

# Statistical study of combustion characteristics and optimal operation factor determination in an emulsion burner fuelled with vegetable oils

*Y. Arroyo,\*<sup>1</sup> M.A. Sanz-Tejedor,\*<sup>1</sup> J. San José<sup>2</sup> and L.A. García-Escudero<sup>3</sup>*

<sup>1</sup>Department of Organic Chemistry, ITAP, School of Industrial Engineering, University of Valladolid, Paseo del Cauce 59, 47011 Valladolid, Spain

<sup>2</sup>Department of Energy Engineering and Fluid Mechanics, ITAP, School of Industrial Engineering, University of Valladolid, Paseo del Cauce 59, 47011 Valladolid, Spain;

<sup>3</sup>Department of Statistics and Operational Research, Faculty of Science, University of Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain

*Keywords:* vegetable oils, emulsion burner, combustion, PCA, ANOVA.

*Paper type:* Primary Research

## **Abstract**

This work experimentally investigates the combustion characteristics of refined soya, sunflower and rapeseed vegetable oils and, by means of statistical techniques, determines the optimal operating factors of an emulsion burner to obtain the best combustion performance and low pollutant emissions. Given the high dimensionality of the study, the PCA provides a descriptive study of the variables involved in the combustion process and of the physicochemical properties of the vegetable oils so as to establish the correlations between them. ANOVA was then performed to identify which factors (type of vegetable oil, fuel flow, and airflow), as well as any possible interactions, have the greatest impact on the combustion results (performance as well as CO<sub>2</sub>, CO, NO<sub>x</sub>, C<sub>x</sub>H<sub>y</sub> and SO<sub>x</sub> emissions). ANOVA results showed that almost all of the factors and their interactions were significant, which makes it essential to analyse the interaction plots to see the optimal combinations of levels. This study showed that fuel flow rate was quite an important factor affecting combustion characteristics, that the type of vegetable oil influenced C<sub>x</sub>H<sub>y</sub> emissions, and that the airflow rate displayed no clear trend. Furthermore, the best combustion performance coupled with pollutant emissions that were below the lowest limits established by current legislation were achieved for a combination of maximum fuel flow and minimum airflow rates, with soya exhibiting the best performance. In general, good combustion performances were obtained with extremely low NO<sub>x</sub> emissions, and SO<sub>x</sub> emissions were not detected in any of the combustion experiments performed.

## Introduction

The growing demand for energy, the environmental impact of fossil fuels, and energy supply security are the main worries in today's energy scene. Within this context, the use of vegetable oils (VOs) as a potential source of energy for heating purposes, has grown in popularity as an alternative to fossil fuels [1], due to the fact they are renewable sources, are eco-friendly, non-toxic and biodegradable. One key aspect in the composition of VOs is their virtually negligible sulphur and nitrogen content, which contributes significantly towards curbing emissions of SO<sub>x</sub> and NO<sub>x</sub>, thus avoiding any harmful environmental impact. Furthermore, production of VOs has spread worldwide and many countries are now producing different types of VOs, depending on their climate, which might contribute towards the energy sustainability of areas where fossil resources are unavailable.

The main drawback of using VOs as biofuels in domestic and industrial boilers is their high viscosity and low volatility, which hinders the atomization process and might lead to incomplete combustion and even carbon deposits in the combustion chamber. One solution to this problem is to chemically transform VOs in order to produce biodiesel, which has been widely documented in the literature [2]. However, this method evidences certain drawbacks such as: long reaction times, high energy consumption during preparation and subsequent purification processes [3] as well as the large amount of glycerol obtained as a by-product of little added value [4]. Another strategy widely used by a number of researchers to reduce the viscosity of VOs involves blending them with lower viscosity oil derivatives. In this regard, San José et al. used a conventional facility equipped with a mechanical pulverization burner to burn blends of diesel fuel with a range of VOs such as sunflower (SfO) [5,6] soya (SyO) [7,8] and rapeseed oil (RpO) [9]. Using injection pressures between  $1 \times 10^6$  and  $1.4 \times 10^6$  Pa and different VO-

diesel fuel blends (up to 40 % in VO), combustion performances above 85% and NO<sub>x</sub> emissions below 53 ppm were attained by the authors. In another study [10], the combustion of diesel fuel-animal fat blends, not apt for human consumption, in a residential oil burning facility was carried out. The best combustion performances were obtained for blends with 10% animal fat, using an injection pressure of  $1 \times 10^5$  Pa. Daho et al. [11] studied the performance and emissions of different coconut vegetable oil (CnO)-diesel fuel blends in a domestic boiler, and reported that CO, NO<sub>x</sub> and CO<sub>2</sub> emissions were the same for all blends studied, when the boiler worked at an injection pressure of  $2 \times 10^6$  Pa. Jiru et al. [12] evidenced that it is possible to burn blends of SyO degummed fuel oil (20% SyO) in an unmodified commercial burner. The combustion of blends of palm oil (PIO)-diesel fuel in an industrial oil burner with and without secondary air was studied by Mohd Jaafar et al. [13]. The lowest emissions of CO and NO<sub>x</sub> were obtained with blends containing 25% PIO. Recently, Esarte et al. [14] studied the performance and emissions of different blends of fossil fuels with renewable fuels such as VOs and their fatty acid methyl esters (FAMES) in a domestic condensing boiler.

Despite their high viscosity, direct combustion of VOs in commercial burners can be carried out by simply correctly adjusting the device parameters. Good examples of this are the studies by Vaitilingom and Daho, who analysed the combustion of RpO [15] and CnO [16], respectively, in a modified fuel oil burner using injection pressures of  $2.8 \times 10^6$  Pa and preheating the VOs ( $T \geq 125$  °C). By applying these conditions, quite low CO emissions ( $\leq 13$  ppm) and high combustion efficiencies (around 93%) were achieved. Combustion of raw SyO, pre-heated to 70-80 °C, in a 2 MW pilot boiler has also been studied [17]. The CO and NO<sub>x</sub> emissions obtained were similar to those of diesel fuel ( $250 \text{ mg} \cdot \text{m}^{-3}$  and  $145 \text{ mg} \cdot \text{m}^{-3}$ , respectively).

One crucial issue to be taken into account for the correct combustion of VOs is the type of burner used, since it must be suitable for high viscosity liquid fuels. In this regard, Holt et al. [18] used a multi-fuelled burner to perform the combustion of crude and semi-refined CnO, although high polluting gases were obtained. Recently, Józsa et al. [19] studied the combustion of raw RpO in a lean premixed pre-vaporized burner, although stable combustions were limited by inadequate atomization. Giovannoni et al. [20] assessed the performance of SfO in a small-scale flat flame regenerative combustion chamber. Despite the viability of the experiment, obstruction problems in the combustion chamber channels were found 40 minutes into operation. San José et al. [21] showed that the use of a low-pressure auxiliary air fluid pulverization burner is the best option for burning liquid fuels, such as VOs, with a kinematic viscosity between 26 and 112 mm<sup>2</sup>·s<sup>-1</sup> (at 50 °C). Using this burner, which operates with an injection pressure of 1x10<sup>5</sup> Pa, the authors carried out the combustion of VOs, rich in unsaturated fatty acids (SfO, RpO, SyO) as well as CnO and PIO with a high content of saturated fatty acids [22,23]. A relationship between the VOs' degree of unsaturation and certain combustion parameters was established in these works, which found that CO emissions decreased and that combustion efficiencies increased as the degree of VO unsaturation rises [23]. They also achieved NOx emissions below 46 ppm in all the experiments performed, regardless of the VO used. Recently, this research group studied the atomization and combustion processes of PIO in the same emulsion burner. They found that the greater the spray cone angle, the less the spray tip penetration length and, in most of the tests performed, the lower the spray cone angle the greater the combustion performance [24].

