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Survey of Straight Vegetable Oil Composition Impact on Combustion Properties

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ABSTRACT

The combustion of straight vegetable oil (SVO) in internal combustion engines has shown conflicting results in emissions, power, and engine longevity. Many early studies suggested that SVO should not be considered for long term use in diesel engines. However, waste vegetable oil has been fueling adapted vehicles in progressive communities for years. The issues involved in the combustion of SVO or pure plant oils are complex. Engine injection systems, oil type, lipid acid ratio, and fuel temperature all have significant impact on the engine performance and emissions. A review of published studies of SVO combustion with a focus on known SVO composition and chemical structure reveals trends which merit further study. Future engine tests with known vegetable oil profiles will add significantly to the progression of SVO use in engines.

INTRODUCTION

SVO has been a recurring subject of study as a fuel for compression ignition engines. Rudolph Diesel developed the diesel cycle engine with peanut oil as the original fuel (3). More recent studies have examined the suitability of various agriculturally derived fuel oils as alternatives to petroleum products [1, 2, 3, 4, 9, 10…]. SVO studies generate interest because of the potential benefits of SVO, compared to petroleum derived fuels, such as low cost, local production, and carbon-neutrality. These studies have considered a wide range of assessments of fuel quality, including combustion efficiency, emissions, and engine longevity.

Carbon balance concerns can be addressed using a carbon-neutral agriculturally derived fuel source. Various oilseed crops can be grown in multiple climates and be locally processed in a low impact manner. Oilseed processing byproducts can be used as livestock feed or fertilizer. Local production also reduces transportation between refinement locations to point of use. The process of producing SVO is very scalable as it has low energy consumption per output ratio. With simple engine applications, SVO could be used in 3rd world domestic situations, producing electricity to help children study, refrigeration for food safety, and transportation. Farmers could reduce reliance upon fossil fuels by using SVO in farm equipment, including irrigation and tractors, thereby lowering the impact on local food prices.

SVO CHALLENGES

Although we use the term SVO in the singular, SVO is a category of products derived from many possible oilseed sources. Focusing on the specific chemical structure of SVO fuels can provide critical insight into interpreting the results of previous studies of SVO performance in engines.

SVO is a possible replacement for Diesel #2 in some engines. One common problem is that most SVO has a much higher viscosity than diesel. The viscosity and chemical property differences between SVO and the fuel for which direct inject diesel engines are designed, lead to several issues. Increased viscosity creates injector and line backpressure problems in direct inject engines [1]. Coking of injectors is the most serious problem for engine longevity. The buildup on injectors results in improper mixture of the fuel and air. When the injectors improperly spray fuel into the cylinder, the SVO hits the cylinder walls, improperly combusts and polymerizes [2]. The unburned fuel buildup can also infiltrate the engine lubrication oil, potentially leading to the engine seizing. When these poor burning conditions exist, they lead to

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poor combustion resulting in increased pollutant emissions including THCs, CO, PM and NO_x [3]. It is under partially loaded, long term situations that the impact of SVO in a non prepared engine is the worst [4].

LIPID ACID INTRODUCTION

Vegetable oil is primarily composed of triglycerides, which consist of three fatty acids attached to a single glycerol as shown in Figure 1. The chemical structure of the carbon chains (i.e. chain length, number of double bonds, location of the double bonds) differs between different vegetable oil, resulting in different physical and chemical properties for each vegetable oil.

The fatty acids can be either saturated or unsaturated. Saturation indicates a lack of carbon double bonds in the fatty acid chain. Many SVO's have a high percentage of palmitic (Cx:0) and stearic (Cx:0) fatty acids (Figure 2 and 3). Saturated fatty acids influence the temperature dependent viscosity of the vegetable oil and saturated fatty acids have higher melting points (Table 1).

