Chapter-4

Tribological evaluation of raw biolubricants

This chapter discusses the tribological performance of vegetable based biolubricants without any additives. The explored biolubricants were the oil of castor, rapeseed, sunflower, cottonseed, olive, neemseed and sesame oil. The role of the fatty acid composition of the biolubricants on the performance of antiwear and antifriction is reported.

4.1. Composition of the selected vegetable oils

The fatty acids composition of the biolubricants obtained using gas chromatography mass spectroscopy (GC-MS) presented in Table 4.1 and detailed composition in Table 4.2. It was observed that saturation and unsaturation varied distinctly for different biolubricants. Among the biolubricants, saturation varies (minimum to maximum) from 4 to 37%, mono-unsaturation ranges from 17.8 to 88.9 and poly-unsaturation from 6.8 to 51.9%, respectively.

Table 4.1. List of saturates and unsaturates in percentage for different biolubricants.

Base oil	Saturates (%)	Mono-unsaturate (%)	Poly-unsaturate(%)
Castor oil (CO)	4.0	88.9 (4.41 oleic + 84.5 ricinoleic acid)	6.8
Rapeseed oil (RO)	6.3	72.8	20.9
Sunflower oil (SO)	8.9	70.0	21.1
Cottonseed oil (CTO)	25.9	17.8	51.9
Olive oil (OO)	19.4	68.2	18.0
Neemseed oil (NO)	37.0	42.1	20.0
Sesame oil (SSO)	16.9	42.0	41.2

Castor, rapeseed and sunflower oils have low saturation as compare to cottonseed, olive, neemseed and sesame oils. However, castor, rapeseed and sunflower oils dominate with mono-unsaturation as compared to rest of the oils (Table 4.1). The number of doubles bond represents the degree of unsaturation and attributes the quality of the vegetable oil. This is because these double bonds act as an active site for different thermo-chemical reactions. Therefore, characteristic of the vegetable oil is greatly dependent on zero or minimum counts of double bonds in the fatty acid structure. Castor oil is only biolubricant with the majority of ricinoleic acid (84.5%), which is mono-unsaturates (Table 4.2). Therefore, castor oil is on the top for mono-unsaturated fatty acid as compared to the other explored biolubricants in this study.

Table 4.2. Detailed composition of fatty acid structure (in %) of biolubricants.

Composition	CO	RO	SO	CTO	OO	NO	SSO
C 12:0	-	-	0.02	-	-	-	-
C 14:0	1.0	-	0.06	0.86	-	-	-
C 16:0	1.48	4.6	6.2	22.6	16.5	15.59	9.7
C 18:0	1.58	1.7	2.6	2.13	2.3	18.71	6.5
C 20:0	-	-	0.11	0.28	0.43	1.33	0.56
C 22:0	-	-	-	-	0.15	0.86	0.14
C 16:1	-	0.21	0.12	0.59	1.8	0.12	0.11
C 18:1	4.41	64.4	69.9	17.2	63.3	41.91	41.5
C 20:1	-	8.18	0.18	-	0.30	0.08	0.32
C 18:2	6.10	19.6	20.9	51.67	16.4	19.59	40.9
C 18:3	0.68	1.2	0.16	0.21	1.6	0.44	0.21
12-OH-9-cis C18:1	84.51	-	-	-	-	-	-

[Note that typical C xy: z represents xy length of the carbon chain with z number of double bonds. For example C 18:1 represents the fatty acid structure for 18-carbon chain with one double bond.]

Here, ***C12:0*** referred as Lauric acid, ***C14:0*** Myristic acid, ***C16:0*** Palmitic acid, ***C18:0*** Stearic acid, ***C20:0*** Arachidic acid, ***C22:0*** Behenic acid, ***C16:1*** Palmitoleic acid, ***C18:1*** Oleic acid, ***C20:1*** Eicosenoic acid, ***C18:2*** Linoleic acid, ***C18:3*** Linolenic acid, and ***12-OH*-9-cis *C18*:*1*** Ricinoleic acid.

