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Research Article

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Storage stability of fatty acid methyl esters from *Hevea brasiliensis*

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ABSTRACT

Biodiesel is a fast emerging alternate fuel but with its own disadvantage of having limited oxidative stability. Fatty acid methyl esters (FAMEs) obtained from high acid value (46.41 mgKOHg^{-1}) rubber seed oil (RSO) was characterized by GC-MS and ^{1}H-NMR. Fuel properties analysed were found to fit the required ASTM D6751 standard. Moreover, the possibility of monitoring the conversion efficiency of RSO to its corresponding methyl esters using FT-IR and NIR techniques was also analysed. As an important specification of bio-fuel quality, the fuel must have a minimum of three hours of oxidative stability (110^{o}C) as per ASTM D6751 standard. Influence of metal contaminants, air, moisture and light on oxidative stability was studied on biodiesel having high iodine value. Acid value, peroxide value and induction period were recorded for samples under six different environments such as open (light exposed), closed (light exposed), open (dark), closed (dark), open (metal contaminated) and closed with metal contamination. Significant impact was observed only when metals are present as contaminants. Extent of degradation (oxidation) is higher when the samples are contaminated by metals, limiting the storage stability to thirty days. Higher oxidative stability was achieved under dark in the closed environment but in the absence of any metal contaminant.

Keywords: oxidative stability, autoxidation, hydrolysis, degradation, induction period.

INTRODUCTION

Biodiesel (Fatty acid alkyl esters) an emerging fuel [1-4] has its main disadvantage because of its inadequate oxidative stability, besides its acceptable fuel properties. The fatty acid profile plays the major role in its stability against oxidation. Extensive unsaturation, especially the presence of bis-allylic carbons deteriorates biodiesel besides other factors such as light, heat, oxygen and metal contaminants [5, 6]. Number of studies so far emerged based on different sources including both edible and non-edible oil has revealed that unsaturation plays an important role in assessing the fuel quality since it initiates the formation of free radicals and consequently hydroperoxides and organic compounds, such as aldehydes, ketones, or acids [6-10]. Also, dimerization and oligomerization can be initiated, from peroxides formed from the reactions of free radicals through autoxidation [11-15] which degrades the fuel adversely resulting in the formation of insoluble products causing problems within the fuel system, especially in the fuel injection pump [16].

Both edible as well as non-edible sources have been used as sources for bio-fuel production. But in the light of possible strains in food production while using edible sources, especially in developing countries, non-edible sources have advanced for efficient fuel production. In this way, *Hevea Brasiliensis* (Natural Rubber) a cheap feedstock from a very popular plantation in the experimental locality is attempted as an alternate fuel source.

Fatty acid methyl esters (FAMEs) from rubber seed oil (RSO) is found to have high degree of unsaturation with iodine value 121 $gI_2 10^{-2} g^{-1}$ and it is important to study its oxidative stability for long term use. The mechanism for the autoxidation of FAMEs has been well established in lot of studies [6, 17]. In the present study, storage stability of the FAMEs is established and, the influence of some of the important parameters over the oxidative stability such as light, air and metal contamination has been studied by monitoring the acid value, peroxide value and induction period. Also the analytical possibility of monitoring the reaction progress in order to claim maximum efficiency for transesterification of rubber seed oil has established.

EXPERIMENTAL SECTION

FAMEs used for the study was produced from rubber seed oil of high acid value 46.41mgKOHg^{-1} by adopting the two step protocol – transesterification *via* acid esterification because of its high acid value [23] (Acid value – 46.41 mgKOHg^{-1}). All the chemicals used were of analytical grade. The reaction was monitored by ^{1}H-NMR also using Brucker FT AC-200 and MSL 300 MHz instruments, apart from GC-MS technique and further characterization was done by GC-MS hyphenated technique using Shimadzu, QP-2010. Possibility of monitoring the transesterification for producing FAMEs from RSO, by FT-IR (Thermo Nicolet, Avatar 370) and NIR (Elico SL 153) techniques was also analysed. Fuel properties were also tested as per ASTM standard to meet ASTM standard D6751. Acid value, peroxide value and induction period (120°C) were recorded at regular intervals for samples maintained in six different environments *viz*. light (open), light (closed), dark (open), dark (closed), metal container (open-dark) and metal container (closed-dark). Transition metal analysis was performed by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) using Perkin Elmer - Optima 2100 DV. Induction period (120°C) was measured by following IP 306 method explained by Mittelbach and Gangl [24], storing the FAMEs samples at 30°C.

