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Study on Effect of Aging and Aging Temperature on Frictional Properties of Coconut Oil Samples

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The present study evaluates the effect of aging and aging temperature on the frictional properties of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO) and Virgin Coconut oil (VCO) samples using four ball tester. It was observed that the variations in the physicochemical properties of fresh URCO, RCO and VCO samples were attributed to the difference in their composition. This study showed that URCO, RCO and VCO samples followed same trend in their physicochemical and tribological properties when subjected to aging. The drop in flash point of aged oil samples with aging was attributed to the increased content of free fatty acids generated due to the degradation of triglyceride molecules. It was observed that the degradation of peroxide molecules has resulted in the stabilization in the peroxide content of URCO, RCO and VCO samples when aged at 100 ^{0}C.

Keywords: Coconut Oil, Oxidative Stability, Lubrication and Coefficient of Friction

Introduction

Mineral oil based lubricants consist of hydro-carbons posing a threat to ecology due to their inherent toxicity and non-biodegradable nature. The stringent regulations and increased public awareness over the last two decades have increased interest in the use of environmentally friendly lubricants[1-3]. One major drawback with vegetable oils is their poor oxidation, thermal and hydrolytic stability, due to the presence of unsaturation in the triglyceride molecule as the double bonds act as active sites for reactions. Thus evaluating the oxidation stability of vegetable oils by subjecting them to accelerated aging will provide useful information. One of the major issues with accelerated aging tests is that the test conditions are no longer representative of storage at ambient conditions if the storage temperature rises above 80^{0}C, the oxidation mechanism of vegetable oil changes and hydro peroxides decompose more rapidly and also leads to the several side reactions[4]. The present work analyzes the effect of these factors on the lubrication properties of VCO, RCO and URCO samples by subjecting them to accelerated aging at different temperatures.

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Materials and Methods

In the present work "*Schaal Oven Test*" was used for evaluating the oxidation stability of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO) and Virgin Coconut oil (VCO) samples. This test is based on the conditions as described in the AOCS Recommended Practice Cg 5-97; Oven Storage Test for Accelerated Aging of Oils. Where the test samples stored in an oven at a temperature at elevated temperature and are periodically monitored for changes in the primary oxidation compounds. Though the method is slow and requires a large number of analyses, the major advantage of this method the conditions and thus results are truly representative of storage at ambient conditions when tested at 60 ^{0}C. One of the major issues with accelerated aging tests is that the test conditions are no longer representative of storage at ambient conditions if the temperature rises above 80^{0}C. Once the temperature crosses this limit the oxidation mechanism of vegetable oil changes and hydro peroxides decompose more rapidly and also leads to the several side reactions. The present work analyzes the effect of these factors on the lubrication properties of VCO, RCO and URCO samples by subjecting them to accelerated aging at different temperatures. The fresh and aged oil samples collected at a different interval of time were subsequently analyzed in terms of various parameters. Fatty acid methyl esters (FAME) of the coconut oil samples were prepared and were analyzed as per the standard procedure[5].

The kinematic viscosity of the fresh and aged oil samples collected at a different interval of time was carried out using SVM 3000 Stabinger viscometer as per ASTM standard. In addition to this flash point, free fatty acid and peroxide value of fresh and aged oil samples were also evaluated. The frictional properties of fresh and aged oil samples collected at different interval of time were evaluated using four-ball tester using chrome alloy steel balls of 12.7 mm diameter, confirming to AISI specification E-52100. The experiments were repeated twice to confirm the repeatability.

Results and Discussion

The presence of long, polar fatty acid chains provides high strength lubricant films, reducing both friction and wear. The earlier study showed that the variations in the composition due to the extraction and refining will have marked effect on the tribological properties of vegetable oils[6]. The fatty acid profile of selected coconut oil samples was evaluated as per the procedure specified in the previous section and is as shown in Table 1. Quantification of free fatty acid is a important factor in estimating the quality of vegetable oils. Formation of free fatty acids is influenced by the duration of storage, temperature and the moisture content present in the vegetable oil. Fatty acids are released from the triglyceride molecule by the elimination of β hydrogen and also by the hydrolysis of triglyceride molecule. The variation in Free fatty acids present in fresh and aged URCO, RCO and VCO samples collected at different interval of time is as shown in section A of Table 2. It was observed that FFA content in RCO was 0.064, where as for fresh VCO and URCO samples it was 0.352 and 0.386 respectively. It was observed that with aging the FFA content in the RCO was increased to 0.551 and 0.985 when aged at 60 and 100 ^{0}C, Whereas for the VCO and URCO samples FFA was increased to 0.677 and 0.633 when aged at 60 ^{0}C. and 1.05 and 1.15 when aged at 100 ^{0}C. This clearly shows that with increasing the aging time has resulted in increased content of FFAsOne major drawback with vegetable oils is their poor oxidation, thermal and hydrolytic stability. This is, due to the presence of unsaturation in the triglyceride molecule as the double bonds act as active sites for chemical reactions. This process gets further accelerated in presence of other variables such as temperature, pressure, and catalysts. Oxidation stability limits the use of vegetable oils in lubricant application. The presence of double bonds in the triglyceride molecule functions as active sites for many reactions. This starts with the removal of hydrogen atom from the methylene group forming

