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Measurement of the Oxidation Stability of Biodiesel Using a Modified Karl Fischer Apparatus

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Abstract Oxidative stability is an important parameter in the characterisation of fats and oils. The determination of this parameter with a Rancimat apparatus is very costly. The alternative modified Karl Fischer (KF) apparatus works on the same principle as the Rancimat, i.e., a conductivity based determination of volatile degradation products and automatic plotting of the conductivity against time. The apparatuses were compared by taking five different samples of methyl esters at different temperature ranges. The results indicate that the modified KF apparatus can be used for the determination of oxidation stability of biodiesel with comparable values of sensitivity, repeatability and reproducibility.

Keywords Oxidation stability · Rancimat · Karl Fischer · Induction period

Abbreviations

BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
TBHQ	*tert*-Butyl hydroquinone
PY	Pyrogallol
PG	Propyl gallate
FAME	Fatty acid methyl ester(s)
ME	Methyl ester(s)
KF	Karl Fischer
IP	Induction period
SD	Standard deviation
f	Temperature coefficient
R^2	Linear regression value
n	Number of samples
R & R	Repeatability and reproducibility
L/h	Liter/hour

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Introduction

Oxidative stability is an important parameter for the quality assessment of animal and vegetable fats, oils and biodiesel from them. Autoxidation is caused by atmospheric oxygen. The oxidation process is initiated by free radical reactions involving unsaturated fatty acids [1–3]. The primary products formed are hydroperoxides, which are further broken down into a number of complex reaction products, the exact nature of which is still under investigation. The secondary oxidation products include alcohols and carbonyl compounds that can be further oxidised to carboxylic acids [1–4].

The method developed for the European standard EN 14112 [5] used in the 743 Rancimat (METROHM AG, CH-9100 Herisau, Switzerland) [6] is based on the fact that the greater proportion of the volatile products consists of formic acid [7]. These volatile components are trapped in distilled water, ultimately increasing the conductivity of the water which will be plotted automatically in the form of a graph. The progress of oxidation curves determined in this manner virtually parallels the development of the peroxide value [5]. The point of greatest inflection (IP) is

determined graphically after the completion of the experiment (tangential intersection point, Fig. 1).

Xin et al. [8] have worked on the kinetics of oxidation of biodiesel using the Rancimat method at temperatures from 100 to 120 °C. The oxidative stability of sunflower (*Helianthus annuus*) oil methyl ester samples with different antioxidant blends was studied according to EN 14112 [5] using a Rancimat apparatus model 743 (Metrohm, Herisau, Switzerland), which was operated under the following conditions: air flow rate, 10 L/h, a 3-g biodiesel sample was placed in a heating block with the temperature set from 100 to 120 °C, the vapours were discharged to a flask containing 0.06 L distilled water and the change in conductivity was recorded by a computer simultaneously. Several researchers have used the Rancimat apparatus for the measurement of oxidation stability of biodiesel. Sarin et al. [9] and studied the effect of metal contaminants and antioxidants on the oxidation stability of the methyl esters of *Pongamia* (*Pongamia pinnata*) oil using the Rancimat apparatus. Park et al. [10] studied the blending effects of biodiesel on oxidation stability and low temperature flow properties using the Rancimat apparatus.

Das et al. [11] studied the long-term storage stability of biodiesel produced from *Pongamia* oil using the Rancimat apparatus. The thermal oxidation stability of the biodiesel sample was determined using a Rancimat 873 instrument (Metrohm, Switzerland). The sample was heated at a constant temperature with an excess airflow, passed through a conductivity cell placed in distilled water. During this oxidation process, volatile acids are formed and conductivity increases rapidly to a point, which is called ''induction period''. The induction period of *Pongamia* oil methyl ester was determined without antioxidant at different temperatures (90, 100, 110 and 120 °C) and with antioxidants [butylated hydroxytoluene (BHT), *tert*-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), propyl gallate (PG), and pyrogallol (PY)] with 100 ppm at 110 °C. Sarin et al. [12] studied the stability of *Jatropha* (*Jatropha curcas*) oil methyl ester and palm (*Elaeis guineensis*) oil methyl ester blends using a Rancimat equipment model 743. Sarin et al. [13] studied the influence of metal contaminants on the oxidation stability of *J. curcas* biodiesel using a Rancimat apparatus model 743 according to EN-14112 and Indian IS-15607 specifications.