In light of the above information, the combustion results of VOs depend on many factors such as the uniqueness of their fatty acid profile, the type of burner used and the

operating conditions. Therefore, the burning characteristics of VOs still require exhaustive research in order to understand how they are affected by different factors. By applying appropriate statistical tools, the aim of this work is to analyse the combustion results of refined SyO, SfO and RpO in an emulsion burner, modifying three fuel flows and three secondary airflows. First a descriptive study is carried out applying a PCA technique on the combustion variables and on the physicochemical properties of VOs so as to establish possible correlations between them. Subsequently, from a more inferential approach, an ANOVA analysis of the combustion results is then carried out to establish the significance of the different operating factors as well as their possible interactions on emissions ( $\text{CO}_2$ , CO,  $\text{NO}_x$  and  $\text{C}_x\text{H}_y$ ) and combustion performance. Finally, the optimal operating conditions for the burner, in terms of performance and emissions, are also established.

## **Materials and methods**

### *Materials*

The refined SfO, SyO and RpO used in this work are commercially available and all of them were used without prior purification. The elemental composition and physicochemical properties of the three VOs studied were determined at the Castilla y León Regional Laboratory (LARECOM), in Spain, which is an accredited laboratory for fuel analysis. The results of these analyses, together with the standard procedures applied to determine each property, are shown in Table 1. Studying the physicochemical properties is important since these affect the combustion process. Elemental analysis is used to calculate the excess air required for combustion, and both the viscosity and density of the fuel determine the atomisation process.

VOs are triacylglycerols whose fatty acids profile displays different substitution patterns with regard to length, degree of unsaturation and chain geometry of the hydrocarbon chains. The fatty acid composition of each VO is unique, affects the state of aggregation, and impacts the physical properties such as density, viscosity and heating value [23, 25-28]. As a result, fatty acid composition determines the VO's behaviour during the combustion process, as recently shown by [28] when analysing the combustion characteristics of crude vegetable oil droplets. The chemical composition of the VOs studied was determined using gas chromatography, in accordance with ISO 12966. The percentages calculated of each fatty acid for SyO, SfO and RpO are shown in Table 2. As can be seen, the main unsaturated fatty acids were oleic, O (C18:1), linoleic, L (C18:2), linolenic, Ln (C18:3) and for the saturated fatty acids, palmitic, (C16:0) and stearic (C18:0). For SfO and SyO, linoleic fatty acid was the main component (62.5 and 50.1%, respectively) while RpO had the highest percentage of oleic fatty acid (64.4%). Ln fatty acid was detected in SyO and RpO, (6% and 8.5%, respectively). A low content in saturated fatty acids was obtained in all the VOs analysed, ranging from 7.2% to 16.1%.

#### *Combustion equipment and procedure*

The experimental facility used to burn the VOs was designed by the authors and was composed of several clearly distinguishable elements shown in Table 3. The burner feed system consists of two tanks and a network of valves and pipes enabling the fuel to be changed easily without turning off the facility. Each tank was equipped with a heating device, controlled by a thermostat, which allows the sample temperature to be adjusted.

In the commercial burner used in this work (AR-CO model BR5), the fuel flow was mixed with primary air through a rotary vane compressor, forming a vegetable oil fuel-

air emulsion. With this technology, an almost perfect blend of air and fuel, and good pulverization in the nozzle was achieved, enabling it to burn liquid fuels that cover a wide range of viscosities.

Combustion was carried out in a boiler connected to a chimney which contains a flap valve that allows the back-pressure inside as well as the chimney draught to be adjusted. The device is also equipped with a gas analyser, TESTO 350, with a probe inserted at a central point of the interior section of the chimney. This device measures the concentration in flue gas of O<sub>2</sub>, in percentage, and those of CO, NO<sub>x</sub>, SO<sub>2</sub> and C<sub>x</sub>H<sub>y</sub> in ppm. as well as the flue gas temperature and input temperature of combustion air.

Combustion of the VOs was performed following a technique [22-24] which involved the following stages; starting up the burner with diesel fuel until steady state was achieved, feeding the VO fuel, adjusting the conditions of each assay, and measuring the emissions and temperatures using the gas analyser. Finally, the pipes were cleaned with diesel fuel and the burner was turned off.

The experiments were carried out in similar weather conditions so as to reduce the possible impact of room temperature and environmental humidity on the combustion results. All of the VOs studied were pre-heated to 40 °C and the fuel injection pressure in the emulsion was kept at  $1 \times 10^5$  Pa.

The gases produced as a result of the combustion process are CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>x</sub> (if the fuel contains sulphur compounds). Also formed are the so-called unburnt gases, CO and C<sub>x</sub>H<sub>y</sub>, which are the result of incomplete combustion, as well as nitrogen oxides, NO<sub>x</sub>, which depend on the amount of nitrogen in the fuel and the flame temperature. The concentrations of pollutant gases in flue gases are strictly regulated by law, and must be  $\leq 130$  ppm for CO [29],  $\leq 150$  ppm for NO<sub>x</sub> [30] and  $\leq 134$  ppm for SO<sub>x</sub> [30].



An imperfect fuel-air blend is the main cause of the formation of unburnt species. In an effort to minimise this problem, excess air is used in industrial and domestic boilers. As a result, a certain amount of oxygen (% O<sub>2</sub>) is also found in the combustion gases. With this value, two characteristic parameters of combustion were calculated: excess air index ( $\lambda$ ), and CO<sub>2</sub> in the flue gas. The three parameters are related through the expression:

$$1 + \alpha \frac{[O_2]}{21 - [O_2]} = \lambda = \alpha \left( \frac{[CO_2]_{max}}{[CO_2]_{real}} - 1 \right) + 1 \quad \text{Eq. 1}$$

$$[\alpha = 0.9429 \text{ (SyO)}, 0.9428 \text{ (SfO)}, 0.9424 \text{ (RpO)}]$$

with  $\alpha$  being a coefficient characteristic of each vegetable oil fuel, given by the relationship between the volume of stoichiometric flue gas and the volume of stoichiometric air. Both values are calculated taking into account the elemental composition of each VO fuel, following a procedure described in ASHRAE [31].  $[CO_2]_{max}$  is the concentration in flue gas in a stoichiometric combustion, and  $[CO_2]_{real}$  is the concentration in flue gas in a combustion with excess air.  $[CO_2]$  and  $[O_2]$  are expressed as a percentage.

