NOx Emission Impacts of Biodiesel Blends

1. Introduction

In the Alternative Diesel Fuels rulemaking, the California Air Resources Board (ARB) is attempting to create a regulatory framework that will permit biodiesel and other alternative diesel fuels to increase their penetration of the California market. Biodiesel is known to increase emissions of nitrogen oxides (NOx). NOx emissions are an important precursor to smog and have historically been subject to stringent emission standards and mitigation programs to prevent growth in emissions over time. A crucial issue with respect to biodiesel is how to "… safeguard against potential increases in oxides of nitrogen (NOx) emissions."[1]

In July 2014, ARB released two datasets that represent the fruit of their efforts to compile biodiesel NOx emissions test data available in the literature on heavy-duty truck (HDT) engines. This document and the companion file *"Biodiesel Emissions Analysis Technical Summary 102014.pdf"* present the results of a statistical analysis of the data sets released by ARB that was performed by Rincon Ranch Consulting at the request of Growth Energy.

This analysis focused on whether soy and animal blends will increase NOx at low blend levels. The following issues were examined:

- The NOx impacts of soy and animal blends at B5 and B10;
- The NOx emission differences observed among animal feedstocks and blends;
- For animal blends, the effect on NOx emissions of the Cetane Number (CN) change relative to base fuel that is caused by blending of the animal feedstock; and
- The development of a cetane-based model of the biodiesel NOx impacts of soy and animal blends.

The key results and conclusions of the study are summarized here. For additional information, the reader is directed to *"Biodiesel Emissions Analysis Technical Summary 102014.pdf"* which has been provided along with this document.

2. Data Used in the Analysis

As noted above, in July 2014, ARB released two datasets of NOx emissions data from testing of biodiesel blends in HDT engines. One file ("B5 & B10 Raw NOx Data") contains the subset of testing for B5 and B10 blends (soy and animal). The test data generated in the four ARB-sponsored UCR studies are present in the form of the individual test run measurements. Because test run information was not reported in their publications, the B5 soy data from Nikanjam 2010 and the B10 soy data from Thompson 2010 are present in the form of emission averages. No animal blends have been tested at the B5 or B10 levels except in the ARB-sponsored emissions testing. A second file ("2014 Biodiesel

[1] "Proposed Regulation on the Commercialization of New Alternative Diesel Fuels. Staff Report: Initial Statement of Reason." California Air Resources Board, Stationary Source Division, Alternative Fuels Branch. October 23, 2013. http://www.arb.ca.gov/regact/2013/adf2013/adf2013isor.pdf.

Literature Search Database") contains all of the biodiesel testing available in the literature through the B20 level (soy and animal), including ARB-sponsored testing and the literature search. The data are in the form of emission averages by engine, test cycle, feedstock type, and blend level.

For purposes of this analysis, the following information was added to the ARB datasets:

- The number of test replications for emissions averages for each study (estimated when the source did not report the number);
- The CN for CARB diesel, the biodiesel blends, and the biodiesel feedstocks; and
- Additional NOx emissions testing at the B50 and B100 levels (where available).

Appendix Table A presents a list of the studies included in the dataset and the author references used in citations here.

3. NOx Emissions from Soy Biodiesel Blends

Most past research on biodiesel emissions has focused on soy blends. As a result, the literature is relatively large and diverse. The dataset assembled by ARB is derived from 10 different studies, covers 13 different vegetable feedstocks (10 soy, 2 used cooking oil [UCO], 1 canola), and was conducted using 7 different test cycles on a wide variety of engines in different labs. Most of the data, in terms of number of data points, is derived from the three UCR studies (Durbin 2011, Durbin 2013B, and Karavalakis 2014) sponsored by ARB.

We subjected the soy dataset to a number of different analyses using different statistical techniques and selections of the data to ensure that the conclusions we drew were robust across analytical techniques and datasets. The statistical analysis included the T-Test for the difference in mean values (e.g., between B5 and CARB diesel) and linear regression analysis using several different models. The data subsets were selected to use either individual test runs or emission averages and to contain testing through maximum blend levels of B5, B10, B20, B50, and B100.

