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Pinzi, Sara; Lopez, I; Leiva-Candia, David; Redel-Macias, Maria Dolores; Herreros, Jose; Cubero-Atienza, A; Dorado, Maria Pilar

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Castor oil enhanced effect on fuel ethanol-diesel fuel blend properties

S. Pinzi^a, I. López^b, D.E. Leiva-Candia^a, M.D. Redel-Macías^c, J.M. Herreros^d, A. Cubero-Atienza^c, M.P. Dorado^{a,*}

^a*Dep. Physical Chemistry and Applied Thermodynamics, Ed Leonardo da Vinci, Campus de Rabanales, Universidad de Cordoba, Campus de Excelencia Internacional Agroalimentario, ceiA3, 14071 Cordoba, Spain*

^b*Center of Energy Studies and Environmental Technologies (CEETA), Universidad Central de Las Villas, Santa Clara, Cuba*

^c*Dep. Rural Engineering, Ed Leonardo da Vinci, Campus de Rabanales, Universidad de Cordoba, Campus de Excelencia Internacional Agroalimentario, ceiA3, 14071 Cordoba, Spain*

^d*Dep. Mechanical Engineering, School of Engineering, University of Birmingham, Edgbaston B15 2TT Birmingham, United Kingdom*

* Corresponding author. Tel.: +34 957 218332; fax: +34 957 218417. E-mail address: pilar.dorado@uco.es

Abstract

Ethanol is a low chain alcohol that could partially substitute diesel fuel to operate compression ignition engines. Its renewable origin and oxygenated structure make ethanol a candidate fuel for internal combustion engines. Main drawbacks of ethanol as a fuel are its low heating value, viscosity, lubricity, cetane number and limited miscibility if mixed with diesel fuel. Additives may enhance its solubility, although with a cost increase. In the present study, castor oil is proposed as an additional component to be added to ethanol-diesel fuel blends. Castor oil and its seeds are not suitable as food neither for humans nor for animals, thus avoiding the possible conflict about the use of land for food or energy, as arises from the use of edible oil/seeds. The presence of a hydroxyl group in the ricinoleic acid increases the polarity of this oil, enhancing ethanol-diesel fuel miscibility. As a result, ternary blends of ethanol, ultra-low sulfur diesel fuel and castor oil have been analyzed considering blend solubility, heating value, kinematic viscosity and cold flow properties, among most critical properties of diesel fuels. Ternary-component mixture prediction models of relevant fuel properties, i.e. kinematic viscosity, cold filter plugging point and high calorific value have been developed. Blend composition that simultaneously optimizes the three fuel properties has been proposed using the desirability function of Derringer. Results from simulation have been experimentally validated, providing a fuel blend composed by diesel fuel, ethanol and castor oil that shows satisfactory values of the most significant physical and chemical fuel properties. The presence of a hydroxyl group in the ricinoleic acid provides superior ignitability, lubricant and solubility characteristics with respect to other additives/components, making it a potential suitable candidate as a blend component to enhance ethanol/diesel fuel blends.

Keywords: solubility; viscosity; lower alcohol; desirability function; simulation model

The short version of the paper was presented at IC AE2017, Aug 21-24, Cardiff, UK. This paper is a substantial extension of the short version of the conference paper.

1. Introduction

In 2012, the EU transport sector demanded up to 70% of total diesel fuel consumed in the whole European Union (2.5 Mt) [1]. Diesel fuel combustion has been reported as the major contributor of atmospheric levels of particulate matter and nitric oxides emissions, being hazardous to both environment and human beings [2]. In addition, as it is stated by the Paris agreement about climate change, reducing the use of non-renewable fuels is urgent to keep the world temperature rise below 2°C above pre-industrial levels. Therefore, a solution to energy, mobility and transport needs could be provided by fossil-fuel replacement with renewable and advanced fuels. It has been reported that optimized use of advanced biofuel in combination with other engine technologies, i.e. EGR could produce favorable particle-NO_x trade-off [3, 4], mainly when oxygenate fuels are employed [5]. In this context, it is important to notice that alcohols include oxygen in the fuel molecule and could be blended with fossil-based fuel to operate both spark and compression ignition engines [6, 7]. Alcohols, both short chain (namely methanol [8], ethanol [9, 10] and butanol [11]) and longer chain alcohols [12], i.e. 1-hexanol [13], cyclohexanol [14] and n-octanol [15] have been used in compression ignition engines, promoting a better combustion and lower gaseous and particle emissions. For instance, Ajav and others [16] tested, in a single-cylinder engine at constant speed (1500 rpm) and four levels of load (25, 50, 75 and 100%), mixtures of ethanol/diesel fuel (5, 10, 15 and 20% ethanol in the blends). These oxygenated mixtures led to a reduction of carbon monoxide and nitrogen oxide emissions. However, most studies proposing the use of ethanol blended with diesel fuel recommend low percentages of alcohol due to several detrimental properties of alcohol fuels when used in compression ignition engines, i.e. low solubility, ignitability, heating value and lubricity [17].