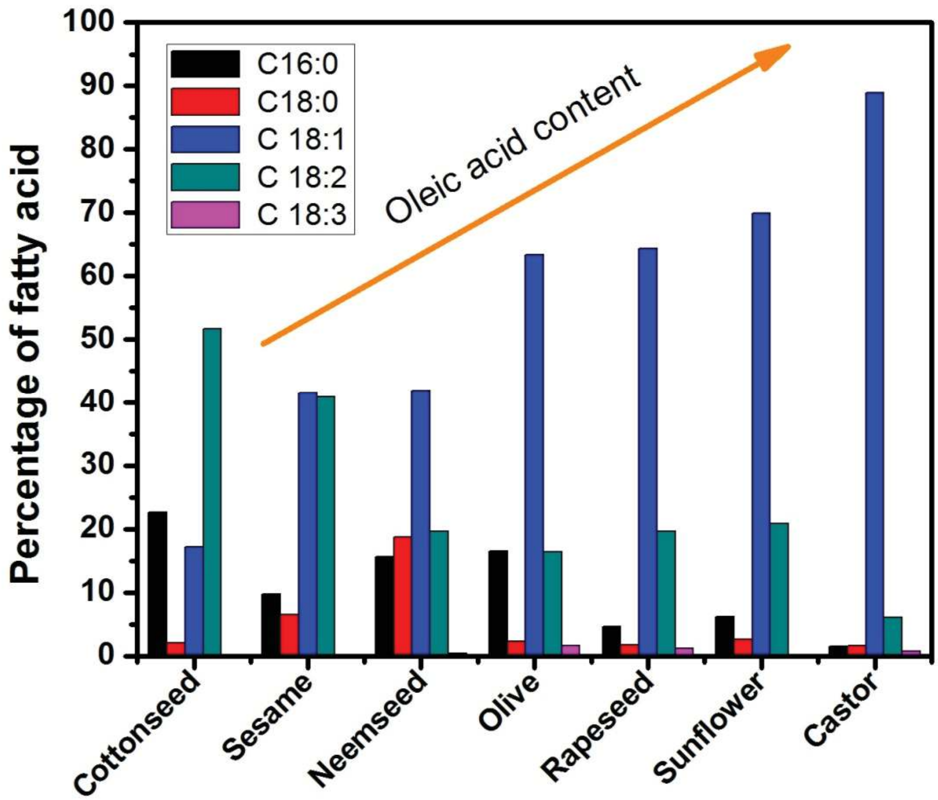

Figure 4.1. Variation in fatty acid composition for different biolubricants.

It was reported that these saturates and unsaturates have a significant role in the physical and tribological behavior of the biolubricants (Koshy et al., 2015). Erhan et al. (2006) also reported that oxidation and low temperature stability of the vegetable based biolubricants is the function of unsaturation in the fatty acid chain. Oil oxidation is an undesirable chemical reaction involving oxygen that degrades the quality of the oil. The presence of the high poly-unsaturation (like linoleic and linolenic acid) in triglycerides reduces the thermo-oxidative stability. On the contrary, high saturated contents (like palmitic and stearic acid) and mono-unsaturation (i.e. oleic acid) increase the same (Erhan et al., 2006).

Figure 4.1 depicts the variation of the main constituents in the fatty acid chain for different vegetable oils as per the obtained composition analysis. It is evident that the variation of the palmitic, stearic and linolenic acid was found random for the explored vegetable oils. In other words, no particular trend observed. However, oleic acid and linoleic acid have shown a specific trend from cottonseed to castor oil (Figure 4.1). Oleic acid has shown increasing trend while linoleic acid is almost decreasing from cottonseed to castor oil. This variation is fascinating and showed vital correlation in the performance of the biolubricants with tribological behavior and thermo-oxidation stability.

4.2. Evaluation of antiwear performance

The tribological behavior of the raw biolubricants, without any additive, was evaluated with four-ball tester. The operating parameters were 392 N load, 1200 r.p.m. spindle speed, oil temperature 75°C and test run of one hour. The antiwear properties of the biolubricants were examined by the wear scar diameter (WSD) on the tested balls (which represents material loss) during the sliding.

Table 4.3 summarized the average WSD size on the test specimen for all the explored biolubricants, and Figure 4.2 depicts the corresponding variation in WSD. The size of WSD tagged with the white lines in SEM images of the wear scar. It shows that the WSD varied from 759.8 (for cottonseed oil) to 906.4 μm (for castor oil) among all the biolubricants in the antiwear test. Table 4.3 also shows the obtained WSD is higher compared to calculated Hertzian diameter (i.e. 405.4 μm, Appendix-A). This is because Hertzian theory assumes all the distortion within the elastic limit. SEM images of the worn-out surfaces lubricated with all explored biolubricants separately presented in Figure 4.3 to 4.9.

