Chemistry and Technology of Fuels and Oils, Vol. 49, No. 5, November, 2013 (Russian Original No. 5, September–October, 2013)

MATHEMATICAL MODELS FOR CALCULATING THE DENSITY OF PETROLEUM DIESEL FUEL/BIODIESEL BLENDS

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We measured the density of blends of petroleum diesel fuel and two types of biodiesel, with different ratios of the components. Using statistical data, we have obtained empirical equations allowing us to calculate the density of these blends.

Key words: *diesel fuel, biodiesel, statistical analysis, density, linear equation.*

Interest in alternative fuels and engines which can run on biofuels and their blends with petroleum fuels has been stimulated by the need to control environmental pollution and by the pursuit of energy independence [1, 2]. Accordingly, in this work we have analyzed the relationship between the content of two types of biodiesel in blends with petroleum diesel fuel and the density of these blends. The major objective of this work was to obtain linear equations relating the density of the blend to the biodiesel content and allowing us to make a preliminary estimate of the applicability of formulated biofuel recipes.

As we know, biodiesel is obtained by transesterification of oil or fat by alcohol, usually methanol, in the presence of a catalyst: sodium or potassium hydroxides, or increasingly more often, alkoxides [3, 4]. Besides biodiesel, the product contains unreacted starting materials plus alcohol, catalyst, and glycerol. The glycerol is separated in the biodiesel purification stage, but nevertheless commercial biodiesel may contain glycerol in trace amounts.

Biodiesel obtained in the laboratory was analyzed to determine how its characteristics corresponded to the specifications of the standards. Table 1 gives the characteristics of the two types of biodiesel studied, the specifications of the standard EN14214 for biodiesel, and also the characteristics of the petroleum diesel fuel used in this work and the specifications of the Greek standard for this fuel. Biodiesel based on blended feedstock (synthetic biodiesel) was obtained from a mixture of 30% waste cooking oil, 5% waste household cooking oil, 5% palm oil, 5% animal fat, and 55% sunflower oil.

The following blends were formulated using the fuel samples provided:

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0009-3092/13/4905–0399

Table 1

Indices	Analyte fuel			EN14214 specifications	Specifications of Greek standard* for petroleum diesel fuel	ASTM analysis method
	biodiesel based on		petroleum diesel fuel			
	soybean oil	blended feedstock (synthetic biodiesel)				
Density at 15°C, g/mL	0.87814	0.86324	0.82266	0.860-0.900	0.820-0.845	D1298-99 (2005)
Kinematic viscosity at 40°C, mm^2/s	4.54	4.36	2.49	1.9-6	2-4.5	D445-06
Water content, mg/kg	296	322	50	max 500	max 200	D 1744-92 (2000)
Total acid number, mg KOH/g	0.24	0.08	-	max 0.50	-	D 664

Note. Standard FEK 332/B/11-2-2004, harmonized with EN 590:1999 [5].

Table 2

Biodiesel content in blend, vol.%	Density at 15°C, g/mL		
	blend I	blend II	blend III
0	0.82266	0.82266	0.82266
10	0.82477	0.83763	0.83133
20	0.82754	0.83986	0.83198
30	0.82990	0.84224	0.84478
40	0.83416	0.84558	0.84410
50	0.84386	0.84716	0.84922
60	0.84724	0.84948	0.85008
70	0.84996	0.85160	0.85562
80	0.85786	0.85357	0.85911
90	0.86278	0.85672	0.86270
100	0.87814	0.86324	0.86754

I : petroleum diesel fuel + biodiesel based on soybean oil;

II : petroleum diesel fuel + biodiesel based on blended feedstock (synthetic biodiesel);

III : petroleum diesel fuel + the two types of biodiesel in 1:1 ratio.

The densities of the blends, measured according to ASTM D1298-99 (2005) at a temperature of 15°C, are given in Table 2.

Preliminary statistical analysis allowed us to propose three linear equations of the following general form that relate the density to the composition of the three studied blends:

$$Y_i = b_0 + b_1 X + U_t$$

where Y_i is the dependent variable (the density); X is the independent variable (the mix, i.e., the composition of the blend); b_0, b_1 are constants; U_t is the residual which we assume follows a normal distribution.

