Emulsified Biodiesel Fuel Effects on Regulated Emissions

P. Grimes, W. Hagstrand, A. Psaila, J. Seth, J. Waldron
Alternative Petroleum Technologies,
Reno, Nevada 89502, USA

Abstract

In the Fall of 2011, APT successfully completed a four-month evaluation of emulsified biodiesel fuel operations in top-handler units at the Port of Los Angeles. Data records for this demonstration show that a 6.5% (by mass) water content in the emulsified B20 biodiesel fuel effectively "neutralized" any NOx emissions increases previously witnessed with regular B20 biodiesel fuel use in diesel engines. Moreover, emulsion technology significantly reduced particulate matter (PM) emissions on the order of 42% as compared to the levels witnessed with ULSD fuel. One final result of the waterfront demonstration was the successful coupling of emulsion fuel technology with an after-treatment hardware technology – a diesel oxidation catalyst (DOC) unit. This serial combination of diesel emissions mitigation technologies reduced PM emissions on the order of 56%. The record of this demonstration is now presented in detail.

Introduction

Several studies [1] have been conducted which quantify the emissions associated with biodiesel containing fuels relative to diesel fuels. An often quoted study [2] was posted by US EPA in 2002. In this study it was shown that PM, CO and HC are significantly reduced with biodiesel fuel whereas NOx emissions increase. Figure 1 illustrates this increase in NOx. It is worth noting that (1) the increase is linear with biodiesel content in the blended diesel-biodiesel blend; (2) for B20 (20% volume of biodiesel in the fuel blend) shows an increase of around 3% NOx and, in the worst case, for B100 of around 17% NOx; (3) the increase depends on the origin of the fatty acid methyl ester. Soybean derived biodiesel shows the highest increase in NOx level while animal-based material shows the lowest increase - with rapeseed based biofuel in between the two levels – at all concentrations of biofuel.

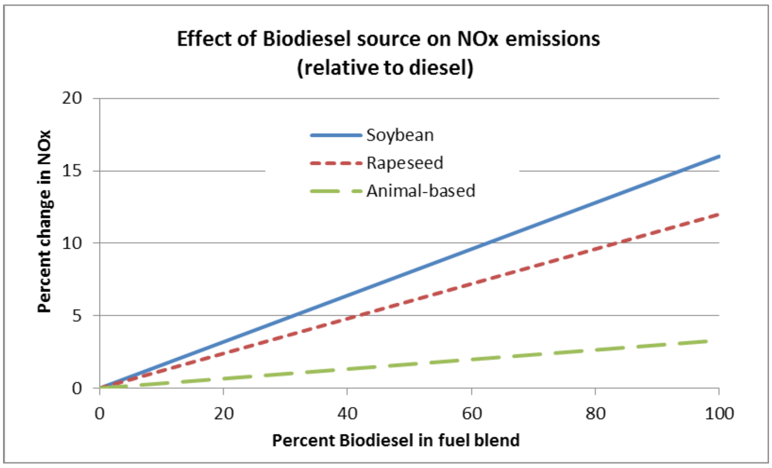


Fig. 1. NOx Increase for Various Fatty Acid Methyl Esters (FAMEs) in Biodiesel Blends

Alternative Petroleum Technologies (APT) had previously shown that emulsion technology was effective in decreasing NOx emissions in regular diesel fuels. [3]. Believing that emulsion technology could alleviate the NOx increases in biodiesel fuels, APT applied to the Technology Advancement Program (TAP) of the Ports of Long Beach/Los Angeles to test the hypothesis. The subsequent effort was accomplished in three phases. The program is now delineated in detail.

Phase 1 – Fuel Screening Tests

Fuel screening tests were conducted at the Southwest Research Institute (SwRI) laboratories in San Antonio, TX. The test engine was a CARB registered Detroit-Diesel (DDEC-60) inline, six-cylinder engine rated for 365hp at 1800rpm. It was turbocharged and used a laboratory water-to-air heat exchanger for a charge air intercooler.

The US Federal Test Procedure (FTP) was used in this work. The EPA transient cycle under the FTP is described by means of the percent of maximum torque and percent of rated speed for each one second interval over a cycle of 1199 seconds. In order to generate the transient cycle, the engine full load torque curve is obtained from an engine speed below curb idle speed to maximum no-load engine speed. Data from this torque map are used with specified speed and load percentages to form a transient cycle. Only hot starts were used, in triplicates, for this study. Hot starts involved running the engine over a "prep" cycle. It was then stopped and allowed to stand for 20 minutes after which the hot-start EPA transient cycle was begun with engine cranking. All the test cycles were within with the tolerances set by the Code of Federal Regulations (CFR).