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

Fatty acid profile	Oil samples		
(in%)	URCO	RCO	VCO
C 6:0*	0.63	0.57	0.44
C 8:0	8.05	8.16	8.65
C 10:0	6.46	6.85	6.21
C 12:0	47.35	47.42	46.73
C 14:0	17.93	18.09	18.51
C 16:0	8.76	8.46	9.06
C 18:0	3.26	3.06	3.54
C 18:1	6.03	6.02	5.61
C 18:2	1.53	1.37	1.25

*C(X:Y) where X corresponds to number of carbon atoms and Y represents number of double bonds

Table — 2 Variation in the percentage of free fatty acid, peroxide value and Flash point of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO), Virgin Coconut oil (VCO) samples with aging time and temperature

Section A					
Test Sample	Percentage of free fatty acid				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	0.352	0.455	0.677	0.882	1.05
RCO	0.064	0.288	0.551	0.753	0.985
VCO	0.386	0.463	0.663	0.885	1.15
Section B					
Test Sample	Peroxide value (in me equiv oxygen/kg)				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	0.45	0.45	0.45	0.45	0.45
RCO	0.08	0.08	0.08	0.08	0.08
VCO	0.49	0.49	0.49	0.49	0.49
Section C					
Test Sample	Kinematic viscosity (in cSt)				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	29.68	30.71	32.73	32.64	35.49
RCO	28.87	29. 16	30.26	32.53	34.73
VCO	29.77	31.24	32.67	33.04	35.11

a free radical, which in turn can attack another lipid molecule propagating the oxidation process resulting in the formation of peroxide molecules. Thus peroxide value quantifies the oxidation level of vegetable oils and evaluating their impact on the lubrication process will allow the development of more effective, and durable, vegetable based lubricants[7-9]. The formation of free fatty acids due to the hydrolysis is as shown in the following section

3 RCOOR$_1$ + 3 H$_2$o --------> Glycerin + 3R$_1$COOH … (1)

Where the COO represents the ester linkage between glycerin molecule and fatty acids present in the triglyceride. The representative reactions leading to the peroxide formation are shown in the following section.

Initiation

RH-------->R^0 + H^0

R^0+O$_2$ -------->ROO

Propagation

ROO^0+RH -------->ROOH+R^0

ROOH--------> RO^0 + ^{0}OH

Branching

RO^0+RH+O$_2$ --------> ROH + ROO^0

^{0}OH +RH +O$_2$ --------> H$_2$O + ROO^0

ROO^0 +ROO^0 --------> ROOH +O$_2$

Termination

ROO^0 +R^0 --------> ROOH

R^0+ R^0 --------> R-R

In the present work, it can be seen that fresh RCO has very lowperoxides content 0.08 mequiv oxygen/ kg and the peroxide level in fresh URCO and VCO was found to be 0.66 and 0.87 mequiv oxygen/kg. The URCO, RCO and VCO samples when subjected to ageing at 60 ^{0}C for 42 days, showed an increase in the peroxide content to 37.22, 32.63 and 38.71 mequiv oxygen/kg, due to the oxidation of unsaturated fatty acids in coconut oil. However, further increase in aging temperature to 100 ^{0}C has shown increase in peroxide content during the initial three weeks and after that peroxide content was stabilized at 38.54, 37.04 and 38.25 mequiv oxygen/kg for URCO, RCO and VCO samples respectively as shown in section B of Table 2., where with increasing temperature has not resulted in the peroxide content to a higher level. The one possibility is the degradation of peroxide molecules leading to the formation of various secondary products and also leading to polymerization reaction which would increase the viscosity of test samples. Viscosity, measures flow characteristics of oils is useful in monitoring the oxidation and contamination of oil samples. High molecular weight compounds represent the final stages of the oxidation process and are usually formed by the cyclisation and polymerization reactions at elevated temperatures. The variation in kinematic viscosity of fresh and aged URCO, RCO and VCO samples collected at different interval of time is as shown in section C of Table 2. In the present study it was observed that kinematic viscosity of fresh URCO, RCO and VCO samples was 29.68 and 28.87 cSt when compared to 29.77 cSt for RCO samples. It was observed with aging the kinematic viscosity of URCO, VCO and RCO has increased to 32.73, 30.26 and 32.67 cSt when samples were aged at 60 ^{0}C and 35.49, 34.73 and 35.11 cSt when samples were aged at 100 ^{0}C. This confirms that the URCO, RCO and VCO samples which have undergone aging at 60 and 100 ^{0}C have shown

