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Validation of thermophysical properties for biodiesel production using waste vegetable oil

Bahman Najafi, Javad Jannatkhah, Hassan Malek Ajhdar

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Abstract

In this present study, we applied validation techniques like specificity, accuracy, precision and robustness to find the thermophysical properties of biodiesel produced using waste vegetable oil and waste cooking oil collected from local restaurants in Ardabil City, Iran. The validation techniques helped in improving the accuracy of the estimation of thermo-physical properties. The properties investigated in this study includes, density, viscosity, flash point, cloud point and heating value. We believe that this validation technique will have wide applications in biodiesel production.

Keywords: Validation, vegetable oils, biodiesel fuel, thermo-physical properties

Introduction

Method validation is an important requirement in pharmaceutical industries for any information submitted to international regulatory agencies in support of new product marketing or clinical trials applications. These validation techniques include, specificity, accuracy, precision and robustness (Shabir 2005; Marfil et al. 2016). One of the most important factors in evaluating the quality of biodiesel is to find the basic thermophysical properties and compare them with US ASTM standards (Chhetri et al. 2008). Researchers usually perform experiments directly and compare the results with ASTM standards. For improving the accuracy of the results and for reproducibility, for the first time, we are applied these validation techniques in biodiesel research for accurate estimation of thermophysical properties.

Materials and Methods

Used sunflower, corn, soybean and canole oils and waste cooking oil were collected from various restaurants present in Ardabil, Iran and pure oils were purchased from local market, Ardabil, Iran. The following thermophysical properties including, viscosity, density, flash point, cloud point and heat value were found for used cooking oil and pure oil samples and compared with US ASTM standards.

The validation parameters of the proposed estimation of thermophysical properties were selected based on the recommendations of the current legislation of Resolution RE 899, of May 25, 2003 and of the document DOQ-CGCRE-008, according to Category I - quantitative tests for determination of active ingredient in pharmaceutical products or raw materials. Thus, specificity, precision, accuracy, and robustness were evaluated (Marfil et al. 2016). The first step in method validation is to prepare a protocol, preferably written, with the instructions in a clear step by step format, and approved prior to their initiation (Shabir 2005).

Specificity: Specificity is the ability to measure accurately and specifically the compound of interest in the presence of other components that may be expected to be present in the sample matrix. In this currently study the thermophysical properties were measured from five different restaurants from Ardabil, Iran. The analysis of the results were done using ANOVA and Statistica 6.0, Statsoft, USA was used for this study (Green 1996).

Precision: Precision is the degree of agreement among individual test results when an analytical method is used repeatedly to multiple samplings of a homogeneous sample. The thermophysical property of the oil was measured five times for checking the precision (Green 1996).

Accuracy: Accuracy is the closeness of test results to the true value. The thermophysical properties of each oil measured in specificity component were compared with the pure oil data and ANOVA was applied to check the level of deviation (Green 1996).

Robustness: Robustness is the capacity of a method to remain unaffected by small, deliberate variations in method parameters; a measure of the reliability of a method. The thermophysical properties of these oils were measured by adulterating all these oils with 2% of palm oil to validate the

Bahman Najafi, Javad Jannatkhah, Hassan Malek Ajhdar

Department of Biosystem Engineering, Mohaghegh Ardabili University, Ardabil, Iran

Table 2: Validation of the thermophysical properties of waste oil collected from local market in Ardabil, Iran .