The exhaust gases were routed to a full constant volume sampler (CVS) that utilised a positive displacement pump (PDP). Total flow in the tunnel was maintained at a nominal flow rate of about 2000 SCFM. Sample zone particulate, heated NOx, heated hydrocarbons THC, CO, CO_2 measurements were connected to the main tunnel. Probes for background gas measurements were connected downstream of the dilution air filter pack, but upstream of the mixing section. The dilution system was equipped with pressure and temperature sensors at various locations in order to obtain all necessary information required by the 40 CFR, Part 86, Subpart N.

Phase 1 – Test Fuels

The reference and untreated candidate fuels were both ultra-low sulfur diesels (<15ppm S) which meet fuel specifications under TCEQ Chapter 114, Subchapter H. The B100 biodiesel obtained commercially met the specification ASTM D6751. The biodiesel blended fuels were prepared using the base diesel and the B100 biodiesel. Emulsions of varying water content were prepared by APT using a pilot scale blender. The final emulsions were characterised for stability and water content was measured using the Karl Fisher method. The proprietary additive treat rate was fixed for all emulsion fuels, irrespective of the water content.

Twenty five test runs were recorded during the testing - each one in triplicate. They include a range of biodiesel and water contents in the fuels. Conventionally a 20% biodiesel in diesel blend is referred to as B20, to indicate the volume of the fatty acid methyl ester (FAME) or neat biodiesel (20% vol.) and volume of diesel making up the balance (80% vol.) of the test fuel. However in the case of water-in-diesel emulsion fuels the convention is to refer to the *mass* of water in the fuel. So a 13%m diesel emulsion fuel contains 13g of water in 100g of fuel (and equates to 11.2% vol. water).

All the fuels were able to complete the test transient cycles which is required for valid measurements to be conducted. Seventeen of these experiments were performed on the engine without after-treatment device (Fig. 2). Eight experiments were carried out on the same engine fitted with a diesel oxidation catalyst (DOC) unit (Fig. 3).

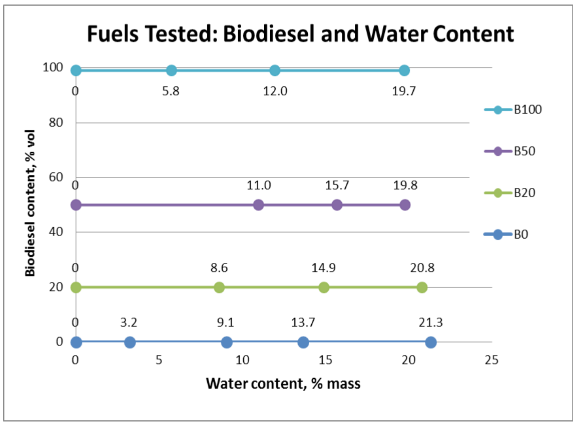


Fig.2: Seventeen Fuels Tested without DOC; Biodiesel and Water Contents

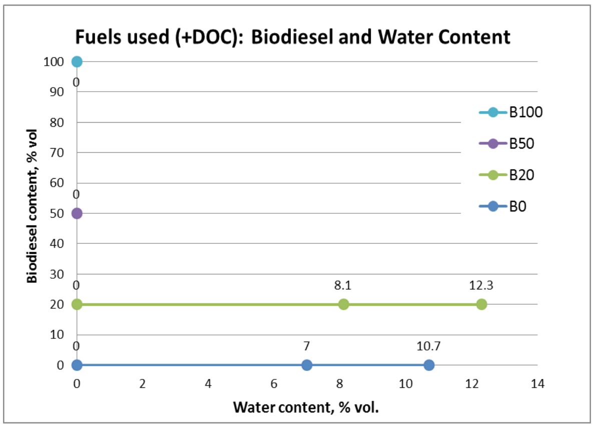


Fig.3: Eight Fuels Tested with DOC; Biodiesel and Water Contents

Phase 2 – B20 Fuel Tests

This study was conducted at the Olson-EcoLogic Engine Testing Laboratories in Fullerton, California. The test engine was a Tier 2 Model year 2004 Cummins QSM 11C engine rated for 330hp at 2100 rpm. The EPA and ARB standards for this engine are 4.9g per bhp-hr for NOx and 0.15g per bhp-hr. Test engine emissions were shown to comply with these standards. The test engine was the same model engine that operated in the three top handler units that used emulsified biodiesel fuel in the final phase of the demonstration at the Port of Los Angeles waterfront.