Our analyses show that there is a consensus among the studies on the NOx impact of soy biodiesel without regard to the specific analytical methods or data used. Soy biodiesel increases NOx emissions by amounts that can be estimated with good statistical confidence because of the large size of the available dataset. The key conclusions are as follows:

- Soy biodiesel increases NOx emissions by ~1% at B5 and ~2% at B10;
- NOx emissions increase in a linear fashion with increasing blend level to reach ~4% at B20 and proportionately larger values at higher blend levels; and
- There is no evidence in the data for a threshold level below which soy biodiesel does not increase NOx.

These conclusions are supported by all of the available studies and data. None of the studies disagree substantially, and while the results for individual blends, engines, and test cycles will vary to some extent, the evidence across a wide range of engines and test cycles is clear. NOx increases can be expected for UCO, canola, and other vegetable biodiesels, but the data are very limited and it is not possible to draw definitive conclusions for these blends.

4. NOx Emissions from Animal Biodiesel Blends

The literature on NOx emissions from animal blends is much smaller. It consists of only four studies, three of which (Durbin 2011, Durbin 2013A, and Karavalakis 2014) were sponsored by ARB. Except for the McCormick 2005 study, the emissions testing was conducted at the UCR CE-CERT lab. A variety of test cycles were used, but most of the testing was conducted on the hot-start FTP cycle. Table 1 presents a summary of the emissions studies for animal biodiesel.

Table 1. Scope of Emissions Testing for Animal Biodiesel

	McCormick 2005	Durbin 2011	Durbin 2013A	Karavalakis 2014
Biodiesel Feedstock	Animal #1	Animal #2	Animal #3	Animal #4
Blend Levels Tested	B20	B5, B20, B50, B100	B5	B5, B10
Engines Tested	2 on-road	3 on-road, 1 off-road	1 on-road	1 on-road
Test Cycles	FTP	FTP, UDDS, 50 mph, ISO 8178	FTP	FTP, SET, UDDS
Test Replications on Biodiesel	6	126	26	80
Is NOx Increase Observed?				
At / Below B10	–	Yes	No	No
Above B10	Yes	Yes	–	–

It is important to understand the limitations of this small dataset. Without the ARB-sponsored testing, we would have only the six test replications (individual runs) conducted in the McCormick 2005 study. While the three UCR studies accumulated 232 test replications, the work involved only three different animal feedstocks. Including the McCormick 2005 study, the entire literature on NOx emissions from animal biodiesel is based on only four different animal feedstocks. The small number is an important limitation because animal feedstocks are much less homogenous than soy due the greater variety possible in animal sources and compositions. Further, there are notable differences among the four studies as to whether animal biodiesel increases NOx at the B5 and B10 levels (as indicated by the red circles in the table).

As in the soy analysis, we subjected the animal biodiesel data to a number of different analyses using different statistical techniques and selections of the data to ensure that the conclusions we drew were robust. The T-Test is the most direct method to assess whether NOx emissions are higher at B5 compared to CARB diesel. Using the individual test run data available from the three UCR studies, we find the following for animal biodiesel at the B5 blend level:

- The animal feedstock used in Durbin 2011 increases NOx in 2 of 3 engines. The increase is highly significant[2] statistically for one engine.