RESULTS AND DISCUSSION

Some of the fuel properties of the FAMEs tested are found to be in the acceptable limit specified by ASTM D6751 (Table 1). The relevant signals used for monitoring the reaction progress are those of methoxy group in the methyl esters ($-COOCH_3$) at 3.7 ppm as a sharp singlet and of the α-carbonyl methylene group ($-CH_2-COOCH_3$) present in all fatty ester derivatives at 2.3 ppm (Fig.1). Absence of any signal at 4.1-4.3 ppm indicates the absence of mono-, di- and tri glyceride protons [18], which confirms the completion of transesterification reaction. The GC-MS analysis reveals the normal fatty acid profile - 18:2, 18:1, 18:0, 16:0 and 18:3 (Fig.2). The fatty acid profile (Table 2) proves its high extent of unsaturation, with all the double bonds in polyunsaturated fatty esters oriented in bis-allylic position. For 18:2 fatty ester double bonds are situated in C-9 and C-12 having one bisallylic carbon at C-11 and for the 18:3 fatty ester the double bonds are situated in C-9, C-12 and C-15 exhibiting two bis-allylic carbons at C-11 and C-14.

Table 1. Fuel characteristics of FAMEs obtained from RSO

Property	ASTM D6751 Limit	FAMEs from Rubber Seed Oil
Acid number [mgKOH/g]	0.5 max	0.10
Iodine Value [gI_2/100g]	-	121
Peroxide value [meqvO_2/kg]	-	0.60
Flash Point [°C]	130 min	179
Kinematic Viscosity, 40°C [mm^2/s]	1.9 - 6.0	5.45
Moisture and Sediments [wt. %]	0.03 max	0.022
Sulphated ash [wt. %]	0.020 max	0.013
Free Glycerin [wt%]	0.020 max	0.004
Total Glycerin [wt%]	0.24 max	0.129
Oxidative Stability Index, 110°C [h]	3 min	6.10

Table 2. Fatty acid profile of FAMEs obtained from Rubber seed oil

Fatty acid	%
Linoleic acid	46.26
Oleic acid	23.20
Palmitic acid	10.35
Stearic acid	10.80
Linolenic acid	9.40

