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Fuel Property Effects on Biodiesel

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Abstract. *Biodiesel is an environmentally friendly alternative diesel fuel obtained from renewable resources, such as vegetable oils, animal fats, and recycled restaurant greases. It is described in ASTM standard D 6751-02 as: a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is oxygenated, sulfur-free, biodegradable, and non-toxic. One of the attractive characteristics of biodiesel is that it does not require any significant modifications to the diesel engine, so the engine does not have to be dedicated for biodiesel. However, due to its different properties, such as a higher cetane number, lower volatility, and lower energy content, biodiesel may cause some changes in the engine performance and emissions.*

These different properties can effect the injection timing and the diesel combustion process causing lower power and higher oxides of nitrogen. The objective of this study was the investigation of biodiesel fuel properties such as cetane number, fuel volatility, and energy content on biodiesel combustion. The results of heat release analysis are presented from measured cylinder pressure data on a turbocharged diesel engine fueled with biodiesel from soybean oil, biodiesel from animal grease, and No. 2 diesel fuel.

Keywords. biodiesel, diesel fuel, alkyl esters, diesel engine, fuel injection, diesel combustion, diesel emission, NOx emission

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Introduction

Biodiesel is an environmentally friendly alternative diesel fuel consisting of the alkyl monoesters of fatty acids. It is obtained from triglycerides through the transesterification process. It is completely soluble in commercial petroleum-based diesel fuel, so biodiesel can be used as a blend and one fuel tank can be used for storage of both fuels. This makes the vehicle flexible. This is a unique advantage compared with most other alternative fuels, because this will give users the opportunity to use the alternative fuel where and when it is available without paying any extra money for engine modifications. Biodiesel has been standardized by ASTM standard D 6751-02 in 2002 and in Europe DIN V 51506 in 1994. Biodiesel is commercially available in Europe and it is becoming more available in the United States. Many large engine and car manufacturers have included biodiesel fuel in their warranties (Korbitz, 1999). Depending on the trade-off between cost and its environmental benefits, biodiesel is most commonly used in the United States as a blend with No. 1 or No. 2 diesel fuels.

The advantageous features of biodiesel result from the fact that biodiesel has different physical and chemical properties than petroleum-based diesel fuel. Eleven percent of biodiesel is oxygen by weight and this appears to result in more complete combustion. Also, it has a higher cetane number that makes the combustion smoother and the engine is less noisy. However, biodiesel has higher values of viscosity, density, speed of sound, and bulk modulus that may cause changes in the injection system and combustion system behavior (Tat and Van Gerpen, 1999; Tat and Van Gerpen, 2000a; and Tat et al., 2000b). Fuel quantity, injection timing, and injection spray pattern in the combustion chamber are directly effected by these parameters. Biodiesel's lower heating value is about 12% less than petroleum-based diesel fuel and this causes a power loss that must be compensated for by increasing the injected fuel amount. When injecting this greater quantity of fuel, some fuel injection systems start the injection earlier and hold the injection needle open longer, changing the fuel injection timing and the start of combustion timing. These differences in physical properties may shift the engine timing settings from their optimized factory settings, leading to earlier combustion. This can result in higher combustion temperatures and pressures causing higher nitrogen oxide (NO_x) emission in the exhaust of a biodiesel-fueled diesel engine. Another reason for the combustion timing change may be the higher cetane number of biodiesel. If the cetane number is higher, this means that the ignition delay time, which is the time between the start of injection and the start of ignition, gets shorter. The start of combustion comes earlier, which tends to increase NO_x, but shorter ignition delay also tends to decrease premixed combustion, which usually decreases NO_x. Which effect is dominant depends on the specific situation.

Therefore, more research is required about the physical and chemical properties of biodiesel fuel and their effects on the diesel fuel injection system and diesel combustion. Biodiesel use in diesel engines reduces diesel engine exhaust emissions with the exception of nitrogen oxides (NO_x). The objective of this project is to determine the reasons for the higher nitrogen oxide emission of the diesel engine fueled by biodiesel fuel.

