

A Study on Chemical and Lubrication Properties of Unrefined, Refined and Virgin Coconut Oil Samples

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In the present work four samples each of unrefined coconut oil (URCO), refined coconut oil (RCO) and virgin coconut oil (VCO) samples collected from different places were evaluated in terms of physicochemical and lubrication parameters. The physicochemical properties of URCO, RCO and VCO were analyzed in terms of kinematic viscosity, Fatty acid profile, Iodine number, Saponification number, free fatty acid, Peroxide value and flash point. The lubrication properties of the oil samples were compared with the aid of four ball tester. The study revealed that fatty acid profile of VCO samples was slightly different from that of URCO and RCO samples. The saponification and Iodine value of VCO samples was also slightly lower than that of URCO and RCO samples. The four ball test results showed that the average coefficient of friction under tested condition was slightly less for URCO and VCO samples when compared to RCO samples. This difference in frictional property was due to the presence of free acid in the URCO and VCO which acted as boundary lubricant. The increased wear observed with VCO and URCO samples was linked to the presence of peroxides.

Keywords: Coconut Oil, Lubrication, Free Fatty Acids, Peroxide Value, Four Ball Tester

Introduction

Oils and fats have been used for lubrication for centuries. The bulk of the lubricants used today are derived from petroleum, which are causing considerable amount of damage to the environment. The increased environmental awareness and stringent regulations imposed by the government has renewed interest in lubricants derived from vegetable oils as it is derived from renewable sources and will also have a value addition to agriculture. Coconut oil is considered as a premium commodity as in addition to being consumed as food supplement, it is used in pharmaceuticals, cosmetics and also as a raw material to synthesize oleo chemicals¹⁻³. It is known that quality of the oil plays significant role its physicochemical properties, which in turn is also expected to reflect in their lubrication properties. The present work evaluates the physicochemical and frictional properties of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO) and Virgin Coconut oil (VCO) samples subjected to different level of refining.

Materials and Methods

In the present work, four unrefined Coconut oil (URCO-1, URCCO-2, URCO-3 and URCO-4), four refined Coconut oil ((RCO-1, RCO-2, RCO-3 and RCO-4) and four virgin Coconut oil (VCO-1, VCO-2, VCO-3 and VCO-4) purchased from the different places in Kerala, India were used for analysis. All the samples used in the present investigations were not more than three weeks old when they were purchased from the market. In the present investigation fatty acid profile of URCO, RCO and VCO was evaluated by means of GC-MS. The URCO, RCO and VCO samples were subsequently analyzed in terms of kinematic viscosity, percentage of free fatty acid and peroxide number. All the chemicals used in the present investigation were of analytical grade. Further to these frictional properties of URCO, RCO and VCO samples were evaluated by using a four ball tester. Kinematic viscosity of the oil samples was carried out with the aid of SVM 3000 Stabinger viscometer as per ASTM standard D7042. The equipment has an inbuilt Peltier thermo electric system, which helps to perform the temperature scans or measure viscosity at a desired temperature without the requirement of thermal baths. In the present work

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kinematic viscosity of oil samples were measured at 40 °C and 100 °C. The tests were repeated three times to get the concurrent results. Fatty acid methyl esters (FAMES) of coconut oil were prepared dissolving the oil sample in mixture of hexane and sodium methoxide followed by subsequent analysis using gas chromatography fitted with a FID detector. Standard FAMES were used for authentication.

The chemical analysis of URCO, RCO and VCO were carried out in terms of Saponification number, Iodine number, peroxide number, flash point and percentage of free fatty acid as per ASTM standard procedures. The four ball tester equipment originated with the work of Boerlage to test the lubricants having high content of additives. Initial configuration of equipment had a single, heavily loaded ball spinning in a nest having three balls clamped in a plane. It was later modified by Blok, Larson and Perry to include all the features which are common in a standard four ball tester allowing one to make more precise measurements under variety of conditions. In the present work, frictional properties of URCO, RCO and VCO were evaluated using a four-ball tester. The experiments were conducted at 1200 rpm, 75°C, 60 minutes at 400N load. Chrome alloy steel balls of 12.7 mm diameter, conforming to AISI specification E-52100 were used for the experiments. The test balls were thoroughly cleaned by soaking them in Hexane for two minutes followed by sonic agitation for another five minutes. The cleaned balls were washed with fresh Hexane, wiped with tissue paper and dried with a hot air blower. The ball pot, locking ring and the top were also cleaned using hexane. The ball pot was assembled with steel balls and filled with test sample. Tests were carried out at specified conditions. The experimental process is completely automated with auto cut-off feature available in case of emergency. A schematic representation of ball pot with chuck is shown in Figure 1. Once the experiment was over, the tested steel balls were thoroughly cleaned and the wear scar images were captured using image capturing system. The scar diameter was subsequently measured later using the software with an accuracy of $\pm 2 \mu\text{m}$. The experiments were repeated twice and the average value was taken for further analysis.