X and Y represent the attributes of the variables which they express. According to the attributes, the signal connecting the two model variables has a plus (+) sign, and the connection can be expressed by an equation of the form $Y = \alpha X + \beta$. Obviously according to this equation, a higher value of X (i.e., higher biodiesel content in the blend) means a higher density of the blend. For blend I:

$$Y = 0.817461 + 0.000521X \quad (1)$$

For Eq. (1), the value of the Fisher statistic is F = 174.0493 and the p-value is equal to 0, which is evidence for statistical significance of this model.

For blend II, we can propose the equation:

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$$Y = 0.830749 + 0.00031X \quad (2)$$

Analogously for blend III:

$$Y = 0.826332 + 0.00041X \quad (3)$$

It was established that the dependent variable Y is statistically significant in all the equations. The positive values of the coefficient of determination R^2, close to 1, are evidence for partial or complete dependence of the density of the blend on the biodiesel content in the blend. In other words, the closer R^2 is to 1, the higher the significance of the model. The coefficient of determination (R^2) for model (1) is equal to 0.95; 0.9 for model (2); 0.96 for model (3). Consequently, in these equations, the independent variable determines the dependent variable by respectively 95%, 90%, and 96%.

Table 3

Indices	Model (1)		Model (2)		Model (3)	
	b_0	b_1	b_0	b_1	b_0	b_1
Student's t-statistic	349.58	13.192	420.85	9.345	542.73	16.211
p-value	0*	0	0	0	0	0

Note. * Not equal to 0, but very close to 0

Table 4

Lag	Standardized residuals			Squared standardized residuals		
	autocorrelation	partial correlation	*LB(n)*	autocorrelation	partial correlation	*LB(n)*
			Model (1)			
1	0.145	0.145	0.3009	-0.090	-0.090	0.1161
2	-0.039	-0.061	0.3245	-0.176	-0.186	0.6103
3	-0.234	-0.225	1.3016	0.129	0.097	0.9076
4	-0.100	-0.039	1.5069	-0.052	-0.067	0.9637
5	0.088	0.100	1.6925	-0.199	-0.179	1.9039
6	-0.298	-0.412	4.2323	0.051	-0.016	1.9792
7	-0.326	-0.326	8.0212	0.018	-0.033	1.9907
8	-0.085	0.024	8.3690	-0.191	-0.170	3.7219
9	0.061	-0.135	8.6384	-0.157	-0.249	5.4942
			Model (2)			
1	-0.025	-0.025	0.0087	0.172	0.172	0.4244
2	-0.075	-0.075	0.0970	0.062	0.034	0.4860
3	-0.103	-0.108	0.2873	-0.007	-0.024	0.4869
4	-0.224	-0.241	1.3144	-0.016	-0.014	0.4925
5	-0.161	-0.215	1.9333	-0.116	-0.113	0.8131
6	-0.103	-0.212	2.2364	-0.146	-0.112	1.4186
7	-0.030	-0.194	2.2688	-0.133	-0.086	2.0482
8	0.119	-0.082	2.9394	-0.089	-0.050	2.4225
9	0.198	0.034	5.7509	-0.098	-0.079	3.1084
			Model (3)			
1	-0.215	-0.215	0.6621	-0.019	-0.019	0.0052
2	0.361	0.330	2.7334	-0.081	-0.082	0.1102
3	-0.513	-0.459	7.4349	0.189	0.188	0.7515
4	-0.011	-0.300	7.4373	-0.132	-0.140	1.1083
5	-0.223	0.085	8.6185	-0.118	-0.091	1.4392
6	-0.018	-0.269	8.6274	-0.104	-0.171	1.7458
7	-0.010	-0.221	8.6311	-0.170	-0.151	2.7769
8	0.040	0.026	8.7065	-0.023	-0.035	2.8023
9	0.060	-0.148	8.9612	-0.004	-0.014	2.8034

Table 3 gives the Student's t-statistics and the p-values for the variables b_0 and b_1 for the three models obtained. The p-value for models (1) and (2) is close to 0, which confirms that they have high statistical significance.

