

A NEW HIERARCHICAL APPROACH FOR MAXIMIZING BIODIESEL MIXING RATIO BASED ON THE FINAL PRODUCT SPECIFICATIONS

Abeer M. Shoaib, Ahmed A. Bhran

*Department of Refining Engineering and Petrochemicals, Faculty of Petroleum and Mining Engineering, Suez University, Suez, Egypt, [*abeershoaib2@yahoo.com](mailto:abeershoaib2@yahoo.com)
abhrane@yahoo.com*

Received September 17, 2013, Accepted December 20, 2013

Abstract

In recent days, fossil fuel resources are decreasing day by day while the population number is continually increasing. This is why many researchers make their efforts to find new sources of energy, especially the renewable ones to compensate the deficiency of fossil energy. Biodiesel fuels are making its place as a key future renewable source and are attracting increasing attention worldwide as blending components or direct replacements for diesel fuel in vehicle engines. The principle objective of the present work is to maximize the biodiesel fraction in the diesel/biodiesel mixtures, while taking into consideration all product quality specifications as they are defined by Greek Legislation. The properties examined were density, viscosity, cloud point, pour point, volatility at temperatures 250, 350 and 360°C, cetane index, cetane number, sulfur, water, higher heating value, flash point and cold filter plugging point. The results concerned the maximum biodiesel ratios of the present work are the same and in some cases are better than that of other authors. In addition to the principle objective stated earlier, this work discusses a new idea directed to predict the maximum mixing ratio of biodiesel when blended with a mixture of more than one type of fossil diesel.

Keywords: Biodiesel; Diesel engine; blends properties; and performance characteristics.

1. Introduction

The biggest problem of the 21st century is linked with increasing prices of mineral fuels, the scarcity of conventional fossil fuels and growing society concern about global warming and transportations. So, different alternate energy sources like wind energy, geothermal energy, solar energy, energy from biomass etc. are under focus these days. The depletion of petroleum reserves and ever growing vehicle population will make renewable energy sources more attractive^[1-4].

In present days, about 95% of the world market is based on compression ignition engine propulsion technologies consuming fossil fuels^[2]. But combustion of fossil fuels inside these engines contributes in higher environmental pollution which leads to climate changes because of air pollution by harmful NO, NO_x, CO, CO₂ and hydrocarbons (HC) emissions that all together lead to frequent hurricanes, heavy rains and deadly floods. To extend the variety of environment friendly energy sources, a special interest among researchers has been focused towards reducing dependence on fossil fuels, replacing them as much as possible by viable and renewable biofuels, which could curb the carbon dioxide CO₂ emission in a global cycle. The environmental advantages that could be achieved by using cleaner and renewable biofuels would be essentially important for reducing air pollution caused by activities in transportation and agricultural sectors in order that the amount of the exhaust gases of off-road vehicles powered by the diesel engines should comply with the ISO 8178 emission standards. Promising alternate fuels for Internal Combustion (I.C.) engines are biodiesel, bio-ethanol, methanol, biogas, producer gas, etc.^[1,5].

Biodiesels offer a very promising alternative to diesel oil, since they are renewable and have properties similar to or better than diesel fuel^[6]. Biodiesel is manufactured from domestically

produced oils such as soybean oil, recycled cooking oils, or animal fats. To manufacture biodiesel, these fats and oils are chemically reacted with a short chain alcohol (such as methanol) and a catalyst to produce biodiesel and a glycerin co-product [7-12]. Biodiesel fuels used as substitutes for conventional petroleum fuel in diesel engines have recently received increased attention. This interest is based on a number of properties of biodiesel including its biodegradability and the fact that it is produced from a renewable resource. These features of biodiesel lead to its greatest advantage, which is its potential for emission reduction [13-15].

Biodiesel contains no petroleum, but it can be blended with petroleum diesel in any percentage. Biodiesel blends from 2 percent to 20 percent can be used in most diesel equipment with no or minor modifications. The biodiesel percentage varies from 2 to 20 according to the properties of both biodiesel and petrol diesel. Statistical regression analysis of data from the numerous research reports and test programs showed that as the percent of biodiesel in blends increases, emissions of HC, CO, and particulate matter (PM) all decrease, but the amount of nitrogen oxides (NO_x) increases. B20 (20% volume biodiesel and 80% volume petrol diesel), one of the most common biodiesel blends, decreases emission constituents of HC, CO, and PM by 21.1, 11.0, and 10.1% respectively, and increases NO_x by 2.0%. When 100% biodiesel is compared to petroleum diesel, there is a 67% decrease in HC, 48% decrease in CO and PM, and 10% increase in NO_x [16,17].

