Properties of Rapeseed Oil for Use as a Diesel Fuel Extender

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ABSTRACT: Chemical and thermal analyses were carried out on degummed and filtered (5 μm) rapeseed oil (referred to as SRO, i.e., semirefined rapeseed oil) to determine its suitability as a diesel fuel extender. The upper rate for inclusion of SRO with diesel fuel is 25%. This fuel blend had a phosphorus level of 2.5 ppm, which was comparable to rape methyl esters (1.0 ppm phosphorus). Thermogravimetric analyses were used to estimate the cetane ratings of the fuels. A 25% SRO/diesel blend had an estimated cetane index of 32.4 compared to 38.1 for diesel fuel only. Differential scanning calorimetry and thermogravimetric analyses were used to compare the volatility ranges of the fuels. SRO needed higher temperatures for volatilization (i.e., 70–260°C for diesel fuel vs. 280–520°C for SRO). This indicated poorer cold-starting performance of SRO compared with diesel fuel. SRO fuel is a low-sulfur, high-oxygen fuel giving SRO a more favorable emissions profile than pure diesel fuel.

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Since the 1970s there has been renewed interest in the use of vegetable oils as alternative fuels for diesel engines. This interest is politically and environmentally motivated. There are two potential methods for utilizing vegetable oils as fuels for diesel engines. One is to convert the vegetable oil into a product with properties similar to that of diesel fuel by chemically altering its structure by either cracking or transesterifying the oil with low molecular weight alcohols. Cracking the oil produces a variable mixture of compounds whereas transesterification produces a more uniform product; hence transesterification is the preferred method for chemical alteration of vegetable oils. The other method is to utilize the oil with a minimal amount of refining and blend it with diesel fuel to form a biofuel blend. This paper focuses on the latter (using semirefined rapeseed oil, SRO).

The 15% lower energy value of vegetable oils compared with diesel fuel is reduced to 10% by volume due to the higher specific gravity of the vegetable oils (1). Because diesel fuel injection equipment meters by volume, the maximal fuel energy delivery without modification of the injection equipment is reduced by only 10%. This will be significant only in the maximal overdesign power region. A 10% longer injection period does not cause problems over the normal engine load range (1).

Engine performance achievable with vegetable oils depends on the quality of the vegetable oil used (1–4). Researchers have used different vegetable oil analysis techniques, heightening the variation in engine performance results (1–4). In Europe, there has been considerable research into rapeseed methyl ester (RME) (5–7), which has led to a series of proposed specifications and standards for RME. Specifications for vegetable oil methyl ester fuel for diesel engines have been drafted (8).

In the United States, a list of research priorities regarding the development of vegetable oil technology was compiled (9). Among these is the need to describe the specifications for a diesel fuel extender, particularly chemical characterization. Also, more complete engine performance analysis of all oils is needed, and reference is made to the American Society of Agricultural Engineers (ASAE) fuel characterization tests for ethyl esters (10). This involves testing for a series of both fuel-specific properties (e.g., viscosity, pour point, cetane number, elemental analysis) and ester-specific properties (e.g., percent glycerine, free fatty acids, alcohol content).

A study evaluating and comparing the fuel characteristics of 11 vegetable oils and relating the fuel properties to their chemical properties was conducted (11). The study concluded that the flash points (ASTM Test No. D93) (12) of all the vegetable oils (rapeseed oil = 246°C) were far above that of diesel fuel (minimum 52°C), reflecting the involatile nature of the vegetable oils. Ignition quality of these fuels is dependent on a number of factors such as molecular weight, structure and volatility. The volatility of a fuel is an important feature for compression ignition engines. These results are in general agreement with those of others (3,4).

The present paper describes a series of chemical and thermal tests carried out on SRO, RME, and diesel fuel in order to evaluate the suitability of SRO for use as a diesel fuel extender (13,14).

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EXPERIMENTAL PROCEDURES

Crude vegetable oils are contaminated by sugars, resins, proteinaceous compounds, trace metals, and phosphatides. These "gums," or "slimes" or "mucilaginous materials" are removed by de-sliming or degumming treatments (15). The rapeseed oil used in these tests was degummed using both water and acidified water techniques (16), and then the oil was filtered through a 5-μm filter.

Phosphorus content. Phosphorus content, as an estimate of gum content, is a benchmark test for the quality of RME (8). The oils used for this test were commercial RME, crude rapeseed oil, SRO, and semisolid precipitate removed from the 5-μm filter used in filtering SRO. Tests were performed in triplicate.