The engine was tested according to the Non Road Transient cycle (NRTC), an engine dynamometer transient driving schedule of total duration of 1200 seconds. Dilute exhaust gases from the dilution tunnel were continuously collected and routed to calibrated instruments (Fig. 4) for analysis by corrected volume and for final calculation of corrected mass concentrations using temperature, barometric pressure and humidity. All engine test related variables were automatically integrated from the second by second raw dilution data record and automatically corrected in accordance with the applicable 40 CFR Part 89 for dilution ratio, temperature, humidity and mass. They were automatically calculated by the laboratory computer program to provide second-by-second integrated final results in g/bhp-hr and g/kWh.

Simultaneously and continuously dilute exhaust samples were routed to an AVL particulate sampler for capture of secondary diluted samples over the test cycle on a pre-weighed paper filter media and weighed again to determine the mass concentration of PM. All PM filter preparation and subsequent weighing was done in accordance with 40 CFR Part 86. The computer software program captured and integrated (when appropriate) all raw data continuously over the test cycle and collected the data every second over the full duration of the1200 second test.

Table 4: Emission Testing Equipment

Pollutant	Instrument	Instrument Description
CO	Horiba AIA-23	NDIR
CO_2	Horiba AIA-23	NDIR
CH_4	CAI Model 600	HFID
HC	CAI Model 300	HFID
NOx	CAI Model 400	HCLD
NO	CAI Model 400	HCLD
PM	AVL PM Sampler	1ary tunnel dilution followed by 2ary dilution/gravimetric
Dynamometer	Baldor controlled 450 HP	Full Electric

In addition to correction of the raw data for temperature, barometric pressure and humidity, the data were corrected for any hydrocarbons and carbon monoxide present in the dilution air introduced through the dilution tunnel. This was done by continuously collecting a dilution air sample over the test cycle in a bag for analysis of the background dilution air at the end of the engine test cycle. The measured dilution air bag concentrations of selected gases were subtracted from the continuously integrated dilute exhaust gas samples to provide the corrected exhaust gas values. Engine and related test variables, including automatically calculated values, were recorded second-by-second at all times during testing.

The baseline diesel fuel was a commercial California ultra-low sulfur diesel fuel. The B100 Biodiesel was prepared by Community Fuels in Stockton, CA from 100% soybean biodiesel feed stock. The B20 blend was prepared by Ramos Oil in West Sacramento, CA. The emulsified fuel, EmB20 used in this study contained 6.55% mass water (verified by the Karl Fisher method). The fuel compositions and characteristics are shown in Table 5. Stable emulsions were prepared using an APT commercial blender and additive. Tests with each fuel were carried in dublicate (Table 6).

Table 5. Composition of EmB20

Fuel	Density (19°C)	% mass	% vol.
B20	0.842	93.45	94.43
Water		6.55	5.57
EmB20	0.855	100.00	100.00

Table 6. Engine Test Plan

Fuel	Test No.
Diesel (B0)	A1
	A2
B20	B1
	B2
EmB20	C1
	C2
EmB20DOC	D1
	D2

Phase 2 – Results Without a DOC

The effects of changes in the biodiesel content and water content of the fuel on the NOx and PM emissions for the first 17 test runs (no DOC) are illustrated in Figs 4 and 5. In both of these graphs the intercept on the y-axis is the effect of changing from diesel (B0) to B20 to B50 and to B100 (and no water present). In the case of NOx, the intercept is at higher values indicative of an increase in NOx as the biodiesel content increases, whereas in the PM graph the y-axis intercepts decreases as biodiesel content increases. PM emissions steadily decrease and NOx emissions increase with increasing biodiesel content. This is consistent with published data [5], [7]. Figure 4 shows the NOx emissions for all fuels diminish as the water content increases and converge to around 4 g/bhp-hr at high water content (around 20% mass water). Figure 5 shows the PM emissions with increasing water content converge asymptotically to around 0.07 g/bhp-hr PM for all the fuels. Exceptionally, for the neat biodiesel, B100, the PM emissions are so low that addition of water has virtually no incremental effect.