One of the major shortcomings derived from the use of methanol or ethanol mixed with diesel fuel is their reduced solubility, forcing to lower the presence of alcohol to percentages below 20%. Although solubility of ethanol in ultra-low sulphur diesel fuel (ULSD) is higher than that of methanol blends (methanol presents higher polarity due to a shorter hydrocarbon chain, which means it is almost not soluble in diesel fuel), its solubility depends on the number of hydrocarbons present in diesel fuel, wax content, temperature and moisture content of the blend [18]. For this reason, additives in percentages below 10% are often used to improve solubility of blends [10, 19]; although, the cost of these additives is a major limitation. Torres-Jiménez and others [20] studied the physicochemical properties of ethanol/ULSD blends, with percentages of ethanol from 5 to 15% v/v. They concluded that the presence of ethanol did not influence fuel properties, excepting flash point and blend stability. Authors found that 15% v/v ethanol could be used directly and without additives in blends with diesel fuel, but the use of an additive is needed to improve stability and flash point of the blend. Moreover, they found that to keep a single phase, blend temperature should be above 30°C; however, for temperatures below 30°C, two phases were formed in less than a month. Similarly, Huang and others [21] studied solubility and behavior of ethanol (from 10 to 30% v/v)/diesel fuel mixtures using n-butanol as additive. Stability and solubility tests showed that no mixture was stable after three days. Lapuerta et al. [17] measured stability of ethanol-diesel fuel blends using optical equipment, specifically designed for the characterization of liquid emulsions, suspensions and solutions. Authors found out that at 25°C, blends with more than 20% v/v ethanol were not

miscible. Li and others [22] used a stabilizing additive (1.5%) in blends of diesel fuel with ethanol (5 to 20% in volume) and achieved a significant reduction of smoke and NO_x emissions.

Vegetable oils and biodiesel have also been researched as a fuel component to alcohol-diesel fuel blends, forming a so-called ternary fuel blend. The high lubricity of biodiesel and vegetable oil as well as their potential to enhance both ethanol/diesel fuel and butanol/diesel fuel blend stability has been demonstrated in several works [11, 23, 24]. Castor oil (CO) has been traditionally used in cosmetics and even in the biodiesel industry, among others [25]. Provided that castor oil/seeds cannot be used for feeding purposes, alternative industrial uses, i.e. promoting business opportunities for marginal rural areas, become an attractive idea [26]. According to this, the effectivity of CO used as lubricating oil for engines has been demonstrated [27]. According to FAO database (FAOSTAT), four countries (India, China, Mozambique and Brazil) produce 96% of the world's supply of castor oil (1 700 000 t of seeds, in 2016). Total castor production may vary yearly due to changes in rainfall and the size of cultivated areas. In a recent study [28], it was concluded that diversification of cultivation areas and the use of irrigation are needed for an extensive use of CO.

CO presents low solubility with diesel fuel, but acceptable in case of alcohol. Other authors have used different strategies to enable the use of higher percentages of alcohols in compression ignition engines. Wei et al. [8] proposed the strategy of a high premixed ratio to directly inject into the chamber 70% methanol blended with diesel fuel, finding out a high decrease of soot and NO_x . Ethanol-diesel blends also feature an increase in auto-ignition delay times [29] due to decrease in cetane number, which could be around 35 for 25% ethanol and 25 for 45% ethanol. Increase in auto-ignition delay times can be overcome if pressure and temperature levels at the injection timing, inside the combustion chamber, are increased, for example by varying the compression ratio [30]. Cross effects of compression ratio and low cetane numbers have already been highlighted for ethanol-diesel fuel blends, biodiesel fuels and naphta-like fuels [31]. Variable compression ratio could be able to overcome variation in cetane number by adapting compression ratio for different amounts of ethanol up to 45%, while for higher ethanol content, the required compression ratio would be very high for diesel fuel. Surface ignition [32] could also be employed to overcome the low cetane number of alcohol fuels. In the present study, the potential of CO as solubility, lubricity and energy density enhancer to improve ethanol/ULSD blends has been studied. CO composition comprises one hydroxyl group in the fatty acid and one apolar group in other long-chain fatty acids, making castor oil a surfactant material. The hydroxyl group also has superior ignitability and lubricant properties as well as higher flash point compared to other fatty acids, making it a potential suitable candidate as a blend component to enhance ethanol/diesel fuel blends. In this sense, for the first time, a comprehensive study to select optimal ethanol, CO and diesel fuel blend has been performed. Solubility and viscosity of several ternary blends comprising ethanol, ULSD and CO are analyzed to pre-select ternary fuel blends. Besides, mixture optimization based on fuel properties (Derringer method) has been carried out, and property prediction models have been designed. To validate the model, relevant chemical and physical properties of the predicted optimum mixture have been experimentally measured.

2. Materials and methods

2.1. Fuels

Ethanol 99.8% v/v was provided by SCHARLAB (Barcelona, Spain). Castor oil (*Ricinus communis*) was purchased from GUINAMA (Valencia, Spain). Fuel ternary blends include ethanol, castor oil and ULSD fuel (meeting EN 590 standard). Straight ULSD (with no biodiesel addition) was provided by CEPSA oil refinery (Huelva, Spain).

Table 1 shows some of the most representative fuel properties of ternary blend components. For solubility reasons, the mixing order must be met in the following way: firstly, oil and ethanol were mixed together; later, ULSD was added. To produce a homogeneous blend, it was vigorously shaken for one minute. Blends were kept in a glass container to check solubility and physical stability with time.

