

Evaluation of Diesel Oxidation Catalyst Conversion of Hydrocarbons and Particulate Matter from Premixed Low Temperature Combustion of Biodiesel

2011-01-1186

Published
04/12/2011William F. Northrop
Univ. of Michigan-Ann ArborDennis Assanis and Stani Bohac
Univ of Michigan

Copyright © 2011 SAE International

doi:10.4271/2011-01-1186

ABSTRACT

Premixed low temperature combustion (LTC) in diesel engines simultaneously reduces soot and NO_x at the expense of increased hydrocarbon (HC) and CO emissions. The use of biodiesel in the LTC regime has been shown to produce lower HC emissions than petroleum diesel; however, unburned methyl esters from biodiesel are more susceptible to particulate matter (PM) formation following atmospheric dilution due to their low volatility. In this study, the efficacy of a production-type diesel oxidation catalyst (DOC) for the conversion of light hydrocarbons species and heavier, semi-volatile species like those in unburned fuel is examined. Experimental data were taken from a high speed direct-injection diesel engine operating in a mid-load, late injection partially premixed LTC mode on ultra low sulfur diesel (ULSD) and neat soy-based biodiesel (B100). Gaseous emissions were recorded using a conventional suite of analyzers and individual light HCs were measured using an FT-IR analyzer. PM emissions data were collected from filter samples taken before and after the DOC using gravimetric analysis, Soxhlet extraction with speciation of extracted HCs, and total organic versus elemental carbon (OCEC) analysis. The previous results were confirmed with LTC of B100 resulting in over an order of magnitude increase in engine-out PM. It was found in the experimental study that 76% of the unburned fuel species responsible for this increase can be converted by a production-type DOC with an inlet temperature of 240°C and gas hourly space velocity (GHSV)

of 85,000 hr^{-1} . Unfortunately, the remaining unburned biodiesel left unconverted by the DOC still contributed significantly to the PM following dilution. Methyl esters from biodiesel were found to be the primary species contributing to the higher total organic fraction (>95%) on the PM for biodiesel LTC following a DOC.

INTRODUCTION

Motivated by ever stringent regulatory requirements, the reduction of emissions from diesel engines is a thriving area of research. Three general approaches can be used to decrease emissions from an engine operating at a given speed and load: reducing engine-out emissions through the alteration of the combustion process; using fuel that inherently forms less pollutants when combusted; and implementing aftertreatment systems. Combining these three strategies can provide additional advantages unattainable with one alone but can also create further complications.

Premixed low temperature combustion (LTC) is a well known combustion strategy for the simultaneous engine-out reduction of soot and oxides of nitrogen (NO_x) [1]. It is enabled by high levels of cooled exhaust gas recirculation (EGR) and high injection pressures, extending ignition delay and creating a primarily premixed combustion event. Local equivalence ratios are thereby reduced allowing the avoidance of soot formation while the increased dilution from EGR lowers NO_x formation by reducing local combustion

temperatures. The disadvantages of premixed LTC in diesel engines include an order of magnitude increase in hydrocarbon (HC) emissions due to mixture over-leaning and restriction on speed and load due to excessive heat release rates.

Biodiesel consists of alkyl esters from the transesterification of triglycerides with an alcohol. Its use is well known to reduce soot emissions in conventional diesel combustion due to embedded oxygen [2]. Biodiesel has been shown to have a combined benefit in the reduction of soot when used in premixed LTC modes as well as lead to the reduction of HC and carbon monoxide (CO) emissions while retaining equal NO_x emissions compared to petroleum diesel [3, 4]. Biodiesel LTC also has been shown to have disadvantages. Previous work by the authors proved that biodiesel LTC leads to an increase in engine-out particulate matter (PM) emissions due to condensation of unburned, low volatility biodiesel species following dilution [5]. Since this process occurs upon a reduction in temperature due to exhaust dilution, if the concentration of unburned fuel molecules in the gas phase can be lowered prior to exiting the atmosphere, the observed increase in PM could be averted.