In order to assess combustion quality, emissions of CO<sub>2</sub>, CO, NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub> were analysed and combustion performance,  $\eta$ , was calculated, per unit of mass, in accordance with the procedure described in ASRHAE [23,31] (Eq. 2):

$$\eta = 100 \cdot \left( \frac{LHV - \text{Sensible heat loss}}{LHV} \right) = \left( 1 - \frac{Cp_g \cdot m_g \cdot (t_g - t_a)}{LHV} \right) \cdot 100 \quad \text{Eq. 2}$$

$t_g$ : flue gas temperature at the exit of the heating device (°C).

$t_a$ : input temperature of combustion air (°C).

$Cp_g$ : specific heat of flue gases, at constant pressure, for  $t_g$  [kJ·(kg·°C)<sup>-1</sup>].

$m_g$ : kg of dry flue gases produced for combustion with excess air per kg of fuel (kg·kg<sub>fuel</sub><sup>-1</sup>).

$LHV$ : low heating value (kJ·kg<sup>-1</sup>)

### *Experimental design*

In this work, three factors were modified in each combustion experiment: the type of vegetable oil, the fuel flow, and the secondary airflow rates. For each VO, three fuel flow rates (C1, C3 and C6) and three airflows (Amin, Amid and Amax) were studied, and a total of 27 different conditions were analysed. Each test was repeated a different number of times, and 75 experiments were carried out in all (results available in the Supporting Information). Table 4 shows the factors with their corresponding levels. Five different variables were studied for each experiment, combustion performance and concentration of CO<sub>2</sub>, CO, NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub> in flue gases.

Fuel flows were determined with a flowmeter, hooked up to the fuel tank that fed the burner. Airflows were determined with a flow nozzle TG-40 (TECNER Engineering model). The values obtained are shown in Table 5.

### *Statistical Analysis*

First, a descriptive study of the variables involved in the combustion process was performed using a principal component analysis (PCA) technique. PCA seeks optimal dimensionality reduction by considering linear combinations of the original variables (principal components) which capture the maximum possible underlying information in those variables. The joint representation (biplot) of the component weights, together with the coordinates (scores) of the optimally projected individuals provides a simple way to visualize higher dimensional data sets. Furthermore, correlations among variables can also be easily visualized in the biplot. We applied PCA to the five output combustion variables: performance, CO<sub>2</sub>, CO, NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub> emissions, together with four other physicochemical variables: viscosity, LHV, monounsaturated fatty acids, MUFA and L, which measure different features of the VOs.

After this simple descriptive study of PCA, a more inferential technique, ANOVA, was used to analyse the dependence of three categorical variables, VO type, and airflow as well as fuel flow levels on the combustion response variables. ANOVA is a widely applied statistical methodology to explore variability in the response variable by considering partitions of that variability into appropriate sums of squares. These sums of squares serve to test the significance of the considered effects, and their interactions, on the five response variables analysed. Statistical analyses were performed by using R statistical programming language and Statgraphics Centurion 18 software.

## **4. Results and discussion**

### **4.1. Principal Component Analysis (PCA)**

PCA was applied on the nine numerical variables mentioned above: combustion performance, (CO<sub>2</sub>, CO, NO<sub>x</sub>, C<sub>x</sub>H<sub>y</sub>) emissions, viscosity, LHV, MUFA, and L. We only focus on the first two principal components. The associated biplot is shown in Figure 1. Each individual experiment is represented by a point, and each variable by an arrow.

The three charts in Figure 1 also highlight different levels of the categorical variables analysed: VO (a), airflow (b) and fuel flow (c), by coding these levels with different colours in the biplot. Variables pointing in the same directions in the plot show clear positive correlations between

- (Viscosity, MUFA) and C<sub>x</sub>H<sub>y</sub>
- LHV and L
- CO<sub>2</sub> and NO<sub>x</sub>

A negative correlation between variables, pointing in opposite directions is observed between

- viscosity with (L and LHV)
- (CO<sub>2</sub>, NO<sub>x</sub>) and CO.

The observed correlations between viscosity and fatty acids content can be explained by considering that viscosity is the result of the forces of cohesion between the molecules of the fluid, with these being greater the more linear the fatty acid chain is. The MUFA chains, with only one *cis* carbon-carbon double bond, barely alter the fatty acid zig-zag arrangement, giving rise to intense inter- and intramolecular forces between adjacent hydrocarbonated chains, mainly van der Waals dispersion forces and  $\pi$ - $\pi$  interactions. In contrast, the chains of linoleic fatty acid with two *cis* carbon-carbon double bonds, display angular shapes increasing the distance between adjacent hydrocarbonated chains and reducing these interactions. From Table 2, it can be seen that RpO exhibits the biggest percentage of MUFA (mainly oleic FA) and is the one with the highest viscosity. On the other hand, SfO is the one that contains the highest percentage of linoleic FA and the lowest viscosity.

Furthermore, high viscosity values give rise to poor fuel atomization, incomplete combustion and unburned hydrocarbon formation, which could explain the positive correlation between C<sub>x</sub>H<sub>y</sub> and viscosity. As regards the negative correlation between viscosity and the lower heating value (LHV), San José et al. [23] observed that the LHV of several VOs, rich and poor in unsaturated fatty acids, increased as the DU (Table 2) increased, contrary to viscosity. In contrast, direct correlation between LHV and viscosity in FAMEs (biodiesel) has been established by some researchers [25-28], evidencing the different behaviour of VOs with regard to the FAMEs as a result of the latter's greater molecular complexity.

Moreover, by examining the relative positions of the scores corresponding to all of the analysed experiments in the two-dimensional biplot (figure 1a), it can be seen that in most of the tests performed, SyO provided relatively high values in combustion performance, coupled with relatively low CO emissions. As regards CO<sub>2</sub>, CO and NO<sub>x</sub> emissions, the groups of scores whose colour codes the type of VO are distributed parallel to the axis marked by CO and CO<sub>2</sub>-NO<sub>x</sub>, which shows there is no clear correlation between these emissions and the physicochemical properties analysed. As for the biplot in Figure 1b shows that fuel flow emerges as quite an important factor with regard to explaining combustion characteristics. Most of the experiments performed with the fuel flow rate at level C1 are associated to relatively large CO emissions and relatively low combustion performances. In contrast, in most of the assays carried out in conditions C3 and C6, good combustion performances, low emissions of CO and relatively high NO<sub>x</sub> emissions were obtained, with these values always being below those permitted by legislation. As regards airflow, a greater dispersion of results was obtained, as can be seen in Figure 1c.

#### **4.2 Analysis of variance (ANOVA)**

ANOVA was performed to identify the most significant factors in the combustion variables: combustion performance and (CO, NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub> and CO<sub>2</sub>) emissions in flue gas, obtained in the different combustion tests. The associated results are shown below, where one table for each of the five considered response variables is provided (Tables 6-10). The significance level of each factor, type of VO, airflow and fuel flow, was characterized in terms of p-values. It is important to note that most of the main factors and interactions between them are significant at standard 0.01 and 0.05 levels. In fact, very small p-values are found in almost all the cases, with the sole exception of the variable C<sub>x</sub>H<sub>y</sub>, for which a p value = 0.4821 (>0.05) was observed for the airflow

factor. For this reason, this factor cannot be considered statistically significant in this case.