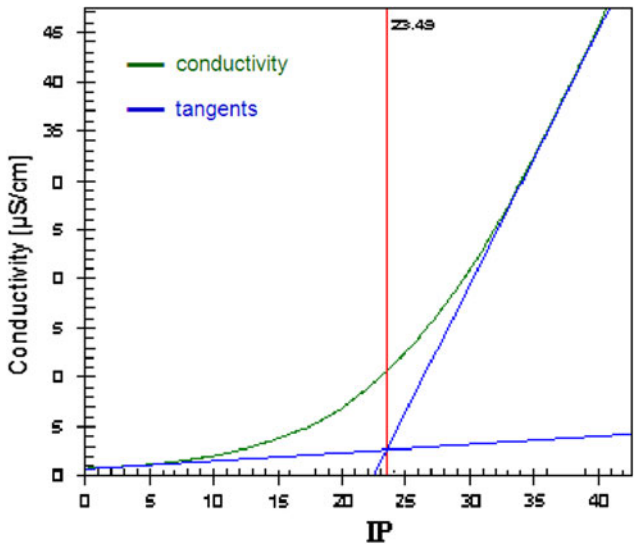

Fig. 1 Graphical determination of induction time (t) by the tangent method

Materials and Methods

The Principle of the Rancimat Test (EN-14112)

The determination of the oxidation stability of oils and fats is the classical application for the Rancimat apparatus model 743. The resulting induction time characterises the resistance of oils and fats to oxidation. In addition to the term IP, the expression 'oil stability index' (OSI) is also in common use. This test, also called the automated swift test or accelerated oxidation test, is in general used today as an automated version of the previously used and extremely complicated active oxygen method (AOM).

During the measurement, a stream of air is passed through the oil or fat sample contained in a sealed and heated reaction vessel as shown in Fig. 2. This treatment results in the oxidation of the oil or fat molecules in the sample to initially produce hydroperoxides as the primary oxidation products. After some time, the hydroperoxides are destroyed. The secondary oxidation products formed include low-molecular organic acids in addition to other volatile organic compounds. These products are transported in the stream of air to a second vessel containing distilled water. The conductivity of this vessel is recorded continuously. The organic acids can be detected by the increase in conductivity as shown by Fig. 1. The time that elapses until these secondary reaction products appear, is

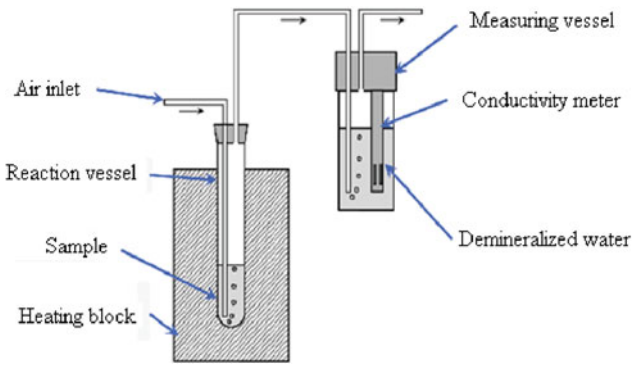

Fig. 2 Schematic of the Rancimat test

known as the IP or OSI. The IP is determined graphically after completion of the experiment (tangential intersection point, see Fig. 1).

This test provides standard quality control parameters for the production of oils and fats in the food industry or for checking incoming goods/feedstocks for further processing. In addition to oils and fats from vegetable sources, the oxidation stability of animal fats such as lard, tallow and fish oil can also be checked with the 743 Rancimat apparatus.