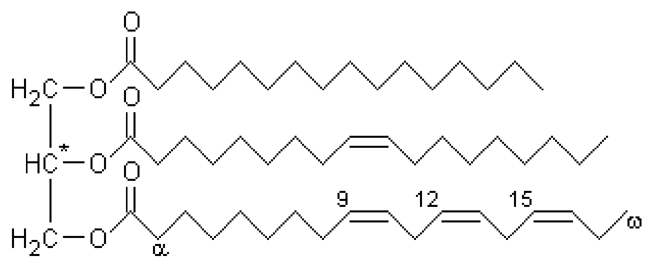

Figure 1: SVO composition, 1 glycerol, 3 fatty acids

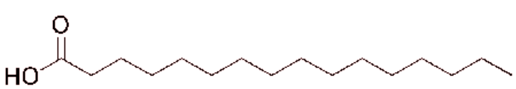

Figure 2: Palmitic Fatty Acid

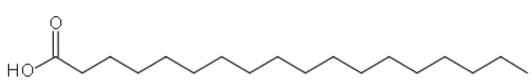

Figure 3: Stearic Fatty Acid

MONO AND POLYUNSATURATED ACIDS -

Table 1 Common Fatty Acid Structures and Melting Points [5]

Fatty Acid	*Carbon atoms*	*Melting Point (°C)*
Palmitic	*16:0*	*63*
Stearic	*18:0*	*70*
Oleic	*18:1*	*13*
Linoleic	*18:2*	*-9*
Linolenic	*18:3*	*-17*

Unsaturated fatty acids include monounsaturated fatty acids and polyunsaturated fatty acids. Monounsaturated fatty acids such as Oleic and Erucic, have 1 double carbon bond, resulting in a slight curvature of the fatty acid chain (Figure 4). This results in a liquid state at lower temperatures than the fully saturated oils (Table 1). Erucic Acid is not easily digested in feedstock and is therefore bred out of oilseed crops when possible.

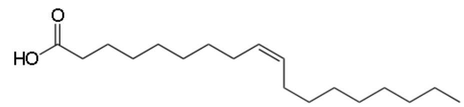

Figure 4 Oleic Fatty Acid C18:1

Polyunsaturated fatty acids have 2 or more double bonds, thereby additionally bending the fatty acid, resulting in a more rigid structure (Figure 5). Each additional unsaturated bond lowers the melting point of the resultant oil (Table 1). Plant oils with high levels of polyunsaturated acids are referred to as drying oils. Drying oils leave a 'varnish' when submitted to an oxidation state. This is caused by the oxidation of the oil, leaving a cross-linked polymer [5].

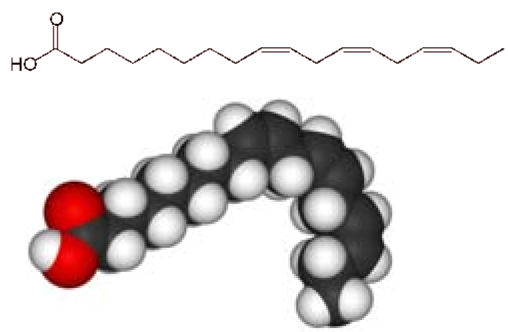

Figure 5 Linolenic Acid C18:3

IODINE VALUE - A vegetable oil's iodine value correlates to the amount of iodine absorbed by the double bonds in the oil. There is no differentiation between polyunsaturated and monounsaturated acids in the iodine number. The iodine value does reflect the total composition of both monounsaturated and polyunsaturated acids [6].

OILSEED CROPS

There are several sources of SVO suitable for use in CI engines. This review focuses on safflower, soybean, coconut, jatropha, rapeseed, and palm oils. Each type of oilseed oil burns differently. This is due to the variation in fatty acid composition of each seed variety (Table 2). The fatty acid composition can vary widely within the same oilseed type. Table 2 illustrates the high variability of multiple crops. The largest factors within an oilseed type are cultivar and growing conditions [7].

	PALMITIC C16	STEARIC C18	OLEIC C18:1	LINOLEIC C18:2	LINOLENIC C18:3	IODINE VALUE	POLYUNSATURATED
HIGH LINOLEIC SAFFLOWER	2-10	1-10	4-7	55-81	1	130-150	56%-82%
HIGH OLEIC SAFFLOWER	4-8	4-8	74-79	11-19		100-130	11%-19%
SOYBEAN OIL	9	4	11-60	25-63	3-12	120-152	28%-75%
RAPESEED	2-5	.7-1.5	12-62	11-22	8-11	81-112	19%-33%
COCONUT	7-12	1-5	3-12	1-4		8-10	1%-4%
JATROPHA	3-16	7	34-47	30-43	0.2	95-105	30%-44%
PALM OIL	10-66	1-9	18-63	5-24	.1-.6	44-58	5%-25%

Table 2: Lipid Acid Composition of Multiple Oilseeds [7]

VEGETABLE OIL TYPES

SAFFLOWER - Safflower oil is used in processed foods, animal feed and paints. There are two dominant varieties of safflower, the first is High Linoleic Safflower and the second is High Oleic Safflower. Safflower is grown in Mexico, Africa, U.S.A., Turkey and Europe, and has been used for hundreds of years. As a result of its wide availability safflower has been studied as an engine fuel [7].