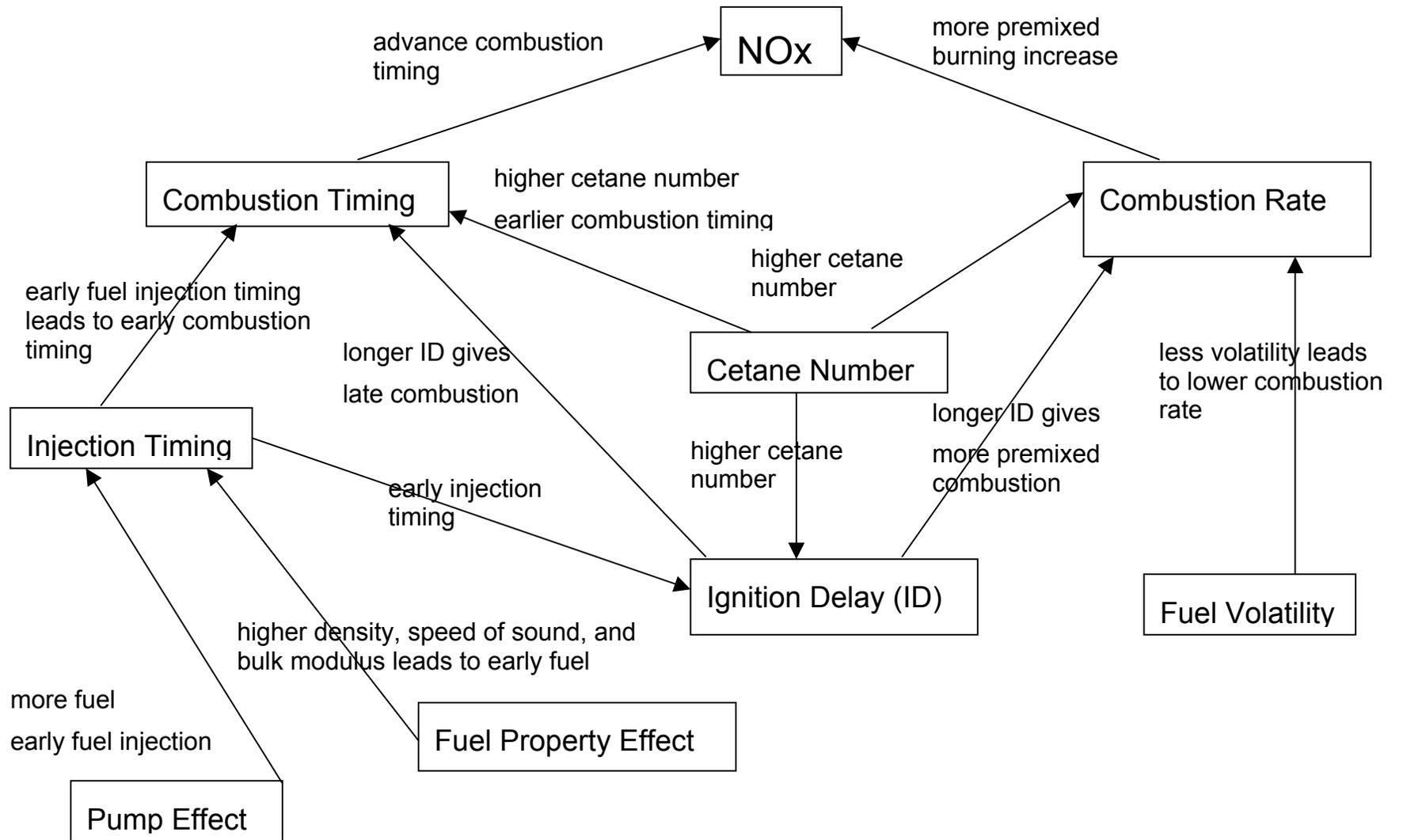
Materials and Methods

The interrelationships between NO_x emissions and diesel engine combustion parameters, such as combustion timing and premixed combustion, are explained in this section and discussed using the concept map shown in Figure 1. Nitrogen oxide emission is primarily a function of high temperature in the combustion chamber (Heywood, 1988; Owen and Coley, 1990; Lavoie, et al. 1970). As shown in Figure 1, there are two main combustion characteristics that will determine the temperature in the cylinder and thus the NO_x emission. These are the combustion timing and combustion rate.

Combustion timing determines the combustion history relative to the piston position at TDC in the cylinder. Early combustion timing causes combustion to occur closer to TDC and perhaps during the compression process, increasing the pressure, temperature, and NO_x emission (Heywood, 1988; Lyn and Valdmanis, 1968; Wong and Steere, 1982). Combustion timing in a diesel engine is mainly affected by injection timing, or the start of injection, and the ignition delay, which is the time between the start of injection and the start of combustion. The ignition delay time is mostly affected by the fuel's cetane number. The cetane number of biodiesel is higher than diesel fuel. Higher cetane number corresponds to ignition delay time and advances the combustion timing. Early injection timing and higher cetane number advance the combustion timing which tends to increase the NO_x emission (Heywood, 1988; Owen and Coley, 1990; Lavoie, et al. 1970; Lyn and Valdmanis, 1968; Wong and Steere, 1982). Biodiesel has a lower energy content than diesel fuel and when a greater volume of fuel is injected to correct for this, some fuel injection pumps will advance the start of injection. Biodiesel also has different physical properties such as higher density, speed of sound, and bulk modulus, which can lead to an earlier start of injection (Tat and Van Gerpen, 1999; Tat and Van Gerpen, 2000a; and Tat et al., 2000b).

Combustion rate, as indicated by the heat release rate, also has an effect on NO_x production. More premixed combustion means a high initial rate of combustion which increases NO_x emission (Heywood, 1988). Cetane number and fuel volatility are the most two important fuel properties that affect combustion rate. High cetane number and low volatility lowers the combustion rate (Freedman and Bagby, 1990; Van Gerpen, 1996). Biodiesel's high cetane number is expected to lower the amount of fuel prepared during the ignition delay period and thus the amount of premixed combustion. This decreased amount of premixed combustion and biodiesel's low fuel volatility are expected the rate of combustion and the NO_x emission (Heywood, 1988). It should be noted that cetane number has two conflicting effects. It advances combustion timing, which tends to increase NO_x and it decreases premixed combustion and the initial rate of combustion, which tends to decrease NO_x.

The engine tests laid out in Table 1 were developed to provide a better understanding of biodiesel fuel property effects on diesel engine combustion and NO_x production. A four-stage test process was planned and is in the process of being completed. For the first stage, the research was started from the bottom of the concept map to investigate the effect of the pump timing advance and the fuel property effect on fuel injection timing. The engine was to be run at different load conditions, and the injection timing and the fuel delivery were recorded in grams per injection for both biodiesel and diesel fuel. This test was to provide information about the fuel property effect and the injection pump effect on the injection timing advancement seen in diesel engines fueled with biodiesel.



For the second stage, the injection pump timing was varied for both fuels so that the engine could be run with equal start of injection timing and the actual start of combustion timing was measured. This allowed any effects of fuel properties on the fuel pump to be eliminated from the comparison. It was possible to distinguish the cetane number effect on the diesel combustion. These tests provided enough information to understand cetane number and fuel injection timing effects on the start of combustion and NOx production due to the effect on the start of combustion.