Table 1. Mixture components fuel properties

	ULSD	CO	Ethanol
Density at 15°C (kg/m ³)	827.1	964	789
Flash point (°C)	70.2	229	13
Kinematic viscosity at 40°C (mm ² /s)	2.47	298	1.07
Cetane index	47.4	28[33]	8[34]
Water content (mg/kg)	4.52	3598.37	419.50
CR (% w/w)	0.1	0.22	0.01
Boiling point** (°C)	180-360*	313	78.2
Melting point** (°C)		-10	-114
Lubricity wear scar at 60°C (µm)	335	203	656
HCV (kJ/kg)	42700	39820	29700
CFPP (°C)	-15.67	***	<-25
C (% w/w)	85.62	73.60	52.14
H (% w/w)	14.38	11.55	13.13
O (% w/w)	0	14.85	34.73

*Boiling Range; **Values provided by supplier

*** CFPP could not be measured because the filter during the test becomes clogged

ULSD: ultra-low sulphur diesel fuel; CFPP: cold filter plugging point; HCV: higher calorific value; CR: carbon residue

2.2. Experimental design

In a starting screening experimental study, a McLean-Anderson design was followed. For each corner of the triangle, the minimum value was 10% vol., while the maximum was 80% vol. of each component in the fuel blends (Figure 1). During the initial preliminary study, 36 runs were performed. Blends were visually examined every hour, during one

day time, to remove blends that were both stratified in two layers during the settling time and depicted viscosity values beyond that of ULSD fuel.

Based on results achieved from the preliminary design, blend values were selected to build the second mixture design of experiments (MDOE). Experimental mixture designs [35] and models allow determination of optimum values of component proportions with the execution of the lowest number of experiments. Mixture models are consequent with general polynomial equation (eq. 1) used in response surface analysis:

$$\hat{y} = b_0 + \sum_{i=1}^q b_i x_i + \sum_{\substack{i=1 \\ i \leq j}}^q \sum_{j=1}^q b_{ij} x_i x_j + \sum_{\substack{i=1 \\ i \leq j \\ i \leq k}}^q \sum_{j=1}^q \sum_{k=1}^q b_{ijk} x_i x_j x_k \dots$$

Eq. 1

Eq. 1 defined a predicted response variable, y , in function of the amount of q experimental factors observed in the experiment. For mixtures, q factor values, or ingredient proportions, x_i , are associated by eq. 2:

$$\sum_{i=1}^q x_i = 1$$

Eq.2

Then, proportions of ingredients in mixtures always sum 1 (or 100%).

Second MDOE includes 14 runs with 3 central points (Table 2). Optimum blend value provided by second MDOE was experimentally validated, and most important physical and chemical properties were measured, as well as its physical stability after 14 days.

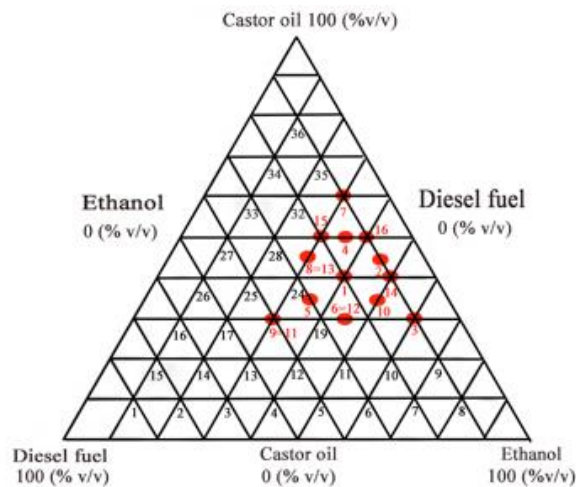


Figure 1. McLean Anderson design of experiments. Numbers include samples from the first screening. Red circles indicate set of samples used for the second design of experiments

Table 2. Second experimental design and fuel properties of ternary mixtures

Sample	% ULSD (v/v)	% Ethanol (v/v)	% Castor oil (v/v)	ν (mm ² /s)*	CFPP (°C)*	HCV (kJ/kg)*	CR (% w/w)*
				EN ISO 3104:1994	EN116:1998	ASTM D2382-88:1994	EN ISO 10370:2014
1	20	40	40	8.04 (0.44)	3 (0.6)	35357 (341)	0.08493 (0.00308)
2	10	45	45	8.48 (0.35)	1 (0.6)	34522 (72)	0.08003 (0.00156)
3	10	60	30	4.82 (0.39)	4 (0.6)	33181 (193)	0.08822 (0.00645)
4	15	35	50	12.00 (1.46)	8 (1.1)	35270 (111)	0.08396 (0.00484)
5	30	35	35	7.51 (0.34)	2 (0.2)	36515 (105)	0.08152 (0.00246)
6	25	45	30	5.43 (0.10)	1 (0.2)	35 116 (70)	0.08475 (0.00230)
7	10	30	60	17.63 (0.77)	19 (0.0)	35360 (35)	0.08332 (0.00291)
8	25	30	45	11.93 (0.23)	8 (1.2)	36424 (73)	0.08343 (0.00586)
10	15	50	35	6.32 (0.29)	2 (0.0)	33910 (96)	0.08329 (0.00591)
12	25	45	30	5.35 (0.17)	0 (0.6)	34892 (28)	0.08415 (0.00168)
13	25	30	45	10.00 (0.34)	6 (0.6)	36475 (105)	0.08557 (0.00508)
14	10	50	40	7.39 (0.49)	-4 (0.6)	31422 (422)	0.08322 (0.00176)
15	20	30	50	13.38 (0.62)	9 (1.1)	36059 (132)	0.08431 (0.00078)
16	10	40	50	11.73 (0.49)	3 (0.6)	34319 (237)	0.08696 (0.00244)

*Errors, in brackets, are expressed as relative standard deviation, in percentage (n=3 replicates)