Correlation between WSD and fatty acid composition

The obtained results of worn surface indicate that antiwear behaviour of the vegetable oil strongly affected by the fatty acid composition. The correlation can be readily understood by comparing Figure 4.1, Table 4.2 with Table 4.3. The increase in the oleic acid content in the biolubricant (which has one double bond in fatty acid chain, i.e. mono-unsaturates), increases the WSD. On the contrary, a higher concentration of linoleic acid improved the WSD in our study. Although the variation in WSD for the explored biolubricants is not significant, however, the influence of oleic and linoleic acid cannot be ignored. It frames the role of these constituents on the tribo-performance of biolubricants. In other words, one can say that tribological property of biolubricants dependent on the fatty acid composition (Karmakar et al., 2017).

Table 4.3. Summary of the average WSD on the test ball lubricated with different biolubricants. (σ: standard deviation and Δ: WSD – Hertzian diameter)

Base oil	WSD (μm)	σ	Δ
Castor	906.4	29.2	501
Sunflower	873.0	18.7	467.6
Rapeseed	788.4	28.3	383
Olive	784.6	22.6	379.2
Neemseed	771.9	13.5	366.5
Sesame	767.2	18.9	361.8
Cottonseed	759.8	23.3	354.4

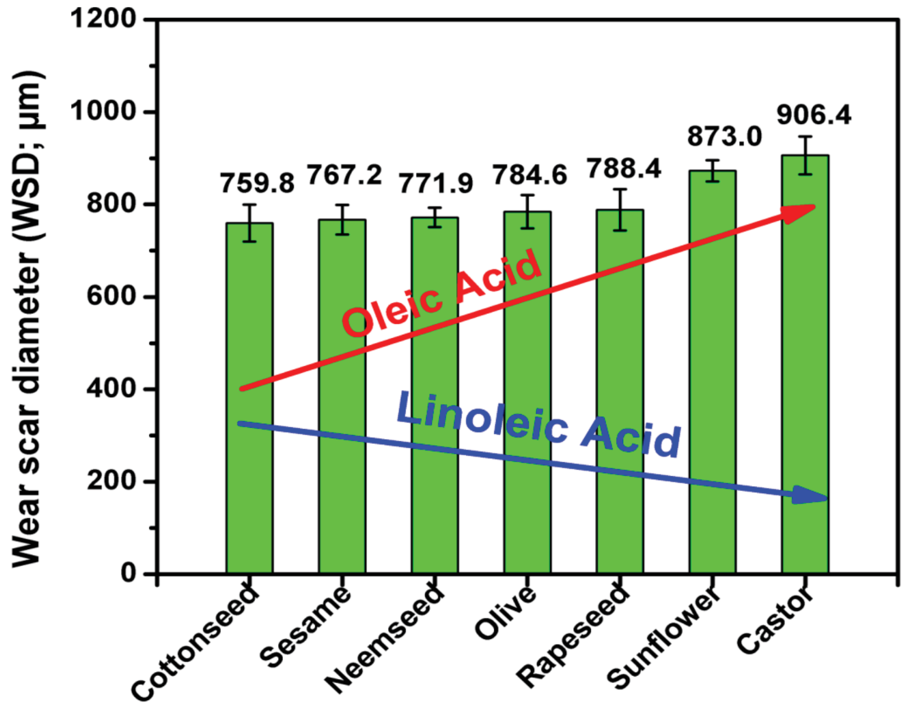

Figure 4.2. Variation in wear scar diameter for different biolubricants.