The third and the fourth stages were combined and the cetane number and the fuel volatility effect on the combustion rate was investigated together. The engine was run on both fuels at the same start of combustion and with the same cetane number, but at different volatility. In order to do this, the cetane number of the diesel fuel was increased using a cetane improver additive, but the volatility of the diesel fuel was still higher than for the biodiesel fuel. This test answered the question about the volatility effect on the combustion rate and NOx emission. Also, with the same start of combustion timing and by using fuels that have same volatility, but different cetane numbers, such as soybean oil-based biodiesel and animal fat-based biodiesel, we should be able to distinguish the cetane number effect on combustion rate and NOx production.

Table 1 Test proposal

<i>Stage Number</i>	<i>Purpose</i>	<i>Variables</i>	<i>Held constant</i>	<i>Monitored</i>
1	Determination of fuel injection pump and fuel physical property (density, speed of sound, and bulk modulus) effect on fuel injection timing and NOx production	Load, (100% to 20%) Fuel, (Soybean biodiesel and No. 2 Diesel fuel)	Engine speed	Injection timing Fuel delivery
2	Determination of cetane number effect on the combustion timing.	Fuel Cetane No.	Injection timing	Combustion timing and NOx
3	Determination of fuel volatility effect on fuel combustion	Fuel Volatility (Soybean biodiesel and No. 2 Diesel with cetane Improver)	Cetane number and Start of combustion	Combustion rate and NOx emission
4	Determination of cetane number effect on fuel combustion	Fuel Cetane number (Soybean and Yellow Grease Biodiesel)	Volatility and Start of combustion	Combustion rate and NOx emission

Experimental Apparatus

A four stroke, four cylinder, turbocharged, direct injected John Deere 4045 TF diesel engine was used for this research. The engine had a bowl-in-piston combustion system and a distributor type fuel pump. The engine had fuel injectors with four 0.305 mm diameter holes with an opening pressure of 250 bar. The basic specifications of the engine are given in Table 2. A 112 kW HP General Electric model TLC2544 direct current dynamometer was used to brake and motor the engine.

Engine temperatures were measured at eight different points during the engine runs, and these points are given in Table 3. The engine's turbocharger boost pressure and lubricating oil pressure were monitored with Bourdon pressure gages. Engine intake air flow rate was measured using a Meriam laminar flow element and the engine fuel flow rate was measured using a digital scale and a stopwatch. Fuel properties of the No. 2 diesel fuel, soybean biodiesel, and yellow grease biodiesel are given in Tables A1 and A2 in Appendix.

The engine exhaust emissions of the diesel engine were measured using the following emission instruments:

- Rosemount Analytical, Inc., model 755R non-dispersive infrared O₂ monitor
- Rosemount Analytical, Inc., model 880A non-dispersive infrared CO analyzer
- Rosemount Analytical, Inc., model 880A non-dispersive infrared CO₂ analyzer
- J.U.M. Engineering, model VE7, flame ionization detector (FID), HC analyzer
- Beckman Industrial Corp., model 955 chemiluminescent NO/NO_x analyzer
- Robert Bosch GMBH, model ETD02050 smoke meter

Table 2 John Deere 4045TF diesel engine specifications

Bore	106.5 mm
Stroke	127.0 mm
Connecting Rod Length	203.0 mm
Compression Ratio	17.0:1
Maximum Power	66.5 kW at 2200 rpm
Peak Torque	374 N-m at 1200 rpm

Table 3 Engine temperature measurement points

1. Engine Oil Temperature	4. Building. Cooling Water Outlet Temperature
2. Engine Cooling Water Outlet Temperature	6. Intake Air Temp
3. Engine Cooling Water Inlet Temperature	7. Intake Manifold Temp.
4. Building. Cooling Water Inlet Temperature	8. Exhaust Temp.

Results

In stage one, No. 2 diesel fuel, soybean biodiesel and yellow grease biodiesel were tested at a standard steady state condition corresponding to the engine's peak torque. NOx emission results, heat release analysis, and a summary of the combustion characteristics are presented in Figures 2 and 3 and Table 4, respectively. Fuel properties of the three fuels are given in appendix Table A1. As can be seen from Figure 2, there was approximately a 14% increase in NOx with soybean biodiesel fuel relative to No. 2 diesel fuel but only a 1% increase in NOx emission with yellow grease biodiesel.

Heat release analysis comparisons are shown in Figure 3. The start of heat release for the yellow grease biodiesel was advanced about 2 degrees, and about 1.5 degrees for soybean biodiesel relative to No. 2 diesel fuel. The premixed combustion is the initial period of rapid combustion that follows ignition. It involves fuel that was prepared to burn during the ignition delay period. High levels of premixed combustion are often associated with high exhaust NOx levels because the combustion occur early and at high temperature and pressure. As shown in Table 4, the premixed combustion portion for the No. 2 diesel fuel includes about 9% of the total heat release, however for soybean and yellow grease biodiesel these percentages were only 6.75 and 4.5%, showing much less premixed combustion. This lower amount of premixed combustion is expected to be a result of a shorter ignition delay, which provides less time for the preparation of premixed fuel, and slower fuel vaporization due to biodiesel's low volatility. The ignition delay period for No. 2 diesel fuel was 4.3 degrees, given in Table 4. The ignition delay period for soybean and yellow grease biodiesel fuels were 3.5 and 3.0 degrees, respectively. The source of the higher NOx level with soybean-based biodiesel is not readily apparent but appears to be a combination of the earlier combustion timing (compared with diesel fuel) and slightly more premixed combustion (compared with yellow grease).

Table 4 shows that the percentage of fuel burned in the premixed mode depends on more than just ignition delay. Diesel fuel's ignition delay is 37% longer than the ignition delay for soybean biodiesel and the percentage of fuel burned as premixed increased by a similar 33%. However, when diesel fuel is compared with yellow grease biodiesel, its ignition delay is 57% longer but the fraction of fuel burned as premixed is 98% larger. This would indicate that perhaps the diesel fuel's greater volatility may be contributing to the greater rate of fuel preparations for this initial phase of contribution. However, when soybean biodiesel and yellow grease biodiesel are compared with each other the ignition delay of soybean biodiesel is only 15% longer while it has 50% more premixed contribution. Since all of the compounds in biodiesel from both sources have similar boiling points, the difference in the fraction of fuel burned as premixed cannot be attributed to volatility differences.