Due to the significance of most of the interaction effects, it is essential to analyse interaction plots (Figures 2-6). These graphs show the effect of each factor and its combinations of values on the variable considered and help to establish the optimal operating conditions for the burner. Optimising the combustion process involves using minimum excess air, obtaining the highest combustion performance and pollutant emissions (CO, NO<sub>x</sub> and C<sub>x</sub>H<sub>y</sub>) below the legally established limits.

Figure 2 shows the variation in the mean percentages of CO<sub>2</sub> obtained in the combustion tests, depending on airflow (right) and fuel flow (left) for the different types of VOs. The greatest variability observed in the mean levels of CO<sub>2</sub> for the various fuel flows, compared to the airflow, would indicate a greater influence of fuel flow in the concentration of CO<sub>2</sub> in flue gases. This might be explained by taking into account that the control parameters used in the burner offer a different variation for the fuel flow than for the airflow. Thus, there is a greater difference between the fuel flow values than between the airflow values, as can be seen in Table 5. Changing from C1 to C3 entails an increase in fuel flow of between 30% and 40% depending on the VO used. This increase varies between 10 and 17% from C3 to C6. In contrast, when changing from Amin to Amid and from Amid to Amax, increases in airflow were substantially lower and varied around 5% and 8%, respectively.

Variations of combustion performance with regard to fuel flows and airflows are shown in Figure 3. For this variable, an improvement could be seen as the fuel flow increased and the airflow was reduced. The relationship between airflow and performance can be explained by considering that sensible heat losses in flue gases decrease as the airflow is reduced (see Eq. 2).

Figures 2 and 3 clearly show how for the three VO<sub>s</sub> studied, the best combination for emissions of CO<sub>2</sub> and performance is C6/Amin, with soya oil, SyO, exhibiting the best performance in the emulsion burner, with regard to the two variables represented. This result evidences the impact of VO fatty acid content on combustion performance. A high percentage of just one type of fatty acid (oleic for RpO and linoleic for SfO) does not appear to be suitable for good combustion, whereas soya oil, with a more balanced proportion in saturated fatty acids (SFA) and unsaturated fatty acids (oleic, linoleic and linolenic fatty acids), performs better. A similar result was seen by [32] when studying the relationship between fatty acid composition of biodiesel on engine performance and emissions.

As expected, the interaction plots for CO emissions (Figure 4) showed that, as with CO<sub>2</sub> emissions, these are more affected by fuel flow than by airflow. Moreover, tests conducted with fuel flows C3 and C6, at any airflow, gave remarkably low CO emissions,  $CO \leq 41$  ppm, which are values well below the 130 ppm established as the most restrictive current legislation [29].

Emissions of NO<sub>x</sub> were seen to increase with fuel flow and airflow, with the lowest emissions being obtained for C1 and Amin (Figure 5). Given that the nitrogen content of VO<sub>s</sub> is virtually negligible, these emissions are mainly formed as a result of the decomposition of nitrogen in air and its subsequent oxidation with oxygen. This process is furthered by high flame temperatures (favoured at high fuel flows) and long dwell times in the combustion chamber (favoured at low airflows), which would explain the values obtained.

A comparative analysis of interaction plots for CO, NO<sub>x</sub> (Figures 4 and 5) reveals that, as NO<sub>x</sub> emissions decreased, CO emissions increased. This result can be explained considering that the conditions favouring complete combustion and, therefore, low CO

emissions, are a high flame temperature and long dwell times in the combustion chamber which are, in fact, what triggers thermal NO<sub>x</sub> formation. It is important to highlight that the NO<sub>x</sub> levels obtained in all the experimental conditions assayed were under 55 ppm, well below the 150 ppm which is the most restrictive limit set by current legislation [30].

For C<sub>x</sub>H<sub>y</sub> emissions, the greater influence of the type of VO is clearly visible in Figure 6, which also shows there is no clear trend in these emissions with regard to fuel flow and airflow. For S<sub>y</sub>O, flows C1 and C6 gave rise to the lowest emissions, whereas for S<sub>f</sub>O and R<sub>p</sub>O these are given by flows C1 and C3. Formation of C<sub>x</sub>H<sub>y</sub> is related to incomplete combustion, probably due to poor atomization of the fuel, which ultimately depends on the physicochemical properties and fatty acids composition of each VO studied.

## **Conclusions**

In this paper, PCA and ANOVA were applied to the combustion results of an emulsion burner fuelled with refined vegetable oils in order to establish the optimal operating conditions that provide the highest combustion performance and pollutant emissions below the limits established by law. On the basis of the results, the following findings may be put forward:

From PCA, an interesting positive correlation between C<sub>x</sub>H<sub>y</sub> and (viscosity and MUFA) as well as a negative correlation between viscosity with (L and LHV) was observed. According to the results obtained from ANOVA, the type of vegetable oil, the control parameters of the burner (airflow and fuel flow rates) together with most of their interactions, are statistically significant for four dependent variables studied, performance combustion, and (CO<sub>2</sub>, CO, NO<sub>x</sub>) emissions. However, for C<sub>x</sub>H<sub>y</sub>



emissions, airflow rate were not seen to have a significant effect. From PCA and the interaction plots, it is clear that However, in all the tests carried out, NO<sub>x</sub> emissions remained well below the current legal limits, and fairly low CO values were obtained. In summary, the optimal conditions in terms of performance and pollutant emissions are those in which the burner works with the maximum fuel flow (C6) and minimum airflow (Amin), with SyO fuel providing the best results. This work demonstrates that vegetable oils are possible alternative fuels for heating purposes and may be used in a commercial emulsion burner without any need to modify it.

**Supporting Information:** The following are available: Table S1. Variations of combustion results with Fuel flow and Secondary Airflow rates of the three vegetable oils studied.

### **Acknowledgments**

The financial support for this work provided by the Spanish government (Ministry of Finance and Competitiveness, grant MTM2017-86061-C2-1-P) and the Regional Government of Castilla y Leon (ERDF, VA272P18, grants VA005P17 and VA002G18), is gratefully acknowledged.

## References

- (1) BP Statistical Review of World Energy 2018. <http://www.bp.com> (accessed March 2019).
- (2) For a review see: N.A. Negm, M.T.H. Abou Kana, M.A. Youssif, M.Y. Mohamed, Biofuels from Vegetable Oils as Alternative Fuels: Advantages and Disadvantages. *Surfactants in Tribology* 51 (2017) 289-368.
- (3) For recent reviews see: (a) M. Erdem Gunay, L. Turker, N. Alper Tapan, Significant parameters and technological advancements in biodiesel production systems, *Fuel* 250 (2019) 27-41 and (b) R. Shan, L. Lu, Y. Shi, H. Yuan, J. Shi, Catalysts from renewable resources for biodiesel production, *Energy Conversion and Management* 178 (2018) 277–289.
- (4) M. Zhang, H. Wu, Effect of major impurities in crude glycerol on solubility and properties of glycerol/methanol/bio-oil blends, *Fuel* 159 (2015) 118–127.
- (5) J.A. López-Sastre, J. San José-Alonso, C. Romero-Ávila, E.J. López Romero, C. Rodríguez Alonso, A study of decrease in fossil CO<sub>2</sub> emissions of energy generation by using vegetable oils as combustible, *Build. Environ.* 38 (2003) 129-133.
- (6) J.F. San José-Alonso, C. Romero-Ávila, J.A. López-Sastre, E.J. López Romero, C. Izquierdo-Iglesias, Using mixtures of diesel and sunflower oil as fuel for heating purposes in Castilla y León, *Energy* 30 (2005) 573-582.
- (7) J.F. San José-Alonso, J.A. López-Sastre, E. Rodríguez-Duque, E.J. López Romero, C. Romero-Avila, Combustion of Soya Oil and Diesel Oil Mixtures for Use in Thermal Energy Production, *Energy Fuels* 22 (2008) 3513–3516.