ULSD: ultra-low sulphur diesel fuel; CFPP: cold filter plugging point; HCV: higher calorific value; CR: carbon residue; V: kinematic viscosity

2.3. Methods

Chemical composition of castor oil was determined following UNE EN-14103 (Table 3). Firstly, oil needed to be esterified (reagents were CH_3ONa , methanol 30% PS and hexane). Gas chromatography was conducted by means of a Perkin Elmer chromatograph GC-FID. Fatty acid C17:0, supplied by Fluka (Steinheim, Germany) was used as internal standard. Rotary viscometer Rheotest RV 2.1 (Moscow, Russia) was used to measure dynamic viscosity (μ). Kinematic viscosity (ν) was analyzed according to European EN ISO 3104 standard, by means of Cannon-Fenske viscometer Proton no. 150.

Table 3. Castor oil fatty acid composition

Methyl esters		% v/v
Palmitic	C16:0	0.68
Stearic	C18:0	1.24
Oleic	C18:1	2.63
Ricinoleic	C18:1OH	89.3
Linoleic	C18:2	4.71
Others		1.44

UNE EN 116 standard was used for the analysis of cold weather behavior of the fuel, namely cold filter plugging point (CFPP). It was measured by means of HCP 842, Herzog by PAC (Lauda-Königshofen, Germany). An IKA model C200 bomb calorimeter (Staufen, Germany) was used to calculate fuel higher calorific value (HCV), according to ASTM D240 standard. Carbon residue (CR) was measured with Alcor microcarbon residue tester, by PAC (Lauda-Königshofen, Germany), following EN ISO 10370:2014 standard. Flash point was calculated using a Stanhope-Seta (Cherstey, UK) Setaflash Series 3 flash point tester, following European ISO 3679 standard. Water content was analyzed using a Karl Fischer titrator, model Mettler Toledo DL 32 (Spain). Lubricating properties of the tested fuels were assessed on a high frequency reciprocating rig (HFRR). An optical microscope was used to measure the size of the wear scar of the ball, which was corrected for standard water vapour pressure 1.4 kPa (WS1.4). All lubricity tests were conducted according to EN ISO 12156. As a precautionary measure, due to the high volatility of ethanol, the fuel bath was also covered with a close-fitting PTFE lid. To calculate final distillation temperature, Optidist automated distillation analyzer, by PAC, was used. For cetane index determination, standard ISO 4264 was followed. Properties were measured in triplicate, to calculate average values and standard deviation.

For optimization purposes, software Statgraphics© centurion XVII (Virginia, USA) was used. To find out the optimum ternary blend, a model applied to each one of the most significant properties (CFPP, HCV and ν) was designed. Despite there are no regulations advising a range to fill, heating value should be maximized to achieve maximum fuel vehicle range, while reducing brake-specific fuel consumption (BSFC); ν should be minimized as all blends analyzed in the second MDOE show large viscosity values, being a critical property for an optimal atomization of fuel spray and accurate operation of fuel injectors. CFPP is a crucial property because high CO content may produce partial

solidification in cold weather and cause blockages of fuel lines and filters, leading to fuel starvation and problems during engine start-up. The convenience surface was described using a Derringer (multifactorial) design. In the present study, the product of single desirability functions provided global desirability, leading to the optimum ternary mixture as a function of most representative fuel properties.

3. Results and discussion

3.1. Initial screening

Initially, solubility and viscosity of 36 fuel mixtures (comprising different quantities of castor oil, diesel fuel and ethanol) were visually and analytically evaluated. As may be seen from Table 1, fuel properties dramatically differ between mixture components, which may lead to different engine performance. As a result, ternary blend optimization considering the most significant properties is crucial.

Further property analysis while looking for the optimum values showed that 16 samples keep the blend physical stability, thus they were considered for subsequent tests. Samples #9 and #11 were removed from the lasting model as they showed phase separation after five-day trial. In sum, first blend stability test provided only 14 miscible samples out of 36. To find out the optimal ternary mixture, a second MDOE was generated, this time only including the set of miscible samples that showed the lowest dynamic viscosity (red circles, in Figure 1), following EN ISO 3104 standard. Second MDOE is shown in Table 2, besides blend property values (ν , CFPP, HCV and CR). As may be seen, viscosity value is directly proportional to the presence of each component viscosity value. In this sense, the higher the presence of low viscosity components, i.e. ULSD and ethanol, the lower the blend viscosity. The opposite trend may be inferred from the presence of CO in the blend.

