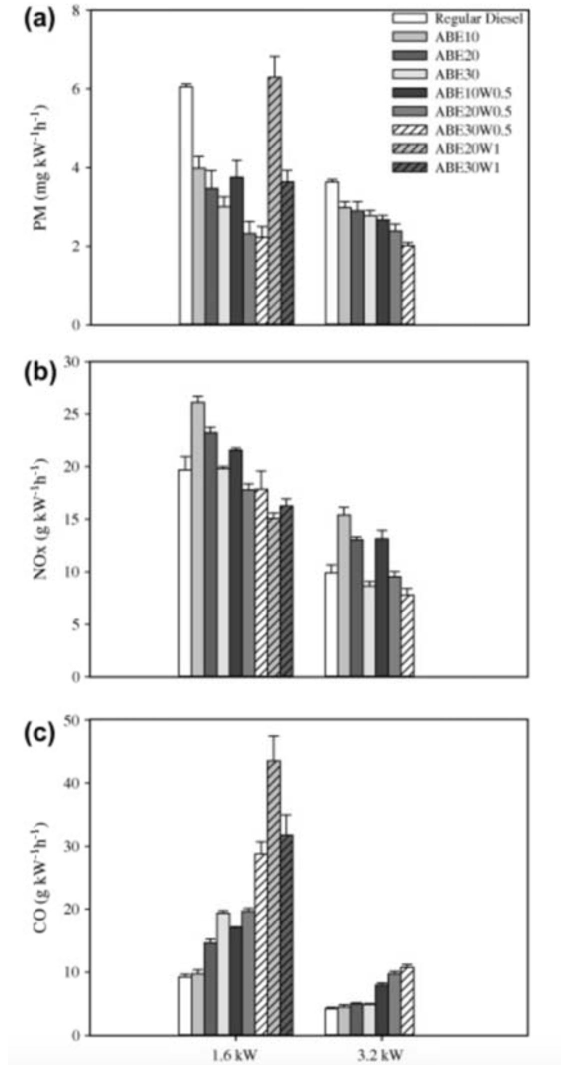

Figure 25. Emission Effects of Water Additive Blends (50)

2) *Water Additive Power Effects*

Multiple studies have shown that increasing the oxygen content enhances the combustion efficiency, therby increasing brake thermal efficiency. Water in particular has been the focus of many studies that support this claim. Again, because of the higher stoichiometric oxygen that water provides, a fuller combustion process is able to take place, providing more power. However, some studies, such as Davis et al. showed that a water-diesel blend into a single cylinder diesel engine actually reduced the brake thermal efficiency (51). That being said, this team is not alone, and other studies have shown the same. Therefore, there exists a need to utilize the water for its lower heating value and extra oxygen without compromising the combustion. This can be done by incorporating other additives into the mixture, as well, which has been done by a few teams but not many.

For example, Chang et al. combined 0.5% water to 20% acetone-butanol-ethanol-diesel blend that improved bte up to 8.56% (50). Because of better atomization due to micro-explosions, combustion improved at high loads and low loads. Interestingly, at higher loads, bte improvements were greater, most likely because of ignition delay in the low load. The high latent heat of vaporization caused by the water slowed combustion by releasing heat late in the expansion stroke. Yet, unsurprisingly, the brake specific fuel consumption increased. This can be seen in Figure 26 below. Again, this exemplifies the tradeoff that with more bte, there may be more fuel consumption needed.