On the other hand, KF apparatus is used to calculate the moisture content in biodiesel, biofuel, diesel, engine oil, gasoline, gear oil, jet lube, solvent or turbine oil based on EN 14214. For the purpose of testing the oxidative stability of biodiesel, the apparatus is modified for the Rancimat test. The detailed procedure is given below.

Jatropha Vikas Sansthaan, Uttarakhand, India has specialised in the production of *Jatropha* (*J. curcas*) oil and its methyl esters used for research and development purpose, therefore, the biodiesels were purchased from this company. The biodiesels purchased were subjected to gas chromatographic analysis to determine their composition [14]. The characteristics of all the biodiesels are given in Table 1. For the purpose of measuring the oxidative stability, a 831 KF Coulometer (Metrohm) and a 743 Rancimat apparatus were used. For the measurement of conductivity in modified KF, a digital conductivity meter (Hack) was used.

To compare the results of the Rancimat apparatus and the modified KF apparatus, samples of biodiesel were tested by these methods as discussed below.

Experimental Procedure for Measurement of IP Using a Rancimat Apparatus

In the Rancimat apparatus, the oxidation is induced by passing a stream of air at the rate of 10 L/h through the biodiesel sample (3 g) kept at constant temperature (100, 110 and 120 °C). The vapours released during the oxidation together with the air, are passed into a flask containing 60 mL of demineralised water and an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. When the conductivity begins to increase rapidly, it is indicative of the end of IP. This accelerated increase in conductivity is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and subsequently absorbed in the water. When the conductivity of the solution is recorded continuously, an oxidation curve is obtained whose point of inflection, known as the IP, can be calculated by the point of intersection of two tangents as shown in Fig. 1.

Experimental Procedure for Measurement of IP Using a Modified Karl Fischer Apparatus

A diagram of the apparatus is shown in Fig. 3. A reaction vessel and a highly calibrated conductivity meter are installed externally as shown in Fig. 3. The sample (3 g) is kept in a reaction vessel and subjected to heating at predecided constant temperature (100, 110 or 120 °C) and an air flow rate of 9 L/h. The maximum air flow used in the KF apparatus is 9 L/h and therefore, the same air flow is used in the test. The remaining part of the test is similar to that of the Rancimat apparatus.

Modifications to the Karl Fischer Apparatus

In the Rancimat apparatus reaction vessel, a conductivity measuring cell, a heating block, and piping to pass air from the atmosphere to the biodiesel and from the biodiesel into the demineralised water are assembled as one apparatus. In order to measure the oxidation stability of the biodiesel sample by the KF apparatus, a digital conductivity meter (manufactured by Hack) and reaction vessel (24 mm in diameter, 150 mm long of quartz glass) is assembled separately with all the necessary piping to pass air as shown in Fig. 3.

Results and Discussion

Induction Times

The induction times (t) of all the biodiesel samples investigated are shown in Tables 2 and 3 for both the apparatuses (Rancimat and modified KF), respectively. Both the tables

Table 1 Fatty acid composition of different oil FAME

S. no.	Name of ME (scientific name)	C14	C16	C18	C18:1	C18:2	C18:3	Saturated fatty acids (%)	Unsaturated fatty acids (%)
1.	*J. curcas* FAME (*J. curcas* Linn.)	–	16.8	7.9	39.1	36	0.2	24.7	75.3
2.	Sunflower FAME (*H. annuus* Linn.)	0.2	5.3	5.7	20.6	67.4	0.8	11.2	88.8
3.	Soybean FAME (*Glycine max* Merr.)	0.1	10.8	4	23.4	53.9	7.8	14.9	85.1
4.	*Pongamia* FAME (*P. pinnata* (Linn.) Merr.)	–	9.8	6.6	71.8	11.8	–	16.4	83.6
5.	Palm FAME (*E. guineensis* Jacq.)	–	41.3	3.5	43.1	12.1	–	44.8	55.2

