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Prediction of Storage Stability of Diesel Fuel Mixture Containing Biocomponents of Primary and Secondary Origin by Multi-Criteria Analysis

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Abstract

In the present study the multi-criteria analysis of storage stability of diesel fuel mixture contained biocomponents of primary and secondary origin was studied and predicted. As a result of the experimental design we obtained the nine objects of biodiesel/diesel blends containing 6% (v/v) biocomponent - 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, which were stored at ambient temperature (appr. 15°C – 25°C) in glass bottles, not accessible to sunlight and moisture. These samples were periodically monitored during the whole storage period by measuring a number of properties, such as distillation temperatures (ASTM D86), density (EN ISO 12185) and a total amount (%, v/v) of biodiesel (gas chromatography method). The results show that the maximum the storage stability of diesel fuel mixture contained biocomponents of primary and secondary origin without loss of fuel quality according to the studied properties is up to the 280th day under the specified conditions.

Keywords: *Biodiesel feedstocks; Biodiesel–diesel fuel blends; Multi-criteria analysis; Fuel properties; Storage stability.*

1. Introduction

Biodiesel fuels are an alternative source of energy, composed of a mixture of fatty acid methyl esters (FAME), which can be produced from vegetable oils, animal fats and waste materials by transesterification reaction. At present, the dominant feedstock (about 80%) is vegetable oils, namely soybean oil in USA, rapeseed and sunflower oil in Europe and palm oil in Southeast Asia. Biodiesel is biodegradable, nontoxic and essentially free of metals, sulfur and carcinogenic aromatics [1-3]. Biodiesel can be used both as an alternative fuel and as an additive for diesel fuels. Pure biodiesel (B100) is generally not used as a fuel, but instead it is blended with petroleum diesel in 2, 5 or 20 volume % (B2, B5, B20) [4].

The quality control of liquid fuels on the territory of Bulgaria for compliance with the requirements to them are specified in the Ordinance on the requirements for the quality of liquid fuels, the conditions, the order and the manner of their control.

According to the Renewable Energy Act, the content of biodiesel in diesel fuel must be a minimum of 6% (v/v), and according to the Ordinance, in force since 24.10.2014, a maximum of 7% (v/v).

The Law on Amendments to the Law on Energy from Renewable Sources states that from April 1, 2019, diesel fuel is required to include at least 1% (v/v) of new generation biofuel [5]. In recent years, more and more attention has paid to research related to the use of waste from industry, agriculture, forestry and household. One of the cheap waste raw materials is coffee grounds. In our previous studies [6-7], we synthesized biodiesel from the oil fraction of coffee grounds and investigated its composition.

However, the fuel properties of biodiesel–diesel fuel blends change with the amount of biodiesel in the fuel mixture because biodiesel has different fuel properties compared to conventional diesel fuels. The instability of biodiesel compared to petroleum diesel leads to many questions and concerns about storing fuel that may contain even low concentrations of biodiesel [8]. Therefore, the long-term storage conditions is a key issue for its markets concerning.

The presence of unsaturated fatty acids ester in biodiesel makes it more susceptible to oxidation or autoxidation during long-term storage [9].

There are key properties, which need to be characterize before using biodiesel–diesel fuel blends in a diesel engine. These properties include kinematic viscosity, density, pour point, flash point and distillation characteristics of the blends [10]. Density is a key fuel property, which directly affects the engine performance characteristics. Many performance characteristics, such as cetane number and heating value, are relate to the density [11].

Distillation includes the determination of the range of boiling points for the fuels and is use to characterize the fuel in terms of the boiling temperatures of its components. Distillation characteristics of a fuel are signs of lots of information for engine performance and safety. The distillation range of the diesel fuel affects the fuel properties such as viscosity, flash point and density [12].

The aim of this study is the investigation and prediction of storage stability of diesel fuel mixture containing biocomponents of primary and secondary origin by multi-criteria analysis.

2. Experimental

2.1. Materials

Commercially available diesel fuel delivered from the refinery Lukoil Neftochim Burgas (Burgas, Bulgaria) with physico-chemical and technical characteristics corresponding to BS EN 590, was used in this study as the reference oil to be blended with biodiesel fuel.

Two biodiesels were used – one originally manufactured by Astra Bioplant (Slivo pole, Ruse, Bulgaria), biodiesel from rapeseed oil, with physico-chemical and technical characteristics corresponding to BS EN 14214:2008, and one was laboratory synthesized by transesterification of spent coffee ground oil according to a methodology previously described [6-7]. B100 biodiesel samples sourced from rapeseed oil and spent coffee ground oil were obtained by blending 99% and 1% (v/v), respectively.

