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Spectroscopic Techniques for Stability and Quality Assessment of Biodiesel

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With the high demand for fuel supply, as well as environmental concerns, the development and production of biodiesel produced from renewable, bio-based raw materials are of great concern. The increase in greenhouse gases has become the driving force for the shift from fossil fuels to alternative fuels. Aging of the biofuels on storage is a major concern for the biofuel production sector as it will degrade the fuel properties. Biofuel get oxidized easily, which affect its properties such as kinematic viscosity and acid value. By adding suitable antioxidants, biodiesel ageing can be controlled to a great extent. The oxidation stability of the biofuels needs to be tested in order to maintain the quality under storage. In this study, the suitability of various spectroscopic techniques such as photochemiluminescence and UV/visible spectrophotometry to access the oxidation stability of the biodiesel produced from rubber seed oil have been assessed. The results suggest that photo chemiluminescence and spectroscopic method can be effectively used to quantify the oxidation stability of the biofuels. This study also confirms that antioxidant use will assure long term storage stability of biodiesel fuels.

Keywords: Biodiesel, Crude rubber seed oil, Oxidation stability, Photochemiluminescence.

INTRODUCTION

Biodiesel is known to have many advantages such as low toxicity, sustainable supply, harmless degradation products, *etc*. Because of these qualities it is considered to be more environmental friendly than fossil fuels. However, compared to its fossil counterpart, it has got a lower stability, reflected in a higher rate of degradation due to aging, primarily by oxidation. The oxidation of biodiesel can produce various acids or polymers, which, if in high enough concentration, can cause fuel system corrosion and deposits, which in turn can lead to filter clogging and fuel system malfunctions. Antioxidants are found to be effective for inhibiting the oxidation process. Depending on the feedstock, some biodiesel may contain naturally occurring antioxidants and crude rubber seed oil is one of the favourable options. In this study, the oxidation stability of the biodiesel produced from rubber seed oil has been analyzed. Also a comparison of the stability of the biodiesel with and without antioxidants by measuring its properties over the time period has been done. For this, the photochemiluminescence and other spectroscopic techniques have been utilized to analyze the storage stability of the biodiesel produced from rubber seed oil [1,2].

Chemiluminescence can be defined as the emission of ultraviolet, visible or infrared radiation from a molecule or atom as the result of the transition of an electronically excited state, having been produced as a consequence of a chemical reaction. This chemical reaction produces energy in sufficient amount to induce the transition of an electron from its ground state to an excited electronic state. This electronic transition is often accompanied by vibrational and rotational changes in the molecule. Photochemiluminescence can be defined as the combination of the light irradiation system by chemiluminescence system and it enables to detect the fluorescence from samples with very high sensitivity [3-5].

EXPERIMENTAL

Crude rubber seed oil is non-edible oil prepared from the commercially available rubber seeds in a private firm. Methanol and butylated hydroxy toluene are purchased from Chemind Chemicals. Commercially available calcium oxide was dipped in ammonium carbonate solution then the mixture was stirred for 0.5 h at room temperature. After filtration and drying at 385 K till constant weight, the dried solid was milled and sieved then calcined at 1123 K for 1.5 h. After cooling in a dessicator to room temperature the base CaO is ready to use. High temperature calcinations of CaO improved the performance of the catalyst. *n*-Hexane is being used as the diluent for the luminescence spectroscopy.

Experiments performed: Biodiesel used for this study was prepared from crude rubber seed oil by a two stage transesterification process using methanol and modified calcium oxide as catalyst (Fig. 1). Samples of biodiesel collected for biodiesel analysis are shown in Fig. 2. Two equal volumes of biodiesel prepared were taken in separate containers for further analysis. To one of the containers, 250 ppm butylated hydroxy toluene is added as an antioxidant. The physical and chemical properties of both the biodiesel samples were analyzed using standard methods. The two samples were stored for 6 months and their properties after 6 months were again analyzed. UV/visible photoluminescence spectroscopy and FTIR spectroscopy studies of the prepared and aged samples were carried out and the oxidation stability were quantified from the analysis of the peak positions [6-8].

Fig. 1. Experimental set up for biodiesel production process

Fig. 2. Biodiesel samples for analysis A, B, A*, B* (A – Fresh sample, B – Sample after 6 months, A* - Fresh sample + 250 ppm BHT and B* - Sample + 250 ppm BHT after 6 months)

Chemiluminescence is defined as the emission of light as a result of chemical reaction. It measures label-free photon emission during the termination stages of oxidation. An excited triplet carbonyl is formed through the combination of radicals in a termination step and on relaxation to ground state, a photon is emitted. The sample can be subjected to elevated temperatures and gas flow and induction period can be determined by tangents set manually by the operator. Sample preparation is minimal, no reagents are required and measurement is continuous [9,10].