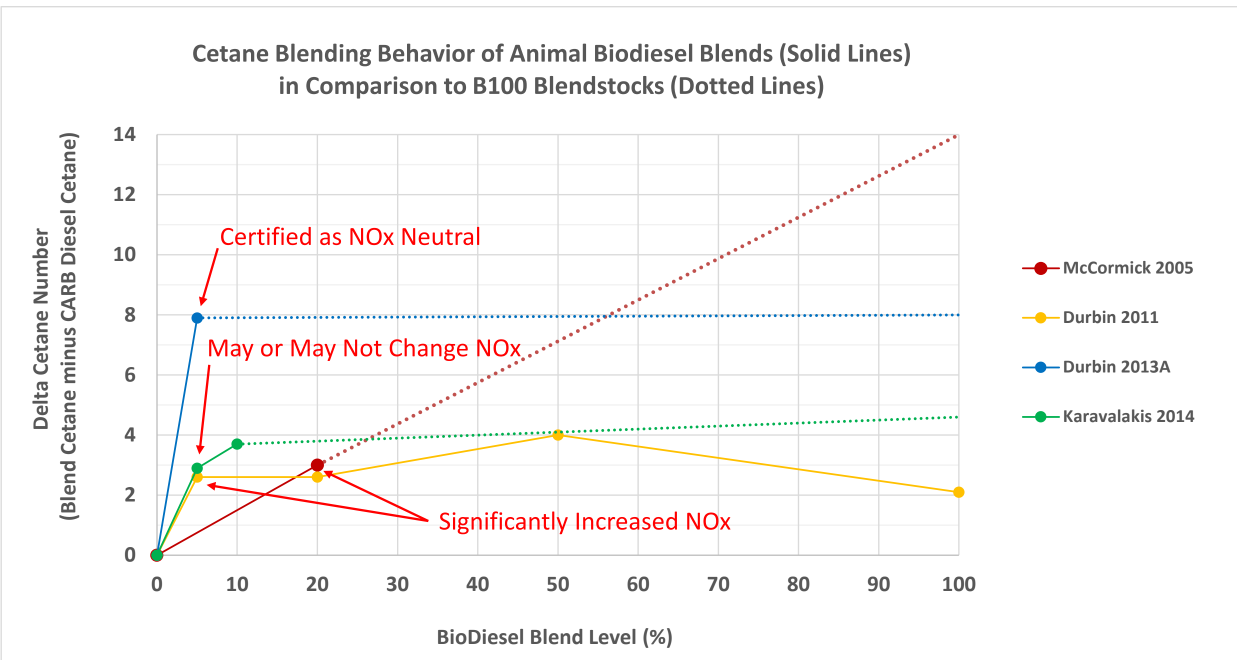
[2] The term "significant" is used in this report only to refer to statistical significance. When a result reaches the p=0.05 level, we can be 95 percent confident that it is real. In such case, and at smaller p values, the result is said to be statistically significant. "Significant" has been used by others to indicate that an emissions increase, even if real, is too small to warrant concern. For example, the Predictive Model for RFG will permit alternative gasoline formulations to increase NOx emissions by up to 0.05% and still be classified as emissions compliant. To our

- The animal feedstock used in Durbin 2013A decreases NOx in one engine. The decrease is statistically significant at the p=0.05 level and the blend was certified as NOx neutral at B5.
- The animal feedstock used in Karavalakis 2014 increases NOx in three of six cases and decreases NOx in the other three cases. None of the changes are statistically significant. The blend may or may not change NOx.

Contrary to Staff's assertion that no NOx increase occurs in B5 animal blends, it is clear that <u>some animal blends will significantly increase NOx emissions, while other animal blends will not</u>. The fundamental issue is then understanding what the NOx impact of a particular animal biodiesel blend will be.

The effect of feedstock blending on the CN of the resulting animal blend is the reason for the apparently discordant results among the studies. Figure 1 plots the four series of animal blends in the literature with the blend level on the horizontal axis and the change in blend CN (relative to CARB diesel) on the vertical axis. CN blended linearly to B20 for the McCormick feedstock, which showed a much smaller CN benefit than the feedstocks used by UCR – only three numbers at B20 (0.6 numbers at B5). In contrast, all three UCR animal blends achieve a large CN boost at low blending levels in which most or all of the CN benefit of the feedstock is achieved at B5.

Figure 1. Cetane Blending Behavior of Animal Blends (Solid Lines) Compared to B100 Feedstocks (Dotted Lines)



In Durbin 2011, the CNs for the blends are above that of the B100 feedstock. This result is probably caused by lab-to-lab differences (blend CN was determined at CE-CERT, while CN for CARB diesel and the

knowledge, ARB has not formulated a position on the level of NOx increase from alternative diesel fuel that is too small to warrant concern.

