

Effects of Methyl Ester Biodiesel Blends on NOx Emissions

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ABSTRACT

Effects of methyl ester biodiesel fuel blends on NOx emissions are studied experimentally and analytically. A precisely controlled single cylinder diesel engine experiment was conducted to determine the impact of a 20% blend of soy methyl ester biodiesel (B20) on NOx emissions. The data were then used to calibrate KIVA chemical kinetics models which were used to determine how the biodiesel blend affects NOx production during the combustion process. In addition, the impact on the engine control system of the lower specific energy content of biodiesel was determined. Both factors, combustion and controls, must be taken into account when determining the net NOx effect of biodiesel compared to conventional diesel fuel. Because the magnitude and even direction of NOx effect changes with engine load, the NOx effect associated with burning biodiesel blends over a duty cycle depends on the duty cycle average power and fuel cetane number. Higher duty cycle average power corresponds to a larger NOx increase. Results also show that for biodiesel blends containing less than 20% biodiesel, the NOx impact over the FTP cycle is proportional to the blend percentage of biodiesel. At B20, the difference in NOx emissions between a biodiesel blend and its base diesel fuel is relatively small, and is less than the difference that can be seen between two commercial diesel fuels within the normal range of aromatics content available in the marketplace.

INTRODUCTION

Recent concerns about energy security, the desire to reduce petroleum imports, emphasis on greenhouse gas reductions through the use of renewable fuels, and interest in locally grown fuel crops have raised the demand for biodiesel use. Many studies have been completed that show biodiesel consumption in diesel engines reduces PM, HC and CO emissions for all methyl ester biodiesel blends [1,2]. This attractive feature of biodiesel has been a key driver for biodiesel use in environmentally sensitive applications, such as transit/school buses, urban municipal fleets and

underground mines. The impact of biodiesel on NOx emissions is not as clear. Several studies have been conducted where NOx emissions associated with various blends of biodiesel have been measured. In studies where pure methyl ester biodiesel is burned (B100), analysis of the results showed an average NOx increase of 10% [1]. However, the limited availability of biodiesel will restrict broad use of that fuel to blends that will typically contain 20% biodiesel or less. In some tests the NOx difference associated with B20 was not statistically significant [3]. In some studies the NOx increased while in other studies the NOx decreased [2,4,5]. The engine architecture and the duty cycle seem to be important factors affecting the NOx impact of these lower blends.

The purpose of this study was to quantify the effect of burning lower blends (20% or less) of soy based methyl ester biodiesel on NOx emissions. The effect was quantified in terms of the impact on the combustion process and the impact on engine controls settings due to the lower energy content of the biodiesel fuel. Finally, the above effects are applied to several key duty cycles to determine the expected change in NOx under typical operating conditions. These results are compared to experimental results available in the literature.

APPROACH

In an attempt to understand the variation in NOx emissions using methyl ester based B20 fuel blends over a wide variety of engine duty cycles and engine architectures, the impact of the engine controls settings was separated from fundamental combustion effects. The approach taken to achieve this purpose was to:

1. Conduct engine experiments under well controlled conditions to quantify the change in NOx emissions associated with B20. A comparison of NOx emissions between #2 diesel fuel (DF2) and B20 was conducted at fixed engine operating conditions to isolate the influence of fuel on combustion. Data was acquired for two commercial DF2 fuels with low

and high aromatic content along with their corresponding B20 blends.

2. Use this data set to calibrate a combustion CFD model.
3. Use the calibrated combustion CFD model to predict the change in NO_x emissions during the closed cycle combustion event for several different engine architectures at different engine speeds and loads.
4. Calculate the impact of the engine controls settings on NO_x emissions due to the lower energy content of biodiesel blends at the same speed and load conditions.
5. Use the contributions at specific speeds and loads to calculate the net impact of burning biodiesel blends over several key duty cycles.