The work described in this paper is part of an on-going project and stage 2 is still incomplete. The results of this part of the study will be presented later.

Based on stages 3 and 4 described in Table 1, engine tests were conducted with No. 2 diesel that had been treated with a cetane enhancing additive to give the same cetane number as soybean biodiesel fuel. The fuels were evaluated at five different start of injection settings to see the effect of fuel volatility on NOx emissions between No. 2 diesel fuel and the biodiesel fuels. Yellow grease biodiesel, representing essentially the same volatility level as soybean biodiesel, was also compared with soybean biodiesel at the same five different start of injection timings. Results are presented in Figures 4-8.

From Figure 4, it can be seen that for the same cetane number and the same start of combustion, NOx emissions are the same for the two fuels. However, for the same level of volatility, the yellow grease biodiesel produced less NOx emission than the soybean biodiesel, as shown in Figure 5. Heat release diagrams are presented for the standard, the most advanced, and the most retarded cases in Figures 6-8. It is seen that when timing advanced, the premixed fraction of the combustion increases and No. 2 diesel fuel, with same cetane number as the soybean biodiesel, has about the same level of premixed combustion.

Tables 5,6, and 7 show the measured data for injection timing, start of combustion, ignition delay, and fraction of fuel burned as premixed for the 3 cases shown in Figures 6-8.

The cetane improver in the diesel fuel brought to ignition delay of the diesel fuel to within .39° of the soybean biodiesel. For the standard timing case, the premixed burn fraction was within 1% (of the total fuel burned) for all three timings. The similarity in premixed burn fraction correlates with the similarity in NOx emissions for the diesel fuel and soy biodiesel. The yellow grease generally had much less premixed combustion than either of the other two fuels and also had less NOx.