3.2. Optimization of ternary blend properties

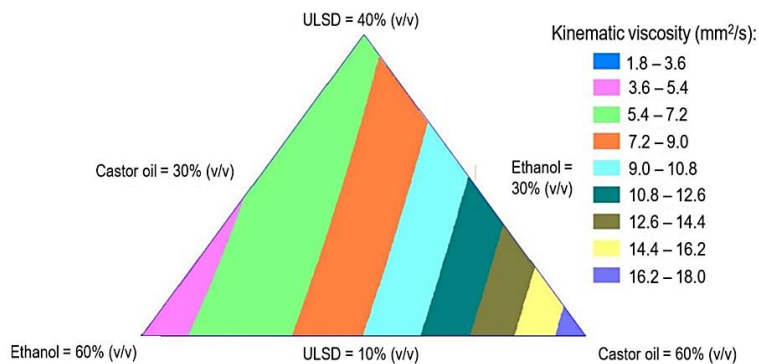
To predict blend physical properties based on mixture composition, four ternary-component mixture models, based on blend measured properties (ν , CFPP, HCV and CR), have been built (Table 4). As may be inferred from the models, they are robust and may accurately predict experimental values. As may be seen from Table 4, kinematic viscosity may be predicted by a second-order model, while a third-order model is needed to predict CFPP. Second order or quadratic model includes three terms that have coefficients indicating synergic or antagonistic interaction effects on response values between two of the mixture ingredients. Second-order model ($R^2 = 98.49$) is preferred to first-order model ($R^2 = 90.31$), due to the higher significance. This means second-order model shows a high capability of kinematic viscosity prediction based on mixture composition. This fact may suggest that both hydroxyl group of ethanol and ricinoleic acid of castor oil (constituting 89.3% castor oil fatty acid composition) could present synergic behavior. Cubic or third-order model implies more complex interaction effects between the three mixture ingredients. Finally, HCV is predicted by a lineal mixture model. In a lineal mixture model, the variability of response variable (HCV) with experimental factor (amount of each component in the blend) may be determined by simply performing response measurements of pure components of the mixture being investigated. These pure components are represented

by points at vertices of the mixture concentration triangle. This fitting is also remarkable in Figures 2 to 4, which depict a three-component plot for each property. They allow to state the relationship between property values and component content included in the ternary mixture. As may be seen, castor oil content increases mixture kinematic viscosity value. Ensuring that the content of CO is below 40%, blends will achieve acceptable kinematic viscosity values, considering ASTM D6751 standard.

Table 4. Prediction of most significant fuel properties considering ternary mixture composition. ULSD: ultra-low sulphur diesel fuel (% v/v); CFPP: cold filter plugging point; HCV: higher calorific value; v: kinematic viscosity; E: ethanol (% v/v); CO: castor oil (% v/v)

Property		R^2 (%)	Adjusted R^2 (%)	P value
v at 40 °C (mm²/s)	$v = 6.71203 \text{ ULSD} + 4.91589 \text{ E} + 17.6693 \text{ CO}$ $- 1.40865 \text{ ULSD E}$ $- 4.33109 \text{ ULSD CO}$ $- 9.09086 \text{ E CO}$	98.49	97.55	0.0010
CFPP (°C)	$\text{CFPP} = 0.22422 \text{ ULSD} + 3.84279 \text{ E} + 18.9492 \text{ CO}$ $- 5.75938 \text{ ULSD E}$ $- 12.3524 \text{ ULSD CO}$ $- 48.5076 \text{ E CO}$ $+ 85.6201 \text{ ULSD E CO}$	96.76	93.98	0.0001
HCV (kJ/kg)	$\text{HCV} = 37796.6 \text{ ULSD} + 32390.6 \text{ E} + 35216.5 \text{ CO}$	80.88	77.40	0.0001

a)



b)

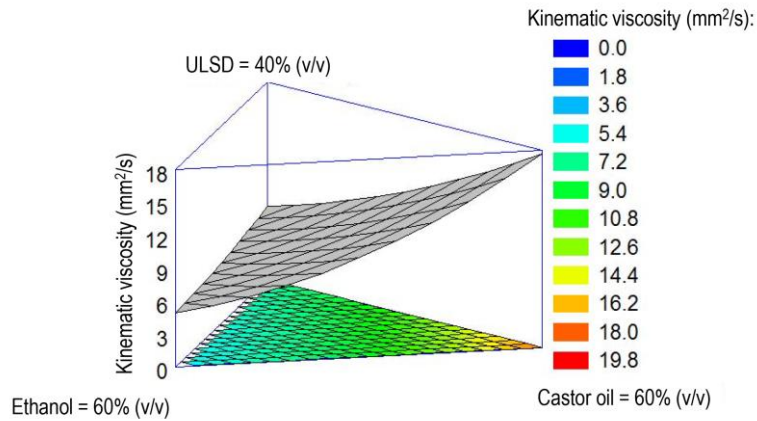
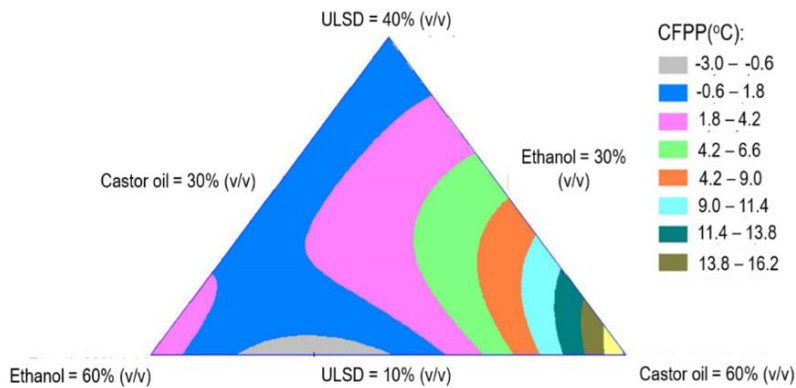


Figure 2. Estimation of ternary mixture kinematic viscosity considering blend composition (%): a) estimated response surface and b) 3D-response surface of ternary plot. ULSD: ultra-low sulphur diesel fuel

a)



b)

