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Advanced Combustion Research for Energy from Vegetable Oils (ACREVO)

Contacts

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Introduction

The objective of the ACREVO project developed by LCSR / CNRS in Orleans (France) is to investigate the burning characteristics of vegetable oil droplets from experiments conducted under high pressure and high temperature conditions. With such investigations, combustion performances of vegetable oils as biofuels for Diesel engines could be improved.

Many studies have examined the performances and pollutants emissions of Diesel engines using vegetable oils. Due to their physical differences as compared to Diesel fuel (especially a significantly higher viscosity), there are problems such as poor atomisation and coking tendencies in long-term test. It appears, therefore, important to study the mechanisms of deposit formation during vegetable oils combustion. To understand the vaporisation and combustion mechanisms of sprays in Diesel engines, it is necessary to isolate and study a droplet of this spray.

In part of the ACREVO project investigated the vaporisation and combustion of a vegetable oil droplet. Few studies provide basic data about the properties and characteristics of vegetable oil droplets vaporisation and combustion, although some single droplet experiments with two biomass oils, produced from the pyrolysis of oak and pine, have been carried out. Liquid-phase polymerisation and pyrolysis of the oxygenate-rich biomass oils lead to the formation of carbonaceous cenospheres. The vaporisation mechanism of a sunflower droplet has been investigated showing a micro-explosion mechanism inside the droplets that was more important, when using vegetable oils than with Diesel fuel.

Depending on the chemical composition of vegetable oils and their esters, the amount of residue formed become more or less. For various vegetable oils, a classification of vaporisation velocity has been established : copra > palm > sunflower > rapeseed > cotton > soy > linseed.

Several methods exist for the study of droplets. These include the fibre- suspended droplet, the freely-falling single droplet and the porous sphere. Many experiments have been conducted concerning the vaporisation and combustion of classic fuel droplets using these various methods. For the present project the fibre-suspended droplet technique was used. This method allowed the droplet to be maintained in a fixed position so that the vaporisation and combustion mechanisms could be monitored using a high speed camera.

To improve the use of vegetable oils as biofuels and decrease their effect on environment, it is also necessary to understand the chemical processes occurring during the combustion and to identify the products formed during pyrolysis and the oxidation. Several studies have investigated the thermal cracking of vegetable oils. Whatever the nature of vegetable oil and the temperature (400-500 ·C) pyrolysis transforms most of ester functions of triglycerides into carboxylic acids. The unsaturated chains are transformed into aromatic hydrocarbons. During the pyrolysis of sunflower oil the following compounds were identified : alcanes, alcenes, diolefins, carboxylic acids and aromatics.

Depending on the temperature, the thermal degradation of vegetable oils is a polymerisation (200-300 °C), a degradation of vegetable oils into acrolein, ketene, fatty acids then formation of alcanes, alcenes above 300 °C and finally a formation of a gas-liquid mixture from around 500 °C up. Information is available concerning the nature of compounds formed during the pyrolysis of rapeseed methyl ester. The main pyrolysis products are alcanes, alcenes, aromatics (benzene and toluene), methyl esters (both saturated and unsaturated). Ethylene is a major product at high temperature (850 °C) while methyl esters decompose to secondary products from around 600 °C and higher.

To complement the few existing studies concerning the oxidation of vegetable oil methyl esters (VOME) experiments have been conducted in a jet-stirred reactor in which it is possible to study the reactivity of VOME and the formation of the main oxidation products. This enables the elaboration of chemical kinetic models for the combustion of rapeseed methyl ester and other VOMEs. These have been investigated in a jet-stirred reactor at high temperature (800-1050 K) and at high pressure (1 Mpa).

Activities

Droplet vaporisation In order to improve combustion performances of vegetable oils as biofuels for Diesel engines, experiments about the vaporisation of vegetable oil methyl ester droplets have been conducted in a high pressure and high temperature droplet burning facility. The fibre- suspended droplet technique was used with high speed video camera to follow the histories of the droplets during their lifetimes. Experimental data agree with the d^2-law, the standard model describing droplet vaporisation. From the $d^2(t)$ curves, it was possible to determine the average and instantaneous vaporisation rates at temperatures between 573 K and 773 K at atmospheric pressure. The vegetable oil methyl esters evaporate like pure components, with a very significant preheating phase. A comparison of experimental results with those predicted by the quasi-steady theory has been completed. The calculation shows that the influence of the quartz fibre is important at the end of the vaporisation, when the droplet size is comparable with the extremity of the quartz fibre.