SOYBEAN - Soybean oil is one of the most frequently studied vegetable oils in diesel engines. It's availability on many continents makes it possible to be used worldwide. However, there are hundreds of varieties of soybean [7], each with different lipid composition. Soybean is especially prone to lipid acid profile changes due to cultivation conditions, even within the same farm (Table 2).

RAPESEED - Rapeseed is most often tested in engine research in Europe, due to its relatively high energy content, only 7% lower than diesel volumetrically [3]. This crop grows best in cool moist climates. The oil composition of the seed varies widely in its percentage of erucic acid. Newly bred, lower erucic acid plants tend to have higher levels of oleic, linoleic, and linolenic acids [7]. Rapeseed oil has less variation in polyunsaturated oil (Table 2). This makes rapeseed oil more desirable as a fuel because the oil profile and subsequent combustion characteristics are more consistent.

COCONUT - Eighty percent of coconuts are grown in Asia, with Indonesia and Philippines producing 60% [7]. Unused coconut plantations offer an ideal source of fuel to the islands. Coconut oil is almost completely saturated (Table 2), consisting of C:12, C:14 and C:16. Coconut oil is solid at room temperature, but when blended with diesel becomes a clear liquid. Coconut oil does have lower energy content than diesel, but it also has a very low iodine value, which helps it to combust completely.

JATROPHA - Jatropha, also known as the Physic nut is found in semi-arid locales. It originates from Central America, but can now be found in South America, Africa and Asia. It can grow in areas that have poor soil [8] preventing it from taking over land for food crops. It is a non edible plant that can be used as hedges to keep animals out of crops. Jatropha seeds contain up to 55% oil by weight; however, the oil harvesting methods vary widely in efficiencies. The fatty acid composition of Jatropha varies according to the local varieties and growing conditions. The linoleic percentage varies from 30 to over 50% (Table 2).

PALM OIL - Palm Oil accounts for a large portion of the edible oil market. It produces 5 to 7 tons of oil per hectare, making it the highest producing oil crop. It also has a lower percentage (Table 2) of linoleic acid, making it perfect oil for engine combustion. This oil is also ideal for human consumption, rendering it less likely to be used as a fuel in third world [7].

IMPACT OF OILSEED CHARACTERISTICS

The effects of viscosity, cloud point and density of vegetable oils are widely known. Table 3 presents a summary of the results compiled from a wide variety of SVO engine studies [1-22]. General trends of SVO properties and their effect on engine performance are valuable when considering future biofuels work. Short term engine tests show that these factors have an immediate impact on engine performance and longevity [9, 10].

VISCOSITY - Room temperature viscosity of vegetable oils varies between 30-90 centistokes. Higher ranges of viscosity can block filters, clog fuel lines and adversely affect fuel atomization [11]. Heating the oil and decreasing viscosity (Figure 13) increases the mixing rate of air and vegetable oil, assisting completion of combustion. Fuel penetration rates into the engine cylinder increase as the fuel is heated [18]. This can contribute to lower CO emissions.