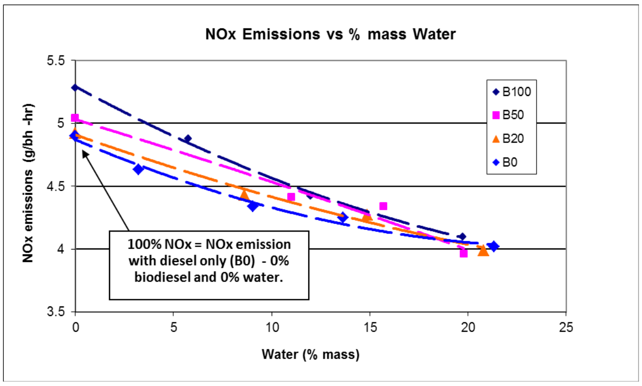


Fig.4: Changes in NOx with changes in Fuels

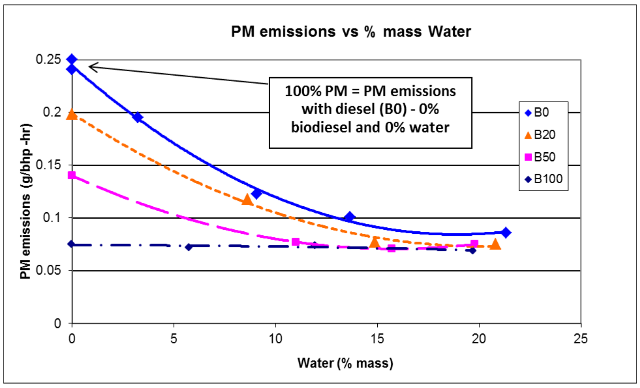


Fig.5: Changes in PM with changes in Fuels

Phase 2 – Results With a DOC

A DOC was fitted to the engine and various fuels with varying level of biodiesel and water were tested (Fig. 3 shows the experimental matrix of fuels tested). DOCs are fitted as exhaust after-treatment system in order to fully oxidize the products and by-products of combustion. As such, CO is converted to CO_2, hydrocarbons - HC or THC (Total Hydrocarbons) - are converted to water and CO_2 and particulate matter, PM, which is primarily unburned carbon, is in part converted to CO_2. The effect of a DOC on NOx is negligible. The results obtained with emulsified B20 test fuels are shown in Figs 6, 7 and 8. As a general point, the changes taking place at the lower water content (below 10% mass water) are more significant and of particular interest. Emulsification has a positive benefit on CO emissions. The incorporation of a DOC catalyst has an additional benefit – it virtually eliminates all CO emissions (Fig. 6).

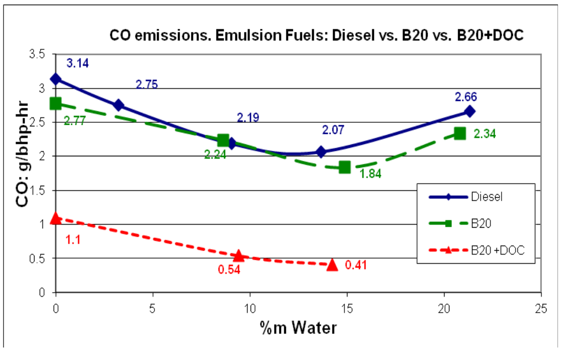


Fig. 6: CO emissions; Effect of Fuel and DOC

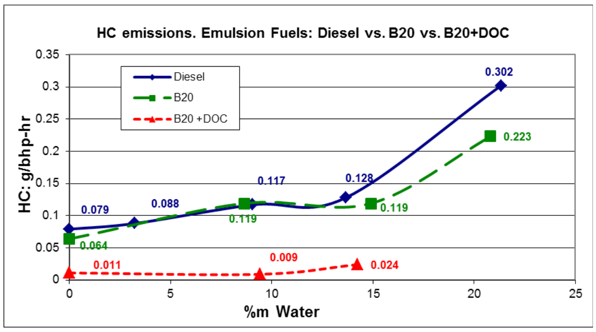


Fig.7: HC emissions; Effect of Fuel and DOC

In Fig. 7 the effect of water is to increase the hydrocarbon emission – hydrocarbon emissions are low in any case and the effect is slight for emulsified fuels containing less than 10% water. The inclusion of a DOC catalyst virtually eliminates HC. Relative to the baseline emission obtained with low sulfur diesel successive PM reductions are achieved when each of the three technologies, water emulsion, B20, and DOC are introduced. The overall reductions achievable are impressive (Fig. 8). Figures 9 and 10 illustrate the % changes in NOx and PM with increasing water content in B20.

From these graphs it is evident that around 6% mass water in B20 emulsion fuel would give at least a 6% reduction in NOx. Figure 11 summarizes the effect of the various emissions abatement technologies on PM reductions. These values for NOx and PM reductions for a 6% water emulsions are read off the graphs shown in Figs 9 and 10. The emulsification of an ultra-low sulfur diesel fuel – with a 6% (by mass) water content - reduces PM emissions levels by 34%. In other words the PM emission levels of an emulsified ultra-low sulfur diesel fuel are only 66% of the PM levels of ultra-low sulfur diesel fuel.