TEST FUELS

Five test fuels were used for engine testing. These fuels were:

1. An ASTM D975 compliant ultra low sulfur diesel (ULSD) #2 fuel sample selected to represent higher aromatic content within the range of fuels typically available in the marketplace. The fuel was obtained from Chevron-Phillips and contained 31.4% total aromatics with a cetane number of 44.4. The aromatics content of this fuel is similar to EPA certification fuel. This fuel is referred to as DF2 (CN 44).
2. An ASTM D975 compliant ULSD #2 fuel sample selected to represent the lower end of typical commercial aromatic values. The fuel was obtained from Haltermann Products and contained 8.4% total aromatics with a cetane number of 51. This fuel is similar to CARB certification fuel and is designated by Haltermann as HF-523. This fuel is referred to as DF2 (CN 51).
3. A high aromatic biodiesel B20 blend obtained by mixing the soy based B100 stock with the high aromatic ULSD fuel DF2 (CN 44). This mixture has an aromatic content of 25.1 with a cetane number of 48. This fuel is referred to as B20 (CN 48).
4. A low aromatic biodiesel B20 blend obtained by mixing the soy based B100 stock with the low aromatic ULSD fuel DF2 (CN 51). This mixture has an aromatic content of 6.7 with a cetane number of 51.5. This fuel is referred to as B20 (CN 52).
5. A B100 soy methyl ester blending stock obtained from Chevron-Phillips, meeting ASTM D6751 and sourced from a BQ9000 Accredited Producer. This fuel has a cetane number of 51.6.

Fuels (3) and (4) were blended under controlled conditions at the Cummins Technical Center (CTC). All five fuels were chemically and physically characterized

at CTC's chemistry laboratory (for sulfur, specific gravity and viscosity), at CORE Laboratories (for aromatics, C/H/N, gross and net heat of combustion, cetane number, and distillation curve) and by the Southwest Research Institute (SwRI) for B100 speciation and aromatic carbon contents. Results and key test methods are summarized in Table 1 below and Tables A-1 through A-4 in the Appendix.

Table 1: Fuel properties.

	Aromatics (%)	Sulfur ppm	Specific Gravity	Viscosity cSt	Cetane No
Method ASTM	D5186	D5453		D445	D613
High Aromatics Fuel - DF2 (CN44)	31.4	8	0.84	2.25	44.4
Low Aromatics Fuel - DF2 (CN51)	8.4	0	0.83	2.41	51
B20/High Aromatics - B20 (CN48)	25.1	6	0.85	2.54	48
B20/Low Aromatics - B20 (CN52)	6.7	0	0.84	2.63	51.5
B100	0	0	0.89	4.14	51.6

Total aromatic content as measured by D5186 can be misleading from a combustion analysis standpoint, as it only reflects the mass fraction of molecular species containing an aromatic ring. To further characterize the base diesel fuels in a manner that more fundamentally describes their combustion attributes, the aromatic hydrogen atom and carbon atom content (expressed as mol %) was measured by nuclear magnetic resonance spectroscopy (ASTM D5292). This analysis revealed a narrower spread in the aromaticity of the two base fuels than is predicted by D5186, and helps to explain the relatively narrow difference in the measured net heat of combustion.

COMBUSTION ANALYSIS APPROACH

With extensive development and validation, combustion modeling based on detailed computational fluid dynamics (CFD) has become an integral part of the Cummins engine design process. In this study, these tools were applied to understand the impact of biodiesel on NO_x emissions. CFD offers a means to gain significant insight into the detailed relationship between biodiesel fuel injection, atomization, and combustion followed by the subsequent formation of exhaust emissions while capturing the influence of the combustion system geometry. A detailed description of the combustion analysis process used in this study can be found in [6].

The combustion model is based on the flamelet concepts developed by [7]. The flamelet approach allows the turbulent diffusion flame to be represented as an ensemble of thin, locally one-dimensional laminar flame structures. Advances made in turbulent combustion modeling offer the potential to greatly improve the ability to resolve the chemical processes involved in biodiesel spray combustion. One such advancement is the Representative Interactive Flamelets (RIF) approach [8]. RIF is a two-dimensional flamelet code which, used in conjunction with the KIVA3

software [9], models interactions between the turbulent flow field and chemical kinetics.