Although there are many advantages in using biodiesel, some problems are achieved in engines used it. The considerable problem of using biodiesel is based on its cold start problems due to the long chains that increase cloud point, pour point, cold-flow plugging point (CFPP) etc. [18]. Biodiesel quality depends on the feedstock utilized and process conditions, which in turn affecting its blending percentage with petrol diesel. For determining the maximum mixing ratio of biodiesel with petrol diesel, it is very important to estimate the quality of the final mixture which consequently based on the properties of these two blending components. Many researchers make their efforts to determine individual properties of biodiesel – diesel blends based on the quality of the two blending components. [19-21]

Present research work is based on a study presented by Bezergianni *et al.* [22]. This work focuses on using a new simulation tool for determining the optimum mixing ratio of biodiesel considering all the constraints imposed on each property of the final biodiesel/petrol diesel blends. The model was evaluated for mixtures between two diesel types (normal diesel and Shell extra diesel) and four biodiesel types (i.e. biodiesel produced from different vegetable oils). The simulation tool used in this paper is software called LINGO software, version 11.

2. Problem statement

The problem given in this paper could be addressed as follows:
Consider we have one type of biodiesel and a number of types of fossil diesel. Data given are as the following:

- The properties of different types of petrol diesel
- Properties of biodiesel to be mixed
- Upper and lower limits for different important properties for produced diesel according to Standards

It is desired to develop a systematic procedure that provides answers to the following questions:

- What is the target for the maximum ratio of biodiesel so as to achieve product specifications within standard limits?
- What are the mixing ratios of other types of diesel?
- What are the properties of the resulted blends?

3. Methodology

LINGO software was utilized to solve the model which predicts the diesel/ biodiesel mixture properties at varying mixing ratio. The proposed optimization model is capable to predict the maximum biodiesel ratio to be blended with petrol diesel without deviation of the constraints imposed over each property of the final mixture according to standard specifications of biodiesel/diesel mixtures. The fossil diesel and biodiesel properties as well as the constraints for the properties of the resulted diesel/biodiesel mixture are the model inputs. The blend mixing rule for each property should also be put in the optimization program.

By studying the behavior of the properties and its variation with different case studies (or blends), it is found that the all properties (except kinematic viscosity and pour point) behave as additive properties. So, the main assumption in the introduced program is that: Density, volatility, cloud point, water content, flash point, higher heating value, cetane index and cetane number are additive properties. All these eight properties can be calculated depending on the following simple blending equation for a blend of two blend components only [21]:

$$prop_A^m = (1 - x).Prop_A^f + x.Prop_A^b \quad (1)$$

where: $Prop_A^f$ is the value of property A for fossil (petrol) diesel; $Prop_A^b$ is the value of property A for biodiesel; x is the mixing ratio of biodiesel to diesel, and $prop_A^m$ is the predicted value of property A for the diesel-biodiesel mixture.

Blend mixing rule for kinematic viscosity is taken as follows [23] :

$$\ln KVm = \sum xi \ln KVi \quad (2)$$

where: KVm is the blend kinematic viscosity; KVi is the kinematic viscosity for each blend component, and xi is the volume fraction for each blend component.

Regarding pour point, correlations have been extracted for each type of biodiesel, since it is found that pour point relation is a quadratic polynomial.

The proposed model can be applied to predict the blend properties as well as the maximum mixing ratio of biodiesel in the final biodiesel/diesel mixture containing more than two blend components. The problem formulation could be summarized in the following equations and their constraints;

The object of the model is to maximize biodiesel ratio (x_1)

$$\text{Maximize } x_1 \quad (3)$$

Subject to

$$\sum xi = 1 \quad (4)$$

$$Dm = \sum Di xi \quad (5)$$

$$\ln KVm = \sum xi \ln KVi \quad (6)$$

$$Vtm = \sum Vti xi \quad (7)$$

where: Vtm is the blend volatility at temperature t

$$CIm = \sum Cii xi \quad (8)$$

$$CNm = \sum Cni xi \quad (9)$$

$$Sm = \sum Si xi \quad (10)$$

$$FPM = \sum FPi xi \quad (11)$$

$$HHVm = \sum HHVi xi \quad (12)$$

$$Wm = \sum Wi xi \quad (13)$$

Constraints for upper and lower bounds of each property are formulated as follows:

$$L_{Dm} \leq Dm \leq U_{Dm} \quad (14)$$

$$L_{KVm} \leq KVm \leq U_{KVm} \quad (15)$$

$$L_{Vtm} \leq Vtm \leq U_{Vtm} \quad (16)$$

$$L_{CIm} \leq CIm \leq U_{CIm} \quad (17)$$

$$L_{Sm} \leq Sm \leq U_{Sm} \quad (18)$$

$$L_{FPM} \leq FPM \leq U_{FPM} \quad (19)$$

$$L_{HHVm} \leq HHVm \leq U_{HHVm} \quad (20)$$

$$L_{Wm} \leq Wm \leq U_{Wm} \quad (21)$$

4. Results and discussion

Our research work is based on a study presented by Bezergianni *et al.* [22] Their model was developed in MATLAB, and the corresponding biodiesel optimization studies were carried out with the MATLAB's optimization toolbox. Their model is employed to predict the properties of diesel-biodiesel mixtures of different mixing ratios and to identify the maximum biodiesel mixing ratio that does not violate the product specifications of the produced mixture. They used two typical fossil diesel types and four biodiesel types. The two fossil diesels are the normal and Shell extra diesel, the properties of which are presented in Table 1. The normal diesel represents the most typical diesel while the Shell extra diesel represents a slightly heavier diesel resulting from heavier crude oil types.

