PROPERTIES OF THE RAPESEED OIL METHYL ESTERS AND COMPARING THEM WITH THE DIESEL OIL PROPERTIES

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Abstract

The paper presents theoretical analysis of the properties of the rapeseed oil methyl esters and comparing them with the diesel oil properties. The essential differences in the physic-chemical properties have been emphasised, such as: Cetane number, viscosity, density, fraction content, calorific value and temperature properties of the rapeseed oil methyl esters in respect to the diesel oil.

The influence of individual properties of fuels on the combustion needs to be comprehensively approached, taking into account mutual relationships between individual characteristics of diesel oil. The numbers of the basic fuel properties depend on the fractional content, such as: viscosity, density, Cetane number or surface tension influencing the course of the physic-chemical processes taking place in the self ignition engine and the combustion. The influence of many fuel properties on the combustion process is sometimes contradictory. The range of the fuel's influence on the combustion depends also on the thermodynamic parameters of the engine. The new and current problem concerning the fuels for the self ignition engines is an introduction into the operation of the rapeseed oil esters and their mixtures with the Diesel oil are an object of the paper. The question, how will the vegetable oils affect the combustion process, remains open.

Keywords: *biofuels, rapeseed oil methyl esters, physic-chemical properties*

1. Introduction

The development of combustion engines follows the requirements of protecting natural environment, while maintaining low fuel consumption. Further lowering the toxicity of the exhaust gasses by selecting solutions and design parameters has a limited range. Other possibilities are being sought out to improve combustion in the self combustion engines by optimising the process, electronic control, high pressure fuel delivery, turbo charging the engines, effective methods of purifying the exhausts and other methods. One of such possibilities is application of the ecological fuels.

The influence of individual properties of fuels on the combustion needs to be comprehensively approached, taking into account mutual relationships between individual characteristics of diesel oil. The operational characteristics of fuel depend mainly on the fractional content of the diesel oil, determined by the content of the individual chemical compounds in the crude oil and the technology of its processing.

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The new and current problem concerning the fuels for the self ignition engines is an introduction into the operation of the rapeseed oil esters and their mixtures with the Diesel oil. The question, how will the vegetable oils affect the combustion process, remains open. According to the literature, the influence of the rapeseed oil esters is varied depending on the engine parameters.

The rapeseed oil esters are formed as a result of the chemical reaction between the raw rapeseed oil and the methyl or ethyl alcohol in the presence of the catalyst. For the economic and technical reasons, commonly produced are rapeseed oil methyl esters (RME – Rapeseed Oil Methyl Ester).

Ester definition differs from the European definition FAME (Fatty Acid Methyl Ester) meaning methyl ester of the higher fatty acids found in the rapeseed oil fats, or other vegetable and animal fats, obtained during processing them. The FAME definition does not cover ethyl esters.

There are various commonly used names in the European Union:
- Austria, Germany – FAME, RME,
- Czech Republic – RME,
- France, Italy, Sweden – VOME,

and USA – BIODIESEL.

The properties of the rapeseed esters depend both on the properties of the raw rapeseed oil, and processing technology. The rapeseed oil methyl esters formed as a result of processing raw oil have significantly better properties than the rapeseed oil. The mole mass decreases (to the value of about 300 kg/kmol). As a result of that, the kinetic viscosity decreased several times which allows improving the process of creating air-fuels mixture and the combustion. The fuel density decreased also slightly. The Cetane number in turn increases up to the values similar to that of the diesel oil. The rapeseed oil methyl esters have significantly lower, than the raw rapeseed oil, cold filter plug point (CFPP) and the Condradson number, characterising coke deposits. The Sulphur content and the ignition temperature also decrease.

The necessary condition for the oil esters as a fuel is as high as possible level of esterification, which means that the esters should not contain the residues of alcohol and unreacted oil particles. The residues of alcohols are the cause of fuel system malfunctions, while the oil residues cause the deposits to collect [3].

In comparison with the diesel oil, both the raw rapeseed oil, and methyl esters of this oil change their physic-chemical properties and characteristics during storage. These differences depend on the storage conditions. Apart from the end quality of fuel and the storage time the changes can be caused by: material the tank is made of, air access, sun exposure, and first of all the temperature.