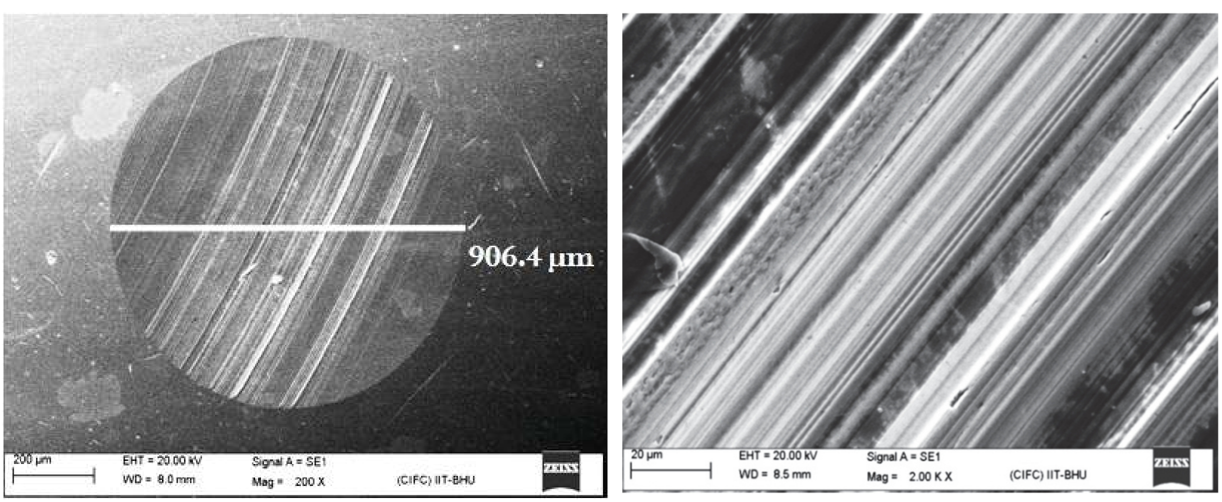

Figure 4.3. SEM images of the worn surface (at different magnifications) tested with castor oil at load 392N, sliding speed 1200 rpm for 1h.

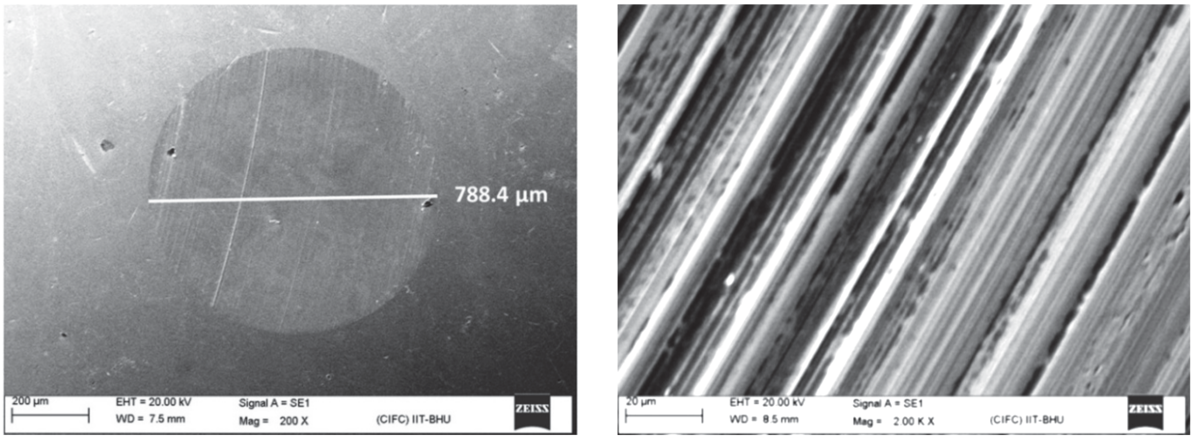

Figure 4.4. SEM images of the worn surface (at different magnifications) tested with rapeseed oil at load 392N, sliding speed 1200 rpm for 1h.

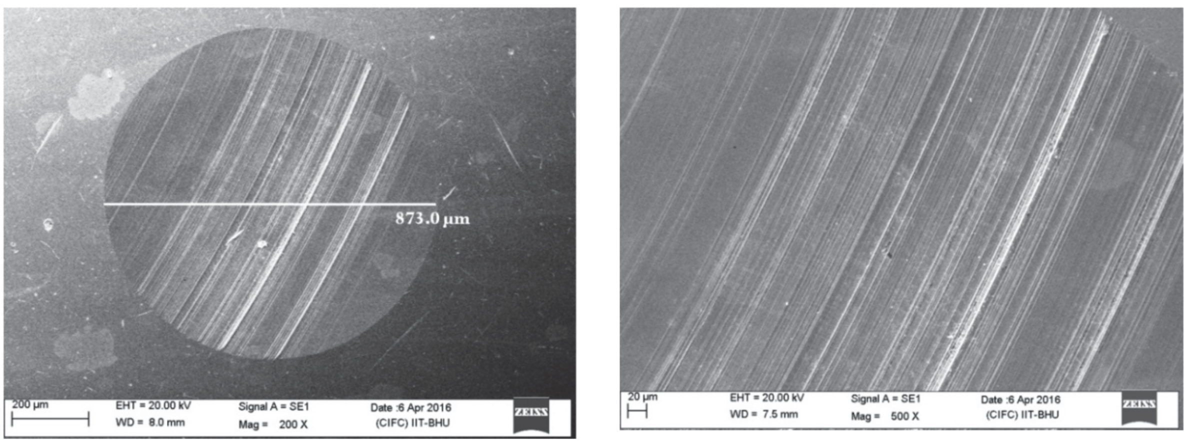

Figure 4.5. SEM images of the worn surface (at different magnifications) tested with sunflower oil at load 392N, sliding speed 1200 rpm for 1h.