Elemental analysis. Six blends of SRO with diesel fuel were prepared: 5, 15, 25, 30, 35, and 50% SRO. These blends, along with 100% RME (Chemoxy, Middlesborough, United Kingdom), 100% diesel fuel, 100% crude nondegummed rapeseed oil, 100% SRO, and the residue from the bottom of the settling tank, were analyzed for carbon, hydrogen, oxygen, sulfur, and nitrogen in a commercial laboratory based at University College Dublin (Dublin, Ireland).

Saponification value, nonsaponifiable matter, iodine value, acid number. Saponification value, nonsaponifiable matter, iodine value, and acid number were determined by standard methods (Refs. 17–20, respectively). Tests were carried out in triplicate.

Thermogravimetric analysis (TGA). TGA measures the changes in sample weight with respect to temperature, i.e., it indicates when a sample is losing weight and quantifies that weight loss in accordance with heating rate (21,22). In this study, 10-mg samples were placed in the sample pan in the TGA chamber along with a reference pan, and the sample + reference were heated in 5°C/min ramp steps up to 750°C in air. The sample weight loss with respect to temperature was logged by the system.

Differential scanning calorimetry (DSC). DSC is a measurement of energy changes, i.e., it detects enthalpy changes that occur in the sample (23,24). All tests in this study were carried out under a nitrogen atmosphere, hence combustion is prevented and volatilization of the sample takes place instead. The DSC pan with the weighed sample was crimped and placed in the chamber. It was then cooled to approximately −30°C using liquid nitrogen. The chamber was then heated to 550°C at 5°C/min. The DSC chamber was continuously purged with N_2 gas using a flow rate of 50 mL/min. The system logged the weight change with respect to the temperature.

RESULTS AND DISCUSSION

Phosphorus as an indicator of gum content. Phosphorus content in rapeseed oil of about 100 ppm corresponds to a phosphatide content of about 0.25% (8). The phosphorus content of rapeseed oil can be reduced to 20–30 ppm by transesterification, which corresponded to a phosphatide content of about 0.04% (8). Combining these values gives the following equation relating gum content to P content:

$$\text{phosphatides} = 0.0021\text{P} \qquad [1]$$

where P = ppm of phosphorus. Using this equation, we compute the gum contents listed in Table 1. Since SRO is used in a blend with diesel fuel and 25% is the upper inclusion limit, the maximal phosphorous content in the blended fuel is 2.5 ppm and the potential problems from using SRO are greatly reduced. It is envisioned that the normal SRO inclusion rate in diesel fuel will be about 10% (14) in which case the phosphorous content is similar to that of RME.

Elemental analysis. The elemental composition of the various blends of SRO is given in Table 2. No additives were used unless otherwise stated. SRO had 9% less carbon and 11% less hydrogen than diesel, hence, the lower specific energy content of SRO compared with diesel fuel. SRO has a barely detectable sulfur content compared with the 0.27% sulfur content of diesel fuel. Fuels with low sulfur contents have the advantage of producing lower sulfur dioxide emissions and, hence, reducing the potential for acid rain production.

Air/fuel ratio for SRO and for diesel. From the elemental analysis one may calculate the stoichiometric air/fuel ratios for both diesel fuel and SRO. Rapeseed oil is approximately a C_{57} compound (15) with one mole having atomic mass of 890. The combustion equation for any hydrocarbon (C_aH_b) compound is as follows:

$$C_aH_b + \left(a + \frac{b}{4}\right)\left(O_2 + 3.773N_2\right) = aCO_2 + H_2O + 3.773\left(a + \frac{b}{4}\right)N_2 \qquad [2]$$

where a and b are the numbers of carbon and hydrogen atoms, respectively (25). This equation gives air/fuel ratios of 14.5 for diesel fuel and 12.66 for SRO. SRO-based fuel would require about 6% less oxygen than diesel fuel for complete

TABLE 1
Chemical Tests of Vegetable Oils[a]

Test fuel	P content (ppm)	Gum content (%, w/w)	Saponification number	Unsaponifiable matter (%)	Iodine number	Acid number
SRO	10	0.021	131.1	0.10	161.6	3.4
RME	1	0.0021	131.7	0.05	165.0	1.0
Crude rapeseed oil	24	0.05	139.8	0.35	152.5	2.8
Filtered residue	105	0.22	145.9	0.58	98.6	50.0
Std. dev. (±)	0.9	0.001	2.3	0.02	1.2	0.7

[a]Sample size = 3. SRO, semirefined rapeseed oil; RME, rapeseed methyl ester.