The emulsification of biodiesel (B20) fuel – with a 6% (by mass) water content - reduces PM emission levels by 42%. The PM emission levels of an emulsified biodiesel (B20) fuel are only 58% of the PM emission levels of ultra-low sulfur diesel fuel. The inclusion of a DOC unit with the emulsified biodiesel (B20) fuel reduces PM emission levels by 56%. The PM emission levels of an engine running on an emulsified biodiesel fuel – with a DOC unit attached to the engine – are only 44% of the PM emission levels of an engine running on ultra-low sulfur diesel fuel. These observations indicate that the PM reductions by DOC after-treatment unit and by water emulsions are complementary. In other words, an emulsified B20 with 6% mass water will neutralize the NOx increase produced by changing from diesel to B20 and a significant additional benefit in PM reductions are anticipated. Furthermore, the expectation is that the loss in maximum power output would be imperceptible.

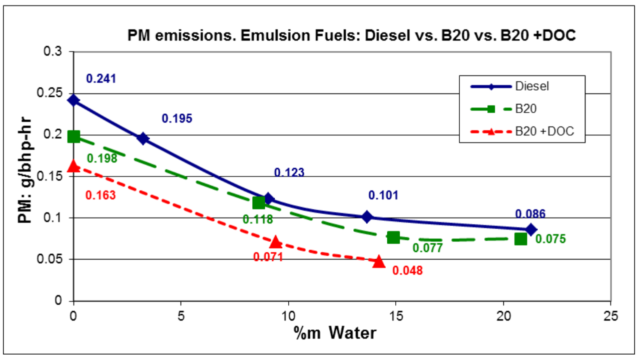


Fig.8: PM emissions; Effect of Fuel and DOC

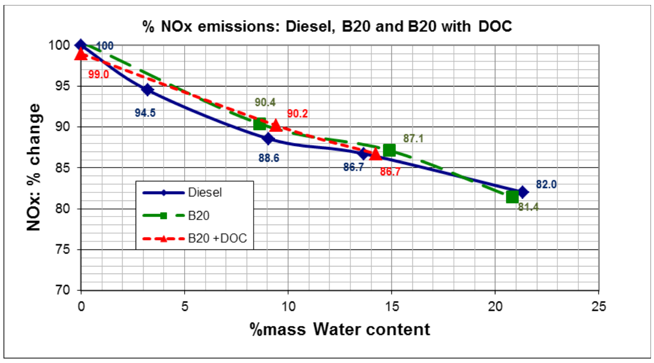


Fig.9: % NOx reductions for B20, Diesel and DOC

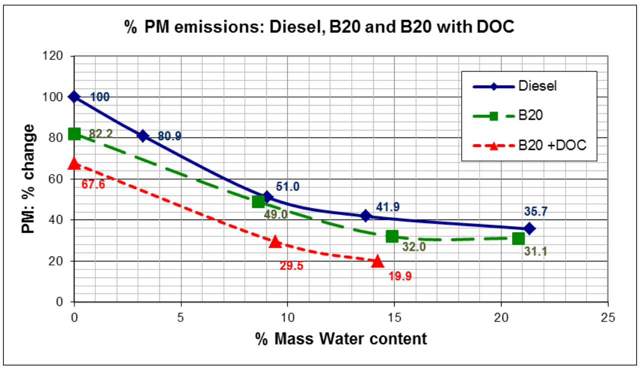


Fig.10: % PM reductions for B20, Diesel and DOC [Note for 6%m H2O the B20 fuel shows a reduction of 42% relative to B0. For same fuel with DOC, the reduction is 58% relative to Diesel Fuel, B0.]

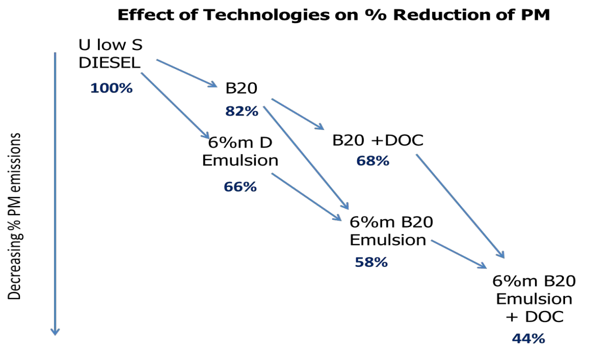
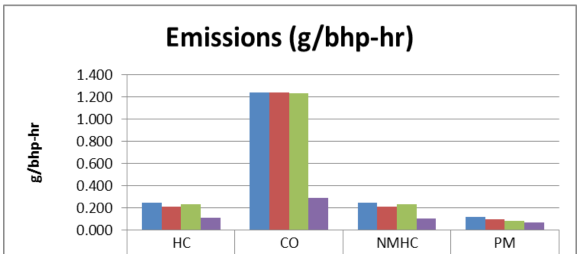