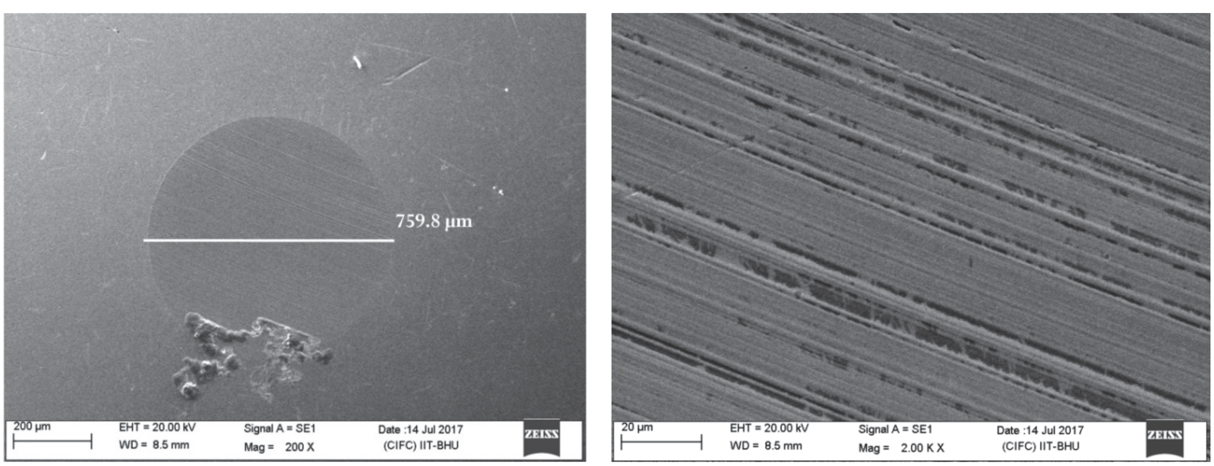

Figure 4.6. SEM images of the worn surface (at different magnifications) tested with cottonseed oil at load 392N, sliding speed 1200 rpm for 1h.

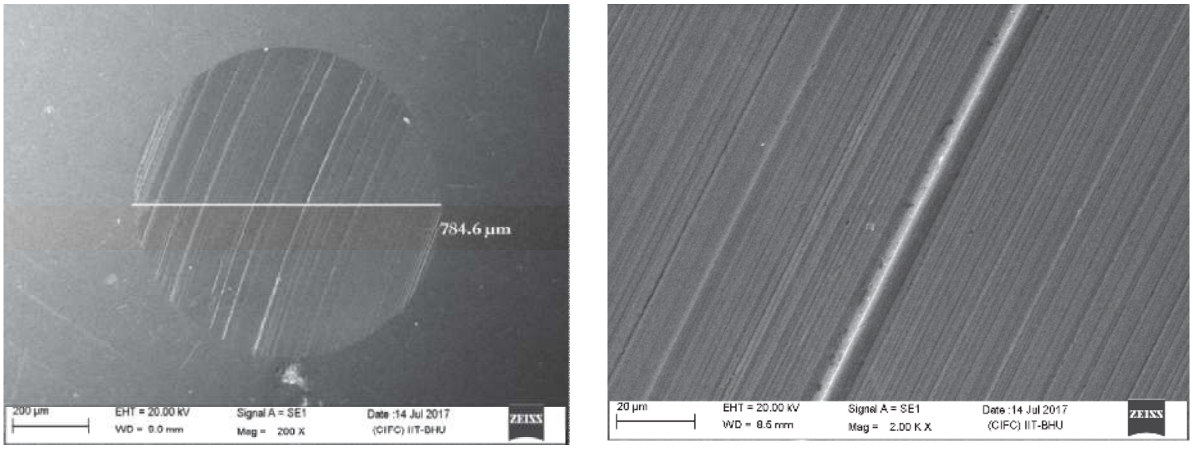

Figure 4.7 SEM images of the worn surface (at different magnifications) tested with olive oil at load 392N, sliding speed 1200 rpm for 1h.