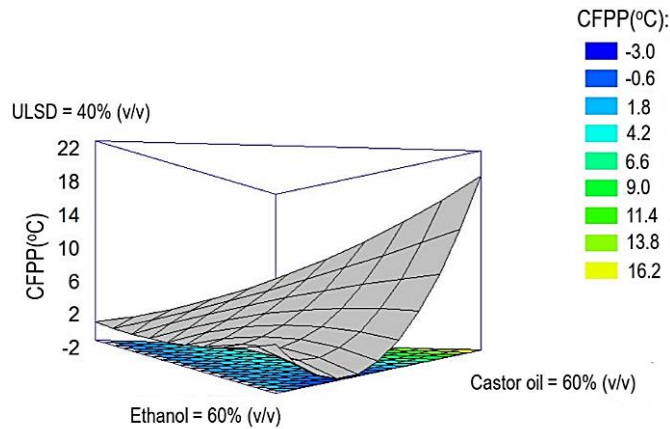


Figure 3. Estimation of ternary mixture cold filter plugging point (CFPP) considering blend composition: a) estimated response surface and b) 3D-response surface of ternary plot. ULSD: ultra-low sulphur diesel fuel

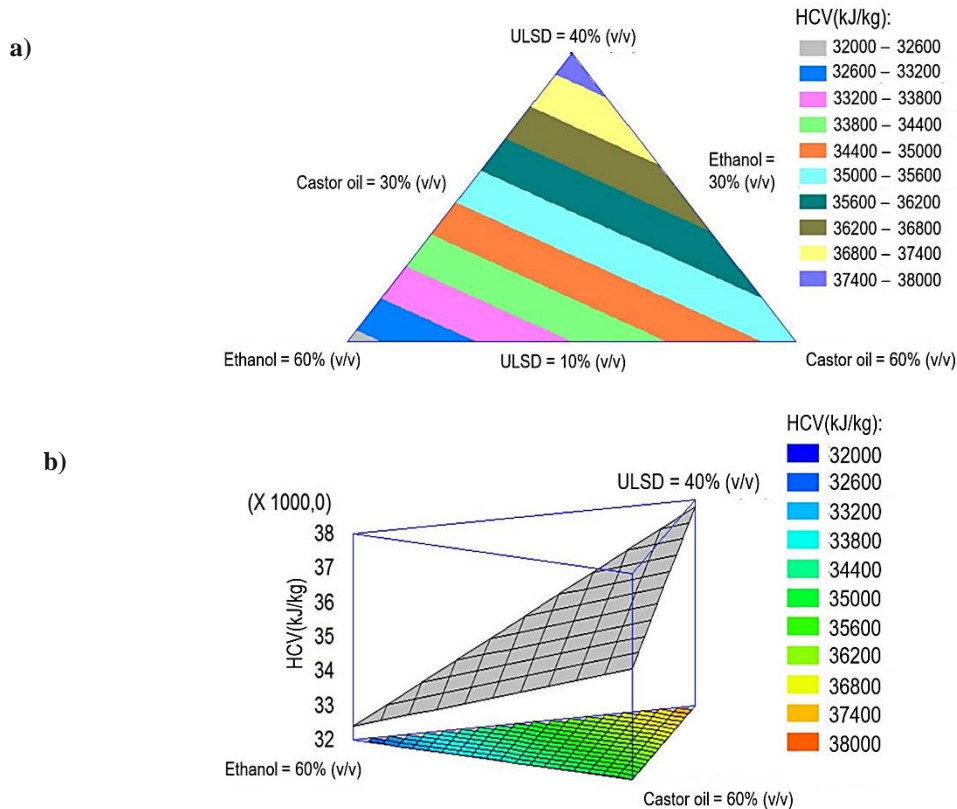


Figure 4. Estimation of higher calorific value (HCV) considering blend composition: a) estimated response surface and b) 3D-response surface of ternary plot. ULSD: ultra-low sulphur diesel fuel

ANOVA statistical analysis of carbon residue prediction model based on blend composition showed a P-value above or equal to 0.39 for a second order model (best option). Therefore, it is possible to state that no significant relation between mixture composition and carbon residue has been demonstrated. For this reason, no prediction model was designed for CR. In fact, CR is a property related to the potential of a fuel to make carbon deposits when working under considerable temperatures (combustion). Carbon residue is expected to depend on ethanol concentration, as it is the most volatile blend compound, although this condition has not been evidenced in this study. It may be explained by a reduction of the evaporation temperature, as a result of interaction forces between components, followed by ternary mixture vapour pressure increase [36]. Eventually, although triglycerides depict reduced polarity, the large presence of ricinoleic acid (88.8% w/w) gives enough polarity to castor oil, favoring interaction forces with ethanol hydroxyl group. Previous researchers have found similar results, when n-butanol [37] or palm oil [38] have been analyzed as potential additives to enhance miscibility between diesel fuel and ethanol.

A 2-D figure, providing blend CFPP value based on the concentration of each component in the ternary blend is shown in Figure 3a. High content of either ethanol (with a melting point of $-114\text{ }^{\circ}\text{C}$) or ULSD fuel leads to the grey and blue areas, representing the lowest CFPP values. This trend should be due to the high melting points of some triglycerides

that constitute CO. Figure 4 shows the lineal correlation between HCV and ternary-component percentages of the blend. According to previous studies [39], this property does not show any synergic or antagonistic interaction with mixture components, so an efficient adjustment may be achieved by a first-order model.

3.3. Derringer function applied to physical properties of ternary-component mixture experiment

Derringer desirability function is based on the idea that the quality of a product or process that depend on multiple quality characteristics, with one of them outside of some desired limits, is completely unacceptable. The method finds the operating conditions that give the most desirable combination of response variables [40].