Originally designed for use in diesel engines for the reduction of organic species from PM [6], the diesel oxidation catalyst (DOC) has become an essential tool for meeting diesel engine emissions targets worldwide [7]. Reviews like that by Zelenka et al. [8] surveyed the use of oxidation catalysts to that point in time and found them a suitable solution for the elimination of semi-volatile organic species within the PM, HC and CO from light and heavy-duty diesel engines. DOCs are usually configured as ceramic monoliths due to a desire for high durability and low pressure drop. The active metal typically used is platinum though palladium is also commonly added to aid in stabilizing the catalyst against thermal aging and sintering [9]. Aluminum oxide (alumina) supports have been commonly used in DOCs. Zeolite-containing supports have also been implemented for adsorbing HC species at lower engine exhaust temperatures where the catalytic material is not active [10]. Cerium oxide (ceria) is also often used as a component in support material for its oxygen storage capacity during rich excitations of the engine and for its ability to oxidize semi-volatile organic species within the PM [11].

The DOC is especially essential for reducing the higher CO and HC emissions generated by premixed LTC modes of operation. Bohac et al. [12] looked at the conversion of CO and HC from an engine operating in the LTC mode over a platinum-based catalyst. They found that the conversion efficiency for CO was near 100% while for hydrocarbons it was near 80%. Methane, being a major component among partially reacted species in premixed combustion did not react at the temperatures found in the DOC for LTC and accounted

for a large portion of the hydrocarbons passing, unreacted, through the catalyst.

Issues related to the use of DOCs in LTC modes arise due to the poisoning effects of engine exhaust species on the catalyst. Knafl et al. [13] in a combined engine and bench reactor study found that catalyst light-off temperature increased for LTC exhaust due to high concentrations of CO. Complicating the effect is low load operation where LTC operating strategies are typically implemented. Here, exhaust temperatures can be as low as 200°C, close or below the light-off temperature of most catalysts. Northrop et al. [14] also examined the self-inhibiting effects of unsaturated hydrocarbon species on a platinum-based DOC catalyst. They found reduced HC conversion efficiency when more of such species were present in the exhaust like the case of a rich LTC mode as described above. Han et al. [15] performed a more detailed study of the hydrocarbon species converted by the DOC from a late LTC mode. They found that alkenes and alkynes were almost completely converted whereas non-methane alkanes like ethane and propane had a conversion efficiency of only 80%. Higher carbon number HCs like those from unburned fuel had conversions that fell from 85% for C_8 to lower than 50% for C_{18} .

Although biodiesel combustion generally creates lower exhaust manifold concentrations of HC and CO than petroleum fuels, conversion of these pollutants through a DOC is still necessary to meet emissions standards. In general, conversions of total hydrocarbon (THC) emissions as measured by a flame ionization detector (FID) and CO are comparable between biodiesel blends and neat diesel fuel [16, 17]. Purcell et al. [18] performed a study where a heavy duty diesel engine was operated over a transient test cycle on commercially available diesel fuel, B50 made with soy-based biodiesel and B100. The results of the average conversion efficiency of THC, CO and formaldehyde (H_2CO) are shown in Table 1. THC conversion for all three fuels remained constant at near 60% and CO conversion was nearly constant at 80% but H_2CO conversion efficiency was significantly reduced for B100.

Table 1. Average conversion efficiencies of THC, CO and H_2CO through a DOC over a vehicle drive cycle calculated from the data presented in Purcell et al. [18] for diesel, B50 and B100

	Diesel	B100
η_{THC}	60%	61%
η_{CO}	77%	76%
$\eta_{\text{H}_2\text{CO}}$	42%	20%

For conventional biodiesel combustion, DOCs have been implemented to reduce higher organic content contributing to PM emissions compared with petroleum fuels. For example,

Sharp et al. [19] tested the effectiveness of a DOC to reduce the total PM emissions on a 5.9L medium-duty engine over the US Federal Test Procedure (FTP) cycle. They found that HC conversion efficiency of the catalyst was reduced but the CO conversion remained the same when comparing 100% biodiesel (B100) to a reference petroleum diesel. However, total PM and soluble organic fraction (SOF) conversion efficiency improved. Others have confirmed this finding [20] showing that the organic content leading to the same or higher PM emissions for biodiesel in conventional combustion are reduced through a DOC since the soot emissions are lower than for petroleum diesel. There are some dissenting findings however. Baik and Han [21] found that conversion of PM through a DOC at 200°C decreased from 37% to 26% for a heavy duty engine operating at part load for B20 compared with petroleum diesel. Peterson et al [16] also found that the conversion of PM for four different modes of combustion was lower for a B20 blend than for ULSD.