Pyrolysis and combustion of vegetable oil fuel sprays These aspects have been examined in a shock tube between 900 and 2000 K at pressures between 3 and 20 + bar and with different fuel/oxygen ratios. High speed video photography has shown how the high pressure spray in injected into the reaction volume and is mixed by natural swirl. Homogeneous or heterogeneous combustion could be produced by injecting the fuel either before or after shock reflection. Combustion occurs near the end-plate where fuel droplets have been conditioned the longest time and near the side wall where the droplet/fuel density is greatest. The combustion spreads very quickly throughout the reactive volume containing the fuel. Fuels which contains either rapeseed oil other methyl esters burn in a different manner to normal Diesel, where the flame was reasonably uniform. With vegetable oil fuels pockets of burning could be seen, some of which persisted for long times suggesting that these were larger droplets which burned as a diffusion flame for times longer than the available than those available in an engine. Thus they were potential carbonising nuclei for the walls of a burner or engine.

A second injection of fuel at a later time directly, under the high temperature pressure conditions, gave a very rapid combustion over the reaction volume where the previous phenomenon was not seen but soot like clouds could be detected by photography. Pyrolysis of fuel at these high temperatures resulted in a much greater light emission which saturated the CCD camera.

Soot could also be seen as the mixture cooled highlighted against the bright background. The amount of soot collected from these combustions and pyrolyses generally gave less than from hydrocarbon fuels with little effect of reaction pressure on the amount found.

The PAHs detected from soot analysis were different to those found with gaseous hydrocarbon fuels such as heptane or toluene with the maximum amounts being acenaphthene, acenaphthylene and fluorene. The yields of PAH (a fraction of a percent of the soot) yields seemed to increase with temperature but showed little, if any, change with total pressure.

Characterisation of soot formed in a rapeseed oil flames. In order to allow complete computations of emitted pollutants, the choice was made of a laminar, diffusion flame of pre-vaporised oil in air. Since the use of vegetable oil was the first constraint, much of the project time has been taken up by the set-up of the process. To measure soot particles with accuracy required the use of laser light scattering (LLS) as a diagnostic. However it is impossible to distinguish soot and fine droplets, if located in the same area of the flame, using the classical optical techniques. The major difficulty, which has been encountered in this project, was to be able to survey the oil vaporisation continuously, and to validate the hypothesis of a gaseous flame. Following a feasibility study described in a previous report, this part of the project has been successfully realised. The main result obtained by the task consists of a vaporising process, for vegetable oil or other viscous fuel, which is optically controlled during the whole experiment duration. This ensemble can be applied to the other activities. The present study includes the design of an experimental oil atomisation set-up with a good knowledge of the droplets formed (stabilities of the sizes distribution and concentrations) and an understanding of the heating of the droplets cloud. The rapeseed oil droplets are completely evaporated when a small amount of butane is added to stabilise the laminar oil diffusion flame.

In order to distinguish the soot particles from the oil droplets, a numerical procedure has been performed to analyse the experimental data obtained by an optical extinction technique. An inversion code has been written and validated to extract the characterisations of residual droplets and soot from the extinction spectra. The presence of gas absorption bands in the flame had to be taken into account, too.

The complete characterisation of soot particles emitted by the laminar rapeseed oil flame, based on LLS technique at several angles has been developed.

Sooting zones Many investigations of soot volume fractions, particle radii and number densities in rapeseed methylester(RME)/nitrogen and acetylene/nitrogen jet diffusion flames have been completed. The measurements were performed using a new laser diagnostic technique which is based on a simultaneous detection of laser light scattering, laser-induced incandescence (LII) and extinction. The sooting zone of an acetylene/nitrogen jet diffusion flame was investigated using this technique and compared with that of a RME/nitrogen jet diffusion flame. The main result is that at the position of the maximum number density a minimum of the particle radius is observed. This result is consistent with the current soot formation mechanism, that predicts incipient soot formation at high number densities and small radii. The surface growth and oxidation of soot is consistent with the measurements. Acetylene showed a much faster formation of soot than the RME, which correlates with the higher soot formation tendency of acetylene as measured by the threshold soot index. In a high turbulent acetylene/nitrogen flame most of the soot is formed under segregated conditions indicating that time scales of soot formation and oxidation are smaller than those under turbulent mixing.