A significant enabling feature of the RIF combustion modeling approach is the ability to utilize extensive biodiesel kinetics mechanisms in a numerically efficient manner. The use of a large biodiesel kinetics mechanism along with diesel fuel kinetics mechanisms enables the model to simulate the various biodiesel blends. Since a large number of species are available with the B20 mechanisms, it also becomes possible to use a more complete soot model that can account for the chemical and physical aspects of soot particle formation, growth and oxidation. An extensive set of NO_x related chemistry is also incorporated into the RIF code [10]. After ignition and after the initial premixed fuel burns, a diffusion flame is established. The mixture fraction based flamelet approach used here is particularly well suited for the modeling of turbulent diffusion flames.

Two different biodiesel mechanisms were explored during this work. The primary mechanism used to simulate the soy methyl ester biodiesel was methyl butanoate proposed by [11] with additional modifications as proposed by [12]. The second mechanism investigated was methyl decanoate as proposed by [13]. The different diesel fuel types were modeled via a kinetics mechanism created using a mixture of n-decane and methyl-naphthalene [14,15].

The methyl butanoate mechanism was used to define simulated biodiesel blends as opposed to using the methyl decanoate mechanism. The methyl butanoate mechanism proved to be more stable and provided an acceptable run time of approximately 17 hours using a single CPU. The final B20 mechanisms representing the two biodiesel blends were not reduced from the reaction mechanisms referenced above and resulted in a combined mechanism with 252 non-steady state species.

In developing the surrogate biodiesel fuel mechanisms, there was the prerequisite that the surrogate fuel adequately predict the autoignition characteristics of the biodiesel blend. A comprehensive review of surrogate fuel selection is contained in [16]. Ignition delay data at the Mode 4 engine operation were used to formulate the blending of the n-decane, α -methyl-naphthalene, and methyl butanoate components. Cetane number was used as an additional fuel property in establishing the fuel blend. For these calculations, the requirement to match gross combustion behavior was given higher priority than a direct matching of fuel chemical structure. α -methyl-naphthalene, which is defined as having a cetane number of 0, was used in combination with long chain aliphatic species like n-decane to simulate fuels of varying cetane number. Our experience is that this practice yields combustion analyses with good capability to predict engine results.

The DF2 (CN 44) diesel fuel was modeled using 47% by volume of n-decane plus 53% by volume of α -methyl-naphthalene. The DF2 (CN 51) was modeled using 54% by volume of n-decane plus 46% by volume of α -methyl-naphthalene. The B20 (CN 48) biodiesel blend was modeled using 15% by volume methyl-butanoate plus 85% by volume of the DF2 (CN 44) diesel. The B20 (CN 52) was modeled using 17% by volume methyl butanoate plus 83% by volume of the DF2 (CN 51).

For this work, the primary atomization of the diesel spray is simulated using the wave break up model originally proposed by [17]. A Rayleigh–Taylor secondary break up mechanism proposed by [18] is also incorporated to account for the instabilities caused by the inertia of the denser fluid when the system experiences an acceleration perpendicular to the interface in the direction of the denser fluid. The fuel properties of biodiesel blends used in the KIVA code were determined using measured data shown in Table 1 and in Tables A-1 through A-3 in the Appendix along with approximation techniques similar to [19].

EXPERIMENTAL APPARATUS AND CALIBRATION

Previously published test results indicate that combusting B20 increased NO_x emissions on the order of 2% [1]. This means that any test regimen would need to have this resolution or better in order to determine the net impact of biodiesel usage on NO_x production. Resolving 2% changes in NO_x emissions represents a significant challenge requiring attention to all details associated with the testing procedure.

A single cylinder test engine facility was used to maximize the accuracy of the results. Test conditions can be more accurately controlled using a properly designed single cylinder test facility. The potential for cylinder-to-cylinder differences to impact the results are eliminated. Also, the charge composition, humidity, temperature, and pressure can be more accurately and precisely controlled in the single cylinder facility due to the availability of conditioned air and high precision flow control valves.