Results and Discussion

The choice of vegetable oils for lubricant applications is favored due to their favorable inherent properties. Since vegetable oils are derived from

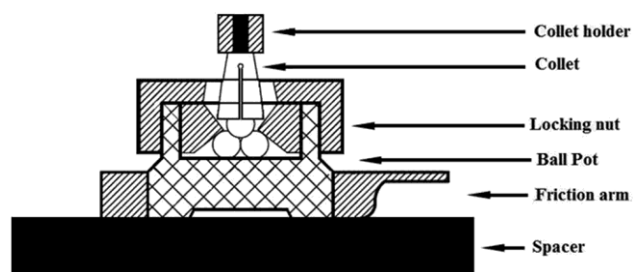


Fig. 1—Schematic representation four ball tester configuration

renewable sources, using them for lubricant application will be beneficial to environment. Coconut oil used in to use in a wide range of edible and non-edible applications due to its unique chemical composition. It has long shelf life due to the presence of high content of saturated fatty acids. In one of the study influence of coconut oil based cutting fluids on tool wear and surface roughness variations during turning of AISI 304 austenitic stainless steel was carried out. It was observed that coconut oil based emulsion was more effective in reducing the tool wear and improving the surface finish compared to conventional mineral oil. In another study reduction in exhaust emission was observed when coconut oil was used as a lubricant and in addition to improved fuel efficiency^{4,6}. The fatty acid profile of coconut oil samples were evaluated as specified in the previous section. The following observations were made with reference to the composition of URCO, RCO and VCO samples. The overall composition of tested oil samples was as expected and comparable to the composition of coconut oil according to the Codex standard. It was observed that the quantity Caprylic(C8:0), Myristic (C14:0), Palmitic(C16:0) and Stearic(C18:0) acids in VCO samples were slightly higher when compared to URCO and RCO. It was slightly lower with reference to Caproic acid (C6:0), Lauric acid (C12:0), oleic acid (C18:1) and linoleic (C18:2) in VCO when compared to URCO and RCO samples. The corresponding fatty acid composition of URCO, RCO and VCO are as shown in Table 1. Commercial grade Coconut oil or unrefined coconut oil (URCO) is extracted from the copra and is not suitable for extended storage. Unsanitary handling and processing of copra also make the URCO susceptible to contamination and oxidative rancidity. This problem can be overcome by means of refining of oil which eliminates the impurities. The close similarity in the composition of URCO and RCO samples reflect the fact that they are extracted from same quality of coconuts. On the other

Table 1—Virgin coconut oil (VCO), Unrefined Coconut oil (URCO) and Refined Coconut oil (RCO) samples

Oil Sample	C 6:0	C 8:0	C 10:0	C 12:0	C 14:0	C 16:0	C 18:0	C 18:1	C 18:2
URCO-1	0.61	8.06	6.49	47.31	17.95	8.79	3.25	6.01	1.53
URCO-2	0.63	8.33	6.55	47.30	17.88	8.34	3.33	6.11	1.53
URCO-3	0.62	8.08	6.56	47.44	18.02	8.47	3.04	6.33	1.44
URCO-4	0.67	8.22	6.88	47.48	17.66	8.52	3.06	6.16	1.35
RCO-1	0.59	8.16	6.84	47.45	18.07	8.48	3.02	6.05	1.34
RCO-2	0.67	8.04	6.53	47.28	18.19	8.22	3.17	6.18	1.72
RCO-3	0.69	8.22	6.41	47.09	18.02	8.69	3.15	6.27	1.46
RCO-4	0.64	8.17	6.72	47.52	17.76	8.25	3.37	6.22	1.35
VCO-1	0.41	8.62	6.28	46.75	18.52	9.01	3.51	5.62	1.28
VCO-2	0.48	8.43	6.24	46.92	18.57	8.92	3.11	5.76	1.48
VCO-3	0.54	8.32	6.75	46.44	18.55	8.90	3.53	5.71	1.26
VCO-4	0.42	8.67	6.43	46.98	18.73	8.62	3.22	5.76	1.17