- (8) J. San José-Alonso, J.A. López-Sastre, C. Romero-Ávila, E.J. López Romero, A note on the combustion of blends of diesel and soya, sunflower and rapeseed vegetable oils in a light boiler, *Biomass Bioenergy* 32 (2008) 880-886.
- (9) J. San José-Alonso, J.A. López-Sastre, C. Romero-Ávila, E.J. López Romero, Combustion of rapeseed oil and diesel oil mixtures for use in the production of heat energy, *Fuel Process. Technol.* 87 (2006) 97-102.
- (10) J.F. San José-Alonso, I. Gobernado-Arribas, S. Alonso-Miñambre, Study of combustion in residential oil burning equipment of animal by-products and derived products not intended for human consumption, *Int. J. Energy Environ. Eng.* 4 (2013) 1-13.
- (11) T. Daho, G. Vaitilingom, O. Sanogo, Optimization of the combustion of blends of domestic fuel oil and cottonseed oil in a non-modified domestic boiler, *Fuel* 88 (2009) 1261-68.
- (12) T.E. Jiru, B.G. Kaufman, K. E. Ileleji, D. R. Ess, H.G. Gibson, D.E. Maier, Testing the performance and compatibility of degummed soybean heating oil blends for use in residential furnaces, *Fuel* 89 (2010) 105–113.
- (13) M. N. Mohd Jaafar, Y. A. Eldrainy, M. F. Mat Ali, W. Z. Wan Omar, M.F.A. Mohd Hizam, Combustion Performance Evaluation of Air Staging of Palm Oil Blends. *Environ. Sci. Technol.* 46 (2012) 2445–2450.
- (14) C. Esarte, J. Delgado, Influence of Heating Oil Formulation on the Combustion and Emissions of Domestic Condensing Boilers Using Fossil Fuel and Renewable Fuel Mixtures, *Energy Fuels* 32 (2018) 10106-10113.

- (15) G. Vaitilingom, Ch. Perilhon, A. Liennard, M. Gandon, Development of rape seed oil burners for drying and heating, *Industrial Crops Products* 7 (1998) 273-279.
- (16) T. Daho, G. Vaitilingom, O. Sanogo, S.K. Ouiminga, A.S. Zongo, B. Piriou, J. Koulidiati, Combustion of vegetable oils under optimized conditions of atomization and granulometry in a modified fuel oil burner, *Fuel* 118 (2014) 329-334.
- (17) I.Oprea, I. Pişă, L. Mihăescu, T. Prisecaru, G. Lăzăroiu, G. Negrean, Research on the combustion of crude vegetable oils for energetic purposes, *Environ. Eng. Manag. J.* 8 (2009) 475-482.
- (18) G. A. Holt, J. D. Hooker, Gaseous emissions from burning diesel, crude and prime bleachable summer yellow cottonseed oil in a burner for drying seed, cotton, *Bioresour. Technol.* 92 (2004) 261-267.
- (19) V. Józsa, A. Kun-Balog, Stability and emission analysis of crude rapeseed oil combustion, *Fuel Process. Technol.* 156 (2017) 204-210.
- (20) V. Giovannoni, R.N. Sharma, R.R. Raine, Experimental Investigation of a Small-Scale Combustion Chamber fueled with Vegetable Oil, *Combustion Science and Technology* (2019) 1-20, <https://doi.org/10.1080/00102202.2019.1565492>.
- (21) J. San José, C. Romero-Ávila, L.M. San José Hernández, A. Al-Kassir, Characterizing biofuels and selecting the most appropriate burner for their combustion, *Fuel Process Technol.* 103 (2012) 39-44.
- (22) J. San José, M.A. Sanz-Tejedor, Y. Arroyo, Effect of fatty acid composition in vegetable oils on combustion processes in an emulsion burner, *Fuel Process. Technol.* 130 (2015) 20-30.

- (23) M. A. Sanz-Tejedor, Y. Arroyo, J. San José, Influence of Degree of Unsaturation on Combustion Efficiency and Flue Gas Emissions of Burning Five Refined Vegetable Oils in an Emulsion Burner, *Energy Fuels* 30 (2016) 7357–7366.
- (24) J. San José, M. A. Sanz-Tejedor, Y. Arroyo, Spray characteristics, combustion performance and palm oil emissions in a low-pressure auxiliary air fluid pulverization burner, *Energy Fuels* 32 (2018) 11502-11510.
- (25) G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, *Fuel Process. Technol.* 86 (2005) 1059-1070.
- (26) A. Demirbas, Relationships derived from physical properties of vegetable oil and biodiesel fuels, *Fuel* 87 (2008) 1743–48.
- (27) G. Martínez, N. Sánchez, J.M. Encinar, J. F. González, Fuel properties of biodiesel from vegetable oils and oil mixtures. Influence of methyl esters distribution, *Biomass Bioenergy* 63 (2014) 22–32.
- (28) H.Y. Nanlohy, I.N.G. Wardana, N. Hamidi, L.Yuliati, T. Ueda, The effect of  $Rh^{3+}$  catalyst on the combustion characteristic of crude vegetable oil droplet, *Fuel* 220 (2018) 220-232.
- (29) RD 815/2013, of 18 October, approving the regulations for industrial emissions, and application of Law 16/2002 of 1 July, on the integrated prevention and control of pollution, BOE 251 of 2013. <https://www.boe.es/eli/es/rd/2013/10/18/815> (accessed May 2019).
- (30) RD 1042/2017, of 22 December, on the limitation of emissions into the atmosphere of certain contaminating agents from medium size combustion facilities and updating

annex IV of Law 34/2007, of 15 November, on air quality and air protection.

<https://www.boe.es/eli/es/rd/2017/12/22/1042/con> (accessed May 2019).

(31) In ASHRAE Handbook Fundamentals. Atlanta GA ed. 2013, chapter 28.