The selected suitable value range for each fuel property is depicted in Table 5. Whereas the goal is to maximize HCV value, ν should be minimized to elude an increase in both injection volume and injection pump pressure [39]. Moreover, CFPP should be minimized to prevent filter plugging due to fuel crystallization under cold weather conditions. According to this, acceptable compromise solution of the model, consisting of a blend composed by 28.6%, 41.4% and 30% v/v of ULSD fuel, ethanol and castor oil, respectively, is shown in Table 5.

Table 5. Optimization of the desirability function

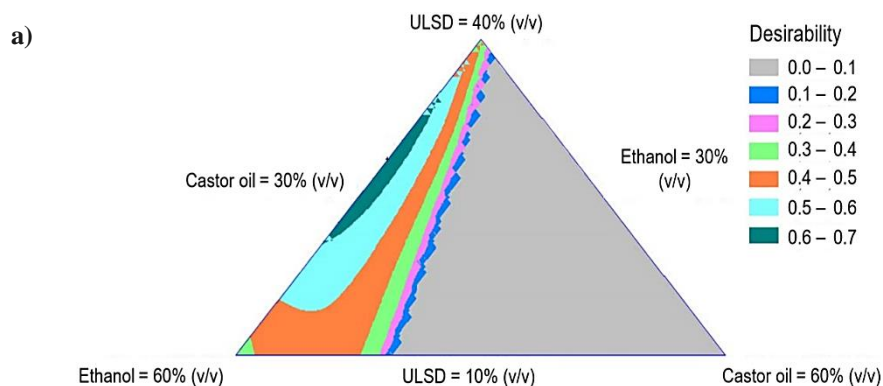
Response	Low Response	High Response	Goal	Parameter	Selected value (low)	Selected value (high)	Calculated optimum value*
CFPP (°C)	-4.0	6.0	Minimize	ULSD (% v/v)	10.0	40.0	28.6
HCV (kJ/kg)	31422	36515	Maximize	% Ethanol (v/v)	30.0	60.0	41.4
ν (mm ² /s)	4.829	7.0	Minimize	% Castor oil (v/v)	30.0	60.0	30.0

*Optimal value of Derringer desirability function: 0.6

ULSD: ultra-low sulphur diesel fuel; CFPP: cold filter plugging point; HCV: higher calorific value; ν : kinematic viscosity

In this work, the result of multiplying single desirability functions provides global desirability, which is equivalent to the most suitable ternary blend (composed by ULSD, castor oil and ethanol) that simultaneously optimizes three main physical fuel properties. This optimal blend was achieved using the effectiveness of Derringer function, combined with a ternary-component mixture experiment, to simultaneously optimize several parameters.

The desirability function is 2-D plotted (Figure 5a). In the plot, grey area corresponds to unsuitable ternary blend (meaning that, at the minimum, one property value is unacceptable, considering Table 4), while remaining areas represent different desirability degree. Figure 5b shows equivalent 3-D ternary figure.



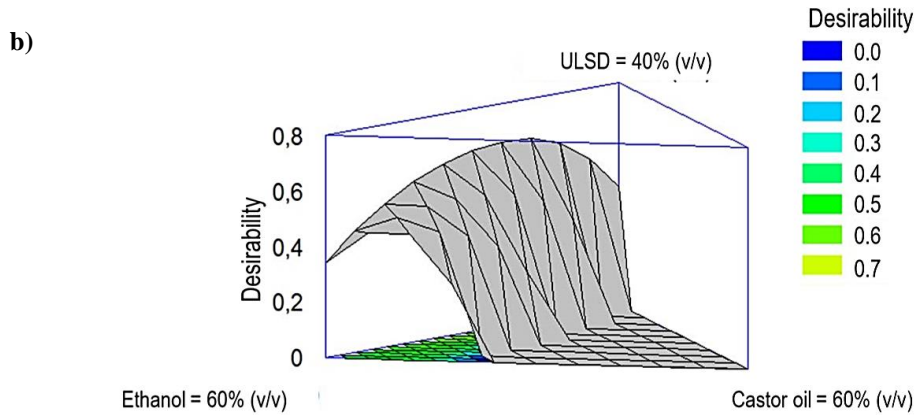


Figure 5. Desirability ternary figure considering mixture composition: a) estimated response surface and b) 3D-response surface.

ULSD: ultra-low sulphur diesel fuel

3.4. Experimental validation of the optimal blend

Optimal blend calculated using Derringer equation simulation has been reproduced under laboratory conditions; predicted physical properties have been validated using experimental data. Table 6 shows experimental values of the most important fuel properties, compared with predicted values provided by optimization statistical studies. Measured properties show more appropriate values than predicted ones, i.e. lower kinematic viscosity, while CFPP and HCV are slightly lower and higher, respectively. These results corroborate synergies between ethanol and castor oil, resulting in a highly renewable fuel blend (70% renewable components), which estimated properties not very dissimilar to conventional diesel fuel. Moreover, the optimal blend has also been fully characterized, to probe its suitability as highly renewable fuel for vehicular applications, as shown in Table 6. In this sense, it may be observed that optimal blend meets limits fixed by European diesel fuel standard (EN 590) in terms of kinematic viscosity, carbon residue, flash point, CFPP, distillation recovered at 250°C and lubricity, while density is marginally higher than fuel standard upper limit. However, water content and density are exceeded, while cetane index is below EN 590 threshold.