Fuel performance of a typical vegetable oil Several studies have been conducted to qualify various oil and their blends from plants and vegetables as alternative renewable energy source. However, these studies were generally conducted with test approach, without considering in detail all the aspects related to atomisation, thermal stability and combustion characteristics of these fuels. So, the performances as a fuel of a typical vegetable oil, the rapeseed oil, as well as blends of rapeseed oil/alcohol have been investigated in a 100 kW pilot plant available at IRC. Preliminary study of physical characteristics as the viscosity and the thermogravimetry profile have been carried out to check the stability of the rapeseed oil with the temperature and a study concerning the miscibility of the rapeseed oil with two different alcohols (methyl and ethyl) was carried out.

In addition the radial distribution of rapeseed oil and rapeseed oil/alcohol blend sprays have been investigated under varying conditions of pressure and temperature by mean of laser-based optical technique according to the Lorenz-Mie theory. The flames have been studied with particular regard to stable gasses (CO, CO_2, NOx, O_2 and hydro carbons), temperature, soot formation and burnout at different rapeseed oil preheating temperatures, All the data have been compared with those obtained with a classical diesel oil under the same burning . Results indicate that rapeseed oil seems is an effective substitute for diesel oil since it produces less soot and similar amounts of other pollutants. The presence of alcohol in the rapeseed oil improves the fuel and allows reduction in the preheating temperature.

Operating characteristics and emissions A comparative evaluation of the operating characteristics as well as the determination of the regulated and non-regulated exhaust gas emissions was carried out, including an investigations of the conversion rates of an oxidising catalyst. In addition engine performance and emission behaviour was characterised in terms of structural parameters relating to vegetable fuels. Finally variations were made in the fuel injection system of the test engine used in order to reduce the specific disadvantages of vegetable fuels. Different vegetable fuels were used and compared to Diesel fuel.

All the fuels had physical and chemical characteristics that allows their use in direct-injection-production-Diesel-engines. One of the fuels used was a rape seed oil mix fuel called TESSOL-NADI®, the others are transesterified from vegetable oils: the fatty acid methyl esters rape seed oil methyl ester (RME), soybean oil methylester (ME SJ), coconut oil methylester (ME K 8-18) and palm kernel oil methylester (ME PK 12-18F).

The experimental engine used was a turbocharged 3-cylinder-direct-injection-Diesel-engine of the type Deutz- MWM TD 226B-3 from the German manufacturer Deutz-Motorenwerke Mannheim AG with a total displacement of 3.12 litres, a compression ratio of 15.5, a maximum power of 54 kW at 2250 revs/min and a maximum torque of 277 Nm at 1500 rev/min.

When using TESSOL or RME there were only slight power and consumption disadvantages in comparison to Diesel fuel. However, with coconut and palm kernel oil methylester the operating characteristics were definitely worse, while soybean oil methylester fell between the two groups.

The emission results of unburned hydrocarbons (HC), carbon monoxide (CO), nitric oxides (NO_X) and particulate matter (PM) confirm the advantages of RME in comparison to Diesel fuel . On one hand soybean, coconut and palm kernel oil methylester show some very good emission values, but on the other hand the restricted power and consumption behaviour has to be taken into account.

The good operating and exhaust gas behaviour of TESSOL was clearly reduced by incomplete combustion and lube oil dilution especially at low load (extreme case:idle). This is not very clear from the results shown, but has been proved definitely while driving the engine on the test bench.

Aldehyde- and ketone-emissions of vegetable fuels are partly similar to those of Diesel fuel, partly clearly richer.

Using an oxidising catalyst no disadvantages of vegetable fuels exist, except for the mix fuel TESSOL with its incomplete combustion. PAH-emissions are distinctly better for all vegetable fuels, so there seems to be a much lower risk of cancer while using fatty acid methylesters as fuel.

The chemical structure of the vegetable fuels has a great influence on engine performance and emission behaviour. NM K and ME PK show best results concerning emissions of hydrocarbons, carbon monoxide, particulate matter and PAH. RME gave the best results in terms of nitric oxides, power and fuel consumption. The mixing of rape seed oil with non-vegetable substances in leads to both negative and positive effects concerning different parameters. Variations of the fuel injection system of the Diesel engine can lead to a clear reduction of the originally high NO_x emissions of vegetable fuels.

Nozzle tests Of the four different injection nozzles tested nozzle S 972 gave the best power results with RME, while nozzles SV 3141475 and SV 3141477 have best consumption behaviour at low speed. They have also got better HC-emissions and smoke number, but NO_X-emissions are slightly worse. A higher nozzle position in the combustion chamber leads to lower emissions of nitric oxides, but over a maximum permissible position other emissions increase and performance decreases significantly. A later start in pump delivery also causes lower NO_X emissions. Nozzle position and start of pump delivery can be changed at the same time, so that both effects add up giving a reduction of up to 75 % of the original value. The corresponding power loss for maximum speed of 2250 revs/min can be up to 17 %, for 2000 revs/min it is less than 10 % and for low speeds it is negligible.