Table 3 Impact of SVO properties on engine performance and durability [1, 2, 3, 9, 13, 14, 18, 20]

Oil Properties	Engine Efficiency	Emissions	Engine Durability
High Viscosity	Results in poor efficiency	Adversely affects emissions	Limits engine life
Cloud point	Lower cloud point corresponds to lower viscosity	Unknown	High cloud point could limit engine life
Lower Heating Value (LHV)	Low LHV results in higher fuel consumption	Increases emissions	Unknown
Phosphates	High levels decrease power output	Unknown	Limits filter life
High Density	More energy per volume decreases fuel consumption	Decreases emissions to a point	Unknown
Elevated Fuel Temperature	Greater than 90 ºC may cause component damage	Could increase NO_x	Increases engine life due to viscosity decrease
Polyunsaturated Fatty Acids	Low levels do not affect performance	Higher levels increase NO_x	Adversely affects engine

POLYUNSATURATED OIL - When high linoleic/linolenic acid oil is used, the engines often cannot last long enough to perform long duration testing [12]. The cylinder buildup and ring corrosion is so severe that catastrophic engine failure occurs [10]. Peterson suggests that vegetable oils with higher concentrations of oleic or erucic oils will limit the formation of combustion chamber deposits. Korus [2] tested high oleic and high linoleic safflower oils in direct injection nozzles. After a series of load variation tests, the injectors were taken out and photographed. The high linoleic safflower test yielded the highest amount of coking on the injectors. These studies definitively demonstrate a significant difference in the performance of monounsaturated oil and polyunsaturated oil in an engine. The monounsaturated oleic oils used in the engine test had relatively minor buildup when compared to the polyunsaturated oils.

Ryan [18] experimented with both IDI and DI engines. He found linolenic/linoleic ratio, nitrogen and iodine number, secondary oxygen content and free fatty acids to have high impact with DI engines. Nitrogen content, oxygen and free fatty acid content were the most significant items with IDI engines. The linoleic/linolenic acids (drying oils) react to heat and oxidation by polymerizing. A properly aerosolized vegetable oil enters a hot engine cylinder in an oxidizing environment resulting in the polyunsaturated oils polymerizing on the cylinder walls and injection tips. Vegetable oils with higher percentages of linoleic and linolenic acids have higher deposition rates [2]. These drying oils also react with metal ions, accelerating solidification in a fluid [5]. This was noted by Adams in soybean oil tests [13]. As unburned soybean oil mixed with the engine's lubricating oil, it caused gelling problems. The soybean oil reacted with the minute particles of manganese and cobalt [13].

IODINE VALUE - Iodine values have long been related to the combustion properties of SVO in an engine. From experimentation, [2, 10, 13] there is a difference between the degree of polymerization of highly monounsaturated oils and polyunsaturated oils. The vegetable oils high in polyunsaturated acids have lower viscosity but result in much higher degrees of engine failure due to buildup in the engine cylinder. Also, the more unsaturated a fuel, the higher the NO_x output [14].

LOWER HEATING VALUE - The lower LHV of oilseeds causes maximum or rated brake power to drop. Brake Specific Energy Consumption (BSEC) allows for a better understanding of the combustion properties of the SVO. When using rapeseed and coconut oil, the BSEC shows a slight increase over diesel BSEC [4, 15, and 16]. This is most likely due to the cetane number of the vegetable oil. Higher cetane number reduces ignition delay and increases efficiency.

MECHANICAL VARIATION FOR SVO PERFORMANCE

Injection method is directly related to SVO performance in an engine. Dual chamber injection systems are ideal for the slower heat release of the vegetable oil. Direct injection engines experience problems with cylinder impingement, reducing engine power and increasing emissions. Duel chamber engines reduce sensitivity to injector design.

Hemmerlein [3] conducted 100% Rapeseed oil fuel tests in multiple engines, with six different injection methods. Hemmerlein tested prechamber, swirlchamber, and direct injection combustion systems. The prechamber engines and the larger swirlchamber engines had the fewest problems with deposition. The high percentage linoleic oils produce ring sticking and result in unburned vegetable oil contaminating the engine lubrication oil in direct inject engines. This is most likely from cylinder wall impingement. The engine tests yielded a decrease in engine performance of about 2% even though the LHV of rapeseed is 7% lower than diesel.

EMISSIONS

Hemmerlein's [3] HC emissions were noted to be significantly higher with the 21.3% linoleic acid composition; however, NO_x emissions were about 25% lower than diesel. A 30-50% reduction in particulate emissions was also noted in engines with divided combustion chambers, while particulate emissions with DI engines had a 90-140% particulate emission increase [3].