Table 1 Properties of two types of diesel utilized.

Properties	Diesel		EN 590:2004	
	Normal	Shell Extra	Min.	Max.
Density (g/cm ³)	0.8368	0.8424	0.8200	0.8450
Viscosity (mm ² /s)	2.7109	3.4301	2	4.5
Cloud point (°C)	-5	-2		
Volatility				
Volatility 250 °C (%. v/v)	22.14	42.00		65.00
Volatility 350 °C (%. v/v)	92.81	93.42	85.00	
Volatility 360 °C (%. v/v)	96.07	96.67	95.00	
T ₁₀	230.00	219.00		
T ₅₀	282.00	264.00		
T ₉₀	341	337		
Cetane index	54.57	49.09	46	
Cetane number	50.00	50.00	51	
Flash point(°C)	12.00	3.20		10.00
HHV (MJ/kg)	34.97	35.32		
Water (ppm)	0.50	0.50		200
CFPP (°C)	-6	NA		-5/+5

The four biodiesel types (A, B, C and D) are FAME biodiesel produced from different vegetable oils (rapeseed, corn, sunflower, and soy). The properties of the four biodiesel types considered are given in Table 2.

Table 2 Properties of four types of biodiesel utilized.

Properties	Biodiesel				EN 590:2004	
	A	B	C	D	Min.	Max.
Density (g/cm ³)	0.8833	0.884	0.884	0.8845	0.8200	0.8450
Viscosity (mm ² /s)	4.4700	4.1769	4.0303	3.9713	2	4.5
Cloud point (°C)	-6.00	NA	NA	NA		
Volatility						
Volatility 250 °C(%. v/v)	1.15	0.00	0.00	0.00		65.00
Volatility 350 °C(%. v/v)	35.00	66.82	3.13	0.00	85.00	
Volatility 360 °C(%. v/v)	41.67	80.14	66.82	3.13	95.00	
T ₁₀	298.33	341.2	351.20	361.20		
T ₅₀	368.89	345.60	355.60	365.60		
T ₉₀	385.00	380.00	390.00	400.00		
Cetane index	46.17	46.15	46.23	45.95	46	
Cetane number	53.00	65.00	49.00	45.00	51	
Flash point(°C)	176.33	169.63	166.26	164.90		10.00
HHV (MJ/kg)	35.82	35.68	35.6	35.58		
Water (ppm)	281.00	300	300	300		200
CFPP (°C)	-13.00	NA	NA	-4		-5/+5

The principle objective of the present work is to identify the maximum biodiesel mixing ratio that does not violate the product specifications of the produced mixture. Furthermore, this work discusses a new idea directed to predict the maximum mixing ratio of biodiesel when blended with a mixture of the two types of fossil diesel (normal and Shell Extra).

Thus the proposed optimization program has been applied for three different cases;

Case 1: Maximizing biodiesel ratio for each biodiesel type (A, B, C, and D) in a mixture of it with the normal diesel (first type of fossil diesel).

Case 2: Maximizing biodiesel ratio for each biodiesel type (A, B, C, and D) in a mixture of it with the shell extra diesel (second type of fossil diesel).

Case 3: Maximizing biodiesel ratio for each biodiesel type (A, B, C, and D) in a mixture of it with the two types of fossil diesel i.e. shell extra and normal diesel.

This last case has been chosen as a new idea to:

- Determine the effect of blending more than one type of fossil diesel on the maximum biodiesel ratio that can be added to the final mixture without violate its standard specifications.
- Determine the optimum blending ratios of the two types of fossil diesel to maximize biodiesel ratio.

4.1 Case 1: Maximizing biodiesel ratio in a mixture with the normal diesel

This case addresses the case of mixing each type of biodiesel with normal diesel to determine the maximum mixing ratio without violating the lower and upper limits for all the 12 properties. The software used to solve the introduced program is LINGO software, version11. The problem is Non-Linear Program (NLP). The solution is global optimum. The overall mathematical formulation for the types of blends entails a number of 13 variables. Two of them are nonlinear (viscosity and pour point).