Fig. 11: Effect of Water Emulsion(%m), Biodiesel (B20) Fuel and After-treatment (+DOC) Technologies on PM Emissions

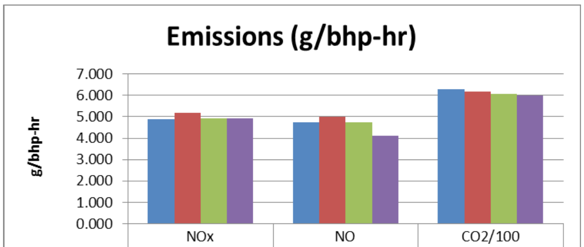
The increase in NOx (Fig. 13) from B0 (diesel) to B20 in study 2 is 5.7%, which is higher than the reported 3-4% increase for B20 (soybean) [3], Fig. 1. Despite this, the 6.55 % water emulsion in B20 fuel effectively mitigated the NO_X increase associated with biodiesel. The baseline NOx emissions measured in both engine tests were both about 4.9g/bhp-hr.



	HC	CO	NMHC	PM
B0	0.249	1.238	0.247	0.120
B20	0.214	1.241	0.212	0.097
EmB20	0.236	1.231	0.234	0.085
EmB20DOC	0.112	0.290	0.110	0.073

Note: NMHC: Non methane hydrocarbons

Fig.12: Emissions obtained with B0 (diesel), B20, EmB20 and EmB20+DOC



	NOx	NO	CO2/100
B0	4.901	4.726	6.269
B20	5.182	4.996	6.196
EmB20	4.930	4.743	6.080
EmB20DOC	4.909	4.108	6.000

Fig.13: Emissions obtained with B0 (diesel), B20, EmB20 and EmB20+DOC

The decrease in PM expected and measured in the two studies for the 6% water in B20 fuels relative to diesel are shown in Fig. 15. The decrease is lower in the second study. However the emissions observed with the low S diesel in the second engine test study is around 50% of that observed in study 1 (0.241 and 0.120 g/bhp-hr for the 1st and 2nd studies respectively). The HC increase in study 2 was effectively controlled by the use of a low water emulsion (a point of contrast with high water containing emulsions in study 1). Indeed the HC and CO emissions for EmB20 are lower than those seen in B0 (diesel), Fig. 12. The DOC unit was able to more than halve the emissions of HC, CO and NMHC (non-methane hydrocarbons) seen in study 1. Figure 14 illustrates the stepwise reduction in PM emissions when the fuel is changed from diesel (100%) to B20 (81%) to EmB20 (71%) and to EmB20+DOC (60%). This is also illustrated in Fig. 15, which shows the reductions measured in both study 1 and 2. Figures 14 and 15 indicate that the PM emissions reductions achieved by using biodiesel (FAME), water emulsions, and DOC complement each other. There is clear advantage in using these technologies in combination as opposed to using them as alternatives.

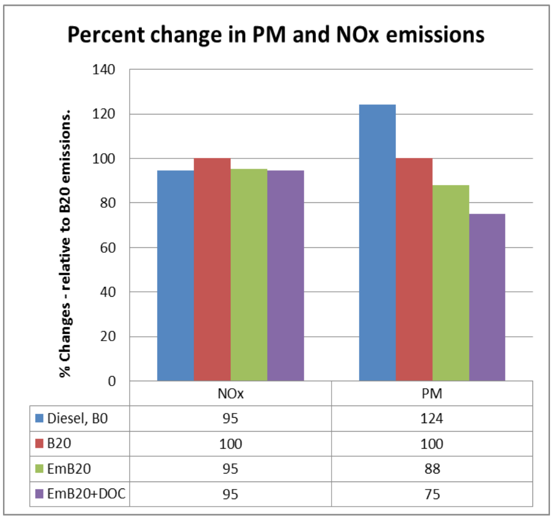


Fig.14: Relative changes in PM and NOx emissions (Note: B20 = 100%)