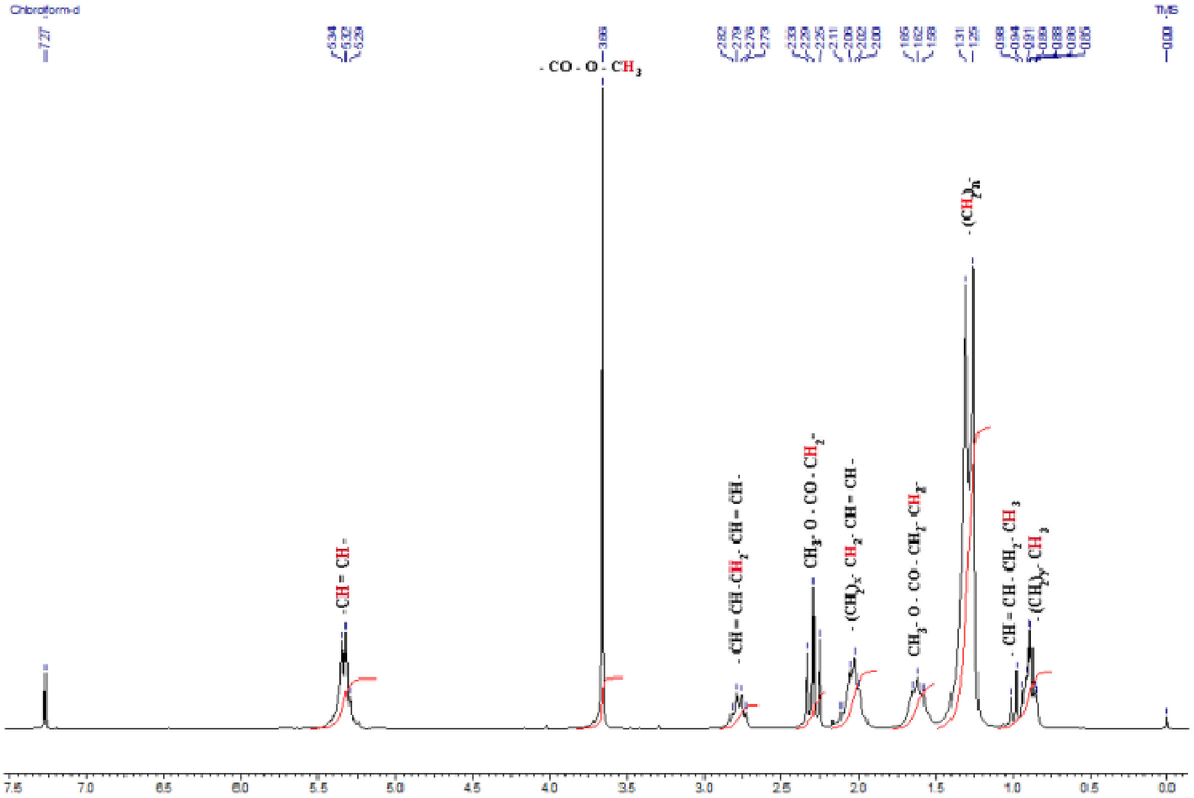

Figure 1. ^{1}H-NMR spectrum of FAMEs from rubber seed oil.

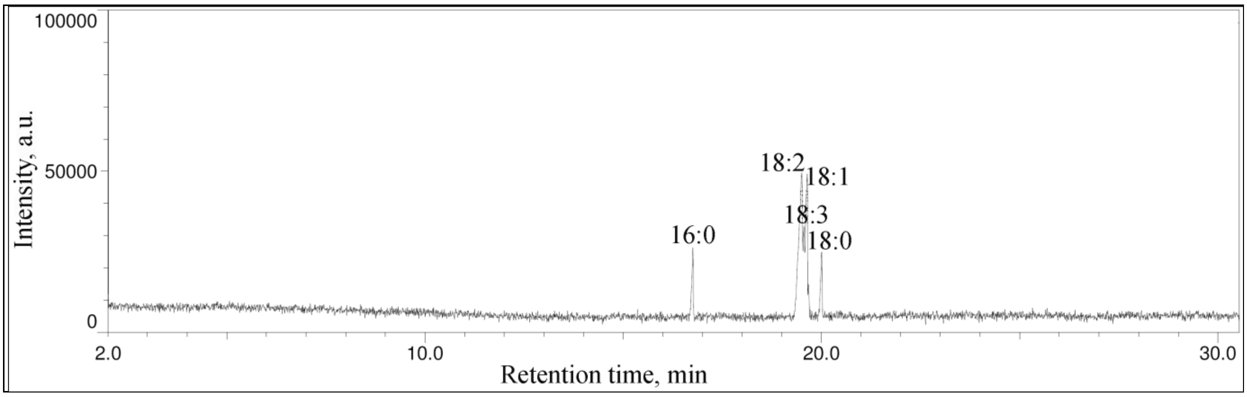

Figure 2. Gas chromatogram obtained for FAMEs from RSO.

For FAMEs obtained from RSO, it is not suitable to monitor the progress of transesterification reaction by FT-IR and NIR spectral techniques since the differences in peak position are not clear as observed from the Figure 3 & 4.