B100 feedstock were determined by an outside lab). The actual CN changes are surely lower than shown here – at or below +2 CNs.

The two animal feedstocks that caused statistically significant NOx increases have the smallest CN benefits: McCormick 2005 (red) at B20 and Durbin 2011 (yellow) at B5. The animal B5 blend that passed certification testing as NOx neutral in Durbin 2013A (blue) has the highest CN benefit, where it achieved the entire B100 CN at just 5 percent blending. The Karavalakis 2014 B5 blend (green) had an intermediate CN benefit and may or may not change NOx.

The blending behavior of the UCR blends is surprising in comparison to the McCormick study, and we find relatively little research on the CN blending behavior of animal feedstocks. All conclusions from this dataset will be influenced by the CN blending behavior of the specific animal feedstocks involved. For such conclusions to be reliable, we must be confident that the large CN boost reported for the UCR blends is both real and representative of all animal feedstocks in California. Also, only limited information is available on the sources and characteristics of the animal feedstocks.

To permit all parties to better understand the animal feedstocks that were tested, ARB should release all information that it has on the following:

- CNs (methods of determination and measured values) for the Durbin 2011 and other UCR studies;
- Physical and chemical properties of the animal feedstocks and biodiesel blends tested;
- The distribution of sources, characteristics, and properties in the population of animal feedstocks that are available for use in the California market; and
- How the specific animal feedstocks tested at UCR were selected, including any information that would demonstrate that the feedstock properties and their CN blending behavior are representative of the animal feedstock population available for use in California.

5. Development of a Cetane-based Model of NOx Impacts from Soy and Animal Biodiesel

The results presented above indicate the important role that CN plays in determining the NOx response for animal blends. Animal feedstocks tend to <u>increase</u> the CN of the blend above that of the CARB diesel and the CN change can be large at low blend levels. Soy feedstocks have generally adverse effects and tend to <u>decrease</u> the CN of the blend below that of the CARB diesel; for soy, the CN change at low blend levels can be smaller than the uncertainty in determining CN. The result of our work on a cetane-based model demonstrates that <u>soy and animal blends are not categorically different fuels once their differing effect on CN is accounted for</u>. Their NOx impacts can be represented by the same model as a function of blend level and the change in CN compared to CARB diesel.

The document that accompanies this report explains the development of the cetane-based model in some detail. In brief, it was developed using conventional linear regression analysis with log(NOx) emissions as the dependent variable. Intercept terms were included to represent the varying emission levels on CARB diesel for each combination of study, feedstock type, engine, and test cycle. A *b* coefficient was included to represent the change in NOx emissions for each 1 percent biodiesel in a blend <u>at constant CN</u>. A *c* coefficient was included to represent the change in NOx emissions for each 1 number change in CN compared to CARB diesel <u>at constant blend level</u>. Both soy and animal blends were included in the estimation, along with the small number of canola and UCO data points, at blend levels up to (and including) B20.

The model estimation shows that the *b* and *c* coefficients are highly significant statistically ($p < 0.0001$). The estimation results also show the following:

- The *b* coefficient has a value of +0.00156, which estimates that soy and animal biodiesel will increase NOx emissions by 0.16% for each 1 percent biodiesel at constant CN or by 0.8% at B5.
- The *c* coefficient estimates that +5 CNs will decrease NOx emissions by 1.5 percent at constant blend level. This result is completely consistent with earlier work[3] on the relationship between CN and NOx emissions in HDT engines, which also found that +5 CNs will decrease NOx emissions by 1.5 percent in base fuels with CN ~50.
- An increase of -b/c = 0.5 CNs is needed to offset the NOx increase expected from each 1% biodiesel added. For B5, an increase of 2.5 CNs is required to offset the expected NOx increase.

The results explain why soy and animal blends appear to be different fuels. Soy blends have an additional, adverse CN effect that increases their NOx impact to ~1% at B5. Animal blends will generally increase CN and that reduces their NOx impact to about one-half the soy level or less depending on the CN change caused by blending. The results also explain why some animal blends do not increase NOx emissions. If an animal feedstock increases CN by more than ~0.5 numbers for each 1% biodiesel blended, then the resulting fuel may not increase NOx emissions.