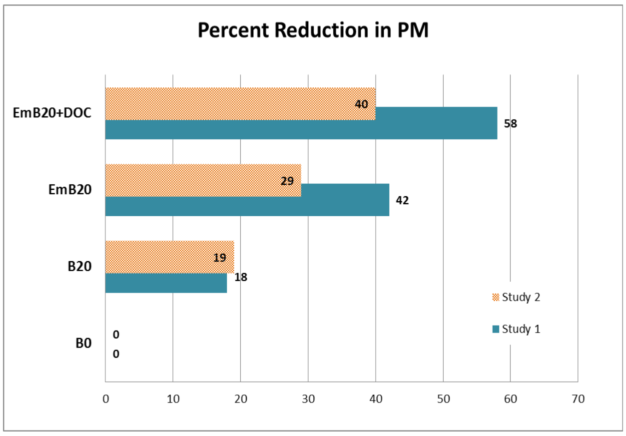


Fig.15: Comparative reduction in PM by B20, EmB20 (~6%m water) and DOC unit from the two studies

Phase 3 – Waterfront Operations

Three primary activities constituted the waterfront demonstration performance for emulsified B20 biodiesel fuel:

1. Operation of three top-handler units on regular B20 biodiesel fuel;
2. Operation of three top-handler units on emulsified B20 biodiesel fuel;
3. Operation of one top-handler unit on emulsified B20 biodiesel fuel with a DOC

Demonstration activities began on August 12, 2010 when "red" (i.e., untaxed) B20 biodiesel fuel was loaded into three MY 2008 Taylor top handler units at the Western Basin Container Terminal (WBCT) in the Port of Long Beach. Each top handler unit was powered by a 330 HP Cummins QSM11 diesel engine. Regular fueling practices were maintained during all subsequent operations at the waterfront. The record of regular B20 biodiesel fuel utilization was as follows:

- 697 hours over 27 days for 3 top-handler units
- 2908 gallons of soy based B20 biodiesel consumed
- 25.8 hours (total) per day average of top handler operation
- 8.6 hours per day average per top handler unit
- 108 gallons per day average fuel consumption
- 4.17 gallons per hour (GPH) average per top handler unit
- An approximate 4.3% increase in gross fuel consumption compared to the 4.0 gallons per hour (GPH) of diesel fuel consumption provided by Ports America for the WBCT top handler fleet
- B20 biodiesel fuel demonstrated a 2.45% increase in brake specific fuel consumption (BSFC) versus ultra-low sulfur diesel (ULSD) fuel during the QSM11 engine dynamometer testing
- Regular/established equipment maintenance schedules were maintained
- No operational issues reported/all processes "transparent" to equipment operators

On September 3, 2010, operations of the top handler fleet on emulsified B20 fuel commenced. Operations of the three units continued – without interruption – until January 21, 2011. The record of emulsified B20 fuel utilization follows:

- 2,742 hours over 118 days (excluding holidays and Sunday)
- 12,300 gallons of soy based emulsified B20 biodiesel consumed
- 23.3 hours per day average total top handler operation
- 7.8 hours per day average per top handler
- 104 gallons per day average fuel consumption
- 4.48 gallons per hour average per top handler

- An approximate 11.0% increase in emulsified fuel consumption (which includes the water content of the emulsified fuel) as compared to the 4.0 GPH of diesel fuel consumption provided by Ports America for the WBCT top handler fleet
- Emulsified B20 biodiesel fuel demonstrated a 10.4% increase in BSFC versus ULSD fuel measured during the QSM11 engine dynamometer testing
- Regular/established equipment maintenance schedule maintained
- No operational issues reported/all processes “transparent” to equipment operators

By achieving NO_X neutrality, biodiesel fuel emulsion technology allows the full benefits of a biofuel to be realized. In this regard, it is instructive to consider the CO_2 reductions wrought by operations at the Los Angeles waterfront. Determination of carbon dioxide level reductions utilizing the emissions calculator at the National Biodiesel Board (NBB) website[1] shows that the 12,300 gallons of which 92% i.e., 11,316 gallons is the actual consumption of B20, the rest being water (adjusted for its relatively heavier specific gravity and additive) reduces total carbon dioxide emission levels on the order of 36.5K pounds (Table 6) during the demonstration period of 118 days.

By extending these initial calculations to consider the application of emulsified biodiesel fuel to the test fleet of three (3) top handler units – for a period of one year – this initial value of 36.5K pounds advances to a value of 112,867 pounds of CO_2 emissions reductions. Finally, by considering the extension of the emulsified biodiesel fuel to a fleet of 100 top handler units for one-year, the NBB emissions calculator indicates that a CO_2 emissions reduction on the order of 3.7 million pounds is plausible. Note that this significant CO_2 emissions reduction would be accompanied by an equally significant reduction in PM levels and a neutralization of the NOx emission increases - that normally result from the use of a biodiesel fuel instead of a ULSD fuel - if the fuel of choice would be emulsified biodiesel fuel. APT would recommend that a case-specific analysis be done before reaching any conclusions of the overall CO_2 reductions; however, this analysis is included for reference purposes only.