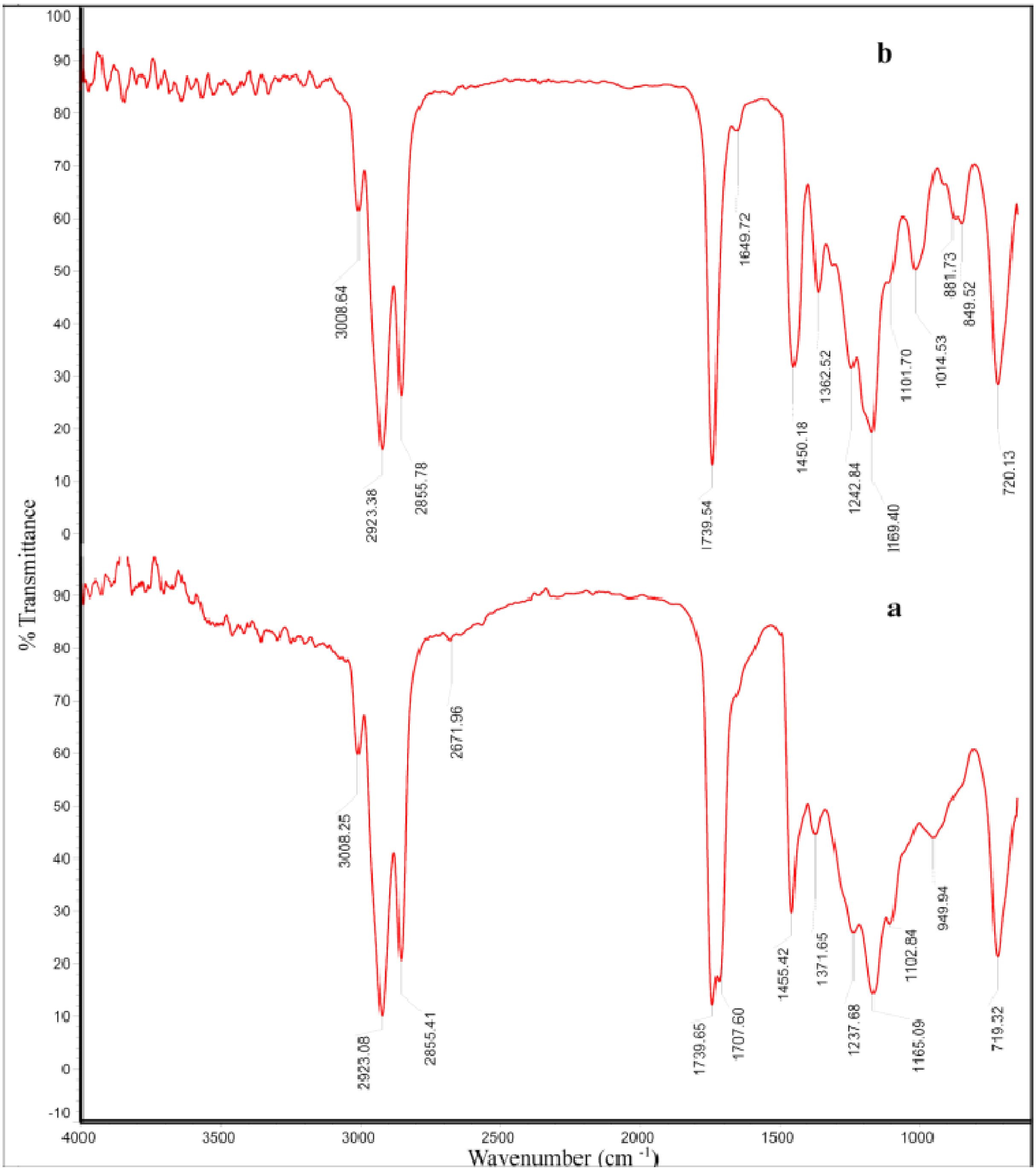

Figure 3. FT-IR spectrum of a) RSO b) FAMEs obtained from RSO.