(32) S. Deshmukh, R. Kumar, K. Bala, Microalgae biodiesel: A review on oil extraction, fatty acid composition, properties and effect on engine performance and emissions, Fuel Process. Technol. 191 (2019) 232-247

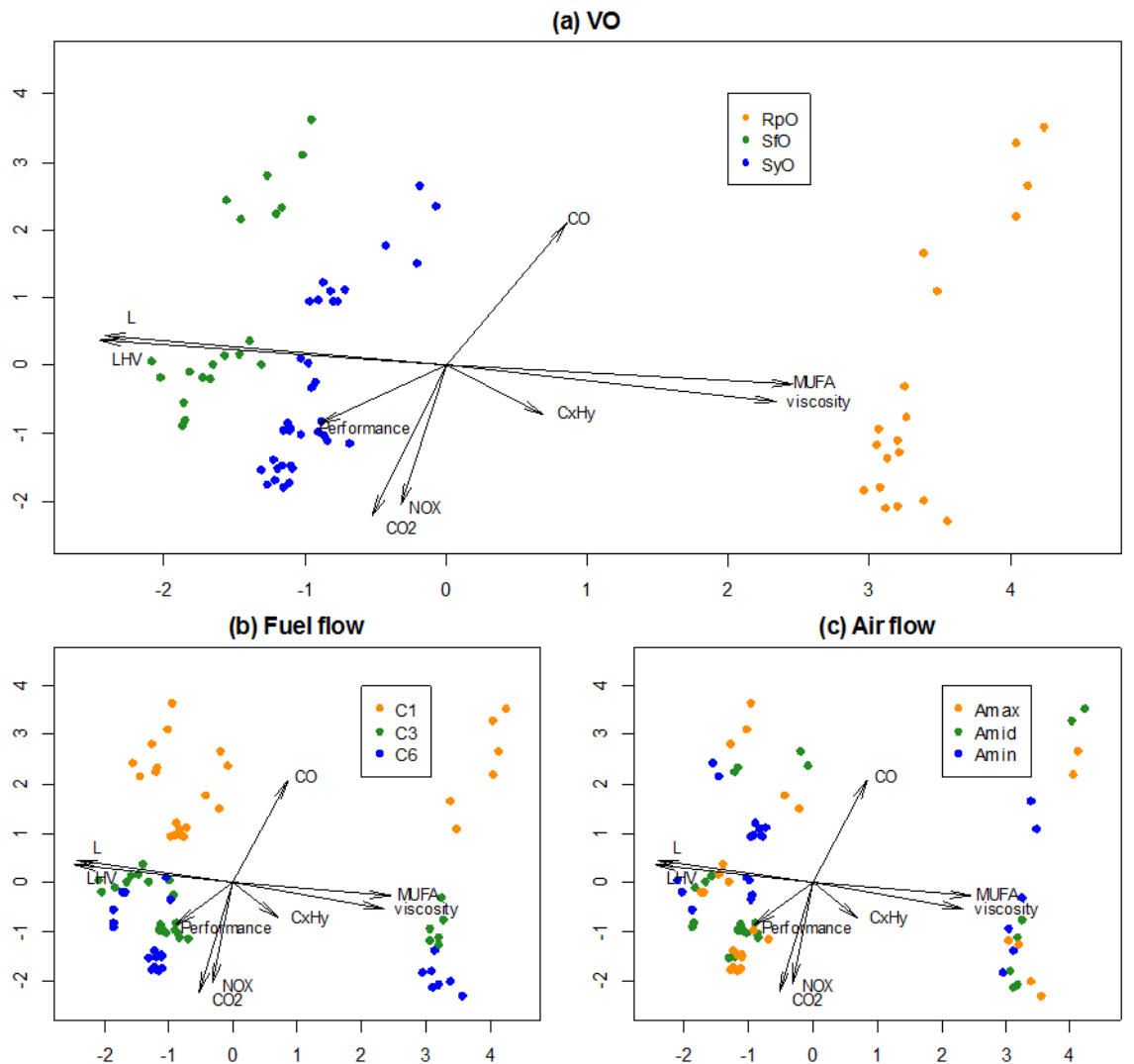
#### Corresponding Authors

\*Tel.: +34983184420. E-mail: [yarroyo@eii.uva.es](mailto:yarroyo@eii.uva.es) (Y.A.).

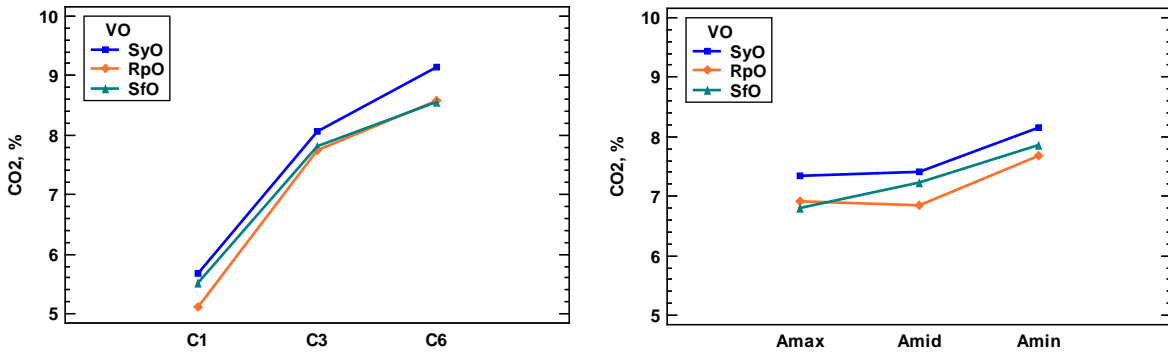
\*Tel.: +34983184418. E-mail: [atejedor@eii.uva.es](mailto:atejedor@eii.uva.es) (M.A.S.-T.).

#### NOTES

The authors declare no competing financial interest.

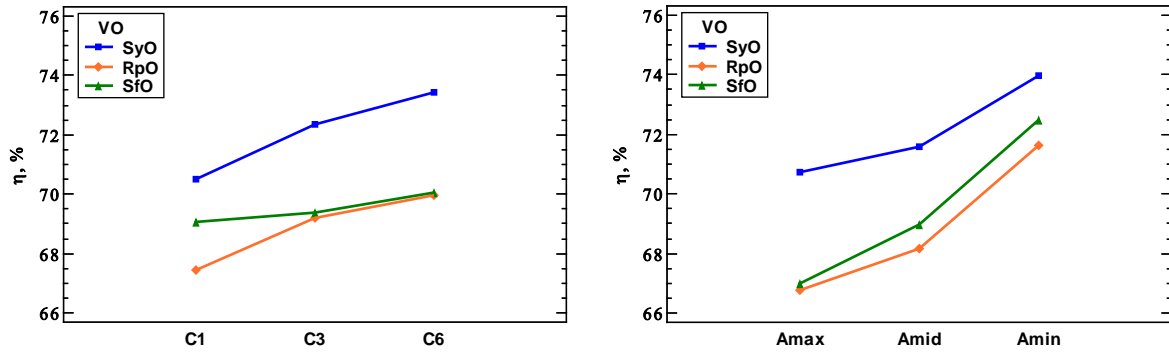


**Figure 1:** Two-dimensional PCA biplots (the x-axis corresponds to the first PCA component and the y-axis to the second) with different code levels: (a) VO, (b) fuel flow (c) airflow. The variability explained by the two first PCA components is 73.58%.