In the 2001 McCormick study, the lipid acid constituents of fatty acid methyl esters (FAME) biodiesel were tested for emissions profiles. The FAME fuels with the lowest number of double bonds had the lowest levels of NO_x emissions. The biodiesel study is consistent with those conducted using straight vegetable oil. Figure 6 shows the results of 3 separate DI engine studies of similar sized engines along with each study's diesel baseline test to allow comparison of NO_x output at 3 rated loads. This figure demonstrates that the oils with higher levels of polyunsaturated fats tend to have higher NO_x emissions. There is a significant decrease in NO_x production in the oils with minor amounts of polyunsaturated fatty acids, such as coconut and palm.

Unfortunately most SVO studies do not publish lipid acid profiles. This makes direct comparison of oils and emissions difficult. Engines also impact emissions. For this reason each study's baseline diesel emissions were used for the oil emission comparison. A plot of emissions data with levels of polyunsaturated oils using Altin's 2004 multi-oil study is shown in Figure 7 [23]. The accuracy of this graph would have been improved with the actual lipid acid profiles of each of these oils. There are indications of possible trending of the NO_x emissions with polyunsaturation percentages, linking higher NO_x emissions with higher polyunsaturation concentrations. Future engine tests with known vegetable oil profiles will add significantly to the advancement of SVO use in engines.

There also is a correlation of higher density and iodine values leading to higher NO_x production [19]. Figure 8 shows a plot of NO_x reduction with respect to baseline as a function of viscosity from Altin's multi oilseed crop emission study [23] (Figure 8, NO_x as a function of viscosity was not analyzed in Altin's study). Generally it is expected that the more viscous a fuel, the higher the NO_x production. However, while preheating the fuel to 75 ºC, the SVOs with higher viscositities had lower NO_x output. Oils with higher viscosities are more saturated and have fewer polyunsaturated fats. It is unclear whether the viscosities quoted in the Atlin [23] study were from the literature or measured directly. There may be a significant variation in soybean oil viscosity, which might explain why the soybean NO_x falls below the line in Fig. 8. The trend for the viscosity/NO_x relationship is strongly evident with an R^2 value of 0.88. As shown in figures 9 and 10, the variation of NO_x does not exhibit the same degree of linearity (R^2 values of 0.48 and 0.52) with respect to heating value and cetane number as compared to viscositiy. Figure 11 demonstrates a trend of higher CO emissions with increasing polyunsaturation. This is unexpected, but may be due to polymerizatrion issues.

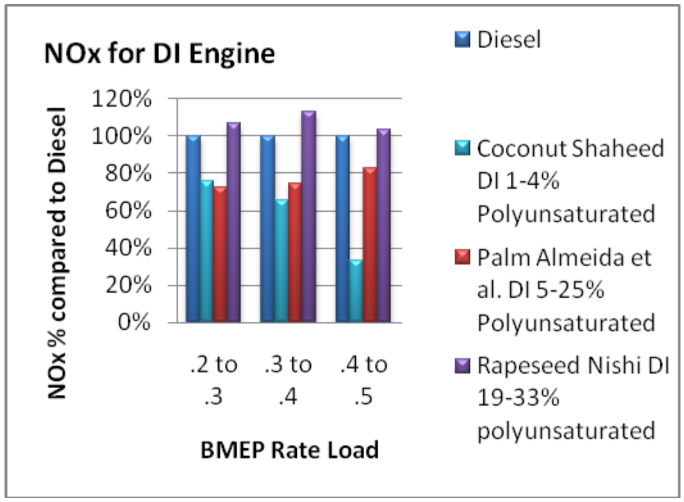

Figure 6 NO production for SVO for polyunsaturation Impact [22, 24, and 21]

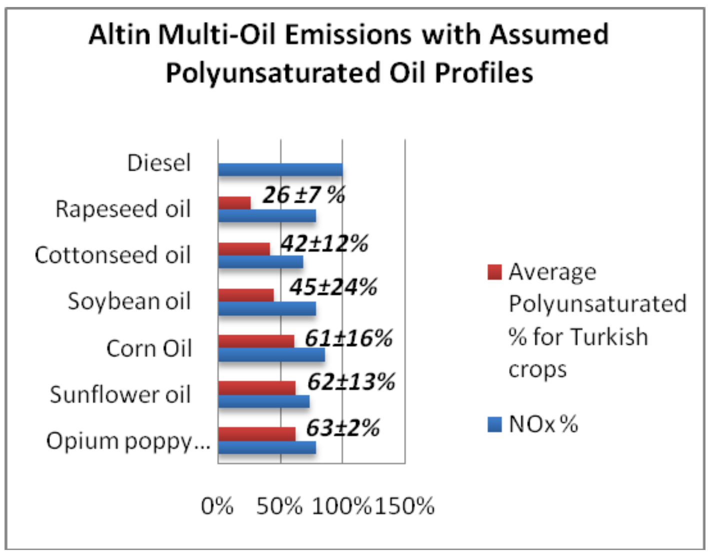

Figure 7 Altin Multi-Oil Emissions and Assumed Oil Profiles [23]