It is observed that the sulfur content of the normal diesel if taken as 12 ppm, then no feasible solution could be found when blended with each type of biodiesel (A, B, C, and D). The solution could be feasible only if maximum value of sulfur content for normal diesel is taken as 10 ppm. The sulfur content of normal diesel can be decreased to 10 ppm by hydrodesulfurization or by blending with the other type of fossil diesel (Shell Extra). There is a big error in the work of Bezergianni *et al.* In their work, all the calculations are carried out using 0.7 ppm as the sulfur content of normal diesel. There is no interpretation presented to discuss why Bezergianni *et al.* used this value of normal diesel sulfur content. The program introduced in their work didn't give any results with sulfur content of 12 ppm for normal diesel. They used the sulfur content for normal diesel as 0.7 ppm, which is wrong value and got dependent wrong results.

Table 3 Comparison between our results with Bezergianni *et al.* results concerning case1: Maximizing biodiesel ratio in a mixture of it with the normal diesel.

Properties	ND-A		ND-B		ND-C		ND-D		EN 590:2004	
	Our result	2011	Min	Max						
Density (g/cm ³)	0.8377		0.839		0.8385		0.8373		0.82	0.845
Viscosity(mm ² /s)	2.7376	2.7456	2.791	2.785	2.75	2.7442	2.7228	2.7198	2.00	4.50
Cloud point (°C)	-5.02	-5.02	NA	NA	NA	NA	NA	NA		
Pour point(°C)	-20.67	-20.66	-19.04	-19.10	-19.93	-19.97	-20.567	-20.61		
Volatility										
Volatility 250 °C	21.727	21.73	20.652	20.70	21.33	21.36	21.885	21.87		65.00
Volatility 350 °C	91.672	91.67	91.064	91.04	89.529	89.91	91.741	91.65	85.00	
Volatility 360 °C	95.00	95.00	95.00	95.00	95.00	95.00	95.00	95.00	95.00	
Cetane index	54.404	54.44	54.004	54.21	54.265	54.37	54.4707	54.50	46.00	
Cetane number	50.059	50.06	51.007	50.98	49.963	49.96	49.9424	49.94	51.00	
Sulfur (ppm)	9.823	0.71	9.462	0.78	9.707	0.75	9.907	0.72		10.00
Flash point (°C)	136.73	136.74	138.20	137.63	137.05	136.70	136.273	136.14		
HHV (Mj/kg)	34.986	34.99	35.017	35.01	34.993	34.99	34.977	34.98		
Water (ppm)	6.0171	6.03	20.617	20.00	11.456	11.02	3.948	4.24		200.0
CFPP (°C)	-6.14	-6.16	NA	NA	NA	NA	-5.98	-6.02		
Maximum biodiesel ratio	1.9669	1.97	6.7168	6.51	3.658	3.51	1.151	1.25		

Table 3 shows a comparison between our program results and results of Bezergianni *et al.*, concerning the determination of maximum mixing ratio for each type of biodiesel when blended with normal diesel. First, it is worth to mention that the optimization methodology used in Bezergianni and coworker is tedious and complex. Their optimization aimed at identifying the effect of maximizing the biodiesel mixing ratio considering a single specification bound each time. Table 4 summarizes the Bezergianni and coworker results of a normal diesel that was mixed with biodiesel A. In their work, every property was examined separately in an effort to determine the maximum ratio of biodiesel, which maintains this property within specification limits, while estimating the remaining properties. Each column in Table 4 represents a different maximization run conducted, considering only a single limitation, while providing the remaining properties for that maximum mixing ratio. For example, in the case of the first optimization run, the biodiesel mixing ratio was maximized until the density reached the corresponding upper bound (0.845 g/cm³) as shown in the column "Density". For this case, the maximum mixing ratio achieved was 17.634% of biodiesel. For this mixing ratio, three other properties violated their specifications: volatility at 350 °C (82.60%, v/v); volatility at 360 °C (86.49%, v/v); and cetane number (50.53). After that, a property by property rather than the density is examined to reach a property (volatility at 350 °C) that doesn't violate the rest of the other properties at its upper limit at which the maximum biodiesel ratio can be determined. As previously described, this optimization methodology is very tedious and boring.

Table 4 Normal diesel–biodiesel. A property predictions when maximizing biodiesel mixing ratio while considering individual property specification constraints [22]