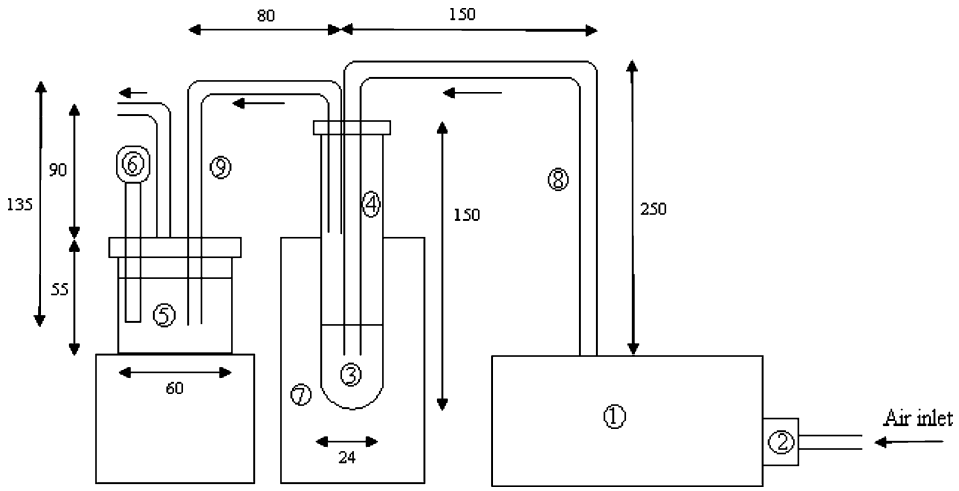

Fig. 3 Schematic of the modified KF apparatus. (*1*) 860 KF Thermoprep, (*2*) absorbent, (*3*) biodiesel sample, (*4*) reaction vessel, (*5*) demineralised water, (*6*) conductivity meter, (*7*) heating block, (*8*) glass tubes, (*9*) glass tubes. (all dimensions are in mm)

showed the results collected by three users with two trials each. The values of standard deviation (2 determinations) are also given in the tables.

Analysis of Variance

The analysis of variance method (ANOVA) is the most accurate method for quantifying repeatability and reproducibility. In addition, the ANOVA method allows the variability of the interaction between the appraisers and the parts to be determined. The ANOVA method for measuring the assurance is similar to the statistical technique used to analyze the effect of different factors in designed experiments. The ANOVA design used is a 'two-way, fixed effect model with replications'.

Based on the above results, repeatability and reproducibility is calculated using the ANOVA method [15, 16]. The results of the ANOVA are shown in Table 4.

Table 2 Induction period determined by the Rancimat method at various temperatures

Temp. (°C)	Sample	Users												Total mean
		1				2				3				
		IP (*t*1)	IP (*t*2)	Mean	SD	IP (*t*1)	IP (*t*2)	Mean	SD	IP (*t*1)	IP (*t*2)	Mean	SD	
100	*J. curcas* FAME	6.1	5.82	5.96	0.197	5.8	5.6	5.7	0.141	6.3	5.7	6	0.424	5.88
	Sunflower FAME	3.8	4	3.9	0.141	3.9	4	3.95	0.070	4.2	3.8	4	0.282	3.95
	Soybean FAME	7	7.4	7.2	0.282	7.3	6.7	7	0.424	7.6	7.2	7.4	0.282	7.2
	Pongamia FAME	4.5	4.8	4.65	0.212	4.4	5	4.7	0.424	4.7	4.3	4.5	0.282	4.61
	Palm FAME	23.1	21.9	22.5	0.848	22.1	23.3	22.7	0.848	22.6	22.2	22.4	0.282	22.53
110	*J. curcas* FAME	3.25	3.29	3.27	0.028	3.25	3.69	3.47	0.311	3.7	3.1	3.4	0.424	3.38
	Sunflower FAME	1.9	1.8	1.85	0.070	2	1.8	1.9	0.141	1.5	1.9	1.7	0.282	1.81
	Soybean FAME	4.2	3.6	3.9	0.424	3.5	4.5	4	0.707	3.6	4	3.8	0.282	3.9
	Pongamia FAME	2.1	2.5	2.3	0.282	2.5	2.3	2.4	0.141	2.7	2.3	2.5	0.282	2.4
	Palm FAME	14.18	14.06	14.12	0.084	13.9	14.7	14.3	0.565	14.7	13.5	14.1	0.848	14.17
120	*J. curcas* FAME	1.82	1.88	1.85	0.042	1.8	2	1.9	0.141	1.9	1.7	1.8	0.141	1.85
	Sunflower FAME	1.1	0.8	0.95	0.212	1.2	1	1.1	0.141	0.9	0.8	0.85	0.070	0.96
	Soybean FAME	2.1	1.8	1.95	0.212	1.9	2.3	2.1	0.282	1.9	2.1	2	0.141	2.01
	Pongamia FAME	1.6	1	1.3	0.424	1.1	1.9	1.5	0.565	1.5	1.1	1.3	0.282	1.36
	Palm FAME	6.8	6.6	6.7	0.141	6.3	6.7	6.5	0.282	7.1	5.9	6.5	0.848	6.56