hand virgin coconut oil (VCO) is extracted typically by wet process directly from the coconut milk obtained from the fresh coconuts under controlled temperature. Thus it is evident from this study that variation in composition of URCO, RCO and VCO samples can be ascribed to the geographical origin of sample and the difference in the extraction process⁷. Saponification value is a measure of the average molecular weight of constituent fatty acids of the vegetable oil. Higher the saponification number shorter will be the fatty acid chain attached to the glycerine backbone in the triglyceride molecule. The study revealed that the saponification values of all the tested oil samples fall within the limit specified by the standards. The saponification value of URCO, RCO and VCO samples is as shown in Table 2. The higher saponification value of URCO, RCO and VCO is further confirmation that coconut oil has predominantly shorter chain fatty acids as compared to other vegetable oils. It was also noticed that URCO and RCO samples had a slightly higher saponification value (255.17–259.54 mg KOH/g) than VCO samples (253.69–255.84 mg KOH/g oil). This difference is attributed to the variations observed in their fatty acid composition. The iodine number is a measure of degree of unsaturation of fats and oils. In the present investigation iodine value of all the oil samples under investigation was evaluated as per ASTM test method D5768. Iodine no. is expressed as number of grams of iodine absorbed by 100g of the oil. The coconut oil samples have low iodine no due to the low content of unsaturated fatty acids. The iodine value of VCO samples was slightly lower than that of URCO and RCO samples and varied from 6.57 to 6.87, indicating a lower level of unsaturated fatty acids in the VCO as shown in the Table 2. Viscosity,

Table 2—Physical and Chemical properties of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO) and Virgin Coconut oil (VCO) samples

Sample	Kinematic Viscosity (in cSt)		Saponification value	Iodine value	Flash Point (in °C)
	40 °C	100 °C			
URCO-1	29.62	5.90	258.96	7.02	316
URCO-2	29.82	5.83	258.32	7.25	319
URCO-3	29.44	5.76	258.62	7.73	320
URCO-4	30.07	5.91	257.41	8.02	313
RCO-1	28.87	5.82	257.68	7.12	322
RCO-2	28.94	5.87	258.44	7.48	327
RCO-3	29.05	5.71	259.54	8.91	328
RCO-4	29.26	5.74	255.17	7.19	322
VCO-1	29.85	5.92	253.69	6.75	311
VCO-2	29.66	5.86	254.22	6.57	317
VCO-3	30.21	5.94	255.08	6.87	318
VCO-4	29.49	5.77	255.84	6.76	310

measures flow characteristic of oil sample and an important parameter from the tribological point of view in selecting the base oil for lubricant application. Viscosity is not only significant from the standpoint of new oils, it is also important in the evaluation of used oil samples. The results show that the viscosity of URCO samples varied from 29.44 to 30.07 and for VCO 29.49 to 30.21 cSt, for RCO it varied from 28.87 to 29.85 cSt at 40 °C. Whereas at 100 °C the viscosity of URCO samples varied from 5.76 to 5.91 and for VCO 5.77 to 5.94 cSt, for RCO it varied from 5.71 to 5.92 cSt. This indicates that the RCO has slightly lower viscosity compared to that of VCO oil samples. Flash point which refers to the volatility, the study showed that flash point of URCO oil samples varied from 313 to 320 °C, for VCO samples it was varied from 310 to 318 °C, whereas for the RCO

samples it varied from 320 to 328 °C. It is clear from the results that the URCO and VCO samples have slightly lower flash point due to the presence of free fatty acids and peroxide which are relatively more volatile when compared to the triglyceride molecules. Free fatty acids (FFA) are formed by the hydrolysis of triglyceride molecule. The level of FFAs in oils depends on several factors. Most important among them are duration of the oil storage, temperature and moisture content of the oils. Since FFAs are less stable than the oils, they are more prone to oxidation and this leads to the undesirable flavor of oils with storage time. Thus quantification of free fatty acid is key factor in accessing the quality and commercial value of oils and fats. The variation in free fatty acid content for URCO, RCO and VCO is as shown in Figure 2a. As expected it has been found that the FFA content in the RCO was lower due to the refining