Table 6: Carbon Dioxide (CO_2) Emission Level Calculations
1. The actual biofuel consumption for 3 top handlers during 118 days of activity was 11,316 GAL Entering this value of Fuel Usage into the NBB computer model gives CO_2 reduction of 36,485 LBS.
2. Annualized EBIOD fuel consumption for 3 top handlers is: 11,316*(365/118) = 35,002 GAL. Entering this value of Fuel Usage into the NBB computer model gives CO_2 reduction of 112,857 LBS.
3. Annualized EBIOD fuel consumption for 100 top handlers is: 35,002*(33) = 1,155,095 GAL. Entering this value of Fuel Usage into the NBB computer model gives CO_2 reduction of 3,724,228 LBS.

Summary

The favorable effects of emulsified biodiesel fuel blends on regulated emissions from diesel engines were proven by an extensive demonstration effort sponsored by the Technology Advancement Program (TAP) at the Port of Los Angeles. The demonstration effort featured a first phase wherein various emulsified biodiesel fuel blends were tested in a CARB certified diesel engine (DDEC-60) to determine the proper water content that could “neutralize” the NOx emission increases associated with regular biodiesel fuel blends. From this testing, it was determined that a 6.5% (by mass) water content could indeed normalize NOx emission levels for emulsified B20 (EmB20) biodiesel fuels to levels equal to those emanating from ultra-low sulfur diesel fuels.

The second phase of the effort showed that the an emulsified B20 biodiesel fuel with a 6.5% water content (by mass) operating in a Tier 2 Model year 2004 Cummins QSM 11C engine not only “neutralized” the NOx levels emanating from the test engine but also significantly reduced (by 42%) the PM emissions emanating from the test engine. One further determination during this second phase of the TAP demonstration effort was the addition of a Diesel Oxidation Catalyst (DOC) after-treatment unit to the emission reduction technology set. The

1 http://www.biodiesel.org/tools/calculator/default.aspx

cost-effective combination of Emulsion Fuel Technology and Engine After-Treatment Technology yielded a 56% reduction in PM emissions.

The final (third) phase of the TAP demonstration effort featured the use of an emulsified B20 biodiesel fuel (with 6.5% - by mass- water content) in three Taylor top-handler units – one fitted with a DOC unit – for four months of commercial operations at the West Basin Container Terminal (WBCT) at the Port of Los Angeles waterfront. All three units performed FLAWLESSLY during this demonstration period according the Area Equipment Services Manager of the Ports America Company who oversaw the operation of the top handler units throughout the demonstration period.

Since the base fuel of an emulsified BIODIESEL fuel is a biofuel, the significant reductions in PM emissions – and neutralization of NOx emissions – is accompanied by an equally significant reduction in CO_2 emissions. As such, emulsified biodiesel fuels can be recognized as a technology worthy of consideration when low carbon fuel standard operations are considered.

It is to be noted that the successful demonstration of EmB20 fuel use at the San Pedro Ports described in this paper was a "California Team" effort involving several Golden State commercial entities. The biodiesel base fuel for the project was supplied by the Community Fuels plant in Stockton, CA to the Ramos Oil terminal in Sacramento, CA where it was blended by APT with water and additive to produce the emulsified biodiesel EmB20 test fuels. The EmB20 test fuels were transported to a fuel truck owned by the General Petroleum (GP) Company in San Pedro, CA. GP distributed the EmB20 Fuel to top handler units that were operated by the Ports America Company in the San Pedro Ports.

References

[1] R. J. McCormick, C. J. Tennant, R. J. Hayes, S. Black, J. Ireland, T.McDaniel, A. Williams, M. Frailey, C. A. Sharp, "Regulating Emissions from Biodiesel Tested in Heavy-Duty Engines Meeting 2004 Emissions Standards" National Renewable Energy Laboratory, NREL/CP-540-37508. SAE 2005-01-2200,

[2] US Environmental Protection Agency "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions, Draft Technical Report." (October 2002), EPA420-P-01_001).

[3] A. F. Psaila, P.M. Grimes, R.L. Ellis, "Improving Biodiesel Blended Fuels: Overcoming the NOx Penalty and Enhancing the Engine's Regulated Emissions Profile" JSAE 20119367 / SAE 2011-01-1949.