Validation Parameter	Conditions	Thermophysical Property				
		Flash point (^{0}C)	Kinematic viscosity (mm^2/s)	Cloud point (^{0}C)	Density (kg/l)	Heating value (MJ/Kg)
Corn Oil						
Specificity	Restaurant - 1	0.912	5.6	-7	38.00	144
Specificity	Restaurant - 2	0.911	5.7	-7	38.12	145
Specificity	Restaurant - 3	0.912	5.4	-7	38.10	144
Specificity	Restaurant - 4	0.913	5.6	-6	38.2	144
Specificity	Restaurant - 5	0.911	5.6	-7	38.13	148
Precision	Replicate - 1	0.913	5.7	-6	38.14	144
Precision	Replicate - 2	0.912	5.4	-8	38.00	146
Precision	Replicate - 3	0.912	5.5	-7	38.11	147
Precision	Replicate - 4	0.912	5.5	-7	38.41	144
Precision	Replicate - 5	0.911	5.6	-7	38.11	148
Accuracy	Pure Oils	**0.861**	**34.9**	**-6**	**39.48**	**320**
Robustness	Adulterated*	0.901	6.2	-8	38.14	152
Sunflower Oil						
Specificity	Restaurant - 1	0.873	5.87	-8	39.34	137
Specificity	Restaurant - 2	0.863	5.82	-8	39.32	137
Specificity	Restaurant - 3	0.888	5.83	-8	39.31	136
Specificity	Restaurant - 4	0.875	5.87	-8	39.38	137
Specificity	Restaurant - 5	0.875	5.87	-7	39.41	135
Precision	Replicate - 1	0.873	5.88	-8	39.40	134
Precision	Replicate - 2	0.876	5.85	-7	39.34	137
Precision	Replicate - 3	0.845	5.86	-8	39.51	137
Precision	Replicate - 4	0.888	5.88	-8	39.34	136
Precision	Replicate - 5	0.862	5.87	-8	39.34	136
Accuracy	Pure Oils	**0.692**	**32.6**	**-5**	**38.81**	**322**
Robustness	Adulterated*	0.801	5.62	-8	39.33	138
Soybean oil						
Specificity	Restaurant - 1	0.882	4.09	-5.5	38.09	137
Specificity	Restaurant - 2	0.882	4.01	-5.5	38.12	136
Specificity	Restaurant - 3	0.881	4.09	-5	38.11	137
Specificity	Restaurant - 4	0.881	4.09	-5	38.09	135
Specificity	Restaurant - 5	0.871	4.08	-5	38.09	134
Precision	Replicate - 1	0.861	4.08	-5.5	38.11	133
Precision	Replicate - 2	0.881	4.09	-5.4	38.12	137
Precision	Replicate - 3	0.861	4.09	-5.5	38.09	137
Precision	Replicate - 4	0.884	4.11	-5	38.09	137
Precision	Replicate - 5	0.881	4.12	-5.5	38.10	135
Accuracy	Pure Oils	**0.852**	**32.9**	**-4**	**44.06**	**318**
Robustness	Adulterated*	0.841	4.15	-5.5	37.78	138
Canola oil						
Specificity	Restaurant - 1	0.875	4.58	-11	35.49	142
Specificity	Restaurant - 2	0.877	4.51	-11	35.49	147
Specificity	Restaurant - 3	0.875	4.52	-11	35.48	147
Specificity	Restaurant - 4	0.877	4.57	-10	35.41	142
Specificity	Restaurant - 5	0.876	4.57	-11	35.42	142
Precision	Replicate - 1	0.875	4.58	-10	35.55	142
Precision	Replicate - 2	0.877	4.51	-10.5	35.49	148
Precision	Replicate - 3	0.876	4.52	-11	35.49	148
Precision	Replicate - 4	0.875	4.58	-11	35.49	147
Precision	Replicate - 5	0.888	4.55	-10.5	35.41	149
Accuracy	Pure Oils	**0.912**	**35.1**	**-8**	**38.85**	**328**
Robustness	Adulterated*	0.845	4.58	-11	34.25	148
Restaurant waste cooking oil						
Specificity	Restaurant - 1	0.861	5.51	-5	38.73	168
Specificity	Restaurant - 2	0.862	5.5	-5	38.73	167
Specificity	Restaurant - 3	0.863	5.51	-5.5	38.77	168
Specificity	Restaurant - 4	0.861	5.51	-5.5	38.12	166
Specificity	Restaurant - 5	0.864	5.41	-5	38.14	167
Precision	Replicate - 1	0.854	5.42	-5	38.7	165
Precision	Replicate - 2	0.861	5.44	-5	38.41	164
Precision	Replicate - 3	0.861	5.51	-5.5	38.1	163
Precision	Replicate - 4	0.865	5.51	-5.8	38.45	168
Precision	Replicate - 5	0.865	5.61	-5	38.41	169
Accuracy	Pure Oils	**0.883**	**36.3**	**-4**	**39.05**	**315**
Robustness	Adulterated*	0.863	5.6	-5	38.5	168