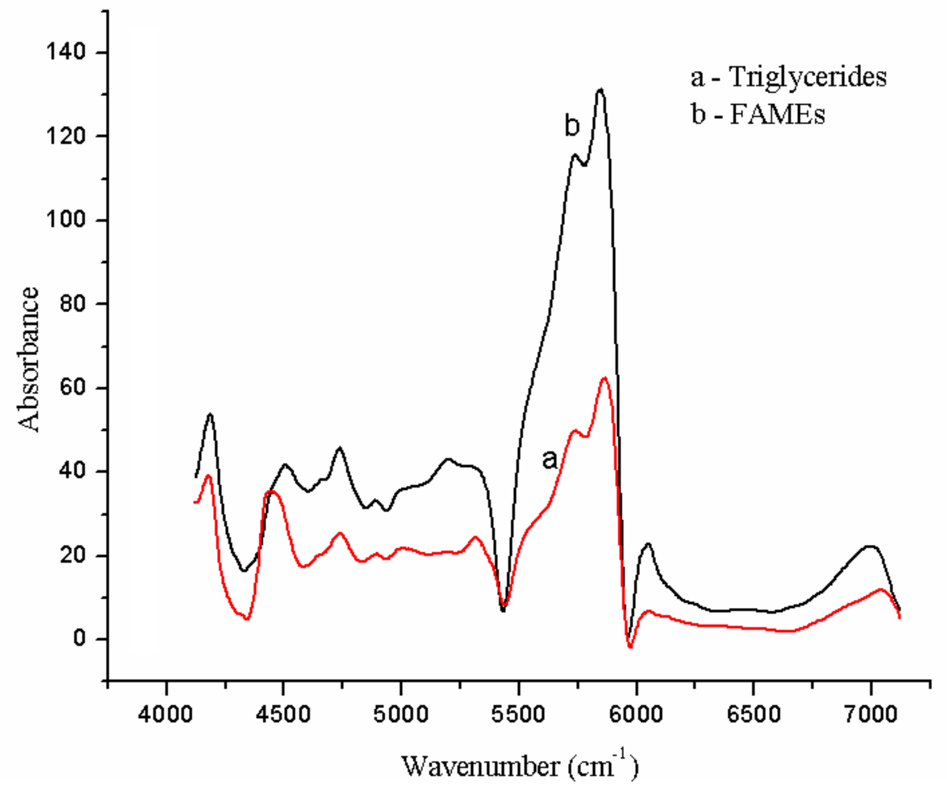

Figure 4. NIR spectrum for a) RSO b) FAMEs from RSO.

3.1. Acid value

All the FAMEs samples kept open and closed, exhibit sign of deterioration due to hydrolytic cleavage of fatty ester bonds, evidenced by the relatively rapid formation of acid content, after ninety days of storage (Fig.5).

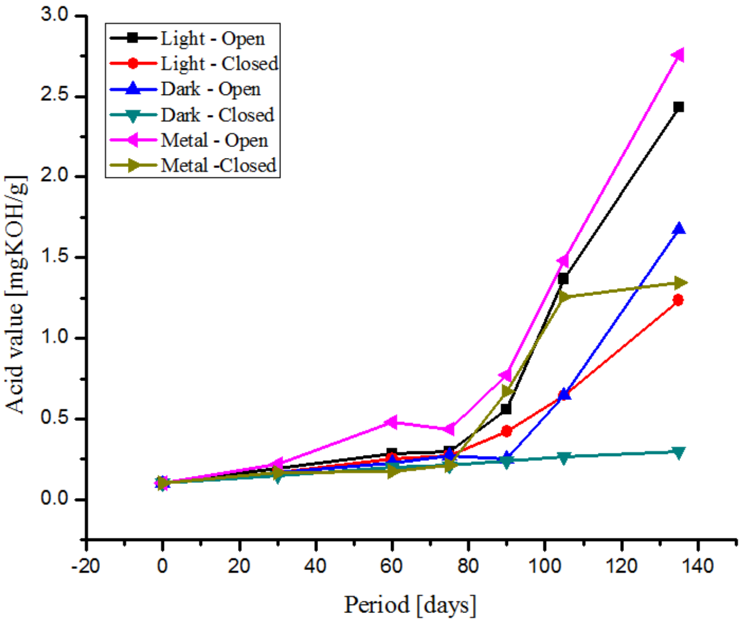

Figure 5. Influence of acid value of FAMEs on storage stability.