A schematic of the Cummins single cylinder test facility is provided in Figure 1. The engine is representative of modern diesel technology, and employs cooled exhaust gas recirculation (EGR) and an electronically controlled high pressure common rail fuel system. Note that a multi-cylinder engine block is employed but only one cylinder of the six is active. Combustion air and EGR flow rates and pressures are precisely controlled using high resolution position feedback control valves made by Sampson. Intake charge temperature is controlled by means of electric heating elements upstream of the intake surge tank. EGR flow rate is controlled by maintaining the pressure difference between the exhaust and intake surge tanks and by the

valve. The rate of EGR is measured in real time by means of a wide range linearized solid state oxygen sensor, made by ECM, that is positioned in the engine intake manifold. EGR temperature is maintained constant by means of a liquid-to-EGR cooler using engine coolant on the liquid side and precisely controlling the rate of engine coolant flow.

Gaseous emissions are quantified by means of a multi-function bench made by California Analytical Instruments (CAI). This bench has a dedicated EGR circuit. Although the rate of EGR is controlled in real time using the intake manifold mounted wide range oxygen sensor, the actual value of EGR is measured to a very high degree of precision using intake Carbon Dioxide measurements provided by the dedicated EGR circuit in the CAI emissions bench. Air flow is measured using a MicroMotion ELITE model coriolis meter. Fuel flow is measured using a high precision mass balance system. In-cylinder pressure is measured using a Kistler model 6067 water cooled transducer. The transducer output is recorded with a Cummins proprietary crankshaft-synchronous data acquisition system.

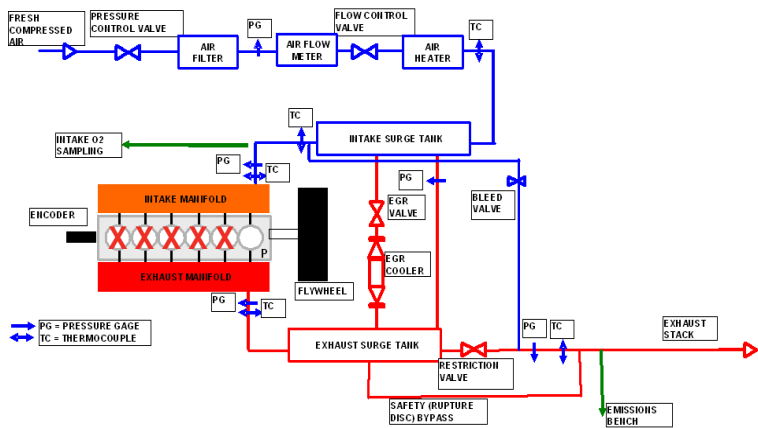


Figure 1: Schematic of Cummins single cylinder test facility.

The single cylinder engine used for this study is a modified Cummins ISB engine. Details of the test engine are provided in Table 2.

Table 2: ISB single cylinder engine specifications.

Bore	107 mm
Stroke	124 mm
Compression Ratio	16.3
Fuel System	Bosch CRIN 3.0 HPCR
Swirl	2.2 DCS
Displacement	1.1 L/cyl
EGR System	High Pressure, Cooled

The software package MINITAB was employed to determine the number of test point replicates required to achieve a test confidence and power of 95% as a function of the coefficient of variability (CoV) of engine out NOx to resolve a 2% change in NOx. A 2 sample t-test was employed for this work because it is effective in determining the differences between sample means. Based on the statistical analysis, 16 replicate points are required to achieve 95% test confidence and power to resolve a 2% difference with a CoV of 1.5%. The single cylinder test cell in which the data were to be acquired exhibited the necessary performance. Table 3 provides evidence that the single cylinder test system achieved better than the needed 1.5% CoV of exhaust NOx repeatability. The replicate points were conducted at the start, twice in the middle, and at the end of a Design of Experiments.

Table 3: Evidence of single cylinder test system achieving required repeatability performance.