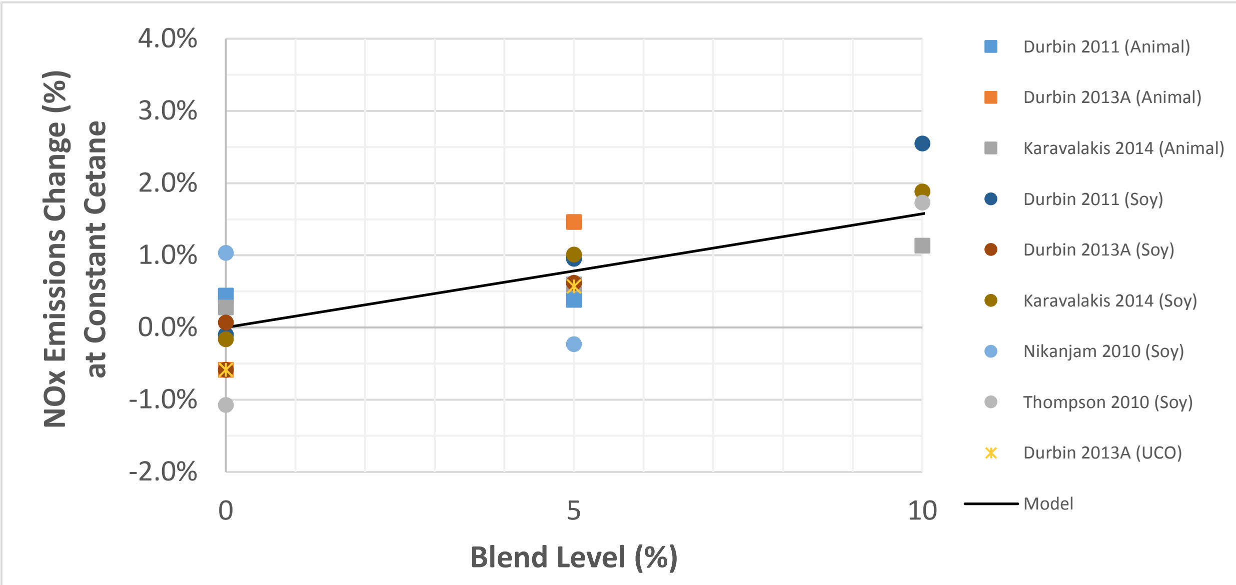
To demonstrate these conclusions, Figure 2 presents NOx emissions as a function of blend level for all fuels used to estimate the model once NOx emissions are adjusted for the CN change observed for each blend (animal blends are plotted as squares, soy blends as circles, and the non-soy vegetable blends as asterisks). For example, if an animal blend increased CN, then its NOx impact is increased as we return it to the base fuel CN. If a soy blend decreases CN, then its NOx impact is decreased as we return it to the base fuel CN. Once adjusted, percent changes in emissions are calculated. As seen in the figure, there is no discernable difference among feedstock types once CN changes are taken into account. Animal and soy blends scatter on both sides of the regression line, indicating that they obey the same blend level model.

Note the scatter of points around the regression line (which gives the "average" response). Some of the scatter is due simply to emissions measurement error. But other factors may be involved in determining the NOx impact for a given feedstock, including differences in the FAME composition and uncertainty in determining CN for the blends. If ARB were to adopt a predictive model to determine the CN improvement needed to mitigate NOx, it should use the model to evaluate a "worst case" feedstock, meaning a point near the upper end of the range at each blend level.

The most important conclusion of this work is that soy and animal biodiesel blends are not categorically different fuels. Their emissions effects are similar, but they show different NOx impacts because they have different effects on CN. Further, this work provides a potential answer to the problem that some animal blends will significantly increase NOx emissions, while other blends will not, by indicating what individual blends may do.