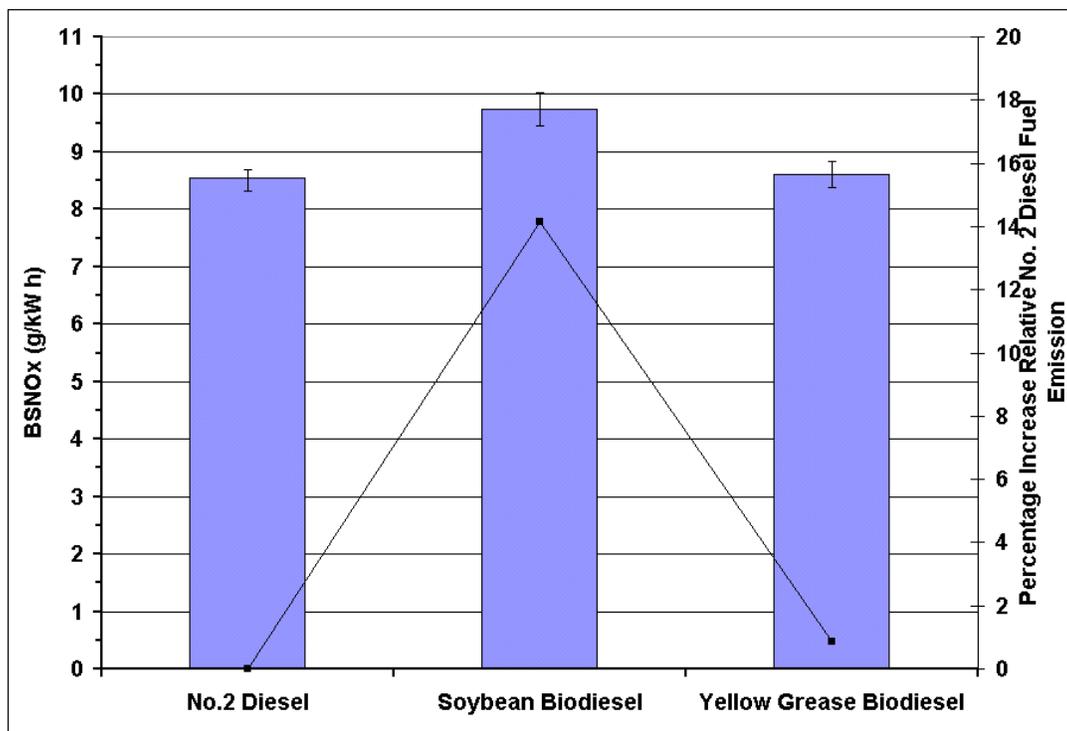


Figure 2. Brake specific NOx emission comparisons at 352.5 N-m and 1400

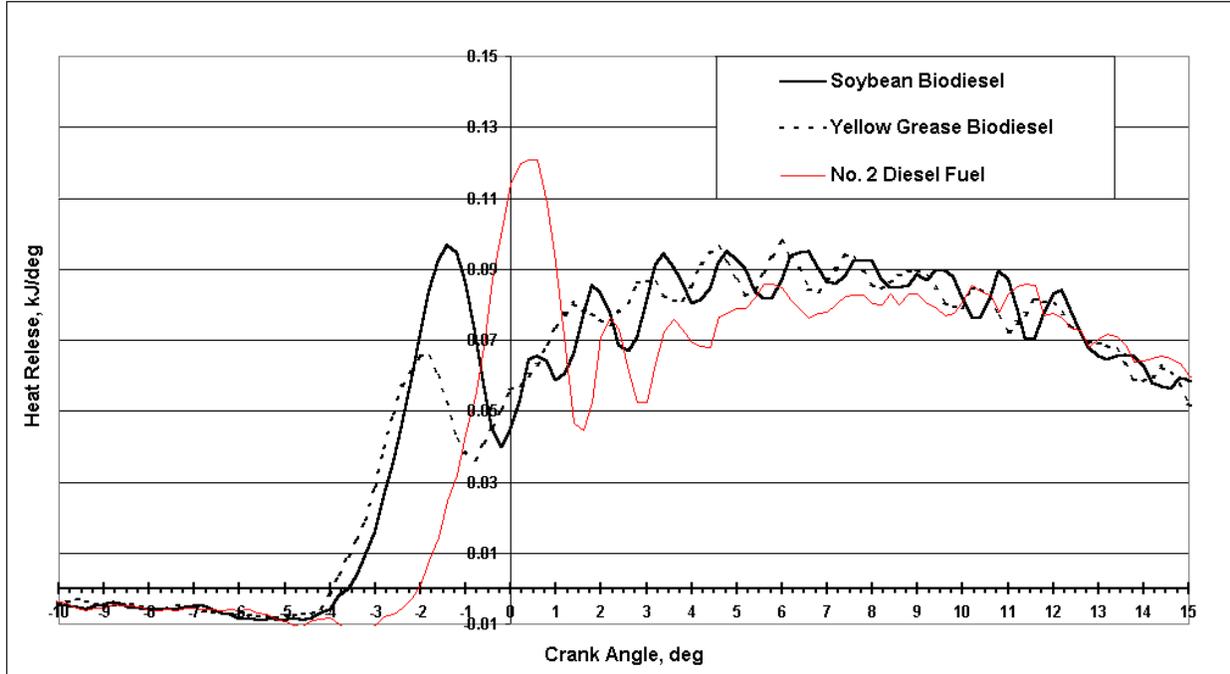


Figure 3. Heat release analysis comparison at 352.5 N-m and 1400 rpm

Table 4. Combustion characteristics of No. 2 diesel, soybean, and yellow grease biodiesel fuels at 352.5 N-m and 1400 rpm.

<i>Combustion Characteristics</i>	<i>No. 2 Diesel Fuel (DIE)</i>	<i>Soybean Biodiesel (SBB)</i>	<i>Yellow Grease Biodiesel (YGB)</i>
Start of Injection, deg	-6.34	-7.13	-7.00
Start of Combustion, deg	-2.05	-3.6	-3.94
Ignition Delay, deg	4.28	3.50	3.05
Total of fuel energy released per injection, kJ/inj-cyl	2.756	2.720	2.760
Percent of fuel energy burned as premixed, %	8.92	6.73	4.5
<i>Comparisons</i>	<i>Ratios of Ignition Delay</i>		<i>Ratios of Percent Energy Release Rates as Premixed</i>
DIE/SBB =	1.37		1.33
DIE/YGB =	1.57		1.98
SBB/YGB =	1.15		1.5

Table 5. Combustion characteristics of No. 2 diesel with cetane improver, soybean, and yellow grease biodiesel fuels at 352.5 N-m and 1400 rpm and standard timing.

<i>Combustion Characteristics</i>	<i>No. 2 Diesel fuel with cetane improver (DIEWI)</i>	<i>Soybean Biodiesel (SBB)</i>	<i>Yellow Grease Biodiesel (YGB)</i>
Start of Injection, deg	-6.47	-7.26	-7.16
Start of Combustion, deg	-2.78	-3.95	-3.87
Ignition Delay, deg	3.69	3.30	3.29
Total of fuel energy released per injection, kJ/inj-cyl	2.76	2.77	2.74
Percent of fuel energy burned as premixed, %	7.04	6.15	6.38
<i>Comparisons</i>	<i>Ratios of Ignition Delay</i>		<i>Ratios of Percent Energy Release Rates as Premixed</i>
DIEWI/SBB =	1.12		1.14
DIEWI/YGB =	1.12		1.10
SBB/YGB =	1.00		0.96

Table 6. Combustion characteristics of No. 2 diesel with cetane improver, soybean, and yellow grease biodiesel fuels at 352.5 N-m and 1400 rpm and advanced timing.

<i>Combustion Characteristics</i>	<i>No. 2 Diesel fuel with cetane improver (DIEWI)</i>	<i>Soybean Biodiesel (SBB)</i>	<i>Yellow Grease Biodiesel (YGB)</i>
Start of Injection, deg	-10.85	-11.99	-11.87
Start of Combustion, deg	-6.79	-8.14	-8.58
Ignition Delay, deg	4.06	3.85	3.30
Total of fuel energy released per injection, kJ/inj-cyl	2.71	2.70	2.72
Percent of fuel energy burned as premixed, %	8.55	8.56	4.65
<i>Comparisons</i>	<i>Ratios of Ignition Delay</i>		<i>Ratios of Percent Energy Release Rates as Premixed</i>
DIEWI/SBB =	1.05		1.00
DIEWI/YGB =	1.23		1.84
SBBWI/YGB =	1.17		1.84

Table 7. Combustion characteristics of No. 2 diesel with cetane improver, soybean, and yellow grease biodiesel fuels at 352.5 N-m and 1400 rpm and retarded timing.