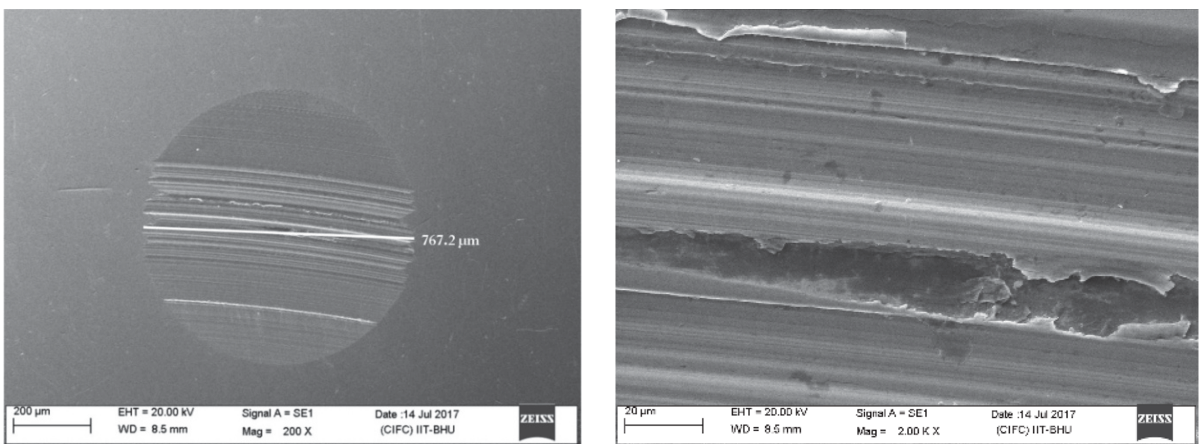

Figure 4.8. SEM images of the worn surface (at different magnifications) tested with sesame oil at load 392N, sliding speed 1200 rpm for 1h.

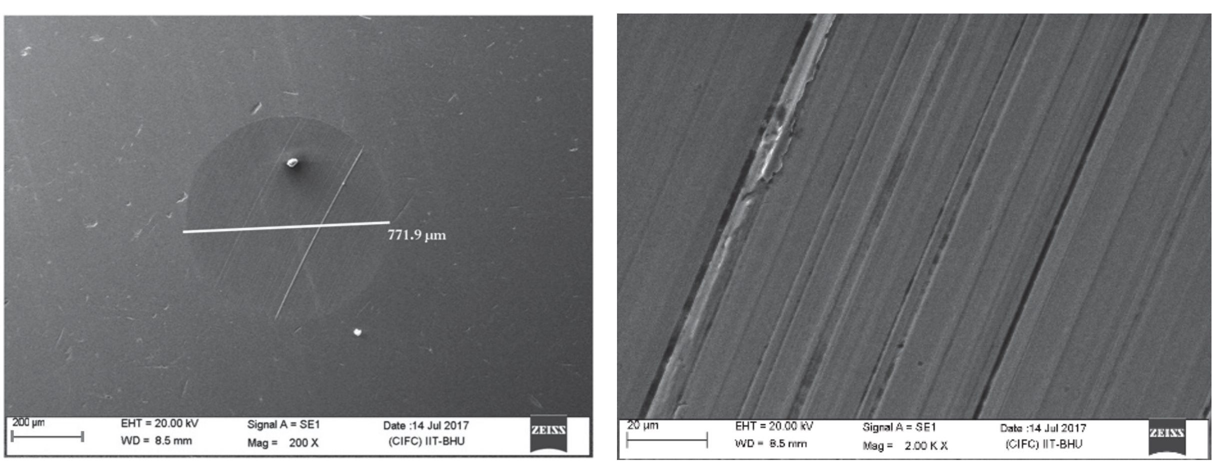

Figure 4.9. SEM images of the worn surface (at different magnifications) tested with neemeed oil at load 392N, sliding speed 1200 rpm for 1h.

The topography of the worn surfaces presented with two different magnifications for each type of the biolubricants as can be seen in Figure 4.3- 4.9. The lower magnification (200x) shown for the measurement of WSD size of the worn surface, while higher magnification (2000x) for the analysis of the wear characteristics. In case of raw biolubricants, both abrasive and adhesive wear were observed (especially with sesame oil adhesive wear dominates). Neemseed oil shows comparatively smoother morphology as compared to the other biolubricants. It can be correlated with the higher amount of the saturation in neemseed, cottonseed, olive, sesame oils as compared to the castor, rapeseed and sunflower oils. It attributes that degree of saturation of the vegetable oil also responsible for such behavior.