Through the preparation of the samples from the previously described raw materials, (Diesel and biodiesel fuel) mixtures containing 6% (v/v) of biodiesel were prepared, which were stored at ambient temperature (appr. 15°C – 25°C) in glass bottles, not accessible to sunlight and moisture. Experimental sampling and analysis of the samples were carried out every month.

2.2. Methods

In order to determine the properties of the diesel fuel, the methyl esters and the blends, the following test methods were used: density at 15°C (EN ISO 12185) [13], distillation temperatures (ASTM D86) [14], and ester content (EN 14103) [15]. To determine of the total amount (% v/v) of biodiesel, added to diesel was done using gas chromatography method reported previously [16]. All the analytical measure point values were determine by the average of three parallel measurements.

To solve the problem associated with stability of diesel fuel mixture containing of primary and secondary biocomponents, we used the method of recommended decision [17-18].

The approach that we used is called "optimistic" because of "optimistic" (high) requirements for recommended values of target parameters (quality indicators) and minimizing the losses, i.e. shortages them.

The choice of operating point (optimal control) x^* (such a multitude of factors ruling in which the target parameters $y_j(x)$ will satisfy the complex requirements of the compromise) in the area of compromise is always associated with certain losses uncompromising optimal solutions. These losses are theoretically zero when the extremes of the m-target functions are coinciding. The losses were obtained in all other cases [17].

The idea of minimizing losses from the optimistically set recommended value y_j^* is illustrated by Figure 1.

Fig. 1. The minimization loss from the recommended value (y_j*)

In our experimental work we set three target parameters, namely:

y_1 – temperature at 95% (v/v) distillation point. For this target parameter we are looking for maximum of 363 Degrees Celsius;

y_2 – density of the product. For this target parameter we are looking for maximum of 845.7 kg/m^3;

y_3 – a total content of biocomponent. For this target parameter we are looking for minimum value of 5.6 % (v/v).

Table 1 shows the requirements for these three target parameters.

Table 1. The requirements to the three target parameters

	Target parameters		
Maximum recommended value y_j^*	y_1, °C	y_2, kg/m^3	y_3, % (v/v)
	364	845.7	5.6

3. Results and discussion

As a result of the experimental design we obtained the nine objects, namely:

Object A – Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 0 days;

Object B – Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 30 days;

Object C – Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 60 days;

Object D - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 90 days;

Object E - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 120 days;

Object F - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 150 days;

Object G - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 180 days;

Object H - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 210 days;

Object I - Diesel fuel mixture contained of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel, stored 240 days.

The results from experiments are present in Table 2.

Table 2. The results of quality parameters for the nine objects using of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel

Object X	**y_1, °C (↑)**	**y_2, kg/m^3 (↑)**	**y_3, % (v/v) (↓)**
Object A	360.0	834.9	6.00
Object B	360.0	834.9	6.00
Object C	360.5	835.1	5.92
Object D	360.5	835.1	5.92
Object E	360.5	835.2	5.90
Object F	361.0	835.3	5.88
Object G	361.0	835.3	5.84
Object H	362.0	835.5	5.82
Object I	362.0	835.6	5.80

The target parameters y_1, y_2, y_3 were transform into losses $\Delta_j(x)$ by the worst result of $y_j(x)$ in equation 1:

$$\Delta_j(x) = \frac{\left[y_j^*(x) - y_j(x)\right]}{\left[y_{j\max}(x) - y_{j\min}(x)\right]}, \qquad (1)$$

where: $y_j(x)$ – the value of the three parameters for each of the nine objects; $y_j^*(x)$ – the worst result for each parameter.

The worst results and limits of the target parameters are present in Table 3. The results for losses (calculated by equation 1), the summary function of losses (calculated by equation 2) are present in Table 4.

Table 3. The limits of the three target parameters /by using of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel

Target parameter, y_j,	y_1, °C	y_2, kg/m^3	y_3, % (v/v)
Limits:			
- y_{jmax}	362	835.6	6.0
- y_{jmin}	360	834.9	5.8

Table 4. The loss function of the objects /by using of a 1% (v/v) of coffee biodiesel and a 5% (v/v) of rapeseed biodiesel/