Table 6. Experimental values of chemical and physical properties of optimal blend provided by the optimization study

Physical and chemical property		Experimental Value	Predicted value	Threshold fixed in EN 590	Standard test
Kinematic viscosity at 40°C	mm ² /s	4.04 (0.03)*	5.70	2-4.5	EN ISO 3104
Density at 15°C	kg/m ³	854.67 (4.73)		820-845	ISO 3675
Carbon residue	%	0.08 (0.01)		< 0.3	EN ISO
	m/m				10370:2014
Flash point	°C	115.6 (3.7)		>55	ISO 3679
CFPP	°C	-0.33 (0.58)	0.24	*	EN116:1998

Water content	mg/kg	1240 (85)		<200	EN590
HCV	kJ/kg	36360 (122)	35741		ASTM D240
Cetane index		37.07 (2.85)		>46	EN ISO 4264
Distillation recovered at 250 °C	% v/v	55		<65	EN ISO 3405
Lubricity wear scar at 60 °C	µm	430		<460	EN ISO 12156-1

CFPP: cold filter plugging point; HCV: high calorific value

*Maximum values of CFPP for grades A, B, C, D, E, F are +5, 0, -5, -10, -15 and -20 respectively.

Density is slightly above standard upper limit, which is due to the high content of CO (30% v/v) that presents, as shown in Table 1, high density value. A density value above that of ULSD standard means that injector might deliver a larger mass of fuel. However, EN590 standard for diesel fuel establishes as upper value of density the limit of 860 kg/m³ (for temperate climate), being this blend suitable for this reference standard, i.e. Mediterranean countries.

Water content (1.2 % v/v) exceeds several times the maximum allowed amount, maybe due to ethanol water content and, in a lower extend, to that of CO (Table 1). Moreover, some problems may occur during storage in non-effectively sealed tank, because the blend can absorb water from ambient moisture, leading to worsen some blend properties. High content of water can affect blend stability. For this purpose, several stability tests have been carried out varying water content and blend temperature. Stable mixture with 4% (v/v) of water was achieved at 15°C of temperature, whereas a content of 5.2% (v/v) of water may be used in a stable blend at 35°C. Moreover, high water content in fuel may cause problems, i.e. water accumulation and microbial growth in fuel tanks and logistic equipment. However, it is very difficult to remove water content from ethanol, because it constitutes an azeotropic mixture with constant boiling point. Microbial growth can be inhibited by applying chemicals (biocides). In this sense, a recent study has demonstrated the long-term efficacy of biocide based on isothiazoline (MIT/CMIT) and oxazolidine (MBO) chemistries [41] or chlorinated fuel additives [42].

Cetane index is lower than EN 590 threshold due to ethanol low cetane index. In any case, fuel blend cetane index is 37, which may be successfully used in conventional compression ignition engines, with different air and fuel injection strategies or even a higher compression ratio. However, the cetane number of this fuel blend can be improved by the use of cetane improvers such as 2-methoxyethyl ether or 2-Ethylhexyl nitrate [43], the effectiveness of adding cetane improvers in alcohol ternary mixture on performances and exhaust emissions has been successfully demonstrate in the literature [44].

Stability of the optimal blend was evaluated, to check whether phase separation could appear after 14 days. Using n-butanol as additive in ethanol-diesel fuel blends, Huang et al. [21] observed phase separation after 11-14 days. In spite of this, in this work, optimum blend fuel composed by 28.6% ULSD, 41.4% ethanol and 30.0% CO showed no phase

separation after 14 days, thus confirming the suitability of the use of CO in ethanol-diesel fuel blend to both improve miscibility and increase physical stability of the blend.

4. Conclusions

Castor oil enhances solubility and stability of ethanol/diesel fuel blends due to hydroxyl group in ricinoleic acid, which shows affinity with polar OH- group of ethanol. Besides, long fatty acid chains show affinity with diesel fuel (apolar). Presence of ethanol in fuel blend reduces both kinematic viscosity and high energy density of the blend, which is counterbalanced with higher kinematic viscosity and energy density of castor oil and diesel fuel.

Due to the antagonistic effects of each component in the blend, the optimal mixture composition should achieve a compromise of physical and chemical property values. For this reason, ternary-component mixture models to predict kinematic viscosity, heating value and cold flow properties based on blend composition were built. A first-order equation model for heating value prediction has been proposed, while kinematic viscosity and cold flow properties were simulated using a second- and a third-order equation-based models, respectively, suggesting synergetic interactions between blend components.

A Derringer optimization has been performed to successfully propose a ternary fuel blend which simultaneously maximizes heating value and minimizes kinematic viscosity and cold flow properties. Results from optimization have been experimentally validated, providing a stable high renewable content fuel blend composed by 28.6% diesel fuel, 41.4% ethanol and 30% castor oil. Optimal fuel blend fulfil most of EN590 standard, including kinematic viscosity, carbon residue, flash point, CFPP and lubricity. It is concluded that the hydroxyl group provides to castor oil superior ignitability and lubricant properties, as well as higher flash point value, compared to other fatty acids. Thus, it makes it a potential suitable candidate as a blend component in ethanol/diesel fuel blends, enabling the formulation of high renewable fuel blends suitable for automotive and power generation applications. However, especial care in fuel handling and storage should be taken due to mixture high water content. Engine calibration (injection settings and air delivery) and modifications (higher compression ratio) might be needed to overcome fuel blend autoignition characteristics, being cetane index below EN 590 threshold.

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