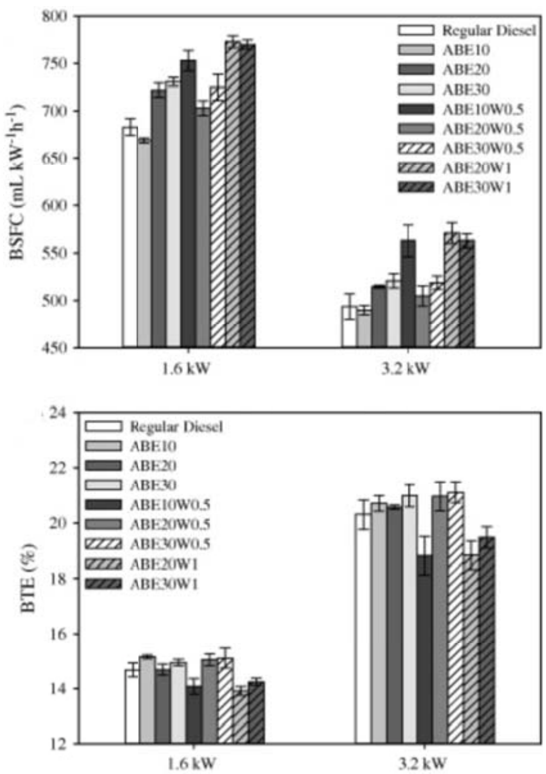

Figure 26. Water Blend BSFC and BTE Effects (50)

Furthermore, interestingly, Abdullah et al. noted that bsfc did not noticeably increase in a water-biodiesel-diesel blend (52). This leads to question what the optimal blend of additives is, rather than just one, and will be discussed further in section 5.

V. Chemical Additives in Biodiesel

When looking at entirely substituting conventional diesel fuel with biodiesel, other issues may arise. Generally, thus far, research has shown that solely using biodiesel could do more harm than good. Because of its low energy content, more fuel may be needed in the long run, which is counterproductive if just as much emissions are produced. Furthermore, much research conducted thus far has shown that biodiesel increased the rate of oxides of nitrogen emitted due to its higher combustion temperature, oxygen concentration, ignition delay, radiative heat loss, and perhaps faster combustion rate (53). This trend can be seen in Fig. 27.

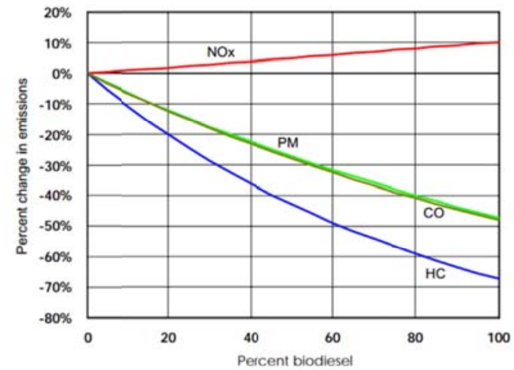

Fig. 27 Percent of Biodiesel vs Percent of Various Emissions (53)

The use of chemical additives in conjunction with biodiesel appears to be an optimal solution if the price is right, instead of completely substituting with biodiesel. A study conducted by Keskin et al., supported the findings of Caton et al. and Valentine et al., showing that metallic based additives with biodiesel decreases carbon emissions and generally NO_x emissions, as well as smoke emissions and opacity (1).

Again, a blend of additives and fuels appears to be the optimal answer, trying to get the best ratio of fuel to air to water to additives to biodiesel, and the list goes on, if internal combustion engines are to continue to be used. More testing is needed, as there are trillions of combinations. However, some successful studies that have been conducted already will be discussed in the section herein.

A. *CNT as Promising Additive in Biodiesel*

Selvan et al. studied cerium oxide nanoparticles and carbon nanotubes integrated with diesel-biodiesel-ethanol (Diesterol). Biodiesel was used to combine diesel and ethanol, as they are immiscible alone. The compounds had to undergo a high-speed mixing and ultrasonic bath, however, which may pose as a problem for commercial use. Nevertheless, the CNT additives accelerated the burning rate, thereby decreasing the ignition delay. The cerium oxide nanoparticles provided extra oxygen and activation energy for better combustion and emissions. In combination, the cerium oxide nanoparticles and carbon nanotubes reduce the exhaust emissions without compromising power too much. The brake thermal efficiency of the different concentrations can be seen in Fig. 28, where CERIA notes ppm of cerium oxide, CNT notes ppm of carbon nanotubes and E20 notes the diesterol blend (54).