Mechanism of oxidation stability: Primary oxidation means that per oxidation occurs by a set of reactions categorized as initiation, propagation and termination. Fig. 1 shows that first set involves the removal of hydrogen from a carbon atom to produce a carbon free radical. If diatomic oxygen is present, the subsequent reaction to form a peroxy radical becomes extremely fast even not to allow significant alternatives for the carbon-based free radical. The peroxy free radical is not reactive compared to carbon free radical, but is sufficiently reactive to quickly abstract hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction terminates when two free radicals react with each other to yield stable products.

Vegetable oils consist of natural antioxidants that tend to increase the stability of fuel but as the vegetable oils are subjected to higher temperature conditions, the natural antioxidants present in the oil start deteriorating at a faster rate, thereby, decreasing its stability. As the biodiesel comes in contact with engine, it gets heated leading to the decrease in fuel stability.

RESULTS AND DISCUSSION

The physico-chemical properties of the fresh and aged samples of biodiesel with and without antioxidant addition are tabulated in Table-1. On comparing the aged samples of the pure biodiesel as well as the one with 250 ppm butylated hydroxy toluene we could observe that most of the physical chemical properties of the both these samples are within the acceptable range. The carbon residue and water sedimentation are found to be slightly higher than the accepted levels for the pure biodiesel samples after aging. This shows that the biodiesel produced from rubber seed oil has got a better stability without the addition of any antioxidants. Fluorescence spectra of the samples are shown in Fig. 3.

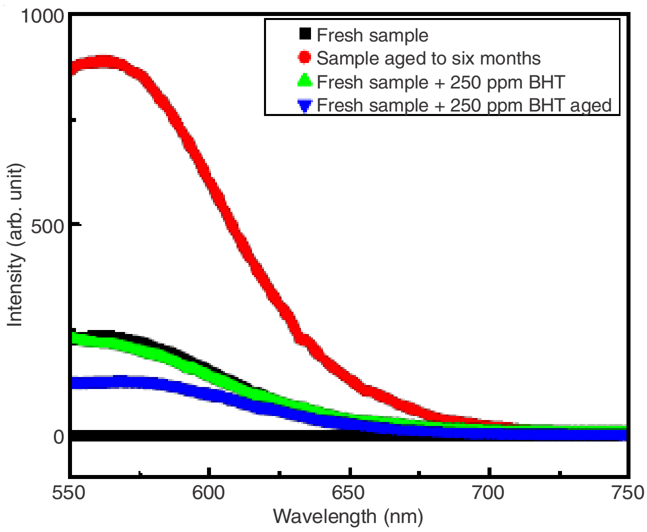

Fig. 3. Fluorescence spectra

Fig. 4(I) and 4(II) show the typical photoluminescence absorption and emission spectra for the fresh and aged biodiesel samples with and without antioxidant additives (butylated hydroxy toluene) for an excitation wavelength of 530 nm. From this Fig. 4(I) (B), it is clear that all the biodiesel samples show a fluorescence band within the measured range of 400 to 800 nm. We could also see an increase in fluorescence intensity for the aged samples (B and B*) compared to that of

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF THE BIODIESEL SAMPLES

BD100	Test	Limit	A	B	A*	B*
Kinematic viscosity [(40 °C) mm^2/s]	D445	1.9-5.0	4.16	4.23	4.11	4.03
Flash point (°C)	D93	120 <	175	173	180	183
Carbon residue (wt %)	D4530	< 0.1	< 0.01	< 0.1	0.01	< 0.01
Sulfur content (mg/kg)	D5453	< 10	< 1	0.0	0.0	0.0
Copper strip corrosion (50 °C, 3 h)	D130	< 1	1	1	1	1
Acid value (mg KOH/g)	EN14104	< 0.50	0.22	0.31	0.26	0.30
Total glycerin (wt %)	EN14105	< 0.24	< 0.01	0.21	0.03	0.02
Oxidation stability (110 °C, h)	EN14112	6 <	1.36	3.4	9	12
Cetane number		48 <	50	48	52	49
Calorific value (MJ/kg)	D240	-	39.8	38.2	39.4	40.1
Water and sediment (vol. %)	D1796	< 0.05	< 0.01	0.086	< 0.01	< 0.005