TABLE 2
Elemental Composition of RME, Diesel Fuel, and SRO/Diesel Fuel Blends[a]

Test materials	Carbon (%)	Hydrogen (%)	Oxygen (%)	Sulfur (%)
5% SRO	85.9	13.2	<0.1	0.2
15% SRO	85.1	13.3	0.5	0.2
25% SRO	85.1	13.1	1.8	0.1
30% SRO	83.9	13.1	3.0	0.1
35% SRO	84.0	13.1	3.1	0.1
50% SRO	82.4	12.6	4.9	0.1
RME	77.3	12.1	10.6	0.1
Diesel	86.4	13.3	0.0	0.3
Crude rapeseed oil	78.1	11.9	10.0	0.0
100% SRO	78.2	11.8	9.9	0.0
Gum residue	75.9	11.9	9.9	<0.1

[a]For abbreviations see Table 1.

combustion. Since test engines are not adjusted either for the lower energy content or for the oxygen content of SRO, the excess oxygen advantage of SRO would have a beneficial effect on the emissions profile of the exhaust gases compared with a similar engine fueled with diesel fuel only.

Chemical analysis of SRO. By degumming rapeseed oil to produce SRO unsaponifiable matter is reduced by approximately 70% compared with a 60% reduction in phosphorus (26,27). Depending on which test is used, a different value for gum content will be determined. The more saturated the vegetable oil, the fewer oxidation and polymerization problems that will arise during both storage and combustion. The differences between the test fuels in Table 1 are unlikely to affect either the combustion or storage of these fuels. Oils with higher gum contents would be more likely to exhibit storage problems. The gum fraction has a large acid number because of the use of phosphoric acid in the degumming. Free fatty acids (in both the fuel and unburnt fuel fraction) act as natural detergents and hence facilitate the decoking of materials deposited in the fuel and exhaust systems of the vehicle being fueled with these fuels. This effect was noted with the vehicles running on 100% RME (i.e., these vehicles had cleaner exhaust systems) and, to a lesser extent, with SRO being used in a 25% blend with diesel fuel.

When using alternative fuels such as SRO, the wet chemistry tests are not definitive in determining the suitability of an alternative fuel for use in diesel engines. These tests reveal very little of how the fuel will behave within the high-temperature, high-pressure complex interactions that exist in a compression ignition engine. These tests are more indicative of how the fuel might be expected to behave in storage.

TGA. The TGA profiles yield useful information about the sample weight losses and temperature range over which a particular sample appears to be either stable or volatile. Crude rapeseed oil and SRO begin to volatilize at about 200°C (which is an indication of the potential onset of combustion), and most of the sample has volatilized by 500°C. Conversely, both diesel fuel and RME begin to combust at lower temperatures (*ca.* 70°C), and have volatilized by approximately 250°C. The weight loss in these tests reached 100% since all of the volatilization products were gaseous and no solid residue was left in the pan. It is clear (Table 3) that both SRO and crude rapeseed oil require considerably higher combustion temperatures than both RME and diesel fuel. The TGA profile of the gum residue shows a higher volatilization rate up to about 400°C. This is consistent with products that contain unsaturated compounds, as saturated materials have higher melting and boiling points (*viz.* gum residue vs. SRO).

Cetane number. The ignition characteristics of a compression ignition fuel affect the ignition delay of the fuel. These fuel properties are very important in determining diesel engine operating characteristics such as fuel conversion efficiency, smoothness of operation, misfire, smoke emissions, noise, and ease of starting. The ignition quality of a fuel is defined by its cetane number. Cetane number is determined by comparing the ignition delay of a test fuel with that of a primary reference fuel mixture in a standardized engine test (ASTM Method D613) (28). This is a complex and expensive method. However, the cetane number can be estimated from TGA data, using the ASTM D976 (29). The distillation values were estimated from the TGA curves for the fuels and the CCI were calculated (Table 4). The CCI values show that SRO fuel performs poorly and reflect the poorer volatilization characteristics compared to diesel, owing mainly to the higher density of this fuel. As the SRO would be used in a blend with diesel (i.e., 25% SRO/75% diesel), this blend would have a CCI of 32.4. Although the cetane number is a measure of the ignition quality of petroleum fuels, the significance of this value for vegetable oils has not been established (11).

DSC. DSC is a method of determining the onset of phase change (e.g., either solid to liquid or liquid to vapor) in a sample. The process is carried out by heating the sample and measuring the resultant enthalpy changes. Volatilization is essential for the onset of combustion. The DSC data analysis package used in these tests established a baseline and an enthalpy flow line. The intersection of these two lines was the onset temperature for the major portion of phase change. The heat input required for this phase change was also calculated. DSC analyses of the test samples are summarized in Table 5. SRO

TABLE 3
Volatilization Temperatures for the Test Fuels

Sample	Onset of volatilization (°C)[a]	End of volatilization (°C)[b]
SRO	280	520
Crude rapeseed oil	280	520
Water degummed and filtered rapeseed oil	280	480
RME	70	250
Diesel	70	260
Gum residue	120	480
Std. dev. (±)[c]	2	2

[a]At 5% weight loss.
[b]At 95% weight loss.
[c]Duplicate samples. For abbreviations see Table 1.