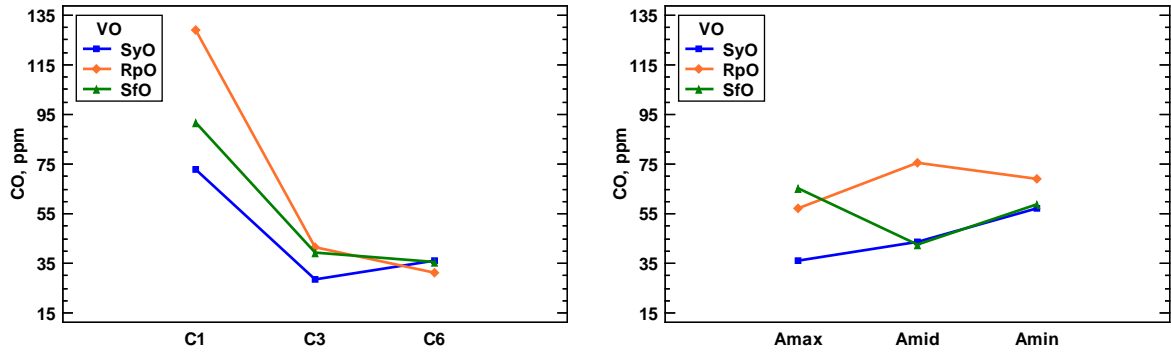


**Figure 2.** Interaction plots of the variability of CO<sub>2</sub>, in %, with the fuel flow (left) and airflow factors (right) for each vegetable oil.

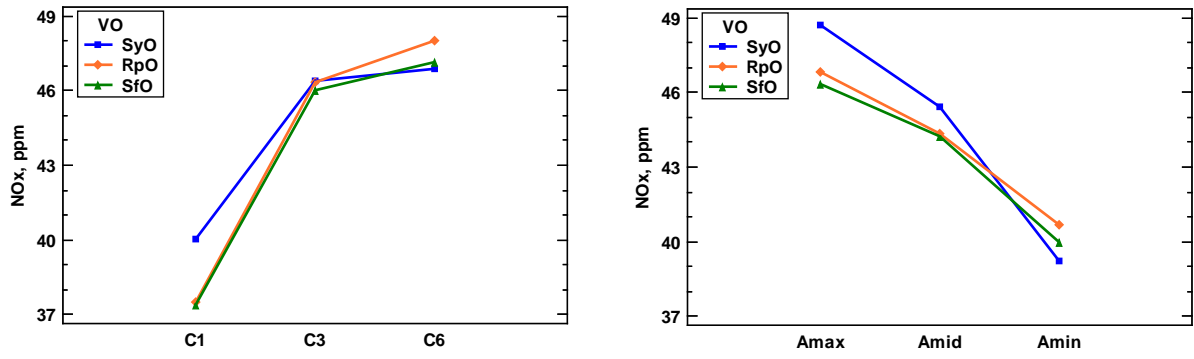




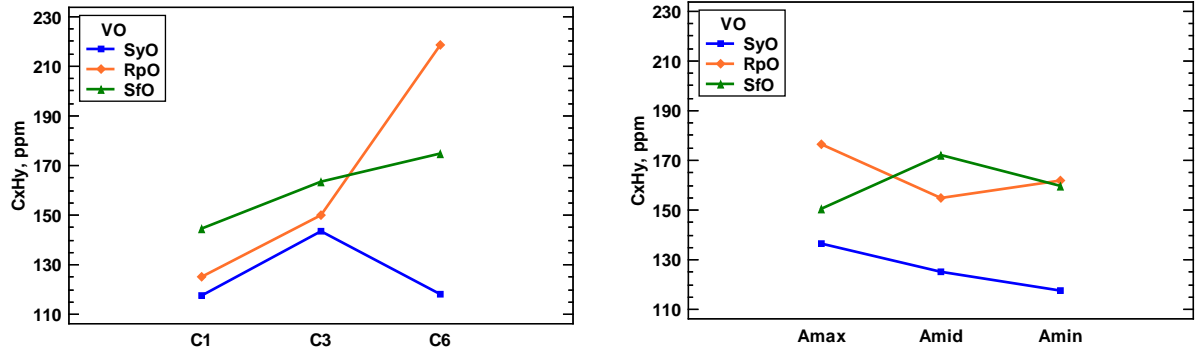
**Figure 3.** Interaction plots of the variability in combustion performance, in %, with the fuel flow (left) and airflow factors (right) for each vegetable oil.



**Figure 4.** Interaction plot of the variability of CO<sub>2</sub> in ppm, with the fuel flow (left) and airflow factors (right) for each vegetable oil.



**Figure 5.** Interaction plot of the variability of NOx emissions, in ppm, with the fuel flow (left) and airflow (right) factors for each vegetable oil.






**Figure 6.** Interaction plot of the variability of CxHy emissions, in ppm, with fuel flow (left) and airflow (right) factors for each vegetable oil.

**Table 1.** Elemental analysis and physical characteristics of the refined vegetable oils studied.

	Unit	SyO	SfO	RpO	Standard
C	% (m·m <sup>-1</sup> )	77.3	77.4	76.9	ASTM5291
H	% (m·m <sup>-1</sup> )	11.2	11.2	11.3	ASTM5291
N	% (m·m <sup>-1</sup> )	<0.05	0.07	<0.05	ASTM5291
S	% (m·m <sup>-1</sup> )	0.04	0.03	0.04	ASTM1552
O <sup>a</sup>	% (m·m <sup>-1</sup> )	11.4	11.2	11.7	-
Ash	% (m·m <sup>-1</sup> )	0.004	0.005	0.007	EN 6245
Humidity	(%)	0.02	0.01	0.06	ISO 662
Acidity	(%)	0.11	0.03	1.73	ISO 660
Density at 15 °C	kg·m <sup>-3</sup>	922.3	922.3	919.9	ISO 12185
Density at 35 °C	kg·m <sup>-3</sup>	909.0	908.9	906.7	ISO 12185
Density at 60 °C	kg·m <sup>-3</sup>	892.4	892.3	890.1	ISO 12185
Kinematic viscosity at 40 °C	mm <sup>2</sup> ·s <sup>-1</sup>	32.53	32.10	35.65	ISO 3104
Kinematic viscosity at 100 °C	mm <sup>2</sup> ·s <sup>-1</sup>	7.79	7.65	8.01	ISO 3104
H.H.V.	kJ·kg <sup>-1</sup>	39,370	39,500	38,840	ASTM 240
L.H.V.	kJ·kg <sup>-1</sup>	36,990	37,120	36,440	ASTM 240

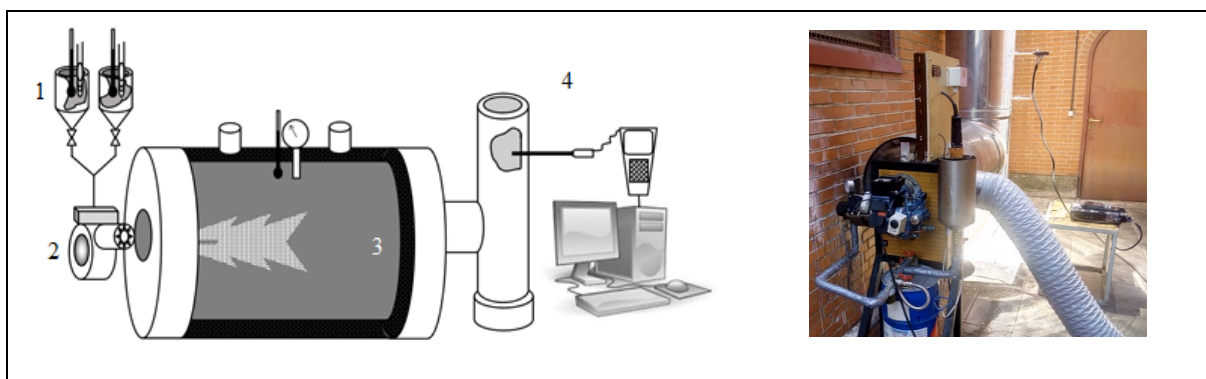
<sup>a</sup> Estimated by difference.