(-)	RPM	LB/HR	LB/HR	NONE	PPM	G/Kgfuel	PSI
run no.	speed	fuelrate	airflow	phi	nox concentration	fuel specific nox	gimep
1	2735	11.14	268.02	0.615	162.83	5.9306	150.24
2	2735	11.08	267.99	0.612	161.35	5.9300	150.29
3	2735	11.11	267.97	0.613	161.74	5.9290	148.05
12	2735	10.99	268.07	0.606	159.04	5.8987	151.51
13	2735	10.96	268.09	0.605	158.66	5.9007	151.21
14	2735	10.96	267.98	0.605	158.85	5.9059	148.66
23	2735	11.02	267.94	0.608	160.02	5.9149	151.35
24	2735	11.01	268.02	0.608	159.30	5.8914	148.16
25	2735	11.05	268.02	0.610	158.87	5.8562	150.15
67	2735	11.07	268.02	0.611	159.51	5.8690	151.66
68	2735	11.07	268.06	0.611	160.20	5.8948	153.53
69	2735	11.07	267.99	0.611	160.30	5.8968	148.33
70	2735	11.07	267.98	0.611	159.21	5.8577	154.04
Max	2735	11.14	268.09	0.62	162.83	5.95	154.04
Min	2735	10.96	267.94	0.60	158.66	5.86	148.05
Ave	2735	11.04	268.01	0.61	159.99	5.90	150.55
Stdev	0.010	0.06	0.04	0.00	1.26	0.03	1.94
CoV %	0.00037	0.50	0.02	0.51	0.80	0.47	1.29

ENGINE OPERATING CONDITIONS FOR ACQUIRING SINGLE CYLINDER ENGINE DATA

The speed/load conditions selected are shown in Figure 2 along with specific engine parameters specified in Table A-5 in the Appendix. Transformation between the multi-cylinder reference engine brake torque and single cylinder engine net indicated mean effective pressure (NIMEP) was required to compensate for the abnormally high friction mean effective pressure (FMEP) typically demonstrated by single cylinder test engines. Nominal conditions for the multi-cylinder engine are shown along with the computed similitude conditions for the single cylinder engine in Table A-5.

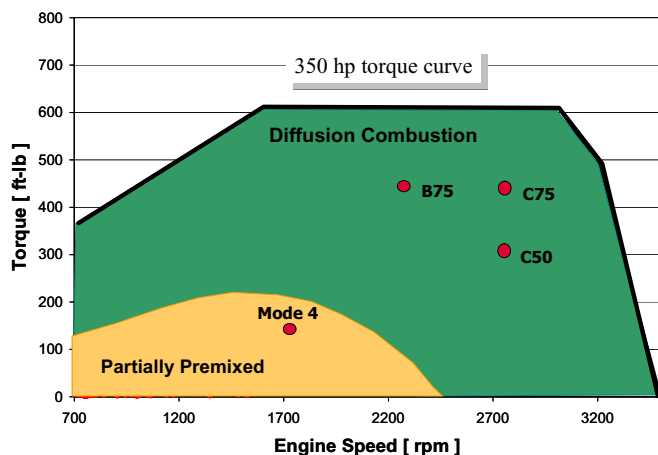


Figure 2: ISB 6.7L engine operating conditions used for single cylinder engine testing.

Equal EGR fraction was set for all of the test fuels at each of the speed/load points because of the extreme sensitivity of engine out NO_x to EGR. The single cylinder test system employed a linearized wide range zirconia based oxygen sensor positioned in the intake manifold to provide a “real-time” measure of EGR. The test system also utilized a control loop to obtain a desired level of intake oxygen for a given EGR fraction. Data analysis used intake manifold measured carbon dioxide concentration from a gaseous analyzer to determine actual test EGR to improve overall accuracy. The analyzer is too slow for real time control. EGR was varied for each test fuel to insure that engine out NO_x from all fuels could be compared at equal EGR rates.

The requirement of varying EGR throughout the test sequence, however, raises the issue of replicating test points in order to achieve the required test confidence and power of 95%. To address this, a linear regression of the Raw Exhaust NO_x data as a function of EGR fraction was generated. If the regression exhibited 95% confidence limits within 1% of the predicted NO_x regression function and if selected replicated points within the test sequence exhibited engine out NO_x CoV of 1% or less, then the requirements for 95% confidence and power would be achieved. Consequently, three replicate points were conducted at the lowest, mean and maximum EGR set point fractions of each test sequence to insure the CoV limit of 1% or less on the replicate points was achieved.