*Adulterated with 2% palm oil

Table 3: One way ANOVA

Corn Oil						Canola oil				
	Value	**F**	**Effect**	**Error**	**p**	**Value**	**F**	**Effect**	**Error**	**p**
Intercept	0.000000	18093610	4	5.00000	0.000000	0.000000	3931498	5	4.00000	0.000000
Flash Point ((^{0}C)	0.000001	184	12	13.52026	0.040000	0.000154	18	15	11.44364	0.000010
Intercept	0.000023	34891.59	5	4.00000	0.005000	0.000001	1134587	5	4.00000	0.000154
Kinematic viscosity (mm2/s)	0.000004	69.17	15	11.44364	0.03240	0.000000	184	15	11.44364	0.003200
Intercept	0.000294	6802.000	3	6.00000	0.000522	0.000031	25511.78	5	4.00000	0.000000
Cloud point (^{0}C)	0.001389	22.834	9	14.75303	0.004110	0.000987	8.60	15	11.44364	0.000387
Intercept	0.000000	256224773	5	4.00000	0.007410	0.000000	7177394	5	4.00000	0.000000
Density (kg/l)	0.000006	58	15	11.44364	0.000000	0.000001	100	15	11.44364	0.000441
Intercept	0.000002	381876.2	5	4.00000	0.000000	0.000002	486502.1	5	4.00000	0.000000
Heating value (MJ/Kg)	0.000007	56.2	15	11.44364	0.000000	0.000000	165.1	15	11.44364	0.000410
Sunflower Oil						**Waste oil**				
Intercept	0.000000	8517166	5	4.00000	0.005000	0.000000	9660210	5	4.00000	0.000000
Flash Point ((^{0}C)	0.000000	185	15	11.44364	0.003500	0.000103	20	15	11.44364	0.000005
Intercept	0.000001	1130966	5	4.00000	0.000000	0.000006	208272.2	4	5.00000	0.000000
Kinematic viscosity (mm2/s)	0.000001	135	15	11.44364	0.000000	0.000003	136.2	12	13.52026	0.000000
Intercept	0.000099	8105.477	5	4.00000	0.002600	0.000015	53560.10	5	4.00000	0.000000
Cloud point (^{0}C)	0.001201	7.955	15	11.44364	0.000560	0.000837	9.17	15	11.44364	0.000282
Intercept	0.000007	276696.8	3	6.00000	0.004000	0.000004	346804.8	4	5.00000	0.000000
Density (kg/l)	0.001426	22.6	9	14.75303	0.041000	0.004960	7.2	12	13.52026	0.000487
Intercept	0.000001	1103866	5	4.00000	0.005000	0.000002	391510.5	5	4.00000	0.000000
Heating value (MJ/Kg)	0.000001	135	15	11.44364	0.000400	0.000000	238.2	15	11.44364	0.000000
Soybean oil										
Intercept	0.000000	263382284	5	4.00000	0.000000					
Flash Point ((^{0}C)	0.000000	696	15	11.44364	0.000000					
Intercept	0.000007	487340.1	2	7	0.00045					
Kinematic viscosity (mm2/s)	0.000005	1043.0	6	14	0.00052					
Intercept	0.002786	1252.945	2	7	0.000000					
Cloud point (^{0}C)	0.323702	1.768	6	14	0.177925					
Intercept	0.000002	1648390	2	7	0.000000					
Density (kg/l)	0.000364	120	6	14	0.004141					
Intercept	0.000001	540595.1	5	4.00000	0.000000					
Heating value (MJ/Kg)	0.000001	135.0	15	11.44364	0.003200					

robustness of the process (Green 1996). All experiments were done in triplicates and the average value was reported.

The following thermophysical parameters were included in this current study.

Table 1: US ASTM standards (Volli and Purkait 2014)

Characteristics	Standard Test Method	Allowable limit	Unit	Conditions or Methods
Flash point	ASTM D-92	Minimum 130	°C	Open-cup method
Kinematic viscosity	ASTM D-445	1.9 - 6	mm^2/s	At 40^{0}C
Cloud point	ASTM D-2500	-	°C	-
Density	ASTM D1298	0.86-0.90	kg/l	At 15^{0}C
Heating value	ASTM D-240	-	MJ/Kg	Bomb calorimeter

Results and Discussion

Validation results

The list of validation studies were shown in Table 2. The analysis of variance was done to the validation data for better understanding of the variations within the groups and for checking the statistical validity of the data.

Based on statistical analysis using one-way ANOVA, the models were highly significant with very low probability values of <0.01. It was noted that the model terms of independent variables were significant at 95% confidence level. Table 2, it is evident that the flash point of pure oil is higher than biodiesel due to high viscosity and long molecular chains of lipids. It is observed that the density and cloud point of biodiesel is higher than the density and cloud point of pure oil. The values were compared with US ASTM standards and were found to be satisfying.

Conclusion

The validation techniques were successfully applied for evaluating the thermophysical properties of biodiesel. We believe that the validation will help in confirming the accuracy of the data and the diversity of the results can be expanded still further for other thermophysical properties of biodiesel.

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