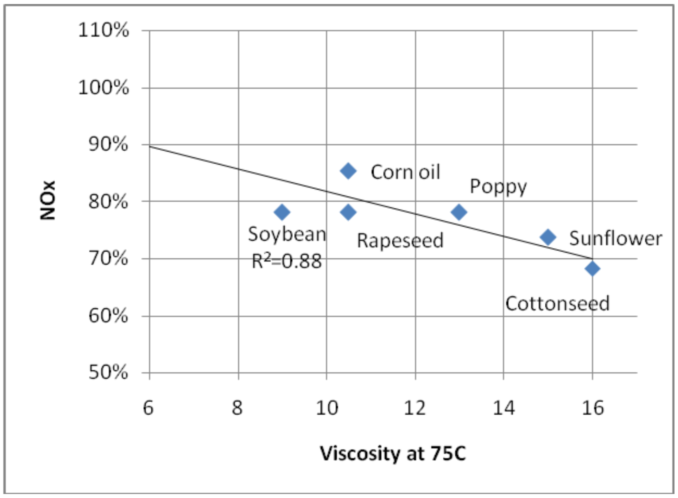

Figure 8 Viscosity of SVO vs. NO_x, Data [23]

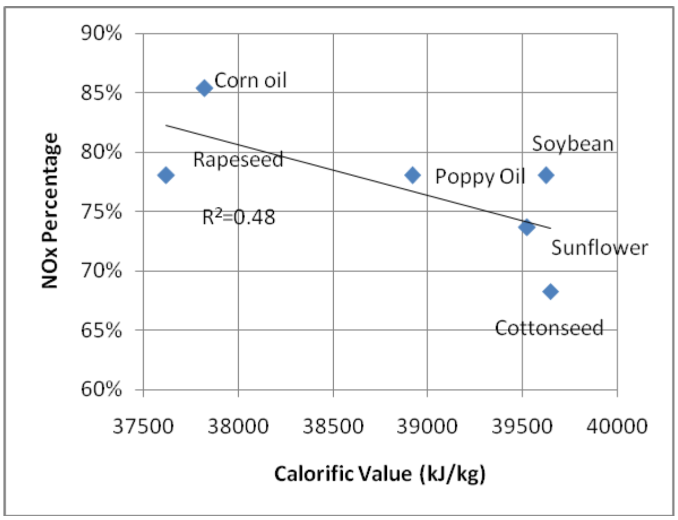

Figure 9 Energy content vs. NO_x, data from [23]

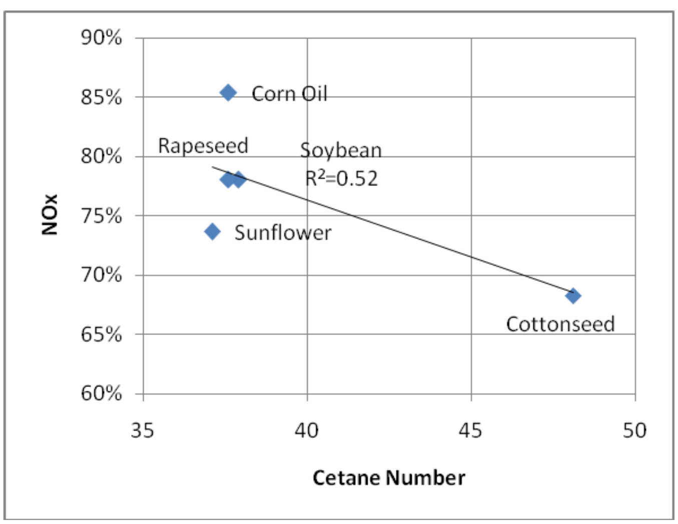

Figure 10 Cetane number vs. NO_x, data [23]