All the lubricants have potential to create the surface protective tribo-film on the mating surfaces by physisorption without any additive (Bhusan and Liu, 2004; Hamrock et al., 2004). And, under the localized frictional heating the chemisorption reaction takes place on the mating surfaces to form the protective film (Bhusan and Liu, 2004). This is the characteristic properties of the lubricating oil without using any additives it forms a boundary lubricating layer. Therefore the capability of the tribo-film formation to separate the asperity-asperity contact depends upon physical properties of the lubricant itself. In case of the vegetable oils triglyceride composition, viscosity, polar nature, and lubricity play a crucial role in forming the tribo-film (Siniawski et al., 2007). Cottonseed oil has excellent capability to create the denser protecting film, thus lower wear. Castor oil also has highest viscosity and good lubricity to form the film but also some ease escaping properties like silicone oils. This may be responsible for the somewhat higher WSD as compared to the other biolubricants. Reeves and Menezes (2017) reported that oleic and linoleic acid content in the biolubricant affect the formation of boundary lubricating tribo-film. The presence of double bonds (one in oleic and two in linoleic acid) in the fatty acid gives an inherent rigidity for the formation of closely packed monolayer on the surface (Doig et al., 2014; Reeves and Menezes, 2017). However, presence of more double bond in the backbone tends to reduce the film packing efficiency. This is because the more disordered film formed when the number of double bond increases in the backbone, which creates obstacles in close packing of the adsorbed film (Sophie 2014).

The images of worn surface roughness lubricated with castor, rapeseed, sunflower, cottonseed, olive, sesame and neemseed depicted in Figure 4.10 - 4.16 respectively. Also, the root mean square (r.m.s.) line roughness (R_q) values enumerated in Table 4.4. Neemseed and cottonseed oil show lower roughness for the worn surfaces, which supports the result as mentioned earlier in the SEM. The roughness R_q varies from minimum 207.1 to maximum 398.5 nm.

Table 4.4. Summary of r.m.s. surface roughness of the worn surfaces lubricated with different biolubricants.

Base oil	Line roughness (R_q; nm)
Castor	398.5
Sunflower	292.6
Rapeseed	272.9
Olive	271.3
Neemseed	207.1
Sesame	276.5
Cottonseed	211.1

At the microscopic level, it was observed that no surface is sound smooth. Every surface consists of numerous asperities/peaks and valleys. During sliding of the mating surfaces asperity-asperity locking takes place and under higher operating load destruction of these asperities result in severity of the surface roughness. Therefore, lubricants help in the easy escape of the asperity contacts. The AFM roughness results (as in Table 4.4) of the worn track showed good agreement with WSD variation. The lower roughness observed with cottonseed oil may be due to the formation of the denser film as compared to the other types of oils tested. Therefore, it is speculated that the presence of high linoleic acid with some oleic acid might have effected on dense film formation.

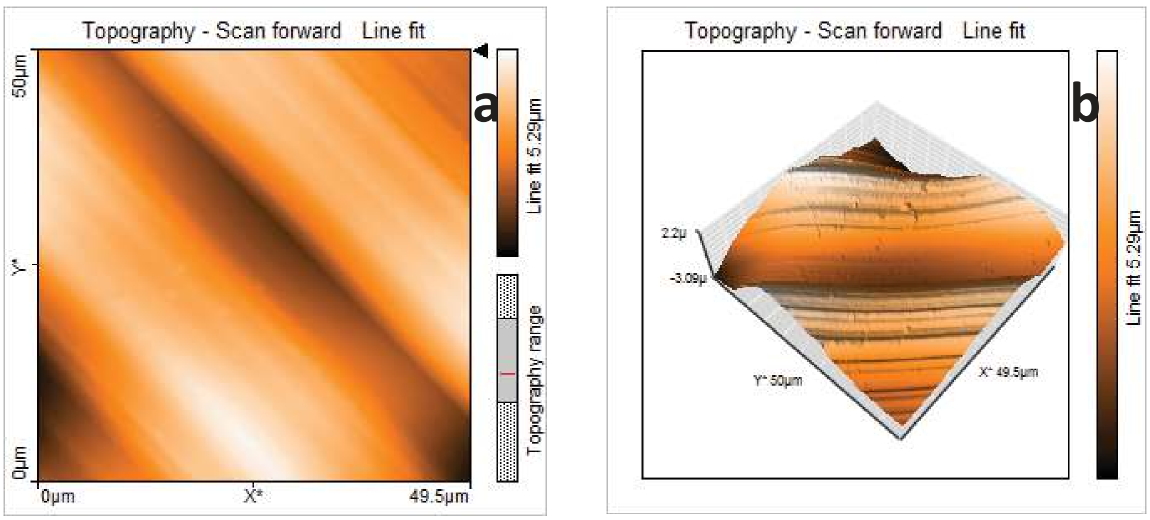

Figure 4.10. AFM roughness topography of the worn surface tested with raw castor oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