Properties	Properties individually examined										
	Density	Viscosity	Volatility 250 °C	Volatility 350 °C	Volatility 360 °C	Cetane index	Cetane number	Sulfur	Flash point	Water	CFPP
1. Density	0.845	0.8833	0.8833	0.8431	0.8377	0.8833	0.8523	0.8833	0.8833	0.8699	0.8833
2. Viscosity	3.0211	4.4700	4.4700	2.9482	2.7456	4.4700	3.2973	4.4700	4.4700	3.962	4.4700
3. Cloud point	-5.17	-6.00	-6.00	-5.13	-5.02	-6.00	-5.33	-6.00	-6.00	-5.71	-6.00
4. Pour point	-17.97	-7.00	-7.00	-18.66	-20.66	-7.00	-15.49	-7.00	-7.00	-10.35	-7.00
5. Volatility											
Volatility 250 °C	18.44	1.15	1.15	19.31	21.73	1.15	15.15	1.15	1.15	7.21	1.15
Volatility 350 °C	82.60	35.00	35.00	85.00	91.67	35.00	73.51	35.00	35.00	51.62	35.00
Volatility 360 °C	86.49	41.67	41.67	88.74	95.00	41.67	77.96	41.67	41.67	57.44	41.67
6. Cetane index	53.41	46.17	46.17	53.69	54.44	46.17	52.60	46.17	46.17	50.07	46.17
7. Cetane number	50.53	53.00	53.00	50.40	50.06	53.00	51.00	53.00	53.00	52.13	53.00
8. Sulfur	0.75	1.00	1.00	0.74	0.71	1.00	0.80	1.00	1.00	0.91	1.00
9. Flash point	143.07	176.37	176.37	141.39	136.74	176.37	149.41	176.37	176.37	164.69	176.37
10. HHV	35.12	35.82	35.82	35.09	34.99	35.82	35.26	35.82	35.82	35.58	35.82
11. Water	49.96	281.00	281.00	38.34	6.03	281.00	94.00	281.00	281.00	200.00	281.00
12. CFPP	-7.31	-13.00	-13.00	-7.01	-6.16	-13.00	-8.43	-13.00	-13.00	-11.12	-13.00
Biodiesel ratio (%)	17.63	100.00	100.00	13.49	1.97	100.00	33.33	100.00	100.00	71.12	100.00

Grey cells indicate the properties that are out of the specification limits. The underlined properties are the properties which are examined each time.

The proposed optimization methodology is easier, in which it searches for the maximum mixing ratio of biodiesel when blended with normal diesel without violating the upper and lower limits of all studied properties simultaneously.

From the results presented in Table 3, our results are nearly the same results of Bezergianni *et al.*. The maximum ratio for individual biodiesel to be blended with normal diesel is determined without violating the constraints of each studied property, except cetane number that will be discussed in details in the following paragraphs. Normal diesel is mixed with biodiesel A and D with maximum mixing ratio of 1.97 and 1.151 respectively that are nearly the same results of Bezergianni *et al.* Moreover, our model gives a better biodiesel maximum mixing ratio in case of biodiesel B and C. As it is listed in table 3, the biodiesel B and C gives maximum mixing ratios of 6.72 and 3.66 respectively when mixed with normal diesel compared to the values of Bezergianni *et al.* which are 6.51 and 3.51 respectively.

As declared by Bezergianni *et al.*, the problematic property is sulfur. The sulfur content of the diesel component is 12 ppm, which is out of the specification limits. However, as biodiesel is normally low sulfur, diesel–biodiesel blends with significant amounts of biodiesel component can solve the excess of sulfur in diesel. In the blends studied, sulfur is within specification limits only for higher biodiesel mixing ratios. Nevertheless, higher biodiesel ratios cause problems to other properties. Therefore, blending biodiesel to diesel can have positive effects as far as the sulfur is concerned, but an optimal ratio has to be chosen so that other properties are not affected. The optimal value is identified only when the sulfur content of normal diesel is decreased

from 12 to 10 ppm. This notice is completely ignored in the research work of Bezergianni and coworkers and consequently there is a big error in their results.

Concerning the cetane number, it is impossible to reach the cetane number lower limit of the final mixture if normal diesel is mixed with biodiesel C or D at any mixing ratio. This is because the cetane number of normal diesel (50) as well as the two types of biodiesel (for C= 49 and for D=45) are lower than the standard minimum value (51) required for the final diesel/biodiesel mixture. Biodiesels A and B have cetane numbers of 53 and 65 respectively. When considering only cetane number limitations for these two types of biodiesel, higher mixing ratios are obtained. On the other hand, at these higher mixing ratios of biodiesel, there are other properties violate their standard limits. For example, as presented in the work of Bezergianni *et al.*, the maximum mixing ratio of biodiesel A obtained was 33.33% (v/v) to reach the lower limit of cetane number (51). At this mixing ratio, however, three other properties were violated: density (0.8523 g/cm³); volatility at 350 °C (73.51%, v/v); and volatility at 360 °C (77.96%, v/v). These three violations are due to the fact that biodiesel is the heavier compound and in such high mixing ratios, this will cause the violation of all properties associated with it (such as density and volatility).

Our results tabulated in table 3 showed that biodiesel B is the only biodiesel type gives a cetane number of 51.007 which is higher than the standard lower limit of diesel/biodiesel mixture cetane number at mixing ratio of 6.72. Regarding the other three types of biodiesel (A, C and D), at their maximum mixing ratios with normal diesel, the cetane numbers violate their lower limits. As stated in the research work of Bezergianni *et al.*, the problem related to cetane number can be easily solved by using additives, called cetane number improvers which are always utilized to upgrade the diesel fuel cetane number.