Table 3 — Variation in the wear scar diameter, coefficient of friction and flash point of Unrefined Coconut oil (URCO), Refined Coconut oil (RCO), Virgin Coconut oil (VCO) samples with aging time and temperature

Section A

Test Sample	Wear Scar diameter (in mm)				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	0.446	0.451	0.458	0.462	0.476
RCO	0.464	0.466	0.482	0.471	0.488
VCO	0.437	0.445	0.464	0.459	0.481

Section B

Test Sample	Coefficient of friction				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	0.092	0.087	0.081	0.084	0.075
RCO	0.11	0.086	0.082	0.088	0.07
VCO	0.088	0.083	0.08	0.083	0.078

Section C

Test Sample	Flash point(in ^{0}C)				
	Fresh oil	Aged oil at 60 ^{0}C		Aged oil at 100 ^{0}C	
		21 days sample	42 days sample	21 days sample	42 days sample
URCO	312	307	298	302	292
RCO	321	315	302	309	297
VCO	314	308	299	304	295

increase in viscosity this was attributed to the chemical changes. The variation in wear scar diameter with aging temperature for URCO, RCO and VCO is as shown in section A of table 3. It can be seen that the scar diameter for fresh URCO and VCO samples was found to be 0.446 and 0.437 mm, where as the wear scar diameter for fresh RCO was found to be 0.466 mm due to the absence of free fatty acids. It was noticed that with aging at 60 ^{0}C the scar diameter for URCO, RCO and VCO has increased to 0.457, 0.483 and 0.465 mm, whereas at the ageing temperature of 100 ^{0}C the scar diameter for URCO, RCO and VCO has increased to 0.477, 0.486 and 0.463 mm. The increased wear scar diameter was observed due to the increased content of peroxides in the oil samples. The variation in coefficient of friction for URCO, VCO and RCO is as shown in section B of table 3. It is clear from frictional data of four ball test experiment that fresh URCO and VCO samples have a coefficient of friction of 0.092 and 0.088 when compared to fresh RCO which has 0.11 the presence of free fatty acids. Further with aging the coefficient of friction for URCO, RCO and VCO has reduced to 0.081, 0.082 and 0.083 at aging temperature of 60 ^{0}C. The coefficient of friction has reduced further to 0.075, 0.07 and 0.078 for samples aged at 100 ^{0}C. The free fatty acids which acted as good boundary lubricants are responsible for the observed variations in the coefficient of friction[10-13]. Flash point measures the volatility of fluid and is a useful tool in quality control. The variation in flash point of fresh and aged URCO, RCO and VCO samples collected at different interval of time is as shown in section C of Table 3. It was observed that flash point of fresh URCO and VCO samples was 312 and 314 ^{0}C when compared to 321^{0}C for RCO samples, which was due to the presence of free fatty acids and peroxides. It was observed with aging the flash point of URCO, VCO and RCO has dropped to 298, 299 and 302 ^{0}C at the when samples were aged at 60 ^{0}C and 292, 295 and 297 when samples were aged at 100 ^{0}C, reflecting the fact with increasing the aging temperature the quantity of oil degradation was also increased resulting in more quantity of peroxide and free fatty acids, which are more volatile than the corresponding triglycerides.

Conclusions

In the present work effect of aging and aging temperature on the frictional properties of URCO, RCO and VCO samples and the following observations were made.

- Variations in the frictional properties of fresh VCO, URCO and RCO were due to the difference in their composition.
- The difference in the flashpoint of VCO, URCO to RCO samples was due to the presence of free fatty acids which are more volatile than the corresponding triglycerides. The decrease in flash point of aged URCO, RCO and VCO samples was due to the increased content of free fatty acids.
- Peroxides present in the fresh VCO and URCO samples are responsible for the increased oxidation of observed with VCO and URCO oil samples when compared to RCO. However it was observed that with increased aging time and temperature the difference in the peroxide content of URCO, VCO to RCO was negligible. The observed stabilization of peroxides levels with aging at 100 ^{0}C was due to the disintegration of peroxides.
- The wear scar diameter for RCO samples was slightly higher possibly due to the absence of free fatty acids which have acted as a boundary lubricant in the case of URCO and VCO samples. It was also reflected in the higher frictional coefficient observed with RCO samples.

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