*t*1, *t*2 showing IP of two trials

Table 3 Induction period determined by the modified KF method at various temperatures

Temp. (°C)	Sample	Users												Total mean
		1				2				2				
		IP (*t*1)	IP (*t*2)	Mean	SD	IP (*t*1)	IP (*t*2)	Mean	SD	IP (*t*1)	IP (*t*2)	Mean	SD	
100	*J. curcas* FAME	6.15	6.25	6.2	0.070	6.2	5.8	6	0.282	6.6	5.8	6.2	0.565	6.13
	Sunflower FAME	4	4.2	4.1	0.141	4.45	4	4.2	0.353	4.4	4	4.2	0.282	4.16
	Soybean FAME	7.25	7.55	7.4	0.212	7.1	7.3	7.2	0.141	7.4	7.2	7.3	0.141	7.3
	Pongamia FAME	4.8	4.6	4.7	0.141	5.2	4.6	4.9	0.424	4.9	4.3	4.6	0.424	4.73
	Palm FAME	22.7	22.5	22.6	0.141	22.1	23	22.5	0.565	22	23	22.6	0.282	22.56
110	*J. curcas* FAME	3.25	3.55	3.4	0.212	3.4	3.8	3.6	0.282	3.6	3.7	3.65	0.070	3.55
	Sunflower FAME	2	2.2	2.1	0.141	2.3	1.7	2	0.424	2.6	1.3	1.9	0.919	2
	Soybean FAME	4.1	4.2	4.15	0.070	4.35	4.3	4.3	0.070	4.5	2.8	3.65	1.202	4.03
	Pongamia FAME	2.4	2.6	2.5	0.141	2.25	2.2	2.2	0.070	2.7	2.4	2.5	0.212	2.4
	Palm FAME	14.4	14.2	14.3	0.141	14.1	14	14.2	0.141	14.4	14	14.3	0.070	14.26
120	*J. curcas* FAME	1.85	1.95	1.9	0.070	1.55	2.2	1.85	0.424	1.7	1.6	1.65	0.070	1.8
	Sunflower FAME	1	1.2	1.1	0.141	1.15	1.5	1.3	0.212	1.2	0.7	0.95	0.353	1.11
	Soybean FAME	2	2.2	2.1	0.141	2.3	2.1	2.2	0.141	2.3	1.9	2.1	0.282	2.13
	Pongamia FAME	1.5	1.1	1.3	0.282	1.45	1.6	1.5	0.070	1.4	1.3	1.3	0.070	1.36
	Palm FAME	7.2	6.8	7	0.282	7.2	6.4	6.8	0.565	7.4	6.2	6.8	0.848	6.86

*t*1, *t*2 showing IP of two trials

Table 4 ANOVA of Rancimat and modified KF

S. no.	Test apparatus	Source	DF	SS	MS	F
1.	Rancimat	Appraiser	2	0.07	0.036	0.25
		Samples	14	2796.26	199.733	1375.19
		Interaction	28	0.76	0.027	0.19
		Error	45	6.54	0.145	–
		Total	89	2803.62	–	–
2.	Modified KF	Appraiser	2	0.11	0.054	0.41
		Samples	14	2789.32	199.237	1511.92
		Interaction	28	1.13	0.04	0.3
		Error	45	5.93	0.132	–
		Total	89	2796.48	–	–