4.2 CAS 2: Maximizing biodiesel ratio in a mixture of it with the Shell Extra diesel

This part discusses the case of mixing each type of biodiesel with shell extra diesel for predicting the maximum mixing ratio for each biodiesel type without violating the limits of the 12 studied properties.

Regarding with an investigated vision, the comparison of our results and the results of Bezergianni *et al.* are listed in table 5. It is clear that there are some errors in the results of Bezergianni *et al.* The noticeable examples are the calculated values of pour point and cetane number. The above researchers stated that they used the equations indicated in Alptekin and Canakci, [24] to calculate the diesel/biodiesel blend pour point and cloud point. But by returning to this reference, no equations are found to calculate neither the pour point nor the cloud point. The pour point of Shell Extra diesel is -6 and for biodiesels B, C and D are -1, -1 and 0 respectively. So, it is reasonable that the pour point for the blend of Shell Extra diesel and any biodiesel type of B, C and D at any mixing ratio is higher than -6. But the results of Bezergianni and coworkers showed that pour point for these blends are lower than -6. The same notice can be applied on the calculated values of cetane number of the Shell Extra/biodiesel blends. The cetane number of Shell Extra is 50 and for biodiesels C and D are 49 and 45 respectively. As the cetane number of the blend is calculated as an additive property, so the cetane number of Shell Extra blended with biodiesel C or D at any mixing ratio must be lower than 50. The results of Bezergianni and coworkers showed calculated values of these blends higher than 50.

Our accurate results concerning the predicting of the maximum mixing ratio of each biodiesel type when blended with Shell Extra diesel and all diesel/biodiesel blends properties including pour points and cetane numbers are presented in Table 5. Considering maximum mixing ratio of each biodiesel type with Shell Extra diesel, it is clear that our results is very near to the results of Bezergianni and coworkers in spite of the variation in the calculated values of some properties as stated above. As shown in Table 5, all the 12 studied properties of all blends are in their suitable limits except the cetane number which violate its lower limit. As indicated earlier, the cetane number of the Shell Extra diesel/biodiesel mixture can reach easily above its lower limit by the addition of cetane number flow improvers as it is familiar for diesel fuel.

Table 5 Comparison between our results with Bezergianni et al results concerning case2: Maximizing biodiesel ratio in a mixture of it with the Shell Extra diesel.

Properties	SE-A		SE-B		SE-C		SE-D		EN 590:2004	
	Our result	2011	Min	Max						
Density (g/cm ³)	0.8436	0.844	0.845	0.845	0.8446	0.845	0.8431	0.843	0.82	0.845
Viscosity (mm ² /s)	3.457	3.46	3.472	3.46	3.461	3.45	3.439	3.43	2	4.5
Cloud point (°C)	-2.12	-2.11	NA	NA	NA	NA	NA	NA		
Pour point (°C)	-6.03	-6.28	-5.69	-6.23	-5.72	-6.22	-5.89	-6.10		
Volatility										
Volatility 250 °C	40.75	35.91	39.375	34.69	39.65	34.93	41.25	36.34		65.00
Volatility 350 °C	91.646	91.65	91.757	91.76	88.368	88.38	91.752	91.76	85.00	
Volatility 360 °C	95.00	95.00	95.636	95.63	95	95.00	95	95.00	95.00	
Cetane index	48.914	49.07	48.906	49.09	48.929	49.09	49.033	49.08	46	
Cetane number	50.091	52.03	50.937	51.81	49.944	51.83	49.911	51.88	51	
Sulfur (ppm)	3.133	3.13	3.125	3.13	3.132	3.13	3.178	3.18		10.00
Flash point (°C)	153.195	153.19	153.542	153.18	153.24	152.87	152.692	152.56		
HHV (MJ/kg)	35.335	35.34	35.342	35.34	35.336	35.33	35.324	35.32		
Water (ppm)	9.017	9.00	19.218	19.22	17.256	17.22	5.847	5.84		200
CFPP (°C)	NA	NA	NA	NA	NA	NA	NA	NA		
Maximum biodiesel ratio	3.0363	3.03	6.25	6.25	5.594	5.58	1.785	1.78		

As a conclusion of this part, with our proposed simple model, the maximum mixing ratios of biodiesel A, B, C and D (3.036, 6.25, 5.56, and 1.785) are carefully determined to be blended with Shell Extra diesel and all blends properties is properly calculated. However, the methodology of Bezergianni and coworkers is tedious and did not give suitable results.