<i>Combustion Characteristics</i>	<i>No. 2 Diesel fuel with cetane improver (DIEWI)</i>	<i>Soybean Biodiesel (SBB)</i>	<i>Yellow Grease Biodiesel (YGB)</i>
Start of Injection, deg	-2.03	-2.48	-2.77
Start of Combustion, deg	1.50	0.75	0.47
Ignition Delay, deg	3.54	3.23	3.24
Total of fuel energy released per injection, kJ/inj-cyl	2.91	2.83	2.86
Percent of fuel energy burned as premixed, %	6.60	5.82	4.12
<i>Comparisons</i>	<i>Ratios of Ignition Delay</i>	<i>Ratios of Percent Energy Release Rates as Premixed</i>	
DIEWI/SBB =	1.10	1.13	
DIEWI/YGB =	1.09	1.60	
SBBWI/YGB =	1.00	1.41	

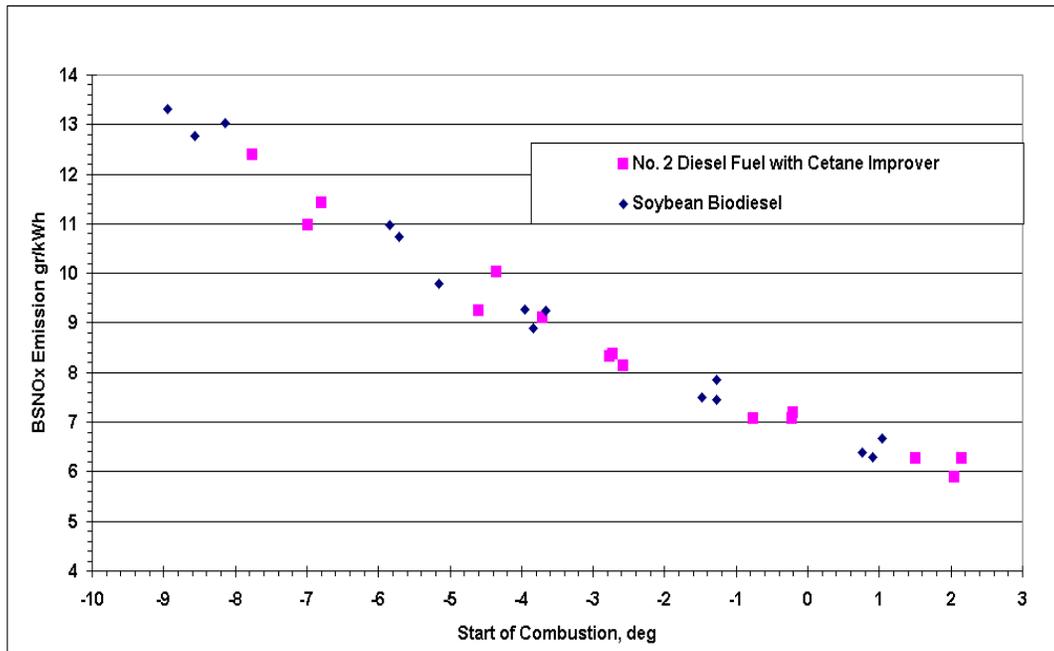


Figure 4. Same cetane number different volatility comparison between biodiesel and No. 2 diesel fuel BSNOx emission at 352.5 N-m and 1400 rpm

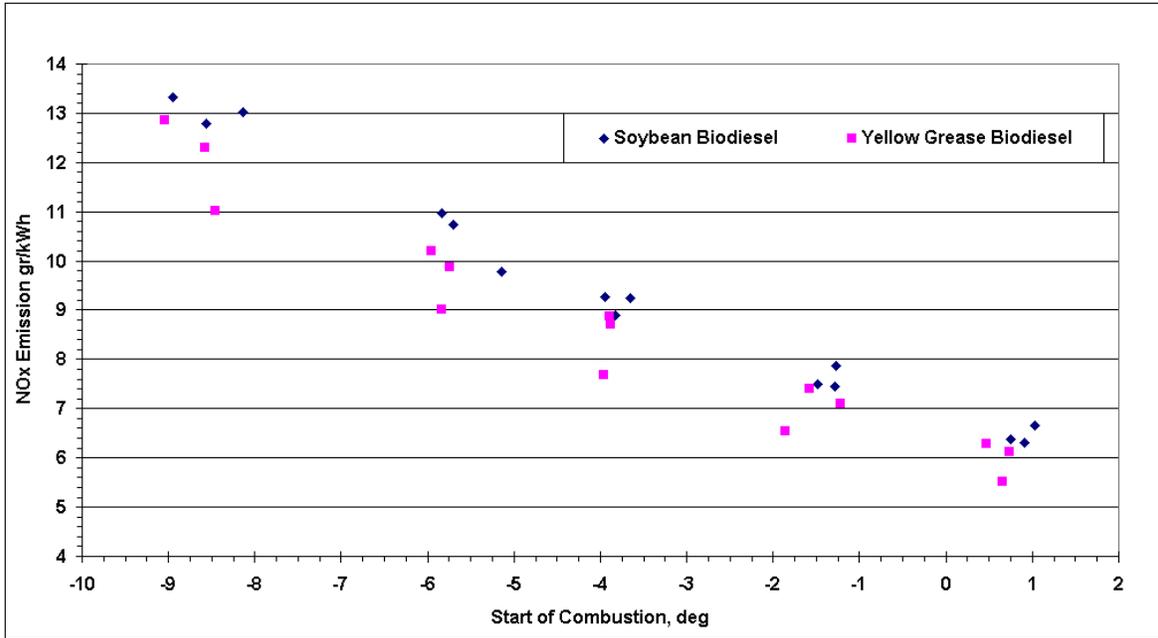


Figure 5. Same volatility different cetane number comparison between biodiesel and No. 2 diesel fuel BSNOx emission at 352.5 N-m and 1400 rpm