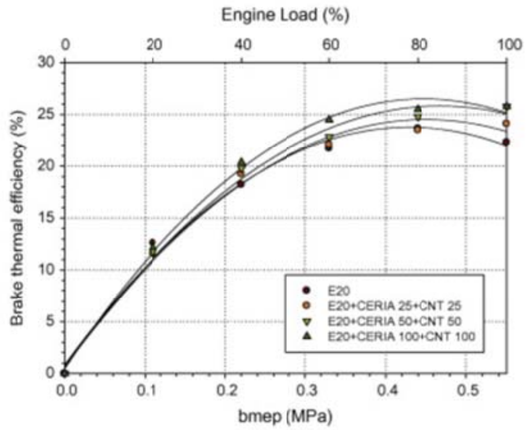

Fig. 28 Brake Thermal Efficiency with Biodiesel Blend (54)

Although these are promising results, showing that the combination of additives has a higher brake thermal efficiency, it was only compared to E20 as a control rather than a commercial fuel such as diesel. That being said, it is still comparable and with the decrease in emissions, as seen in Figures 29-31, it is a somewhat good environmental decision; and as seen in Figure 32, the specific fuel consumption decreased as the additive level increased. Although the main disadvantages of solely using biodiesel, the increase in NO_x and the specific fuel consumption, appear to have been solved, there was a surprising increase in CO emissions. Therefore, further research must be conducted that tests other combinations of additives (54).

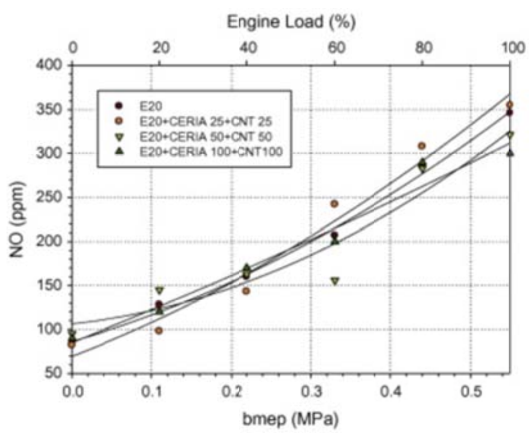

Figure 29. NO emissions with Biodiesel Blend (54)

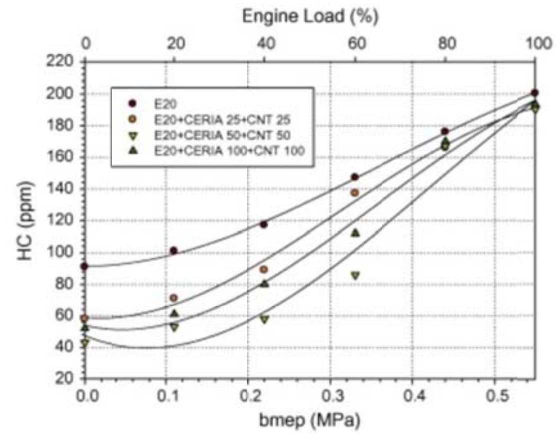

Figure 30. HC emissions with Biodiesel Blend (54)

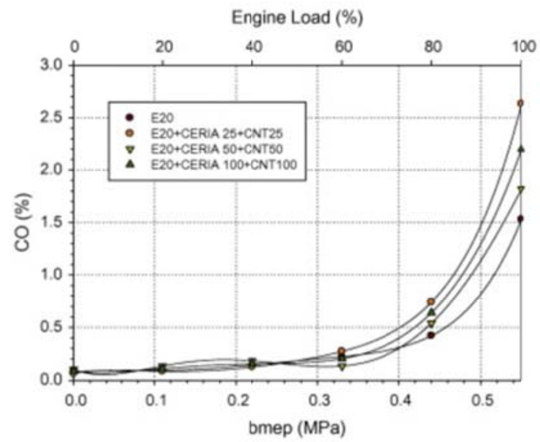

Fig. 31 CO emissions with Biodiesel Blend (54)