The changes affect the, important for combustion, properties of the rapeseed oil and its esters, such as:
- as a result of the sun exposure the viscosity value gets significantly increased, probably by creating polymers following oxidisation,
- Cetane number increases,
- the fuel susceptibility to leaving cock residue gets higher (Condradson number), independently of the storage conditions,
- water vapour content increases.

In order for the ester fuel, approved for use, to have an appropriate quality, it is necessary to have uniform standards developed and implemented as well as methods of testing individual indicators characterising the fuel, and appropriate quality control systems. Such standards are already introduced in some European countries (Germany, Austria, Italy, Sweden, Czech Rep.) as well as in the US.

The correct course of combustion in the self ignition engine is not only determined by the engine design parameters but also physic-chemical properties of the fuels.

Table 1 presents basic physic-chemical properties of the rapeseed oil methyl esters (RME) and diesel oil (ON).

Tab. 1. Basic physic-chemical properties of the rapeseed oil methyl esters (RME) and diesel oil (ON) [2]

No.	Parameter tested	Unit	RME	ON
1.	Density at the 15°C temperature	kg/m^3	886 - 900	817- 856
2.	Cold filter plug point	°C	- 8	- 34
4.	Kinetic viscosity in the temp. of 20°C	mm^2/s	6 - 9	2.9 – 5.5
5.	Calorific value	MJ/kg	37.02 – 37,2	42.7 – 43.5
6.	Cetane number	-	45 - 59	47.1 – 58.6
7.	Clouding temperature	°C	- 3	- 33
8.	Ignition temperature	°C	166	62
9.	Elementary analysis			
	C	%	76.6 - 78	86 – 86.4
	H		12.1	13.4 - 14
	O		10 - 11	
10.	Stoichiometric oxygen demand	kg_{air}/kg_{fuel}	12.5	14.57
11.	Impurities content	mg/kg	14	9
12.	Fractional content	°C		
	20% get distilled to the temperature:		334	
	40% get distilled to the temperature:		336	
	60% get distilled to the temperature:		336	
	80% get distilled to the temperature:		339	
	95% get distilled to the temperature:		343	
	End of distillation		345	
	Up to the temp. of 190°C, gets distilled:	% (V/V)		3.0
	Up to the temp. of 240°C, gets distilled:			59.0
	Up to the temp. of 290°C, gets distilled:			97.0

Physic-chemical properties of the rapeseed oil methyl esters and diesel oil and their influence on the operation of the diesel engines ought to be evaluated based on the following indicators [4].

1.1. Cetane number

Cetane number is one of the most important parameters defining susceptibility of the fuel to self-ignition, expressed by the period of delaying self-ignition. It affects the fuel self-ignition time and the course of its combustion in the engine, and in the consequence also the performance, exhaust composition and the engine noise.

Rapeseed oil methyl esters are characterised by a higher Cetane number (CN) in comparison to the diesel oil. Rapeseed oil methyl esters having higher Cetane number possess shorter self-ignition period than the diesel oil, which results in that the larger amount of RME is supplied after the self-ignition, and the combustion is of a diffusion character.

Too low values of the CN, below 45 units, lead to worsening the engine operating conditions, causing the extension of the self-ignition delay. This may cause excessive increases of pressure and temperature in the combustion chamber, leading to the harsh engine operation resulting in the premature wearing up of the components, with the simultaneous difficulties with starting the cold engine.

Increasing the CN from 50 to 58 causes considerable (even up to 30%) lowering of the CO and HC emission and lowering NOx by several percent, without significantly affecting the PM emission level.

The excessive shortening of the ignition delay period may also be disadvantageous. The combustion process starts then after injecting the fuel and its larger amount is being injected not into the air but the combustion products. The combustion becomes incomplete, the engine power output decreases, and the emission of the toxic substances increases.

At present, the European requirements determine the admissible minimum value of the Cetane number at 51 units, for the fuels used in the moderate climates.