The unique volumetric heating value of each test fuel needed to be considered. For each target operating condition (Table A-5), each fuel was tested at constant air flow rate, constant common rail injection pressure and constant start of injection timing, while maintaining constant coolant, intake charge, and EGR cooler out temperatures. In addition, intake and exhaust system pressures were maintained constant. To compensate for the different volumetric heating values of the test fuels, injector on-time was adjusted to maintain nominal net indicated mean effective pressure as determined by the

net work calculation of the in-cylinder pressure versus crank angle data. Representative data comparing the results of the various test fuels is provided in Figure 3. Analysis of the results is provided in the following section.

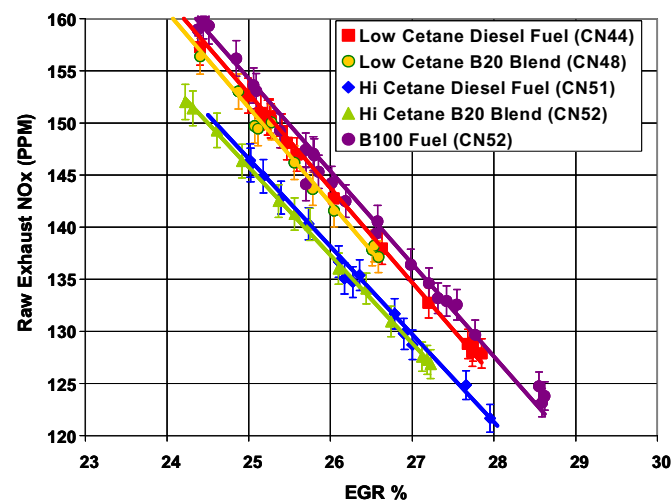


Figure 3: Raw exhaust NO_x variation with %EGR at the C75 condition.

RESULTS

NO_x CHANGES DUE TO THE COMBUSTION PROCESS

There are two primary ways that diesel fuel properties affect NO_x formation during combustion: flame temperature effects and ignition delay effects.

Flame temperature is affected by fuel chemistry (e.g., aromatic hydrocarbon content, methyl ester content). Higher aromatic content produces higher flame temperatures and therefore higher NO_x emissions. This effect is most significant for modes of combustion dominated by diffusion burning, as is characteristic of higher load engine operation. Considering aromatics content alone, one would expect that a B20 blend would have lower NO_x because of the lower aromatics content of the blend compared to the base diesel fuel. However, for biodiesel blends, two additional mechanisms come into play. The methyl ester compounds in the biodiesel have more double bonds than the base diesel fuel. These double bonds have the effect of increasing the flame temperature [20]. Additionally, during the course of the analysis, the combustion behavior of 10 mono-alkylbenzenes and polyalkylbenzenes were tracked. The 10 hydrocarbons include toluene, ethylbenzene, n-propylbenzene, n-butylbenzene, dimethylbenzenes (o, m, p-xylenes), trimethylbenzene (1,2,3 and 1,3,5), and 2-ethyltoluene. These 2 groups can be discriminated based on the pressure and temperature range over which these aromatics react. The first group is toluene, m-xylene, p-xylene, and 1,3,5 trimethylbenzene. This group does not ignite much below 900°C, and the second

group is o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, n-propylbenzene, 2-ethyltoluene, and n-butylbenzene. The second group reacts at low temperatures and pressure. Despite the fact that the simulated fuels are not an exact match to the detailed chemical composition of the experimental fuels, these basic chemical mechanisms are expected to occur and to differentiate between high and low aromatic fuels in this way. In this case, the experimental data are used to quantify the net effect and the analytical model is used to elucidate the underlying chemistry. Since the B20 blends were created with the same quantity of B100 but with different amounts of aromatics, there is a difference in the levels of the first and second groups in each of the blends. The addition of methyl ester to DF2 (CN44) increases the reactivity pathways of the first and second group compared to DF2 (CN44). However, the addition of the methyl ester to DF2 (CN51) does not result in a significant increase in reactivity via the second group but increases the first group compared to DF2 (CN51). The effect of these chemical mechanisms on increasing NOx, then, is more prevalent with the low cetane fuel. A more detailed examination of these mechanisms is beyond the scope of this paper.