Table 3. Metal contamination in FAMEs stored in metal container

Transition metals	**Concentration [ppm]**	
	Metal (Open)	***Metal (Closed)***
Chromium	1.590	1.595
Copper	3.936	3.933
Iron	4.803	4.811
Zinc	5.593	5.590

Significant impact is observed only for FAMEs stored in metal container. The samples stored in metal containers (open), exhibit higher degradation, with relatively higher acid formation. The samples analysed by ICP-OES using Perkin Elmer – Optima 2100 DV reveals the presence of transition metals (leached from the container) chromium, copper, iron and zinc in smaller concentrations (Table 3). Transition metals are reported to have detrimental effect (except zinc which exhibit antioxidant nature) on storage stability of FAMEs [8]. Their presence in traces, is enough to accelerate the acid formation in presence of moisture and oxygen to a greater extent due to the catalytic influence (Cu > Cr > Fe) [19]. Further, the antioxidant nature of zinc [20] (present along with the other metals) is also suppressed due to the strong catalytic effect of copper, chromium and iron.

As for the influence of air, the samples which are kept open (light or dark) also reveal a higher rate of fatty ester hydrolysis (aided by moisture in air) against their counterparts under closed condition. Apart from metals, light is also found to accelerate the fatty ester hydrolysis, since the extent of acid formation is greater for samples exposed to light even under closed condition compared to those samples which are stored in dark (closed).

3.2 Peroxide value

The FAMEs samples kept in different environments are found to undergo sharp degradation due to different levels of peroxide formation. As expected, light exposed samples (closed and open) show relatively higher peroxide formation due to photo-oxidation of unsaturated fatty esters, compared to other samples. But after hundred and five days of storage, FAMEs stored in metal containers exposed to air (kept in dark) show a tremendous increase in the rate of peroxide formation (Fig.6). The rapid rise in peroxide content is due to the fact that metals leached from the container (Cu, Cr and Fe) tend to catalyse oxidation of fatty acids to peroxides in the presence of oxygen, apart from accelerating oxidation of unsaturated fatty esters with bis-allylic carbons (easily prone to oxidation) [6]. The fatty acids formed on storage contribute for peroxide formation in the presence of oxygen due to the catalytic effect of metal contaminants, but in the absence of oxygen, samples stored in metal containers (kept closed in dark) exert no significant increase in the rate of peroxide formation.