Pollutants from oxidation of vegetable oil methyl esters In order to study the formation of the pollutants during oxidation of vegetable oil methyl esters experiments have been performed in a jet-stirred reactor. A study concerning the pyrolysis of three VOMEs at temperatures of 700 ·C and 800 ·C and at a pressure of 1 Mpa, enabled pyrolysis products to be identified. These included heavy compounds (acid methyl esters, from C_{11} to C_{21}, saturated and unsaturated) and light compounds (alcenes, alcynes, benzene, toluene). From the experiments on concentration profiles of oxidation products were obtained by probe sampling and gas chromatography analysis. The following were measured: O_2, H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, I-C_4H_8, 1,3-C_4H_6, CH_2O, CH_3CHO, CH_2:CHCHO. The maximum of mole fractions for CO and oxygenated compounds measured in the present experiments is lower for VOME than for a standard diesel fuel. A chemical kinetic reaction mechanism for the oxidation of VOME has been developed. It is based on that developed for the oxidation of large hydrocarbons (up to C_{10}). A detailed chemical kinetic reaction mechanism has been proposed for the oxidation of a simple methyl ester:methyl acetate.

Results and discussion

The ability of a pure vegetable (VO) oil, the rape seed oil, to be atomised for combustion or engine purposes has been tested. Since the VO is very viscous at low temperatures, it was necessary to heat it to achieve the required increase in atomisation performances. VO was compared to two classical liquids: water, of interest in many fundamental studies of atomisation, and fuel oil, the practical interest of which is evident.

Tests were carried out with two types of atomisers of current use in combustion. Two atomisers were used, one of them (a pressure swirl atomiser) specially designed and built in Rouen for this study, the other was a standard Diesel injector.

The tests were not reduced to simple measurements of particle size distributions, but a complete qualitative and quantitative study of the sprays was conducted from direct optical observation and imaging. The analysis of results depended on the atomiser used. In the case of the pressure swirl atomiser, the processes involved (internal hydrodynamics, sheet instability, break up and drop formation) are sufficiently well known, and some predictions are at the moment possible. The results (cone angles, discharge coefficient, mean drop sizes etc.) could be analysed within the scope of the action of the main parameters (pressure, viscosity...). The study was reduced to atmospheric pressures, since this is the condition generally used use for this kind of injector (industrial furnaces for example). For Diesel sprays, the exact influence of the complex processes involved in liquid jet break up are not yet sufficiently known. Hence, the exploitation of the results was necessarily more elementary. Nevertheless information of primary interest for the practical use of VO in engines could be found in this work.

For use with pressure swirl atomiser, similar values of discharge coefficients may be obtained for fuel oil and heated (90-130 °C) VO. But the injection pressures needed to reach a stable zone (zone of pressure in which these angle or coefficient are independent of injection pressure) are much higher for VO than for fuel oil. This results in greater exit velocities and atomisation processes which are certainly complex. In addition, values of SMD are systematically greater at a given pressure for VO than for fuel oil. Even if these values begin to be comparable between VO at 130 °C and fuel oil, this is only obtained for high injection pressures (more than 20 Bar) As a summary, it may be recommended, for any attempt of using VO in an engine, to use the rape seed oil at relatively high temperature, of order 100-130 °C. An order of magnitude of drop sizes similar for fuel oil and VO may be found. But for Diesel sprays, the sensitivity to ambient air temperature is greater for VO than for FO.

Investigations of turbulent diffusion flames Relative soot volume fractions in a RME/nitrogen jet diffusion flame were carried out. The flame was a moderately turbulent flame with mainly buoyancy driven turbulence. The single shot data showed increasing turbulence with increased height above the burner. At the burner exit the flame showed the same behaviour as a laminar flame. At greater height above the burner the flame becomes unstable and changes from laminar to turbulent. Probability density functions (pdfs) were calculated from this data to show the fluctuations of the soot volume fractions at different locations in the flame. Increasing fluctuations were observed by the broadening of the pdfs with increasing height over burner.