Ignition delay has a less direct but also significant effect. At light load, much of the diesel fuel may burn in the “pre-mixed” mode, i.e., the ignition delay period from start of injection to start of combustion is long enough to allow most or all of the fuel to be injected before combustion begins. This pre-mixing results in a more dilute combustion zone and in lower peak combustion temperatures. This in turn results in lower NOx formation. This effect is contrary to the observations in the literature that indicate premixing the fuel in non-EGR engines increases NOx. Ignition delay is affected by aromatic hydrocarbon content and is generally characterized by cetane number. Higher aromatics fuels generally have lower cetane number, and lower cetane number indicates longer ignition delay. Ironically, although higher cetane diesel fuel is generally regarded as “better” than lower cetane fuel, it decreases the ignition delay and results in higher NOx emissions than lower cetane fuels for engine operation at light load where pre-mixed combustion is dominant.

To better understand the influence of biodiesel blends on each of these combustion mechanisms, we have examined two operating regimes in this study: higher load operation, where diffusion combustion is dominant (points B75, C50, C75 in Figure 2) and lower-load operation where pre-mixed combustion is dominant (Mode 4 in Figure 2).

Higher Load Operation – Diffusion Flame Combustion

A summary of the single cylinder engine results at the C75 (high load) engine operating condition is shown in Figure 4 as a function of intake oxygen concentration for the ISB single cylinder engine. The impact of the various

fuels on NOx emissions are compared at constant intake oxygen concentration to avoid confounding the influences of EGR, A/F, and fuel type on NOx emissions. Under diffusion flame combustion, there are small differences in NOx between a base diesel fuel and its corresponding B20 blend (e.g., comparison of DF2 (CN 44) with B20 (CN 48) and DF2 (CN 51) with B20 (CN52)). However, there are larger NOx differences between the base diesel fuel stocks when comparing DF2 (CN 44) and DF2 (CN 51). As discussed above, the difference in NOx emissions between the two commercial diesel fuels can be attributed to the difference in aromatics content, which is reduced by more than 50% from DF2 (CN 44) to DF2 (CN 51) (Table A-4). The competing effects of the other chemical mechanisms described above in biodiesel offset the aromatics dilution effect. The result is a very small change in NOx for the B20 blends compared to their base fuels. The higher aromatic, lower cetane B20 (CN 48) exhibited slightly higher NOx emissions compared to its based DF2 (CN 44), whereas the lower aromatic, higher cetane B20 (CN 52) produced slightly lower NOx than its base DF2 (CN 51), as would be expected from the previous discussion.

A key conclusion from these results is that at high load conditions where the combustion is dominated by a diffusion flame, there is only a small net combustion impact associated with burning biodiesel. The difference in NOx between either diesel fuel and its B20 blend is considerably less than the difference in NOx between the two commercial diesel fuels.

The KIVA model was calibrated using the engine data for two fuels: DF2 (CN 44) and the B100 fuel. Details of the KIVA calibration technique are summarized in [6]. The KIVA predictions are compared to experimental results in Figure 4. The KIVA code captures the trends in NOx emission between the various fuels well. There are some deviations between predicted and measured data at the lowest intake oxygen concentration. However, the majority of the KIVA NOx predictions are within the uncertainty of the engine data. The B100 NOx data are similar to the DF2 (CN 51) NOx data. Future efforts could focus on relating the detailed NOx formation with B100 to the properties of B100 and their relation to DF2. This investigation is beyond the scope of the current work which is focused on B20 blends.

The result of the heat release calibration for DF2 (CN 44) is shown in Figure 5. Good predictive agreement is also achieved for the B20 (CN 48) blend at the C75 (high load) operating condition where diffusion controlled combustion is the dominant mode of combustion with little to no premixed combustion occurring (see Figure 6).