Object X	y_1	y_2	y_3	Δ_1	Δ_2	Δ_3	F_r°
Object A	360.0	834.9	6.00	2	15.43	-2	5.14
Object B	360.0	834.9	6.00	2	15.43	-2	5.14
Object C	360.5	835.1	5.92	1.75	15.14	-1.75	5.05
Object D	360.5	835.1	5.92	1.75	15.14	-1.60	5.10
Object E	360.5	835.2	5.90	1.75	15.00	-1.50	5.08
Object F	361.0	835.3	5.88	1.5	14.86	-1.40	4.99
Object G	361.0	835.3	5.84	1.5	14.86	-1.20	5.05
Object H	362.0	835.5	5.82	1	14.57	-1.10	4.82
Object I	362.0	835.6	5.80	1	14.43	-1.00	4.81

The average arithmetic function of losses was calculate by the following equation:

$$F_r^0 = \frac{\Delta_1+\Delta_2+\Delta_3}{3} \rightarrow min \qquad (2)$$

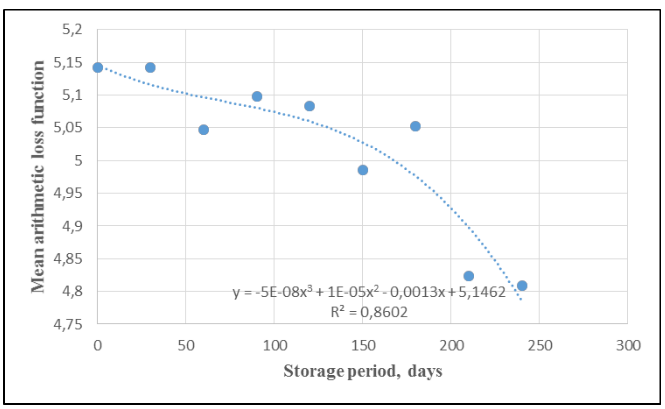

Fig. 2. Dependence of the mean arithmetic loss function from the storage period of the mixtures

Predicting of the maximum storage period according to our proposed model of a multi-criteria solution requires setting thresholds for the arithmetic mean loss function Fr° for each of the studied indicators, at which its loss function Δ will be equal to zero. The results are presented in Table 5. The study of the model of the arithmetic mean loss function (Fr°) from the storage period of the prepared mixtures, is presented in Figure 2.

Table 5. Threshold values of the arithmetic mean loss function for the three target parameters

	Target parameters		
	y_1	y_2	y_3
Threshold value of Fr°	4.48	0	5.81

Following the course of the arithmetic mean loss function (in this case decreasing with increasing days of storage of samples), as well as the losses for the individual indicators, it is seen that the greatest risk is the indicator "Distillation characteristics - Temperature at which distilled 95 % (v/v) of the test sample". Here the threshold value for the arithmetic mean loss function is 4.48 (Table 5).

Using the method of gradual approximation according to the model of Figure 2, with a good probability we can predict the maximum storage period in days, after which the indicator "Distillation characteristics - Temperature at which 95% (v/v) of the test sample is distilled" will exceed the set maximum value of 364°C, as a result of the arithmetic mean loss function, which will fall below the threshold of 4.48. The estimated term in this case will be 280 days.

From the result thus obtained for the maximum storage period of the mixture of pure diesel fuel containing 6% (v/v) biocomponent - 1% (v/v) biodiesel from coffee grounds and 5% (v/v) biodiesel from rapeseed oil, it follows that the fuel will be able to be stored without loss of quality in its performance until the 280th day under the specified conditions (from 15°C to 25°C).

4. Conclusion

The present research demonstrates the successful application of multi-criteria analysis for prediction of storage stability of diesel fuel mixture containing biocomponents of primary and secondary origin by measuring a number of properties, such as distillation temperatures, density and a total amount (%, v/v) of biodiesel.

To predict the maximum storage period according to our proposed model of a multi-criteria solution, threshold values were set for the arithmetic mean loss function Fr° for each of the studied indicators, at which its loss function Δ will be equal to zero. Threshold values of the arithmetic mean loss function for the three target parameters were: 4.48 for distillation characteristics, 0 for density and 5.81 for total amount (% v/v) of biodiesel.

Using the method of gradual approximation according to the model of Figure 2, with a good probability we can predict the maximum storage period in days, after which the indicator "Distillation characteristics - Temperature at which 95% (v/v) of the test sample is distilled" will exceed the set maximum value of 364°C, as a result of the arithmetic mean loss function, which will fall below the threshold of 4.48.

From the result thus obtained for the maximum storage period of the mixture of pure diesel fuel containing 6% (v/v) biocomponent - 1% (v/v) biodiesel from coffee grounds and 5% (v/v) biodiesel from rapeseed oil, it follows that the fuel will be able to be stored without loss of quality in its performance until the 280th day under the specified conditions (from 15°C to 25°C).

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