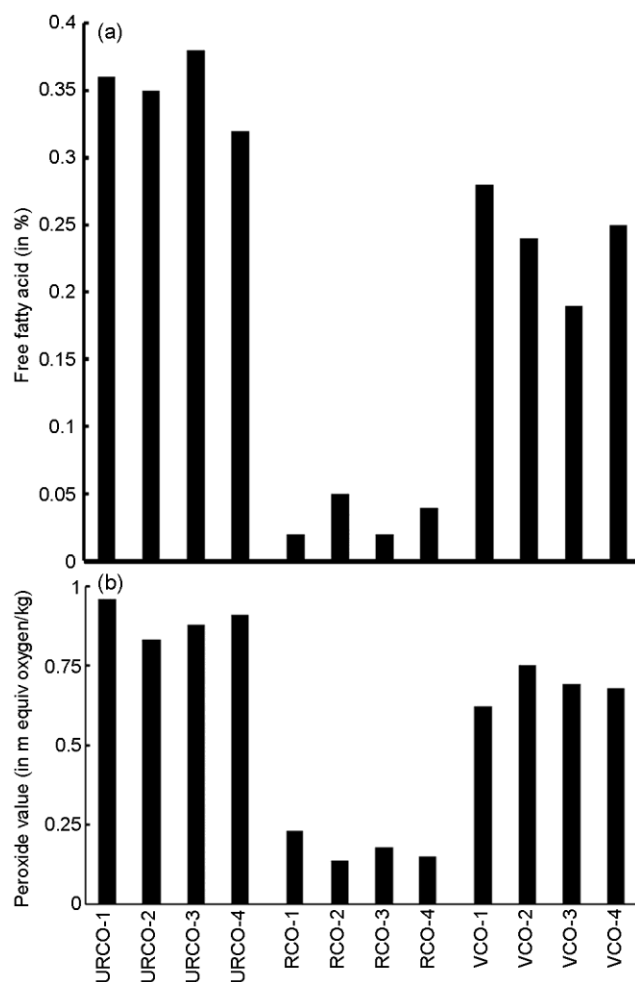


Fig. 2—(a) Variation in free fatty acid content of URCO, RCO and VCO samples, (b) Variation in Peroxide number of URCO, RCO and VCO samples

when compared to URCO and VCO. The refining process results in the removal of impurities such as moisture, fatty acids, metal ions, oxidation products, solid particles and volatiles. It makes the oil suitable for consumption and also improves its shelf life. The observed variations in free fatty acid content of VCO samples were possibly due to the different methods of processing. The VCO produced by fermentation method would have high content of free fatty acid due to the presence of moisture⁸. The peroxide value is a measure of the concentration of peroxides and hydroperoxide present in the oil formed during the initial stages of lipid oxidation. It quantifies the oxidative level of vegetable oils. The variation in peroxide content for URCO, RCO and VCO is as shown in Figure 2b. It can be seen that there is a significant difference in peroxide level of RCO to that of URCO and VCO samples. It was observed that the peroxide values of RCO are low when compared to that of URCO and VCO samples. In the present study peroxide level of RCO samples varied from 0.14 to 0.23 mequiv oxygen/kg oil when compared to 0.62 to 0.96 mequiv oxygen/kg in URCO and VCO samples, which is far below the threshold limit specified by *Codex* indicating that the samples were relatively fresh. However the observed difference in peroxide values for the various samples of RCO to VCO or URCO could be possibly due to the different extraction and processing methods. The variation in wear scar diameter and frictional coefficient for URCO, RCO and VCO is as shown in Figure 3a and 3b. It can be seen that the scar diameter The scar diameter for URCO and VCO samples has varied from 0.435 to 0.453 mm, whereas the wear scar diameter for RCO samples has varied from 0.463 to 0.467 mm which is slightly higher when compared to URCO and VCO and in the same way the coefficient of friction for URCO and VCO samples has varied from 0.082 to 0.096, whereas the coefficient of friction for RCO samples has varied from 0.098 to 0.18. In the present study both wear scar diameter and frictional coefficient for RCO were higher when compared to URCO and VCO samples. This was attributed to the absence of free fatty acids which have act as boundary lubricant in case of URCO and VCO samples reducing the friction. There is also possibility that due to the presence of moisture and the other favorable conditions could facilitate the formation of soaps of fatty acids under sliding conditions to the reduced friction⁹