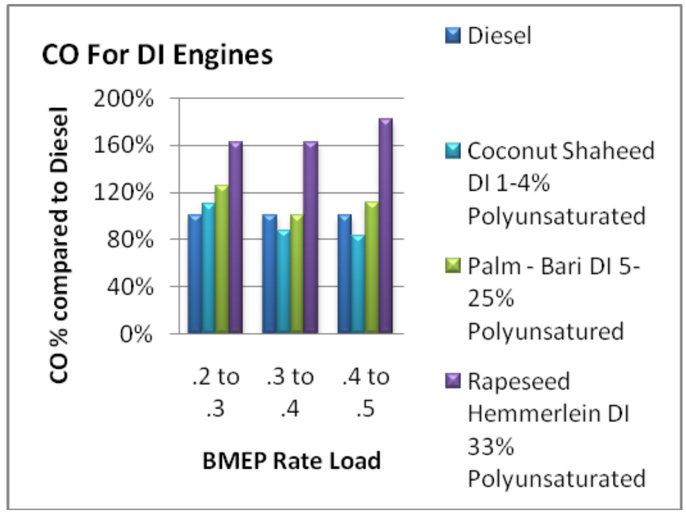

Figure 11 Comparison of Multiple SVO types CO Emissions

As shown in Fig. 12, a comparison between the data of Nishi [21] and Hemmerlein [3] suggests that injection method has a significant impact on emissions. A comparison of DI and IDI with rapeseed oil is more valid than a similar comparison between different studies with soybean oil because the polyunsaturated lipid acid composition for rapeseed varies by only 14% compared to 47% for soybean oil (Table 2).

The majorities of modern engines have DI systems because of reduced fuel consumption and decreased emissions, compared to IDI engines. Using rapeseed oil, direct injection methods increase particulates, CO, CO_2 by up to 140% compared with Diesel, while prechamber engines reduce emissions by 30-50% [3]. In DI engines, the viscosity differences make a larger impact on engine performance and injection quality than in IDI engines. Incomplete mixing of the fuel and air results in pockets of rich mixtures resulting in higher CO emissions. NO_x formation is greater with higher temperatures and more oxygen available [14]. Vegetable oil has fuel-bound oxygen, which can increase NO_x production. There is also a correlation of the number of double bonds in the fuel to the NO_x output [19]. Fuels that have the fewest number of double bonds tend to have lower NO_x output.

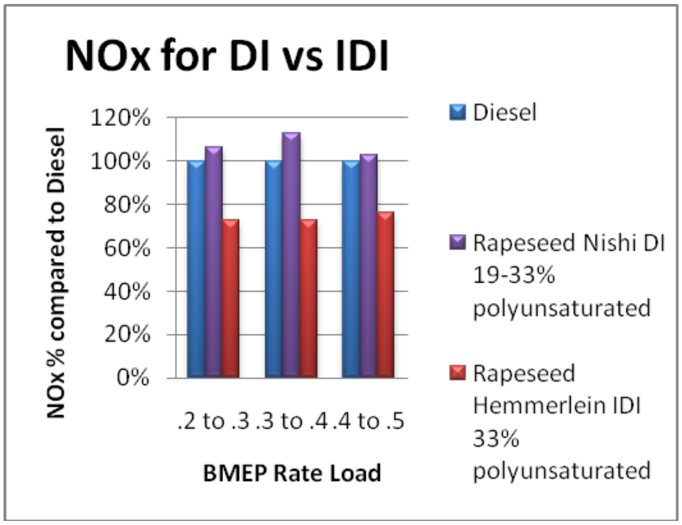

Figure 12 NO_x comparison for Rapeseed in DI and IDI engines

Many of the factors impacting SVO engine performance are interrelated. Improperly combusted fuel leads to higher emissions and buildup in the cylinder. Poor injector design leads to impingement of fuel on the cylinder walls, resulting in non-ideal fuel/air mixtures. During combustion, non-aerosolized fuel goes through thermal polymerization, creating buildup on the cylinder walls and injector.

Consistently, throughout multiple studies, engine noise has been noted to decrease with vegetable oil use. This is attributed to the lower pressures and temperatures in the cylinder, due to the slower heat release in vegetable oils.