**Table 2.** Proportions (% m·m<sup>-1</sup>), obtained by gas chromatography, of the different FAs in SyO, RpO and SfO.

<b>Fatty acid</b>		SyO	SfO	RpO
				
Miristic	C14:0	0.08	0.07	0.05
Palmitic	C16:0	10.4	5.9	4.5
Margaric	C17:0	0.09	0.04	0.06
Stearic	C18:0	4.2	4.3	1.6
Arachidic	C20:0	0.5	0.6	0.3
Behenic	C22:0	0.6	0.8	0.4
Lignoceric	C24:0	0.2	0.3	0.3
Palmitoleic	C16:1	0.09	0.1	0.2
Oleic	C18:1	27.3	25.4	62.7
Gadoleic	C20:1	0.5	0.3	0.6
Linoleic	C18:2	50.1	62.5	19.3
Linolenic	C18:3	6.0	0.09	8.5
DU <sup>a</sup> (%)		146.1	151.1	127.6

<sup>a</sup> Degree of Unsaturation [%MUFA (total monounsaturated fatty acids) + (%L)·2 + (%Ln)·3]

**Table 3.** Characteristics of the combustion facility elements and installation photography.



<b>Characteristics of each element</b>			
<b>1: Fuel feed tanks</b>	<b>2: Burner</b>	<b>3: Boiler</b>	<b>4: Chimney and gas analyser</b>
316 L steel tanks and 5L shut-off valve	Power rating 17-58 kW Fuel viscosity 26 to 112 mm <sup>2</sup> ·s <sup>-1</sup> at 50 °C	42 kW power air-cooled concentric-tube boiler	Testo 350 gas analyser
<b>Adjustable variables</b>			
Fuel temperature	Airflow Fuel flow	Chamber temperature Chamber over-pressure	Initial calibration <sup>a</sup>
<b>Measurement variables</b>			
Fuel flow (L·s <sup>-1</sup> )	Fuel injection pressure	Chamber pressure Chamber temperature	Flue gas and reference temperatures Emissions: O <sub>2</sub> , CO <sub>2</sub> in %; CO, NO <sub>x</sub> , SO <sub>x</sub> , C <sub>x</sub> H <sub>y</sub> in ppm

<sup>a</sup> Prior to each assay, the equipment was calibrated with the oxygen sensor, and in each new test the manufacturer's calibration certificate is obtained.

**Table 4.** Factors with levels

Factors	Level 1	Level 2	Level 3
VO	SyO	SfO	RpO
Fuel flow rate	C1	C3	C6
Airflow rate	A <sub>min</sub>	A <sub>mid</sub>	A <sub>max</sub>



**Table 5:** Fuel flow and airflow rates.

Fuel flow (kg·h <sup>-1</sup> )	C1	C3	C6
SfO	4.92	6.89	8.10
SyO	5.38	6.90	7.56
RpO	5.12	7.23	8.21
Airflows (kg·h <sup>-1</sup> )	A <sub>min</sub>	A <sub>mid</sub>	A <sub>max</sub>
	160	166	180

**Table 6.** ANOVA results for CO<sub>2</sub>.

<b>Factor</b>	<b>Sum of Square</b>	<b>DF*</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Analysis of variance for CO <sub>2</sub>					
VO	2.64086	2	1.32043	75.05	0.0000
airflow	8.95371	2	4.47686	254.46	0.0000
fuel flow	120.987	2	60.4936	3438.33	0.0000
VO*airflow	0.491117	4	0.122779	6.98	0.0002
VO*fuel flow	0.523182	4	0.130795	7.43	0.0001
airflow*fuel flow	1.39186	4	0.347966	19.78	0.0000
VO*airflow*fuel flow	1.07527	8	0.134409	7.64	0.0000
Error	0.844507	48	0.0175939		
Total	146.17	74			

\* Degree of freedom

**Table 7.** ANOVA results for combustion performance.

<b>Factor</b>	<b>Sum of Square</b>	<b>DF</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Analysis of variance for <b>combustion performance</b>					
VO	128.711	2	64.3553	448.62	0.0000
airflow	217.59	2	108.795	758.41	0.0000
fuel flow	47.2	2	23.6	164.52	0.0000
VO*airflow	10.5173	4	2.62933	18.33	0.0000
VO*fuel flow	8.43269	4	2.10817	14.70	0.0000
airflow*fuel flow	5.32697	4	1.33174	9.28	0.0000
VO*air*fuel flow	8.90074	8	1.11259	7.76	0.0000
Error	6.88565	48	0.143451		
Total	427.27	74			

**Table 8.** ANOVA results for CO

<b>Factor</b>	<b>Sum of Square</b>	<b>DF</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Analysis of variance for <b>CO</b>					
VO	4862.31	2	2431.16	89.78	0.0000
airflow	929.709	2	464.854	17.17	0.0000
fuel flow	53740.6	2	26870.3	992.32	0.0000
VO*airflow	3787.48	4	946.869	34.97	0.0000
VO*fuel flow	7122.37	4	1780.59	65.76	0.0000
airflow*fuel flow	23150.7	4	5787.68	213.74	0.0000
VO*airflow*fuel flow	5427.94	8	678.493	25.06	0.0000
Error	1299.76	48	27.0782		
Total	114260	74			

**Table 9.** ANOVA results for NOx

<b>Factor</b>	<b>Sum of Square</b>	<b>DF*</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Analysis of variance for <b>NOx</b>					
VO	9.50985	2	4.75493	3.89	0.0273
airflow	559.299	2	279.649	228.55	0.0000
fuel flow	996.447	2	498.223	407.18	0.0000
VO*airflow	27.5012	4	6.8753	5.62	0.0009
VO*fuel flow	29.2882	4	7.32206	5.98	0.0005
airflow*fuel flow	137.513	4	34.3781	28.10	0.0000
VO*airflow*fuel flow	62.9207	8	7.86509	6.43	0.0000
Error	58.7321	48	1.22359		
Total	2422.67	74			

**Table 10.** ANOVA results for CxHy.

<b>Factor</b>	<b>Sum of Square</b>	<b>DF</b>	<b>Mean Square</b>	<b>F-ratio</b>	<b>P-value</b>
Analysis of variance for CxHy					
VO	19500.5	2	9750.26	21.04	0.0000
airflow	686.613	2	343.306	0.74	0.4821
fuel flow	17690.8	2	8845.38	19.09	0.0000
VO*airflow	4016.59	4	1004.15	2.17	0.0869
VO*fuel flow	20915.2	4	5228.81	11.28	0.0000
airflow*fuel flow	2736.31	4	684.077	1.48	0.2241
VO*airflow*fuel flow	18454.2	8	2306.77	4.98	0.0002
Error	22242.9	48	463.393		
Total	130667	74			