DOC conversion of high concentrations of unburned biodiesel like that found in the exhaust from LTC has been sparsely reported to the date of this writing. The work reported here experimentally evaluates the effectiveness of a production-type DOC to oxidize organic species in the exhaust that contribute to increased PM mass emitted from a vehicle tailpipe using biodiesel in the LTC mode. The overall mass concentrations THC and CO from conventional analyzers and individual light hydrocarbons (LHC) from a Fourier Transform Infrared (FT-IR) analyzer were measured at the inlet and outlet of the DOC with a constant inlet temperature and space velocity. Gravimetric measurement of PM collected before and after the DOC following using a partial flow dilution tunnel and an organic carbon versus elemental carbon (OCEC) analysis was also conducted. Finally the organic species from the gravimetric PM samples were extracted and speciated using a gas chromatograph with flame ionization detector (GC-FID) to determine the biodiesel remaining on the particles following the DOC.

EXPERIMENTAL

TEST ENGINE AND DOC

The experimental study was conducted using a multi-cylinder direct injection diesel engine suitable for use in a mid-sized passenger car. Specifications of the test engine are given in Table 2. The compression ratio of the engine was lowered from the stock engine configuration to enable LTC over a larger range of operation as described in Jacobs et al. [22]. Load and speed were controlled by a direct current dynamometer and the engine was equipped with a programmable electronic control unit (ECU) to allow management of parameters like EGR, fuel injection timing, injection pressure and duration.

Combustion analysis was conducted using in-cylinder pressure measurements using water-cooled Kistler 6041A piezo-electric pressure transducers. An AVL 365C crank angle encoder set at a resolution of 0.25 CA° fitted to the front of the engine was used to time the pressure data. The high speed signals were measured by a Redline CAS II data acquisition system manufactured by A&D Technology Inc. Heat release analysis was accomplished using a code developed at The University of Michigan [23]. This program combined low speed data and the high speed pressure trace from cylinder one to calculate the apparent rate of heat release (RoHR), fuel mass fraction burned and mean cylinder temperature using the first law of thermodynamics for an open system. Thermodynamic properties were calculated using the correlations of Krieger and Borman [24] and Hohenberg's correlation [25] was used to estimate heat transfer from the cylinder during combustion.

Table 2. Specifications of the engine used in the experimental study

Type	Direct-Injected Diesel
Cylinders	4
Displacement (L)	1.7
Bore (m)	0.079
Stroke (m)	0.086
Connecting Rod Length(m)	0.134
Wrist Pin Offset (m)	0.0006
Compression Ratio	16.0*

**Modified from stock engine compression ratio*

A production DOC was mounted in the exhaust stream of the engine following the turbine. It was the standard size and formulation meant to meet EURO IV emissions regulations for the production version of the test engine. Catalyst formulation and other specifications of the DOC are shown in Table 3. The DOC was de-greened prior to the study to ensure steady state activity over the testing period. This process involved maintaining the catalyst at a temperature of 160°C in an air and 10% water environment for 16 hours.

Table 3. Known physical specifications of DOC catalyst used in the study

Monolith length/diameter (mm)	93/74
Fraction engine swept volume	23.5%
Cell density (cm ⁻²)	62
Substrate material	Cordierite
Washcoat materials	Alumina, Silica, Zeolite
Active metals	Platinum, Palladium

FUELS AND OPERATING CONDITIONS

Fuels tested in the study included US specification ultra-low sulfur diesel (ULSD) and 100% soy-based fatty acid methyl ester biodiesel (B100). Physical and ignition properties of the two tested fuels are shown in Table 4. The biodiesel was used within three months of transesterification to avoid extensive fuel oxidation and exceeded the standards defined by ASTM 6751 at the time of engine testing.

Table 4. Properties of fuels tested in the experimental study.