TABLE 4
The Estimated Distillation Temperatures from TGA Curves and Calculated Cetane Index (CCI)[a]

Fuel	Distillation temperature 9°C) 10%	50%	90%	Density (g/cm^3)	CCI
Diesel	85	150	220	0.85	38.1
RME	105	107	242	0.87	39.7
SRO	305	385	500	0.91	15.4
Crude rapeseed oil	310	395	500	0.91	14.6
Water degummed and filtered	310	385	460	0.91	19.7
Std. dev. (±)[a]	2.5	2.1	2.2	0.002	

[a] Duplicate samples. For abbreviations see Table 1.

had a lower energy requirement for phase change (*viz*., volatilization) than crude rapeseed oil and is similar to the requirement for RME and diesel fuel, although it required higher temperature to initiate volatilization. This was attributed to the removal of the gums (24). In Table 5 we see a phase change in the gums (*viz*. transition from gel to liquid) at about 54°C. Below this temperature the gum fraction may impede fuel flow, which will worsen as ambient temperature approaches 0°C. The gum residue volatilized at 383°C and required a heat flow input of 102.5 J/g. This low energy input (relative to SRO) was consistent with the chemical tests, which showed the unsaturated nature of the gum residue. Unsaturated compounds have lower volatilization energy. Diesel fuel volatilizes at a much lower temperature (*ca*. 37°C) than SRO (*ca*. 355°C). As volatilization is essential for onset of combustion, the cold starting performance of SRO will not be so good as with diesel fuel. This difference should not affect performance at normal engine operating temperatures, however, because the energy inflow characteristics of both fuels were similar (Table 5), and hence the heat transfer to SRO and diesel was similar.

From the thermal analyses it can be seen that diesel fuel and RME have similar TGA curves (95–250°C), compared with SRO (280–480°C). However, compression ignition engines generate a nonfiring temperature of about 800°C (25) due to the compression of the air within the combustion chamber. Hence, compression ignition of these fuels should not be a problem.

TABLE 5
DSC Properties of the Test Fuels

Fuel	Onset of phase change (°C)[a]	Energy flow (J/g)[b]
SRO	354.5	338.8
Crude rapeseed oil	351.1	478.3
Water degummed and filtered	348.5	347.4
Acid degummed only	352.9	433.2
RME	178.0	353.4
Diesel fuel	36.7	329.4
Gum residue (gel)	54.6	87.3
Gum residue (vapor)	382.9	102.5
Std. dev. (±)[c]	2.1	2

[a] Volatilization for liquids; gel-to-liquid for gums.
[b] Calculated energy requirement for the phase change.
[c] Duplicate samples. For abbreviations see Table 1.

When fuel is injected into the combustion chamber of an engine, both physical and chemical processes must take place before any significant fraction of the chemical energy of the injected fuel is released (25). The physical processes include atomization of the liquid fuel jet, vaporization of the fuel droplets, and mixing of fuel vapor with air. The chemical processes are the precombustion reactions of the fuel, air, and residual gas mixture which lead to autoignition of the fuel. These processes are affected by engine design, operating variables, and fuel characteristics. Determinination of the thermal characteristics of the fuels using DSC and TGA enables one to evaluate a diesel substitute or extender fuel prior to engine trials.

The CCI is an indictor of the fuel quality in compression ignition engines, and by this method, SRO performs poorly. However, the use of petroleum standards for the evaluation of biological or nonpetroleum fuels has not been established (10,11), which has led to the development of a proposed Engineering Practice for Testing of Fuels from Biological Materials. In this regard, the use of TGA and DSC to estimate the possible behavior of fuels in the combustion chamber of a diesel engine is more appropriate than chemical tests.

SRO proved to be a suitable diesel fuel extender, at inclusion rates up to 25%, when used in direct injection combustion systems (13,14,16). In those studies, power output was reduced by about 0.06% for every 1% increase in SRO inclusion rate, and brake-specific fuel consumption (BSFC) increased by about 0.14% per 1% increase in SRO inclusion rate. Chemical and viscosity analyses of engine lubrication oil (after about 170 h per fuel tested), including metal contamination as an indicator of engine wear, showed that there was no measurable effect on engine lubricating oil due to SRO inclusion in diesel fuel. Degumming and filtering the rapeseed oil and blending it with diesel fuel offer a potentially low-cost, low-technology method for producing an alternative fuel for compression ignition engines.

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