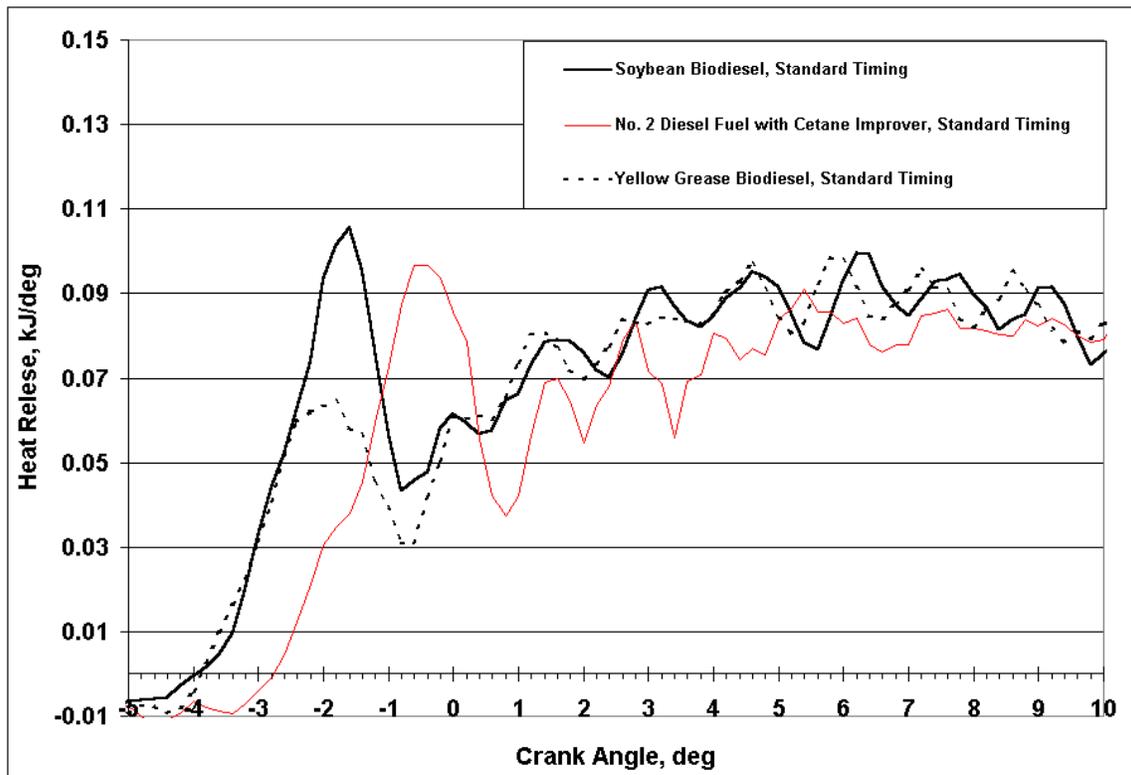


Figure 6. Heat release analysis comparisons at standard timing and 352.5 N-m and 1400 rpm

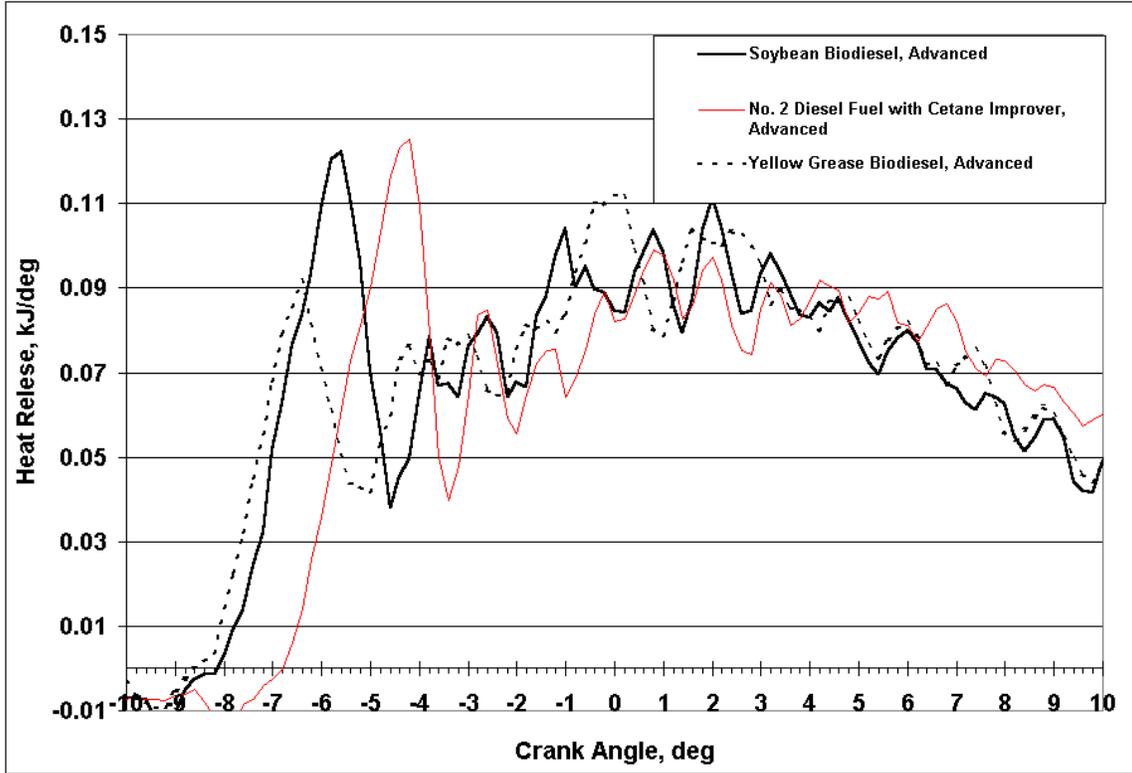


Figure 7. Heat release analysis comparisons at advanced timing and 352.5 N-m and 1400 rpm