The method for measuring of number density, particle radius and soot volume fraction by simultaneous measurement of two-dimensional LII, laser light scattering and extinction was tested with a laminar acetylene/nitrogen jet diffusion flame. A soot zone was mapped by this method. The main result of this investigation is that the maximum number density is located at the location where the minimum mean radius of the soot particles is observed. This observation is consistent with the current soot formation model that predicts the formation of small particles at high number density which then coagulate to larger particles. The maximum of the soot volume fraction was slightly displaced to the fuel lean side which can be explained by the surface growth of the particles. A higher mean radius at the fuel lean side is consistent with the faster oxidation of small particles in the oxidation zone. The data measured is, therefore, fully consistent with the present models of soot formation.

A RME/nitrogen jet diffusion flame was compared with an acetylene/nitrogen jet diffusion flame at the same burning conditions. The fuel flow rates were adjusted to the same stoichiometry. Acetylene forms soot much faster than RME. This result corresponds with the higher threshold soot index of acetylene. The number density and the radii show the same correlation as in the acetylene test flame. At high number densities low radii were found. The single shot measurements showed that the soot zones are very similar. The main difference between the two flames are that soot forms much faster in the acetylene flame. To investigate a high turbulent flame acetylene was used as fuel. The main results did not change. Both the single shot data and the averaged values (1000 shots) show the correlation between number density and radius found

Experiments were carried out in order to compare the atomisation quality of rapeseed oil and rapeseed oil/alcohol with that of a conventional fossil fuel such as diesel oil and to compare performances in terms of soot formation and burnout along the flames for all fuels. First of all the stability of the rapeseed oil with the temperature was checked by thermogravimetry analysis and it comes out that this oil is very stable up to 300°C in inert conditions and up to 200°C under an oxidative atmosphere. Due to this stability with the temperature it is possible to preheat the oil up to 150°C where it attains the same viscosity as the diesel oil. Atomisation tests showed that at 150°C the performance of the rapeseed oil are comparable with that of the diesel oil.

The overall combustion performance of the rapeseed oil are very satisfactory in comparison with the diesel fuel while the rapeseed oil produces almost 40 % less soot than diesel fuel. The different volatility of this fuel respect to the diesel fuel is responsible of the different behaviour of the sampled gas concentrations in the base of the flames while at the end of the flames, both attain almost the same values. It has been established that an addition of 9 % of ethyl alcohol (95 %) bring a great benefit regarding the pre-heating oil temperature. In fact, the presence of alcohol allows a reduction in the inlet oil temperature from 150 °C to 80 °C. Moreover, the combustion of the emulsion produces less soot and, at the exhaust, the amount is almost one half less than that produced by the combustion of rapeseed oil. It should be interesting to investigate more carefully the morphology of the rapeseed oil soot because of its higher reactivity toward oxidation shown by using TG analysis that can be correlated to higher hydrogen content.

Generally all measured operating characteristics power, torque, fuel consumption and efficiency prove, that when using these novel fuels there are only slight power and consumption disadvantages in comparison to Diesel fuel. Only with coconut and palm kernel oil methylester were the operating characteristics definitely worse, while soybean oil methylester is placed between the two groups.

Further it can be stressed, that the shown emission results of unburned hydrocarbons (HC), carbon monoxide (CO), nitric oxides (NO_x) and particulate matter (PM) confirm the advantages of RME in comparison to Diesel fuel. However, in some tests combustion was poor so that part of the fuel went, as liquid, into the exhaust gas system. Consequently modifications are necessary in every case, either of the engine or of the fuel mixture.

Concerning polycyclic aromatic hydrocarbons (PAH) there is significantly better emission behaviour of RME in comparison to Diesel fuel. There are even greater emission advantages for other fatty acid methyl esters and with oxidising catalyst no disadvantages for TESSOL. In general there is a very low PAH-level of vegetable fuels because of chemical structure (there is no PAH in vegetable fuel in contrast to Diesel fuel).

Fuel structure and characteristics have been shown to have great influence on engine performance and emission behaviour. One of the most important parameters is the spectrum of fatty acids. Length of carbon chains and number of double bonds in the fuel molecules affect low temperature suitability, spray formation and carbon residue. Net calorific value and density also affect the energy content of cylinder charge. Short-chained coconut and palm kernel oil methyl ester have distinct emission advantages in terms of hydrocarbons, carbon monoxide, particulate matter and polycyclic aromatic hydrocarbons, but disadvantages as far as nitric oxides are concerned.

Because of their lower calorific values they show low engine power and high fuel consumption. Loner-chained rape seed oil methyl ester (RME) has got, relative to Diesel fuel, advantages concerning HC, CO, PM and PAH, while disadvantages as far as NO_X is concerned are very small.

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