From the ANOVA (Table 4), repeatability and reproducibility (R & R) analysis is carried out and the results are depicted in Table 5 which shows that the interaction between the appraisers and the samples is 0. The R & R for the Rancimat and the modified KF are 1.97 and 1.9, respectively, showing that the apparatus can be used interchangeably for the measurement of the oxidation stability of oils and fats. Also the total measurement system variation (V_T) for the Rancimat and the modified KF was found to be 29.78 and 29.73 indicating that the apparatuses are of equal validity.

The result of linear regression [*t* (Rancimat) vs. *t* (modified KF)] is summarised in Table 6. The induction times determined by both the apparatuses show a very good correlation at 100, 110 and 120 °C with values of R^2 as 0.999, 0.999 and 0.998, respectively and also when all the values are taken into consideration (Fig. 4). This shows that the results obtained from the instruments are well-correlated at different temperatures with an R^2 value of 0.99.

From the Fig. 4 the following relationship was established between the modified KF and Rancimat IP:

$$\text{IP (Modified KF)} = \text{IP (Rancimat)} * 1.01161 + 0.1697$$

The relationship between the Rancimat 743 and the modified KF as shown in Fig. 4 for all the samples at various temperatures has a coefficient of determination value as 0.999 indicating that the new modified KF apparatus can be used with high precision compared to the Rancimat apparatus and may be recommended as an alternative method for measuring the induction period. The accuracy is also very good from the viewpoint that the error is found to be less using the modified KF (±9%).

Using this relation, the Rancimat IP is calculated and an error analysis was carried out on the basis of actual IP (observed) and the Rancimat IP (calculated) using the correlation given in Fig. 5 from which it is seen that there is a maximum of ±9% error between the Rancimat IP (observed) and the IP (calculated).

Table 5 R & R analysis

S. no.	Test apparatus	Repeatability	Reproducibility	Interaction between the appraisers and the samples (I)	R & R	System part variation (V_P)	Total measurement system variation (V_T)
1.	Rancimat	1.96	0.141	0	1.97	29.71	29.78
2.	Modified KF	1.87	0.176	0	1.88	29.67	29.73

Table 6 Results of the linear regression

Temperature (°C)	A	B	R^2	n
100	0.2256	1.0037	0.999	5
110	0.1842	1.0133	0.999	5
120	0.0541	1.0957	0.998	5
100 + 110 + 120	0.1697	1.0116	0.999	15

$Y = A+BX$, where $X =$ the induction period from Rancimat 743 and $Y =$ induction period using modified KF

R^2 is the linear regression value and n is the number of samples

Temperature Dependence of Induction Times

Temperature dependence of induction time is determined through the temperature coefficient (f). In earlier works [17–19], the f, of the induction time for a temperature change of 10 °C was reported as 1.8–2.9. The temperature coefficient was shown in Table 7 to lie between 1.8 and 2.0 with regression coefficients (log t vs. T) better than 0.99. It is an indication of the equal sensitivity of both apparatuses with respect to temperature.

The induction times determined using the Rancimat apparatus correlate extremely well with those of the modified KF apparatus. When experiments are carried out at different temperatures, it is recommended to determine the temperature dependence of the apparatus in order to determine the sensitivity of the apparatus (reduction in the induction period by a factor of nearly two with a temperature increase of 10 °C).

A comparison of Rancimat and modified KF apparatuses is given in Table 8 which shows that the sensitivities of both the apparatuses are equal (1.80) (14, 15 and 16), repeatability is 1.96 and 1.87, respectively and reproducibility is 0.141 and 0.176, respectively showing that the modified KF can give results with more reproducibility. Therefore both the apparatuses can be used with equal sensitivity but with ±4.6% variation in repeatability and ±2.5% variation in reproducibility for the measurement of oxidation stability of fats and oils.