1.2. Viscosity

What can be concluded from the comparison of the properties of the diesel oil and rapeseed oil methyl esters, is that the largest differences can be noticed in the fuel viscosity values [2].

Rapeseed oil esters have larger viscosity than the diesel oil. Diesel oil has a kinetic viscosity of 2.9 to 5.5 mm^2/s at the temp. 20°C, while the rapeseed oil esters from 6 to 9 mm^2/s.

The viscosity is a measure of the internal friction, characterising the resistance that occurs in the fuel flow.

The viscosity has decisive influence on the correct fuel flow through the fuel lines, filter, pomp and the injector, as well as on the course of the pumping and atomising process. Too high viscosity causes poor atomisation of fuel in the cylinder, worse combustion, loss of power and the increase of the HC and CO emission. But lowering the viscosity entails, in turn, worsening of the lubricating properties, which results in the accelerating the wear of the fuel supply system.

In the self ignition engines the size of the fuel portion is controlled volumetrically. For this reason density and viscosity affect the amount of fuel, and thus the chemical energy introduced into the engine cylinder. It is the viscosity that the quality of fuel atomisation depends on, as well as the course of its combustion. If the viscosity is too large, then during the atomisation, the large droplets get created, the range of the fuel stream increases, fuel may settle on the piston tops and the combustion chamber walls creating carbon deposits and then the combustion is incomplete.

On the other hand, with too low fuel viscosity, fine droplets get created, which (during compression, the density of the air increases 12-14 times) swiftly get evaporated and slow down. As a result, not the entire air takes part then in creating the mixture, the local excessive amount of fuel occurs and incomplete combustion follows in the part of the chamber that is closer to the injector. Too low viscosity worsens the lubricating conditions of the injector pump pistons and decreases the range of the stream, causing uneven distribution of the fuel droplets in the combustion chamber, leading to the incomplete combustion and local overheating of the combustion chamber walls.

Because the fuel viscosity decreases with the increase of temperature then through the viscosity changes caused by the temperature, there are changes occurring in the conditions of pumping these fuels. The smallest changes of viscosity together with the temperature alterations can be observed with the paraffin fractions contained in oils. The excess of those fractions, improving the self-ignition properties, worsens significantly the low temperature properties, raising the clouding and solidification temperatures as well as cold filter plugging point.

1.3. Density

Rapeseed oil methyl esters have slightly higher density (886–900 kg/m3) than diesel oil (817-856 kg/m3). The relative fuel density is a mass measurement per volume unit and has a direct influence on the volumetric fuel consumption. Lower density lowers the emission of PM, HC and CO. Lowering the fuel density causes the reduction of the particulates emission. In some cases lower fuel density also causes the decrease of the nitrogen oxides emission.

Decreasing the fuel density is linked with the drop of its calorific value, which affects the engine performance. Depending on the adjustments, the engine either produces less power or uses more fuel volumetrically. If this lowering of the power is stopped by increasing the fuel dose, then the increase in its consumption will eliminate the beneficial effect of particulates emission reduction caused by the lower density of the diesel oil. Despite the increase in the fuel consumption as a result of lowering its density, there is a slight, about 1% reduction of CO_2 emission. Therefore the fuel density should be appropriately low and change only within small limits. Current requirements of the European standards admit density of the diesel oil. not exceeding 845 kg/m3 at the temperature of 15°C.

The changes in the fuels density may also contribute to the emission increase by causing improper operation of the exhaust gasses recirculation system, which regulates recirculation degree depending on the fuel dose.

1.4. Fractional content

Fractional content is a factor characterising the ability of the fuel to turn into the vapour state and is the volatility parameter of the fuel.

Fractional content has considerable influence on the engine operation. If the fuel is too volatile the engine loses power and efficiency. The distillation curve of the rapeseed oil methyl esters differs significantly from that of the diesel oil (Fig. 1).

The temperature of distilling 10% of the diesel oil is lower by about 120°C than that of the rapeseed oil methyl esters, which causes staring difficulties of the engines powered by the esters.