In order to study the applicability of the models, we carried out diagnostic tests. First we found the standardized residuals and the squared standardized residuals (Table 4). As shown by the results, the values of the statistical term of the Ljung—Box (LB) test on the standardized residuals and squared standardized residuals of model (1) are not statistically significant [6]. In lags 1-3 and 5-9, we can see serial correlation of errors, which is confirmed by the values of the Q-statistic in the LB(n) column in Table 4. Serial correlation of errors is also characteristic for the squared standardized residuals, which is evidence for heteroskedasticity. As in model (1), the values of the squared standardized residuals for models (2) and (3) are not statistically significant [6]. As for the standardized residuals, we observe serial correlation of errors.

In order to identify the presence of heteroskedasticity, we carried out the Breusch—Godfrey serial correlation test (Table 5). We see that autocorrelation is not observed for all the models. According to the Breusch-Godfrey tests, for all the models the probability is greater than 0,763661, i.e., the probability is greater than 0.05 (5%).

Testing of the proposed models was continued using the autoregression conditional heteroskedasticity (ARCH) test (Table 6), and the results of the Durbin—Watson test on the standardized residuals and squared standardized residuals was confirmed by the independence test. Heteroskedasticity is not observed according to the test results.

Figure 1 shows the results of the stability studies for models (1)-(3): the trajectory followed by each variable. The graphs plot the growth in the variables with serial number. Thus we have confirmed that there is a linear relationship between the variables Y and X. As we see, the lines on the graphs have the shape of straight lines or straight lines with inflection points, which is associated with the chemical composition of the fuels.

Table 5

Indices	Model (1)	Model (2)	Model (3)
F-statistic / probability	0.280289 / 0.763661	0.022905 / 0.977429	0.637135 / 0.556915
Obs*R-squared/ probability	0.815594 / 0.665114	0.071518 / 0.964873	1.694044 / 0.428690

Note. Obs*R-squared is the LM test statistic for the null hypothesis of no serial correlation. Zero probability strongly indicates the presence of serial correlation in the residuals.

Table 6

Squared standardized residual for lag:				F-statistic	Obs.*_R-squared
-1	-2	-3	-4		
		Model (1)			
4.06E-09	2.79E-09	2.56E-09	1.37E-09	0.98	4.64
(-0.78)	(0.82)	(-0.30)	(-0.97)		
		Model (2)			
3.97E-11	2.80E-11	2.61E-11	1.30E-14	1139.122	6.99
(0.03)	(0.07)	(0.46)	(62.45)		
		Model (3)			
1.04E-09	1.01E-09	9.60E-10	1.08E-12	4.88	6.34
(-0.04)	-0.206573	0.440442	-1.064107		

Note. The t-statistics are given in parentheses.