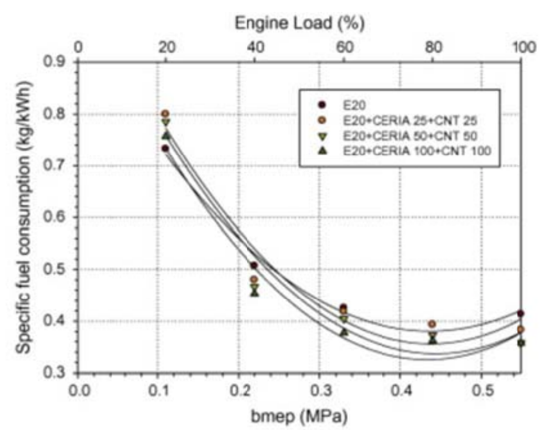

Fig. 32 Specific Fuel Consumption with Biodiesel Blend (54)

Continuing on, looking at a completely different study, inspiring results emerged from a study by Hosseini et al. when using CNT additives in a biodiesel blend of 5% biodiesel and 95% diesel. The biodiesel stemmed from cooking oil waste, and the CNTs were added in doses of 30,60, and 90 ppm. The results can be seen in Fig. 33 (55).

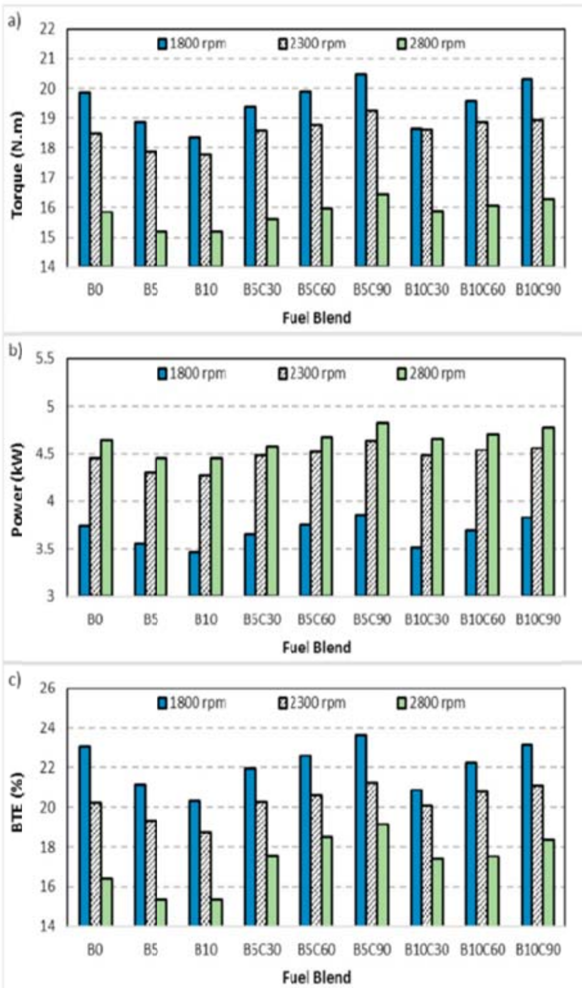

Fig. 33 CNT Additive Results with Biodiesel Blend (55)

Looking at Figure 33a, the results of Hosseini et al. show that the torque of a biodiesel blend with CNT additives exceed the torque of diesel alone (B0) and biodiesel blends alone (B5 and B10). The biodiesel blends alone had a lower torque than diesel alone due to the lower heating value of pure biodiesel, as discussed previously. The reason the torque increased for the CNT additive biodiesel blend is due to the enhanced concentration of nanoparticles, generating energy and more complete combustion inside the cylinder. This increases the quality of the combustion, average pressure, piston force, and piston torque.