The light fractions content is usually determined by distillation temperature of 50% of the fuel volume. The lower it is, the faster liquid fuel turns into vapour, the time to create air-fuel mixture shortens and the engine start up is easier, especially at lower ambient temperatures. The distillation temperature of the 50% of the rapeseed oil methyl esters is higher by about 80°C that the distillation temperature of the same volume of diesel oil.

The distillation beginning temperature affects the ease of starting the engine up. The largest influence on the engine exhausts content has however the number of the heavy fractions, determined by distilling 90% of the fuel volume and the distillation end temperature. Less easy combustible heavy fractions are in large responsible for the presence in the exhaust of the products of the incomplete combustion such as: CO, HC and first of all soot.

The influence of distillation end temperature on the emission of the toxic substances by the self ignition engines was studied as part of the European Auto Oil program. In case of the passenger cars engines (Light Duty Diesel) it was observed, that lowering the distillation end temperature from 375 to 320°C causes reduction of the particulates emission by an average of 7% and increase of the nitrogen oxides emission by an average of 4.6%.

For the trucks engines in turn (Heavy Duty Diesel) the change of the distillation end temperature within the same range brings about only minimal differences in the exhausts content, manifested by lowering NOx emission and the increase of the HC emission.

It has also been established, that high distillation end temperature, regardless of the engine type increases engine smoking and particulates emission. The European Union Directive defines maximum distilling temperature of 95% diesel oils at 360°C. Fast evaporation of the fuel light fractions shortens time necessary to create homogenous combustible mixture. On the other hand however the pressure increases violently, following the mixture self-ignition, causing unfavourable harsh engine operation. Heavy fractions contained in the diesel oil may lead to incomplete fuel combustion, causing occurrence of the thermal brake down of the unevaporated droplets with the emission of large amount of soot in the exhaust and carbon deposits on the tips of the injectors. Unburnt fuel flowing at the same time on the walls of the combustion chamber may wash off the lubricating oil and cause accelerated wear of the cylinder liners.

1.5. Calorific value

The diesel oil is characterised by a higher (by about 10%) calorific value than the rapeseed oil methyl esters. The basic components of the diesel oil are: carbon (86–86.4%) and hydrogen (13.4-14%), while the rapeseed oil methyl esters: carbon (76.6–78%), hydrogen (12.1%) and oxygen (10–11%). The difference in the elementary content of both fuels decides about the calorific value, and also different demands for oxygen necessary for combustion.

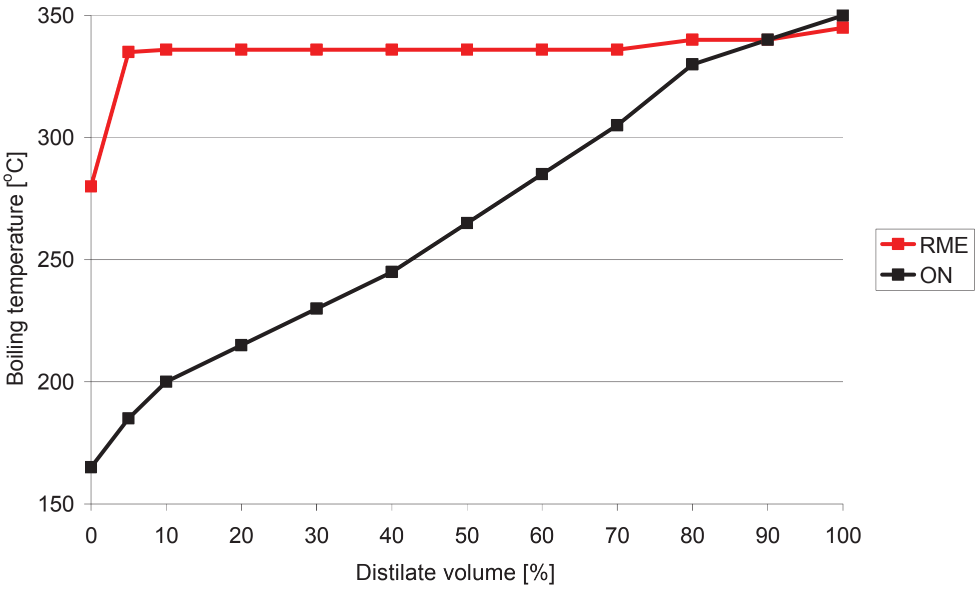

Fig. 1. The course of the relationship between the boiling temperature and the volume of the distilled fuel for the diesel oil and the rapeseed oil methyl esters [5].