Fuel	ULSD	B100
Cetane	45.7	50.1
LHV (MJ/kg)	42.97	37.35
Kin. Viscosity (mm ² /s)	2.35	3.93
Oxygen (Wt %)	0.0	10.9
H/C ratio	1.86	1.83
T10 (°C)	208	n.a.
T90 (°C)	308	340

The engine was operated at a single late-injection premixed LTC point. Table 5 gives the engine parameters held constant for both fuels with the 95% confidence interval error calculated from the standard deviation of all data taken in the study. It has been shown that by setting CA50 to maintain constant combustion phasing, differences in ignition quality can be normalized thus revealing fairer comparisons of emissions from fuels of varying chemical properties [26]. In the test procedure, an operating condition was set using the baseline ULSD fuel. When testing B100 at the same condition, injection timing was altered to maintain the same CA50, thus normalizing for differences in fuel ignition quality.

Three primary factors control the performance of catalytic reactors in exhaust aftertreatment applications; space velocity, catalyst temperature and composition. In this study, only the effects of changing exhaust composition into the DOC per fuel at a given engine condition was desired. Temperature of the DOC inlet was set to a constant value using a co-flow gas to gas heat exchanger installed prior to the DOC. Forced cooling air is provided by a centrifugal blower. The heat exchanger had the capability to lower the temperature by 15°C from a baseline value which was suitable for maintaining a constant DOC inlet condition.

Table 5. Constant Engine Conditions Maintained for the Experimental Study

Speed (rpm)	1500 ± 1
Power (bhp)	11.3 ± 0.1
BMEP (kPa)	397 ± 3
Injections	Single
Inj. Pressure (bar)	1007 ± 11
CA50 (°ATDC)	10.9 ± 0.1
NO _x Range (ppm)	26 – 35
EGR	45.3% ± 0.4%
Φ	0.68 ± 0.02
O ₂ in Intake	13.6% ± 0.2%
Intake Pressure (kPa)	101 ± 1
Coolant Temp. (°C)	86 ± 1
Intake Temp. (°C)	52 ± 1

EMISSIONS MEASUREMENT AND ANALYSIS

Instrumentation and Methods

The results from emissions measurement, including both gaseous species and particulate phase species, are the primary focus of this work. A number of analytical instruments were used to gather the necessary data in pursuit of the research goals. A flow diagram of the instrumentation used both during the operation of the engine and that used in post-processing is given as Figure 1.

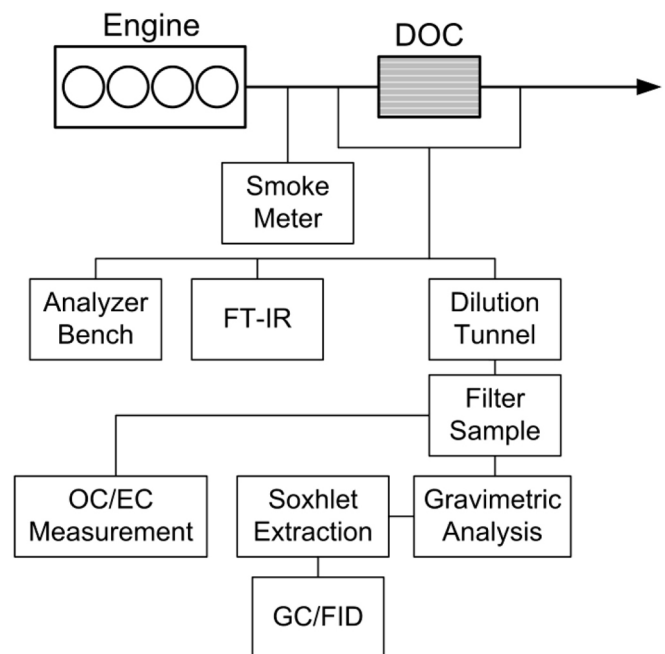


Figure 1. Emissions measurement flow diagram

The primary gaseous emissions from both the engine and the outlet of the DOC were measured by an AVL CEB II emissions analyzer bench. The analyzer bench utilizes non-dispersive infra-red (NDIR) detectors for measurement of CO and CO₂, a paramagnetic detector for O₂, a heated FID for total hydrocarbons (THC) and a chemiluminescence detector for measurement of NO_x consisting of NO and NO₂. Each analyzer has the capability of multiple measurement ranges to increase the accuracy of measurement. For the measurement of NO_x and THC the sample line was heated to 190°C from the sampling point on the engine exhaust line to each detector. Two heated glass micro fiber filters with 95% efficient retention for particles of 0.03 micron diameter of were mounted in the heated sample line to remove PM and other solid material before the analyzer. The O₂, CO, and CO₂ emissions were measured on a dry basis with a cooler to drop out any water from the sample prior to the analyzers.