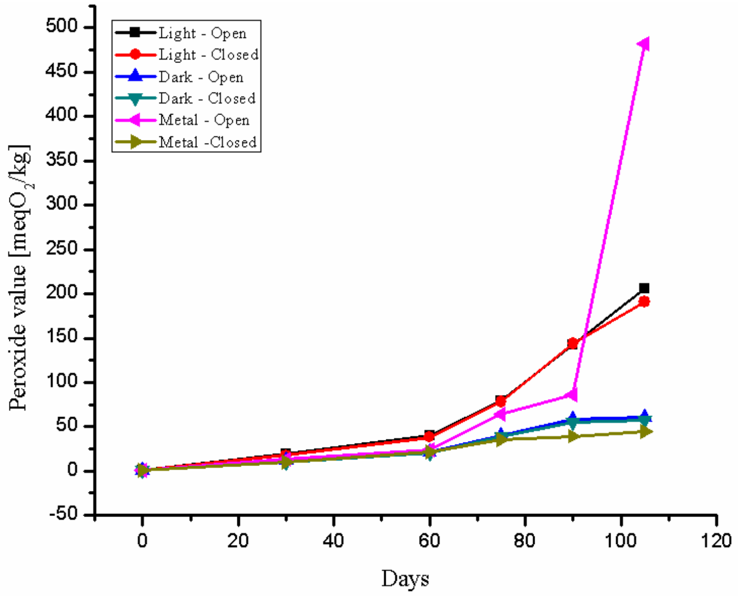

Figure 6. Influence of peroxide value of FAMEs on storage stability

3.3 Induction period

Induction period which is generally influenced by the rate of formation of acids as well as peroxides exhibits linear relationship, except for the FAMEs samples in metal container kept closed. Quite surprisingly, both the metal contaminated samples kept open and closed indicated almost the same extent of degradation (Fig.7), since a higher peroxide value is expected for the FAMEs in the open containers. The controversy is due to the extensive white coloured insoluble depositions observed for the samples contaminated with metals kept closed. Moreover, the colour also gets darkened for metal contaminated samples, due to the catalytic polymerization of unsaturated fatty esters [21] which are present in higher amount (78.86%) thereby reducing the induction period similar to its open counterpart. It has been reported that Cu or Cr can substantially reduce IP at concentrations of ≤ 2 ppm, while the less active metal – iron requires concentrations above 10 ppm to significantly affect the induction period of biodiesel [19].

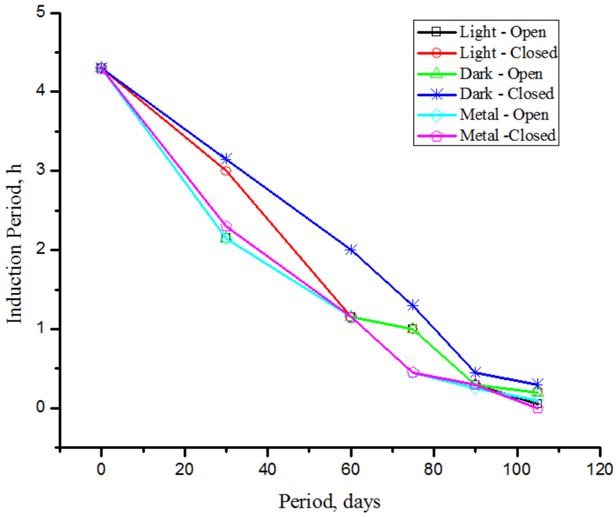

Figure 7. Influence of induction period of FAMEs on storage stability

In general, metal contaminants are found to deteriorate the fatty acid methyl esters in a faster rate due to acceleration of hydrolysis, oxidation and polymerization, limiting the storage stability to approximately one month. Samples kept protected against air, light and metal contaminants exhibit maximum storage stability. Even in such protected condition, the storage stability is restricted to only two months. The fatty acid profile restricts the storage stability of the FAMEs, because of its high degree of unsaturation, especially polyunsaturation (55.66%) with all the double bonds oriented in bis-allylic position. These methylene interrupted carbons in 18:2 and 18:3 fatty esters render more activated sites for autoxidation, since bis-allylic carbons are easily prone to oxidation. The relative rates of autoxidation of purified esters of oleic acid (C18:1):linoleic acid (C18:2):linolenic acid (C18:3) have been reported to be 1:41:98 through oxygen absorption measurements [22]. Consequently, the oxidative stability is limited to just two months (2h at 120^{o}C ≡ 3.15h at 110^{o}C *vide*. Fig.5), beyond which the oxidative stability index could not sustain the specifications of ASTM D6751.

CONCLUSION

Fuel properties of the FAME is found to be within acceptable limits specified by ASTM standard. Monitoring the reaction progress can be made with the help of GC as well as ^{1}H-NMR whereas FT-IR and NIR techniques proves to be inefficient. The high extent of unsaturation with bis-allylic carbons has considerably limited the storage stability of FAMEs to a maximum of just two months, after which it requires addition of antioxidants for long term storage which makes it otherwise unsuitable for long storage. Further, greater degradative effect is observed for metal contaminants over storage stability of FAMEs. Thus acid formation and peroxide formation induced by metals in the presence of air have contributed to higher degradation. In general, influence of air is greater for acid formation, since moisture tends to cleave the ester functions at a higher rate.

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