The calorific value is an amount of energy, which is contained by the fuel and is higher, the higher is the ratio of the hydrogen and carbon contained in the fuel, as the most energy rich element is hydrogen (its Wo = 120 MJ/kg, while that of carbon Wo = 32.7 MJ/kg). The higher in RME (by about 12%) oxygen content benefits better ignition and more complete combustion of RME [1]. The oxygen contained in the fuel may show higher chemical activity in the combustion process than the oxygen contained in the air. The comparable hydrogen content in the fuels tested is beneficial in the environmental protection aspect, as apart from its lower consumption, the exhausts contain less CO2 and CO, and more water.

The lower calorific value of the rapeseed oil methyl esters, with an unchanged adjustment of the fuel system causes lower power output, which is a measurement of the heat generated in the cylinder. The decreasing of the calorific value negatively affects the engine torque, and increases the fuel consumption.

1.6. The temperature properties

The temperatures of ignition, cold filter clogging and clouding are the essential parameters defining flow and ignition properties of the engine fuels. They are varied depending on the season and climatic zone, in which the fuel is being used.

Due to the high ignition temperature of rapeseed oil methyl esters this fuel is not regarded as an explosive substance. The ignition temperature is the lowest temperature, in which the fuel's vapours released in the standardised conditions, together with the air, creates the inflammable mixture in contact with the flame. The diesel oil belongs to the II fire safety class, while rapeseed oil methyl esters to the III class.

The diesel oil is characterised by much lower cold filter plug point than rapeseed oil methyl esters. Therefore, in case of the rapeseed oil methyl esters at about the temperature of –8°C the stoppage of the fuel being supplied to the cylinder, may take place. This is caused by the release of the paraffin crystals and the increase of viscosity, which in time with the fuel flow through the filter, clogs up the filtration system, subsequently stopping the flow of fuel in the filter, causing the complete blockage of the filter. Further lowering of the temperature causes solidification of the fuel, up to the moment of the total loss of it liquidity.

The diesel oil has a lower clouding temperature than that of the rapeseed oil methyl esters. This means that cooling the esters to the temperature about -3°C releases from them the paraffin crystals causing visible clouding of the product.

2. Summary

The presented comparison of the physic-chemical properties of the diesel oil and rapeseed oil methyl esters was aimed at showing the influence of those properties on the combustion process and exhaust toxicity, as well as the usefulness in the operating temperatures.

The physic-chemical properties of the fuels tested are dependent on each other and decide about the course of the basic processes taking place in the engine, such as: atomisation, creating air-fuel mixture or the self-ignition occurrence.

From the features described above there are differences visible in the physic-chemical properties of the diesel oil and RME:

- the Cetane number defines self-ignition properties, which are slightly higher for RME,
- RME viscosity is about 2.5 times higher that that of diesel oil, thus the flow process, injection and atomization of RME will be worse than that of diesel oil,
- RME density is about 8% higher than that of the diesel oil, which affects the volumetric fuel consumption,
- The RME distillation curve runs flat in the upper range of the boiling temperatures of the diesel oil, which means lack of fractions of low boiling temperatures and worse starting up properties,
- RME contains 10.4% of oxygen and less carbon and hydrogen than diesel oil, and this causes the calorific value of RME to be lower by about 10% than that of the diesel oil,
- The cold filter plugging temperature for the diesel oil is much lower that for RME, which causes worse start up engine properties.

Despite the fact that RME differs from diesel oil in the individual properties, taking into account all the parameters affecting the entire combustion process, RME may be used as an independent fuel to power self ignition engines. The application of RME does not require intervening into the engine construction or the supply system. Certain improvement of the rapeseed oil methyl esters properties can be achieved by adding the diesel oil.

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