An FT-IR analyzer was used to measure individual hydrocarbon species from the engine exhaust before and after the DOC. The specific instrument used was a 2030-HS Multigas Analyzer manufactured by MKS Instruments Inc. Although the FT-IR is capable of detecting most HC species found in engine exhaust, it was not used to measure THC since pre-loaded calibrations of all expected organic components in diesel exhaust would introduce too many errors. The value for THC was taken only from the FID incorporated into the analyzer bench. FT-IR sampling was accomplished though a heated sample line maintained at 190°C. When recording from the FT-IR, data were collected at a rate of 5 Hz for two minutes, of which the last minute was logged and averaged.

An AVL 415s smoke meter was used to measure soot from the engine outlet. When taking FSN samples using the smoke meter for the experimental study, 3000ml of gas was passed through the filter and three samples were acquired and consequently averaged per engine condition. FSN was only measured from the engine out location as it was assumed that soot remains unchanged through the DOC.

Particulate was collected from before and after the DOC using a Sierra Instruments BG-2 partial flow dilution tunnel equipped with a 10 µm cyclone separator and 39 mm diameter filter holder implemented in accordance with ISO/DIS 16183. A dilution ratio of 10:1 and filter temperature of 47 ±5°C were used for filter sampling. Whatman 7592 ring-supported PTFE membrane filters with 2 µm pore size were used for PM collection. Three filters were collected for gravimetric analysis for each data point. Conditioning and weighing of filters was done in accordance with EPA 40 CFR 1065 using a Mettler Toledo XP6U microbalance. Particulate was also loaded on quartz filters and organic versus elemental carbon (OCEC) analysis was performed using a thermal optical analyzer manufactured by Sunset Analytical. The

methods used for the OCEC analysis were in accordance with NIOSH 5040 and those described in reference [27].

Soluble organic matter was extracted from the PM filters using the Soxhlet extraction method. Dichloromethane was used as the sole solvent as it has been shown to be effective in the removal of methyl ester compounds as well as species found in petroleum diesel fuel [28]. Extractions of three filters were run in tandem at a rate of 6 minutes per cycle for 15 hours to yield approximately 150 total cycles. A known mass of three internal standard species were injected into the solvent prior to extraction for use in later GC-FID speciation. N-tetradecane was used for identification of hydrocarbons from C₈ to C₁₄, n-nonadecane was used to identify fuel and oil hydrocarbons from C₁₅-C₃₀ and methyl-heptadecanoate (C17:0) was used in the identification of methyl ester species from biodiesel.

A GC-FID analysis was conducted for the identification of unburned petroleum diesel fuel and biodiesel species in the PM. A Shimadzu GC-17A GC with FID was implemented using a pre-set temperature program at constant pressure. Three categories of species were identified: fuel-like light hydrocarbon molecules with carbon number less than C₁₈, methyl ester compounds from biodiesel and heavy hydrocarbon species assumed to be mostly from the engine lubricating oil with carbon number greater than C₁₈. Quantitative analysis was performed using the well known response factor method [29] where the factors for n-alkane species from diesel fuel were estimated using the methods of Scanlon and Willis [30] and methyl ester species factors were from Ulberth et al. [31]. The responses for other species not identified were assumed to be unity.

Emissions-Based Calculations

In measuring the majority of species contained in engine exhaust, the analyzer bench data were used to calculate other parameters useful for the study of emissions and engine performance. First, species measured on a dry basis like CO and CO₂ were calculated on a wet basis using the well established methods in reference [32] such that all emissions data in the study were comparable. Emissions Index (EI) is a near dimensionless parameter used to show the mass flow of a species in the exhaust with respect to the mass flow of fuel into the engine. In this way, emissions can be compared between engine conditions independent of dilution in the exhaust stream or efficiency of the combustion process. Using wet concentrations, the emissions index for each species was found using eq. 1 [33].