[3] *The Effect of Cetane Number Increase Due to Additives on NOx Emissions from Heavy-Duty Highway Engines*. EPA420-R-03-002. February 2004. Figure IV.A-1.

Figure 2. There Are No Detectable Differences Among Feedstock Types Once NOx Emissions Are Adjusted to Constant CN



Note: Animal blends are plotted as squares, soy blends as circles, and the non-soy vegetable blends as asterisks.

6. Summary and Conclusions

Based on the results summarized above, ARB must consider as part of the current rulemaking a regulatory structure in which the NOx impacts of soy and animal biodiesel are accounted for using a statistical model analogous to the Predictive Model for RFG. We see the cetane-based model presented here as a possible draft for a biodiesel predictive model, but further work is needed to:

- Demonstrate that blends mitigated using DTBP obey the same model; and
- Assess whether the four animal feedstocks that have been tested are representative of all animal feedstocks available in the California market.

Additional emissions testing may be needed if it is determined that the four animal feedstocks that have been tested are not representative of the population of animal feedstocks available for use in the California market.

Further, more advanced statistical techniques should be used as was done in developing the Predictive Model for California Reformulated gasoline. The dataset used here is highly unbalanced, meaning that there are varying numbers of data points for each combination of study, feedstock type, engine, and test cycle. In fact, only a fraction of all possible study/feedstock/engine/test cycle cells are represented by one or more data points. A technique known as Mixed Effects Modeling is appropriate in such cases and its use will assure that coefficient estimates are not biased by the unbalanced distribution of the data.

The key conclusions of this study are summarized below.

- Soy and animal blends are not categorically different fuels once their differing effects on blend CN are taken into account.
- There is no evidence in the data of a threshold level below which biodiesel fuels as a group do not increase NOx, whether soy or animal. However, individual blends may not increase NOx if the CN gain caused by blending is sufficiently large to offset the underlying tendency of all biodiesel blends to increase NOx emissions.
- Soy blends clearly and significantly increase NOx by ~1% at B5 and by proportionately larger amounts at higher blend levels. Soy blends require mitigation at all levels to offset increased NOx emissions.
- Animal blends are more complicated. The current research is limited and the evidence is mixed. At least one B5 animal blend significantly increased NOx, while another has been certified as NOx neutral. Other B5 animal blends may or may not increase NOx depending on their effect on CN (and possibly other factors).
- Staff's assertion that no NOx increase occurs at B5 in animal blends is incorrect. Some animal blends will significantly increase NOx emissions, while other animal blends will not.
- Animal blends cannot be assumed to have no impact on NOx emissions without a determination of the impact of feedstock blending on CN.

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APPENDIX TABLE A: REFERENCES TO LITERATURE

Author	Title	Feedstocks Studied	Blends Studied
Clark 1999	Transient Emissions Comparisons of Alternative Compression Ignition Fuel	Soy	B20
McCormick 2002	Fuel Additive and Blending Approaches to Reducing NOx Emissions from Biodiesel	Soy, UCO	B20
McCormick 2005	Regulated Emissions from Biodiesel Tested in Heavy-Duty Engines Meeting 2004 Emissions	Soy, Canola, Animal	B20
Eckerle 2008	Effects of Methyl Ester Biodiesel Blends on NOx Emissions	Soy	B20
Nuszkowski 2009	Evaluation of the NOx emissions from heavy duty diesel engines with the addition of cetane improvers.	Soy	B20
Nikanjam 2010	Performance and emissions of diesel and alternative diesel fuels	Soy	B5, B20
Thompson 2010	Neat fuel influence on biodiesel blend emissions	Soy	B10, B20
Durbin 2011	Biodiesel Characterization and NOx Mitigation Study	Soy, Animal	B5, B10, B20
Durbin 2013A	CARB B5 Preliminary and Certification Testing	Animal	B5
Durbin 2013B	CARB B20 Biodiesel Preliminary and Certification Testing	Soy, UCO	B20
Karavalakis 2014	CARB Comprehensive B5/B10 Biodiesel Blends Heavy-Duty Engine Dynamometer Testing	Soy, Animal	B5, B10