4.3 Case 3: Maximizing biodiesel ratio in a mixture of it with the blend of the two fossil diesels (normal and Shell Extra diesels)

This case concerning the determination of the maximum biodiesel ratio of each type of the four biodiesel types that can be mixed with a blend of Normal and Shell Extra diesels. Sulfur content of normal diesel is taken as 12 ppm and there is no need to reduce it to 10 ppm. The sulfur content of the normal/Shell Extra diesels blend will be lower than 10 ppm due to the lower sulfur content of Shell Extra diesel (3.2 ppm). No problems in running the proposed program. In other words, the problem of high sulfur diesel is overcome by mixing it with another type of diesel have lower value of sulfur content.

Table 6 Maximizing biodiesel B ratio in a mixture of it with a blend of normal (22.55%) and Shell Extra diesels (68.17%).

Properties	Determined value	EN 590:2004	
		Min	Max
Density (g/cm ³)	0.845	0.82	0.845
Viscosity (mm ² /s)	3.313	2	4.5
Cloud point (°C)	NA		
Pour point (°C)	NA		
Volatility			
Volatility 250 °C	33.623		65.00
Volatility 350 °C	90.813	85.00	
Volatility 360 °C	95.00	95.00	
Cetane index	49.991	46	
Cetane number	51.04	51	
Sulfur (ppm)	5.072		10.00
Flash point (°C)	150.337		
HHV (MJ/kg)	35.274		
Water (ppm)	28.307		200
CFPP (°C)	NA		
Maximum biodiesel ratio	9.28		

NA: not available

Mixing more than one type of diesel with biodiesel results in higher biodiesel mixing ratio than if just one type of them is used. The only biodiesel type which gives a higher mixing ratio when blended with a mixture of the two fossil diesel types is biodiesel B. the maximum biodiesel B ratio is 9.28% when blended with 22.55% normal diesel and 68.17% Shell Extra diesel as shown below in Table 6. Pour point and cloud point of that mixture were not determined because there is no sufficient data for extracting equation for each property. The not determining values of pour and cloud points do not affect the performance of the blend mixture because there is no limitations imposed on these properties. The rest of all the mixture properties were determined with values not violating the specification limits with a cetane number higher than 51 (lower limit) and a sulfur content of 5.072 ppm which is below its higher limit (10 ppm).

5. Conclusion

This study is based on the work of Bezergianni *et al.* [22]. In their work, a model developed in MATLAB to predict the properties of mixtures of biodiesel when blended with a fossil diesel at different mixing ratio and also to determine the maximum mixing ratio of biodiesel when blended with petrol diesel without violating the final mixture specifications is used. The model was demonstrated for a normal diesel and a Shell extra diesel mixed with four types of biodiesel. The present work introduced an optimization program to solve such a program and overcome the problems, difficulties and mistakes found in the work of Bezergianni *et al.* The simulation tool used in present work, is LINGO software, version11. After comparing the introduced results with the results of Bezergianni and coworkers, it is clear that the proposed model is successfully applied for predicting 12 properties of diesel/biodiesel mixtures giving nearly the same values of maximum mixing ratios of biodiesel, and in some cases better than that of Bezergianni [22]. All the predicted properties of the biodiesel/diesel mixtures were consistent with the expected quality of the mixtures except of sulfur content and cetane number in the case of blending each type of biodiesel with normal diesel. The problem of higher sulfur content of normal diesel (12 ppm) can be solved by reducing it to 10 ppm by hydrodesulfurization process. The cetane number can be easily improved by using additives such as cetane number improvers. This paper solves some defects presented in the work of Bezergianni [22], for example the problem of using sulfur content of normal diesel of 0.7 ppm which is very far from its accurate value of 12 ppm.

The new idea presented in this work is the determination of maximum biodiesel mixing ratio when blended with more than one type of fossil diesel. The only biodiesel gives the highest mixing ratio of 9.28% is biodiesel B when blended with 22.55% normal diesel and 68.17% Shell Extra diesel. All the determined properties of that mixture are in the specification limits without violating the cetane number and sulfur content limits. The sulfur content of the normal/Shell Extra diesels blend (5.072) is lower than 10 ppm (higher limit) due to the lower sulfur content of Shell Extra diesel (3.2 ppm).

Nomenclature

D	density	CI	cetane index	W	water content
kV	kinematic viscosity	CN	cetane number	CFPP	cold filter plugging point
CP	cloud point	S	sulfur content		
PP	pour point	FP	flash point		
V	volatility	HHV	higher heating value		

Subscripts

m	refers to mixture	t	refers to temperature
i	refers to component number		

References

- [1] Labeckas, G., Slavinskas, S., Mazeika, M., and Laurinaitis, K. (2011). Performance and emission characteristics of diesel engine fuelled with ethanol-diesel-biodiesel blend, *Engineering For Rural Development*, Jelgava, 26.-27.05
- [2] Mytelka L. and Boyle, G. (2006). Hydrogen fuel cells and transport alternatives: Issues for developing countries, Policy Brief No. 3, United Nations University, The Netherlands.
- [3] Kannan, T. K. and Marappan, R. (2010). Study of Performance and Emission Characteristics of a Diesel Engine using Thevetia Peruviana Biodiesel with Diethyl Ether Blends, *European Journal of Scientific Research*, 43, 4, 563-570.