Conclusions

In this paper, the KF apparatus was modified to check the oxidation stability of biodiesel according to EN 14112 and

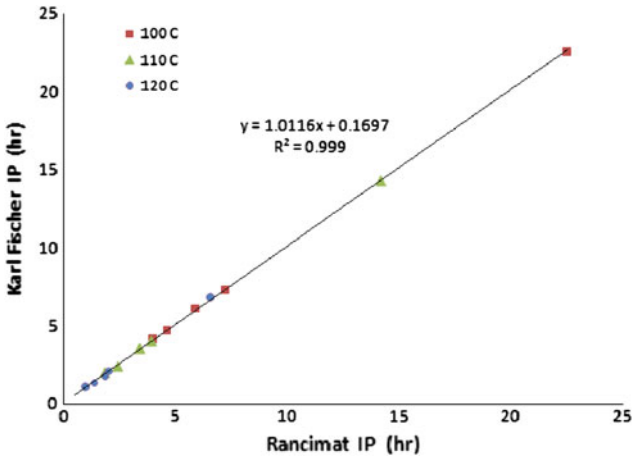

Fig. 4 Correlation between induction periods determined using the Rancimat 743 and modified KF apparatuses

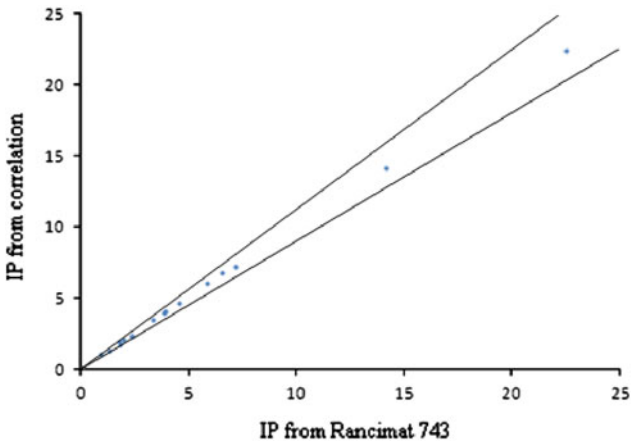

Fig. 5 Error analysis of IP obtained from the Rancimat apparatus and calculated from correlation

to compare it with the Rancimat apparatus. The results of both the tests are comparable. Sensitivity of both the instruments is 1.8 which is also in agreement with the literature (14, 15 and 16). Repeatability of the Rancimat and the modified KF is 1.96 and 1.87, respectively. The reproducibility of the Rancimat and the modified KF is 0.141 and 0.176 respectively showing that the modified KF can give more reproducible results with the same samples. R & R for the Rancimat and the modified KF is 1.97 and 1.9, respectively, showing that both the apparatuses can be

Table 7 Experimental temperature coefficient (f) determined experimentally

Sample	Rancimat		Modified KF	
	f	R^2	f	R^2
J. curcas FAME	1.76	0.999	1.84	0.996
Sunflower FAME	2.01	0.997	1.92	0.995
Soybean FAME	1.87	0.999	1.84	0.999
Pongamia FAME	1.82	0.998	1.86	0.997
Palm FAME	1.84	0.979	1.8	0.982
Average	1.8	0.99	1.8	0.99

f = temperature coefficient and R^2 is linear regression value

Table 8 Comparison of Rancimat and modified KF apparatuses

S. no.	Parameters	Rancimat	Modified KF
1.	Cost of apparatus	30000 US $[a]	15000 US $[a]
2.	Sensitivity	1.8	1.8
3.	Repeatability	1.96	1.87
4.	Reproducibility	0.141	0.176

[a] Including cost of all the necessary items

used interchangeably for the measurement of the oxidation stability of oils and fats. Also the total system variation (V_T) for the Rancimat and the modified KF is 29.78 and 29.73 again showing that both the apparatuses are of equal validity. Further it was also found that the KF apparatus costs less than the Rancimat apparatus but the results from both are comparable. Therefore, it is recommended that the modified KF apparatus can be used in place of the Rancimat apparatus after slight modification as discussed.

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