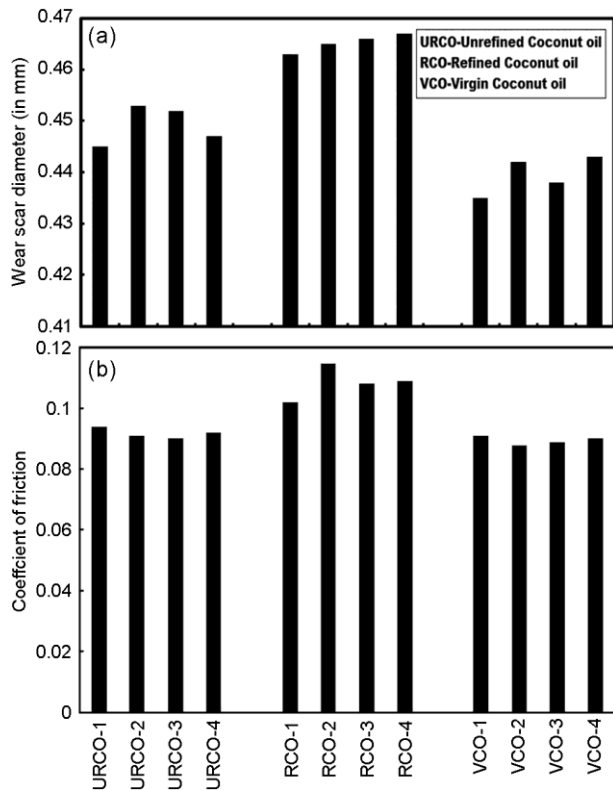


Fig. 3—(a) Variation in wear scar diameter of URCO, RCO and VCO samples, (b) Variation in coefficient of friction of URCO, RCO and VCO samples

Conclusions

In the present work chemical and frictional properties of URCO, RCO and VCO samples were evaluated and the following observations were made. There was close similarity in the composition of URCO and RCO samples collected from the different places reflect the fact that basic extraction of coconut oil was done from same quality of coconuts. The virgin coconut oil (VCO) which is extracted typically by wet process directly from the coconut milk under controlled temperature showed different fatty acid profile when compared to URCO and VCO samples indicates that oil coconuts used were of different quality. The quantity of Caprylic(C8:0), Myristic (C14:0), Palmitic(C16:0) and Stearic(C18:0) acids in VCO samples were slightly higher when compared to URCO and RCO samples. Whereas it was slightly lower with reference to Caproic acid (C6:0), Lauric acid (C12:0), oleic acid (C18:1) and linoleic (C18:2) in VCO when compared to URCO and RCO samples. The URCO and RCO samples had a slightly higher saponification value (255.17–259.54 mg KOH/g) than VCO samples (253.69–255.84 mg KOH/g

oil). This difference is attributed to the observed variation in their fatty acid composition. The iodine value of VCO samples was slightly lower than that of URCO and RCO samples, reflecting the lower level of unsaturated fatty acids in the coconut oil evident from the fatty acid profile. The study showed that the URCO and VCO oil samples have lower flash point compared to RCO samples due to the presence of free fatty acid and peroxide which are more volatile than the triglyceride molecules. As expected it has been found that the FFA content, peroxide value in the RCO was lower due to the refining when compared to URCO and VCO samples. The wear scar diameter for RCO samples was slightly higher possibly due to the absence of free fatty acids which have acted as boundary lubricant in case of URCO and VCO samples. It was also reflected in the higher frictional coefficient observed with RCO samples. The study reveals that for URCO, RCO and VCO samples, the Iodine number, saponification number are influenced by the fatty acid profile of the oil samples. Whereas the tribological properties and flash point were influenced by the peroxide and free fatty acid content in the tested oil samples.

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