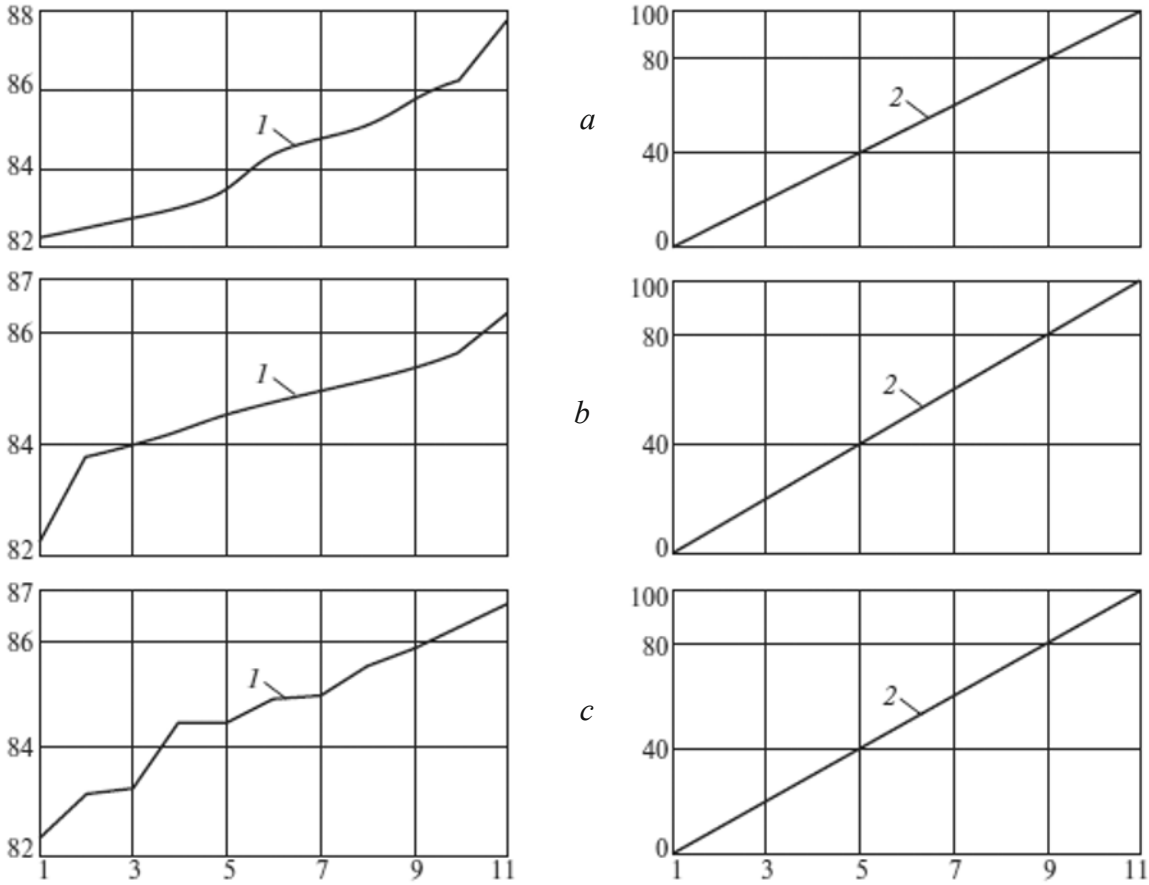

Fig. 1 Results of stability studies for the models: *a*) (1); *b*) (2); *c*) (*3*): density (lines *1*); biodiesel content in blend (lines *2*).

The calculated values of the density of the blended fuels can be used to estimate their calorific value, since the heat of combustion Q can be calculated sufficiently accurately from the equation [8]:

$$Q = a - bd^2$$

where a, b are constants; d is the density at 15°C.

For blend III, we can expect high accuracy of the heat of combustion calculation, since the coefficient of determination R^2 of model (3) is the highest (0.96) among the three models obtained. For a small data file, achieving a high coefficient of determination is complicated. In other words, increasing the number of experiments and accordingly increasing the sample size results in higher accuracy of the models. The equations obtained can be used for a preliminary estimate of the applicability of formulated recipes for blended fuels.

REFERENCES

1. David L. Greene, "Motor Fuel Choice: An econometric analysis," *Transportation Research, Part A: General,* **23**, No. 3, 243–253 (1989).
2. E. Stiakakis and P. Fouliras, "The impact of environmental practices on firms' efficiency: The case of ICT-producing sectors," *Operational Research: An International Journal*, **9**, No. 3, 311-328 (2009).

3. C. G. Tsanaktsidis, S. G. Christidis, and G. T. Tzilantonis, "Study about effect of processed biodiesel in physicochemical properties of mixtures with diesel fuel in order to increase their antifouling action," *International Journal of Environmental Science and Developmen*t, **1**, No. 2, 205-207 (2010).
4. J. J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements, and G. Knothe, "Biodiesel production technology," Subcontractor Report prepared for the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy by Midwest Research Institute, National Renewable Energy Laboratory NREL/SR-510-36244, Battelle (July 2004).
5. Gerhard Knothe, "Analyzing biodiesel: Standards and other methods review," *JAOCS*, **83**, No. 10, 823-833 (2006).
6. G. M. Ljung and G. E. P. Box, "On a measure of a lack of fit in time series models," *Biometrika*, **65**, 297-303 (1978).
7. Robert Engle, "Autoregressive conditional heteroskedasticity with estimates of the variance of United Kingdom inflation," *Econometrica*, **50**, 987-1007 (1982).
8. T. Papaevangelou, *Fuels-Lubricants*, Eugenides Foundation, Athens (1995), p. 173.