Looking at Figure 33b, the 90 ppm CNT biodiesel blend (B5C90) had the greatest power output, far exceeding the diesel alone and biodiesel alone at all rotational speeds. Again, as previously stated, because the CNT has the larger surface area to volume ratio, the energy in the cylinder produced is greater. Furthermore, the CNT acts as a catalyst that greatly reduces the ignition delay and time that combustion occurs, which provides a higher peak cylinder pressure and faster heat release rate (55).

Looking at Figure 33c, the 90ppm CNT blend also produced the greatest brake thermal efficiency, even exceeding the diesel efficiency. Although the BTE decreases with an increasing engine speed, the 90 ppm had the greatest efficiency at all speeds.

As previously discussed, the increasing bsfc is an issue with biodiesel. This can be seen in Fig. 34 as well. That being said, the CNT additive with biodiesel actually decreased the brake specific fuel consumption, with the lowest bsfc being with the 90 ppm (B5C90) including the plain diesel results. This appears to eliminate one of the major fears of using biodiesel in commercial industry.

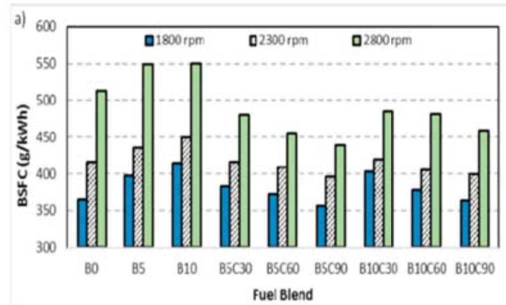

Fig. 34 CNT Additive BSFC Results with Biodiesel Blend (55)

Yet, although the BSFC decreased, the other major concern of using a biodiesel blend, the NO_x emissions, were unphased. This can be seen in Fig. 35, where the NO emissions were still greater than that of using regular diesel due to the higher oxygen content and increased combustion temperature.

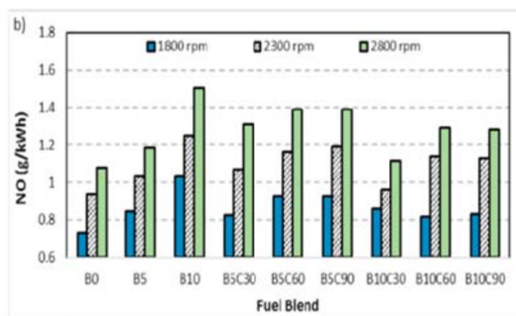

Fig. 35 CNT Additive NO Emissions with Biodiesel Blend (55)

Likewise, it is unfortunate to say that the CO_2 emissions also increased when using the biodiesel blend, ultimately defeating the purpose of alternative fuels in the climate change era. This can be seen in Fig. 36.

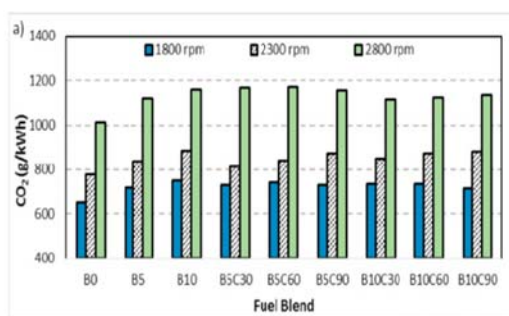

Fig. 36 CNT Additive CO_2 Emissions with Biodiesel Blend (55)

Yet, all other emissions seemed to decrease, including soot, which can be seen in Figures 37, 39, and 39.