- [4] Sheehan J, Cambreco V, Duffield J, Garboski M, Shapouri H. (1998). An overview of biodiesel and petroleum diesel life cycles. A report by US Department of Agriculture and Energy, Washington, DC, 1–35.
- [5] Pandey, S., Sharma, A. and Sahoo, A., K. (2012). Experimental investigation on the performance and emission characteristics of a diesel engine fuelled with ethanol, diesel and jatropha based biodiesel blends, *International Journal of Advances in Engineering & Technology*, 4, 2, 341-353.
- [6] Jaichandar, S. and K. Annamalai, (2011). The Status of Biodiesel as an Alternative Fuel for Diesel Engine – An Overview, *Journal of Sustainable Energy & Environment*. 2, 71-75.
- [7] Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50, 14–34.
- [8] Yin, P., Chen, L., Wang, Z., Qu, R., Liu, X., Xu, Q. and Ren, R. (2012). Biodiesel production from esterification of oleic acid over aminophosphonic acid resin D418, *Fuel* 102, 499–505.
- [9] Hu, S., Wen, L., Wang, Y., Zheng, X. and Han, H. (2012). Gas–liquid countercurrent integration process for continuous biodiesel production using a microporous solid base KF/CaO as catalyst, *Bioresource Technology*. 123, 413–418.
- [10] Shuit, S. H., Ong, Y. T., Lee, K. T. (2012). Subhash, B. and Tan, S. H. Membrane technology as a promising alternative in biodiesel production: A review, *Biotechnology Advances*. 30, 1364 – 1380.
- [11] Motasemi, F. and Ani, F. N. A. (2012). Review on microwave-assisted production of biodiesel, *Renewable and Sustainable Energy Reviews*. 16, 4719–4733.
- [12] Vasconcellos, A., Paula, A. S., Filho, R. A. L., Farias, L. A., Gomes, E., Donato A.G., and Nery, J. G. (2012). Synergistic effect in the catalytic activity of lipase *Rhizomucor miehei* immobilized on zeolites for the production of biodiesel, *Microporous and Mesoporous Materials*. 163, 343–355.
- [13] Xue, J., Grift, T. E. and Hansen, A. C. (2011). Effect of biodiesel on engine performances and emissions, *Renewable and Sustainable Energy Reviews*. 15, 1098–1116.
- [14] Balasubramanian, K. A. (2012). Dual Biodiesel Blends in Diesel Engine - Performance and Emission Analysis, *European Journal of Scientific Research ISSN 1450-216X*. 75, 3, 400-408.
- [15] Yoon, S. H., Park, S. H., and Lee, C. K. (2008). Experimental Investigation on the Fuel Properties of Biodiesel and Its Blends at Various Temperatures, *Energy & Fuels*. 22, 652–656.
- [16] Li, Y.X., McLaughlin, N.B., Patterson, B.S. and Burt, S.D. (2006). Fuel efficiency and exhaust emissions for biodiesel blends in an agricultural tractor, *Canadian Biosystems Engineering*. 48, 2.15-2.22.
- [17] EPA. (2002). A comprehensive analysis of biodiesel impacts on exhaust emissions. EPA420-P-02-001. Washington, DC: United States Environmental Protection Agency. <http://www.obeconline.org/biodieselepreport.pdf> .
- [18] Demirbas. A., (2007). Importance of biodiesel as transportation fuel, *Energy Policy*. 35, 4661–4670.
- [19] Demirbas. A., (2008). Relationships derived from physical properties of vegetable oil and biodiesel fuels, *Fuel*. 87(8-9), 1743-1748.
- [20] Demirbas. A. (2008). Mathematical Relationships Derived from Biodiesel Fuels, *Energy Sources*. Part A. 30, 56–69.
- [21] Kalogeras, K., Bezergianni, S., Kazantzi, V. and Petros A., On the prediction of properties for diesel / biodiesel mixtures featuring new environmental considerations, 20th European Symposium on Computer Aided Process Engineering – ESCAPE20.
- [22] Bezergianni, S., Kalogeras, K., and Petros A. (2011). On maximizing biodiesel mixing ratio based on final product specifications, *Computers and Chemical Engineering*. 35, 936–942.
- [23] Clements, L. C. (1996). Blending rules for Formulating Biodiesel Fuel. Lincoln, NE 68583-0726.
- [24] Alptekin, E., and Canakci, M. (2008). Determination of the density and the viscosities of biodiesel–diesel fuel blends, *Renewable Energy*. 33, 2623.