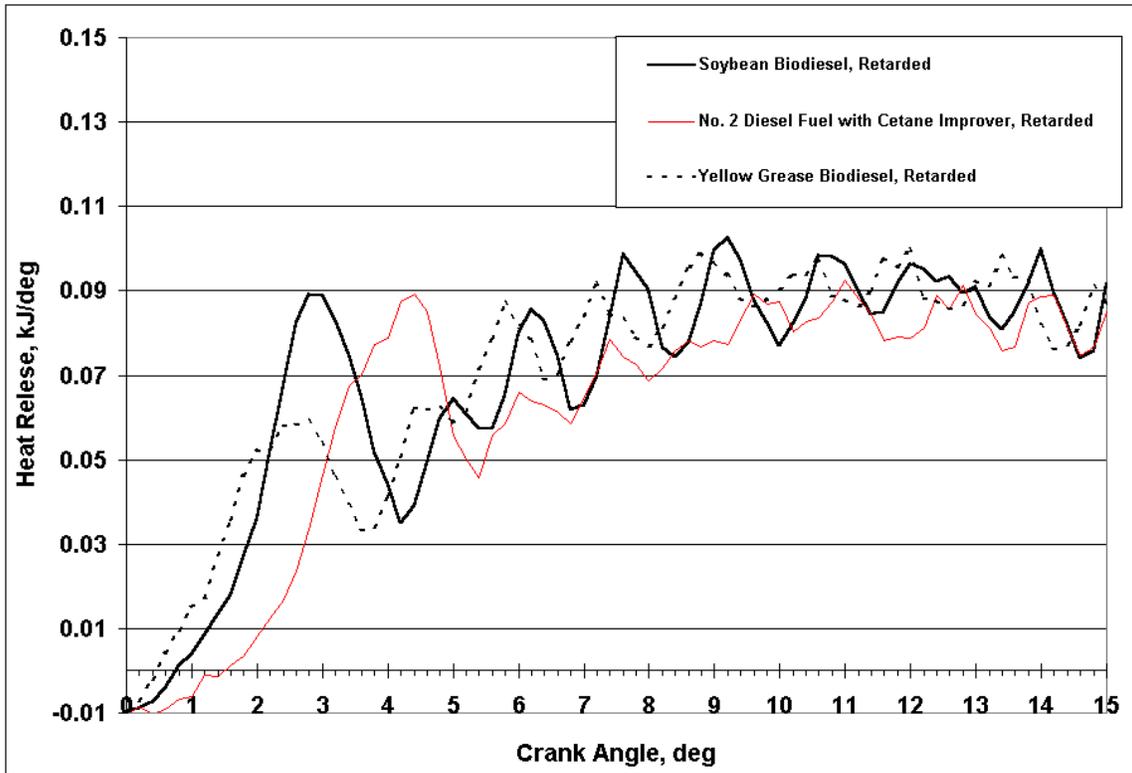


Figure 8. Heat release analysis comparisons at retarded timing and 352.5 N-m and 1400 rpm

Conclusion

At the same start of combustion soybean biodiesel NOx emissions are same as diesel fuel with the same cetane number

At the same start of combustion yellow grease biodiesel has lower NOx emission

Lower volatility of biodiesel decreases premixed burning section of combustion, but NOx emission does not appear to be

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Appendix

Table A1. Fuel properties of fuels used in the engine testing.

<i>Test Property</i>	No 2 diesel fuel	Soybean Oil Methyl Ester	Yellow Grease Methyl Ester
Carbon (% mass) ^d	86.66 ^a	77.00	76.66
Hydrogen (% mass) ^d	12.98 ^a	12.18	12.33
Oxygen (% mass) ^d	-	10.82	11.01
C/H Ratio	6.676	6.322	6.217
Sulfur (% mass) ^a	0.034	<0.005	<0.005
Typical Formula	C _{14.01} H _{25.00} ^b	C _{18.74} H _{34.51} O ₂ ^d	C _{18.40} H _{35.26} O ₂ ^d
Average Molecular Weight	194.14 ^b	291.73 ^d	288.29 ^d
Cetane Number (ASTM D613) ^a	42.2	50.4	62.6
Hydrocarbon Type, FIA (ASTM D1319) ^a			
Saturates	56.6	-	-
Olefins	1.6	-	-
Aromatics	41.8	-	-
Gross Heat of Combustion (Btu/lb) ^a	19419	17183	17252
Net Heat of Combustion (Btu/lb) ^a	18235	16072	16209
Specific Gravity ^c	0.8559	0.8796	0.8722
Kinematic Viscosity (@40°C, mm ² /s) ^c	2.8911	4.5926	5.9156
Total Glycerol (%) ^c	-	0.175	0.194

^aMeasured by Phoenix Chemical Laboratory Inc., Chicago, IL

^bCalculated using UOP Method 375-86

^cMeasured at the Mechanical Engineering Department, Iowa State University

^dCalculated from Fatty Acid Profile unless stated otherwise

Table A2. Fatty Acid Profiles for the Engine Test Fuels

<i>Fatty Acid Profile</i>	Soybean Biodiesel	Yellow Grease Biodiesel
C14:0 Tetradecanoic (Myristic)	<0.10	1.27
C14:1 Tetradecenoic (Myristoleic)	<0.10	0.43
C15:0 Pentadecanoic	<0.10	0.18
C16:0 Hexadecanoic (Palmitic)	10.81	17.44
C16:1 Hexadecenoic (Palmitoleic)	0.11	2.03
C17:0 Heptadecanoic (Margaric)	<0.10	0.51
C17:1 Heptadecenoic (Margaroleic)	<0.10	0.41
C18:0 Octadecanoic (Stearic)	4.54	12.38
C18:1 Octadecenoic (Oleic)	24.96	54.67
C18:2 Octadecadienoic (Linoleic)	50.66	7.96
C18:3 Octadecatrienoic (Linolenic)	7.27	0.69
C18:4 Octadecatetraenoic	<0.10	0.13
C20:0 Eicosanoic (Arachidic)	0.37	0.25
C20:1 Eicosenoic (Gadoleic)	0.32	0.52
C20:2 Eicosadienoic	<0.10	0.11
C22:0 Docosanoic (Behenic)	0.42	0.21
C24:0 Tetracosanoic (Lignoceric)	0.12	0
Unknown	0.32	0.81