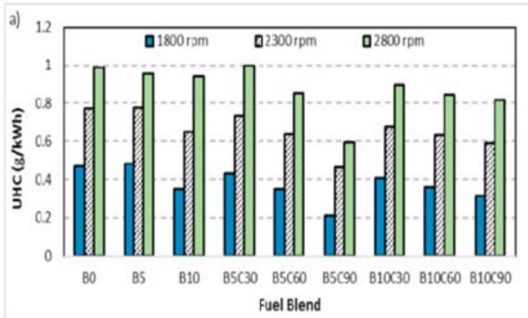

Fig. 37 CNT Additive UHC Emissions with Biodiesel Blend (55)

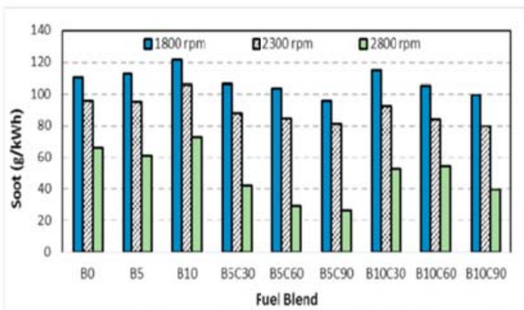

Fig. 38 CNT Additive Soot Emissions with Biodiesel Blend (55)

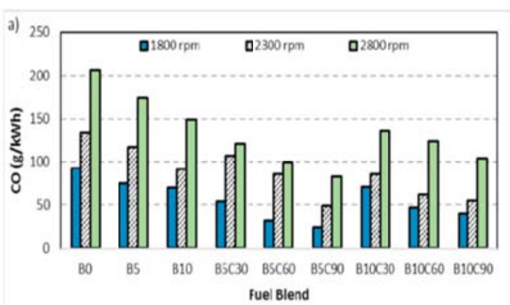

Fig. 39 CNT Additive CO Emissions with Biodiesel Blend (55)

Thus, as seen throughout the entirety of this report, everything is a tradeoff. This begs the question of what the most important parameter is to consider in this day and age.

VI. Conclusion

The most important conclusion made is that more research needs to be conducted regarding additives, tested with and without biodiesel blends. That being said, the use of chemical additives in conjunction with biodiesel appears to be an optimal solution if the price is right, instead of completely substituting with biodiesel. Specifically, the greatest additives based on this compilation include metals such as manganese, oxygenated additives such as cerium oxide, and carbon nanotubes. Carbon nanotubes are especially interesting due to their surface to volume ratio being greater than the norm, and thus improves the fuel's ignition. Overall, however, additives that provide additional oxygen are beneficial for enhanced combustion, acting as if the mixture is burning rich while simultaneously lowering reactivity temperature and viscosity. The mere property of viscosity is especially important, as it has rippling effects on the entire system. Using an additive that lowers the viscosity of the fuel allows for better atomization and ultimately combustion. In some cases, a 'secondary' atomization can occur in the combustion chamber, as was seen with the carbon nanotubes and aqueous additives, which ultimately allows for a better dispersion of fuel particles and thus more efficient combustion with lower emissions. In addition to viscosity, a higher cetane number was also a common cause of better combustion and emissions, as was seen in the manganese additive. In contrast to the manganese additive, the additives that do not appear to be beneficial for combustion include pure biodiesel as well as polymer additives. Polymer waste additives were found to increase harmful emissions and decrease mechanical efficiency, and thus it is recommended to pursue research in other additives. Pure biodiesel research thus far has shown to do more harm than good. Because of its low energy content, more fuel may be needed in the long run, which is counterproductive if more emissions are produced. Furthermore, much research conducted thus far has shown that biodiesel increased the rate of oxides of nitrogen emitted due to its higher combustion temperature, oxygen concentration, ignition delay, radiative heat loss, and perhaps faster combustion rate. That being said, biodiesel in conjunction with another additive has shown to be a very promising fuel alternative, as the additive counteracts some of pure biodiesel's drawbacks, which was seen in the carbon nanotube biodiesel blend. For now, however, much more research is needed regarding fuel additives so that they can be brought to market.

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