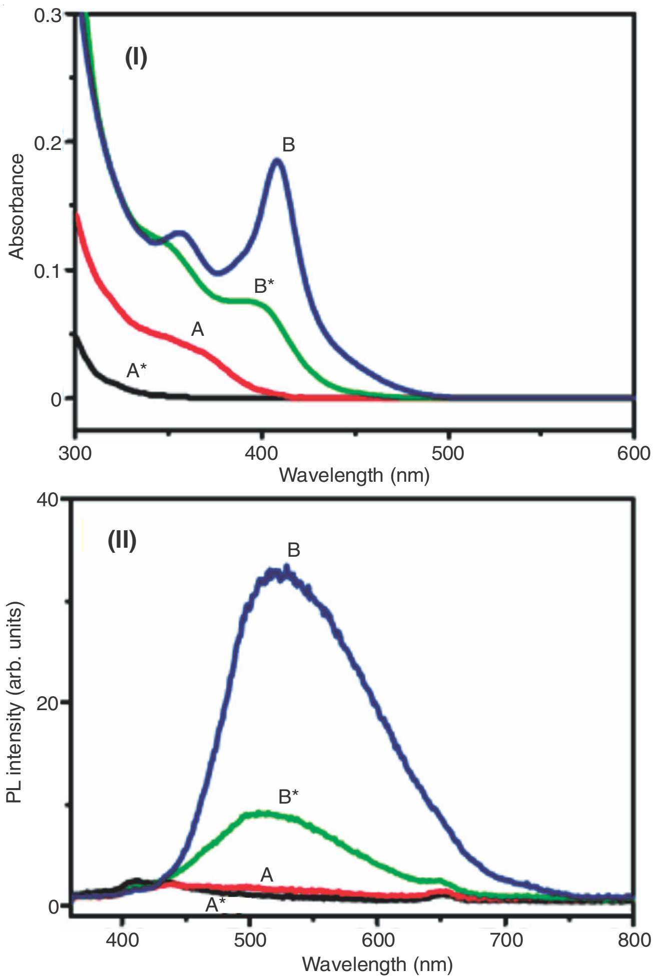

Fig. 4. Photoluminescence (I) absorption and (II) emission spectra of the biodiesel samples: A – Fresh sample, B – Sample after 6 months, A* - Fresh sample + 250 ppm butylated hydroxy toluene & B* - Sample after 6 months + 250 ppm butylated hydroxy toluene

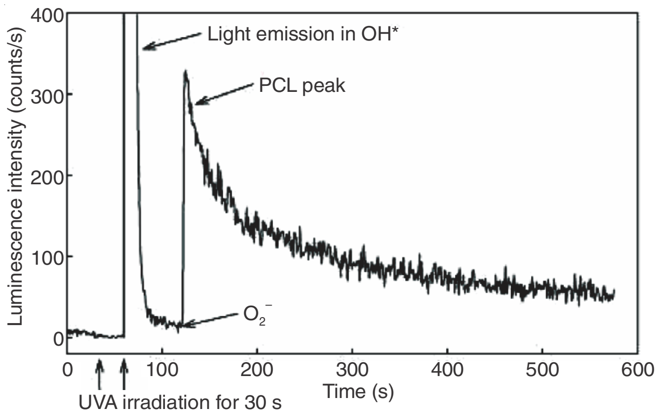

Fig. 5. Luminescence intensity *vs.* time for sample B*

fresh samples with and without additives (A and A*), which implies the formation of some fluorescent active substances upon aging. Similarly, from the photoluminescence absorption spectrum also it can be observed that the aged samples have very good absorption around 400 nm. Fig. 5 shows the luminescence intensity *vs*. time for the sample B*. From this study it can be concluded that aged biodiesel samples show good photoluminescence emission and absorption characteristics and this can be taken as a measure of the quality of the biofuel. As fresh biofuel has not had any emission or absorption bands were as the aged samples do have prominent absorption and emission characteristics [4]. So this study implies that pure biodiesel is prone to some chemical changes may be due to oxidation and can be effectively prevented from the addition of some antioxidants. Moreover the antioxidants are not degrading the physical chemical properties of the biodiesel as well.

Conclusion

The stability and fuel quality of the biodiesel produced from rubber seed oil has been analyzed using chemical fluorescence spectroscopy. This study reveals that physico-chemical properties of the biodiesel produced from crude rubber seed oil is comparable upon ageing with that of mixed with antioxidant substances. But the intensity of the biodiesel sample aged for 6 months is found to be higher than that of the fresh as well as antioxidant added aged samples, which shows that pure biodiesel samples are prone to oxidation. Photochemiluminescence method is about 1000 times faster than the normal conditions, because the presence of an appropriate photosensitizer. Photochemiluminescence is a very quick and sensitive measurement method (in the nanomolar order). The advantage of photochemiluminescence method lies in its high sensitivity, high reproducibility and its short measuring times. The time that is required to perform single measurement of a sample is about 3 min. This time is compared to the other methods available on the market, which is above 6 h, is very short. Not only the measuring times, but also the sample preparation is profitable. It does not require complicated and time-consuming sample preparation. Moreover, the measurement is independent on a particular pH value or temperature. Hence, it opens up the possibility to predict the oxidation stability of biofuels.

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