POTENTIAL SOLUTIONS

Increasing temperature leads to a decrease in the oil's viscosity. The decrease in viscosity leads to an increase in the penetration rate of the fuel injected into the cylinder and a decrease in cone angle [18]. The decrease in viscosity also decreases the overpressure issues in the injection line. There is a possibility that increasing the oil temperature could increase the NO_x output. Advancing the timing for the SVO decreases unburned hydrocarbon Emissions [20].

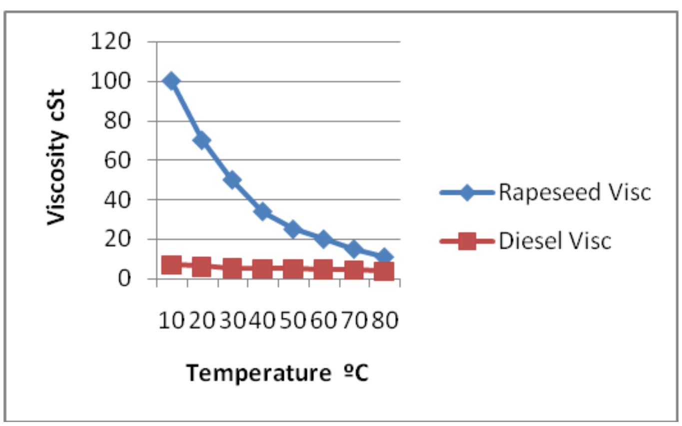

Figure 13 Viscosity vs. Temperature [14]

Heating of the vegetable oil to attain a lower viscosity has helped with the injection of the oil on a limited scale (Figure 13). The viscosity-temperature relationship of Rapeseed oil is very similar to other vegetable oils. To properly reduce the viscosity, the oil must be heated to about 60 ºC. The reduced viscosity does not always improve engine performance but is necessary for an even flow of the fuel through the fuel lines [14]. It is possible to overheat SVO. Several of the oils develop vapor bubbles at 100 ºC. This creates turbulence in the fuel lines, resulting in non-ideal combustion. Due to heat loss along the fuel delivery system, it is recommended to slightly overheat the oil in the fuel tank or to heat fuel lines and filters to prevent viscosity increases in the vegetable oil.

Most tests on SVO's are done in a diesel, vegetable oil blend to decrease potential harm by the SVO. Using pure vegetable oil requires engine modifications to prevent damage to the engine. The fuel tank, fuel lines and filters need to be heated. Most sources recommend that the oil temperature be approximately 70 ºC [17]. The engine oil must be changed on a more frequent basis and the injectors need to be monitored closely. Local temperatures must be accounted for in the testing procedures of the vegetable oil. Two tank fuel systems also reduce the damage done by non-ideal fuels. Diesel can be used to warm the engine to a stable temperature, and then used again to "clean" the fuel system of SVO buildup.

Newer direct inject technology tends to have emission and complete combustion problems with SVO. This may be overcome by adjusting the electronic timing of the engine for the longer heat release profiles of vegetable oil, heating fuel tanks and lines to reduce higher viscosities and examining the injectors for proper spray patterns.

CONCLUSION

Vegetable oils with high percentages of fully saturated fatty acids (e.g. palmitic and stearic acid) have the potential to produce lower NO_x emissions but typically suffer from undesirable physical properties such as high viscosity and high cloud point. Vegetable oils that are high in polyunsaturated fatty acids (e.g. linoleic and linolenic acid) are less viscous, but contribute to cylinder buildup and higher NO_x emissions. It is therefore recommended that SVO be higher in the saturated and monounsaturated fats, and use a retrofit kit/heating system with a new injector for direct inject engines. This will provide a lower emissions profile and increased engine longevity. Further studies are needed to design and test injector nozzles that prevent higher viscosity heated vegetable oil from impinging on the cylinder wall. Indirect inject engines have the potential of using SVO that is low in polyunsaturated fatty acids for long term use without significant engine damage and lower emissions compared to diesel.

The fatty acid constituents of the vegetable oil are very important to the emissions and longevity of the engine. Future SVO engine testing should include a lipid acid profile to facilitate comparison to other SVO testing.

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