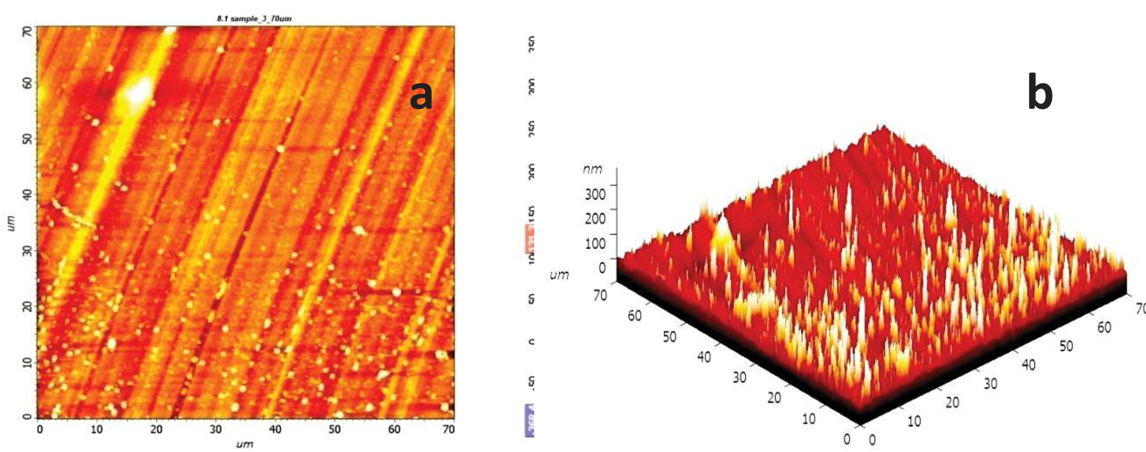

Figure 4.11. AFM roughness topography of the worn surface tested with raw rapeseed oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

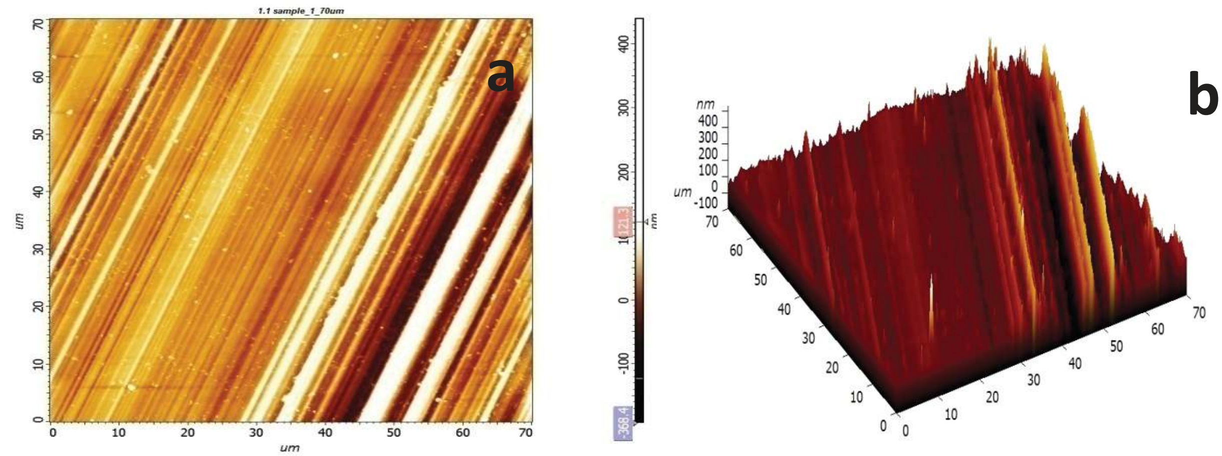

Figure 4.12. AFM roughness topography of the worn surface tested with raw sunflower oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

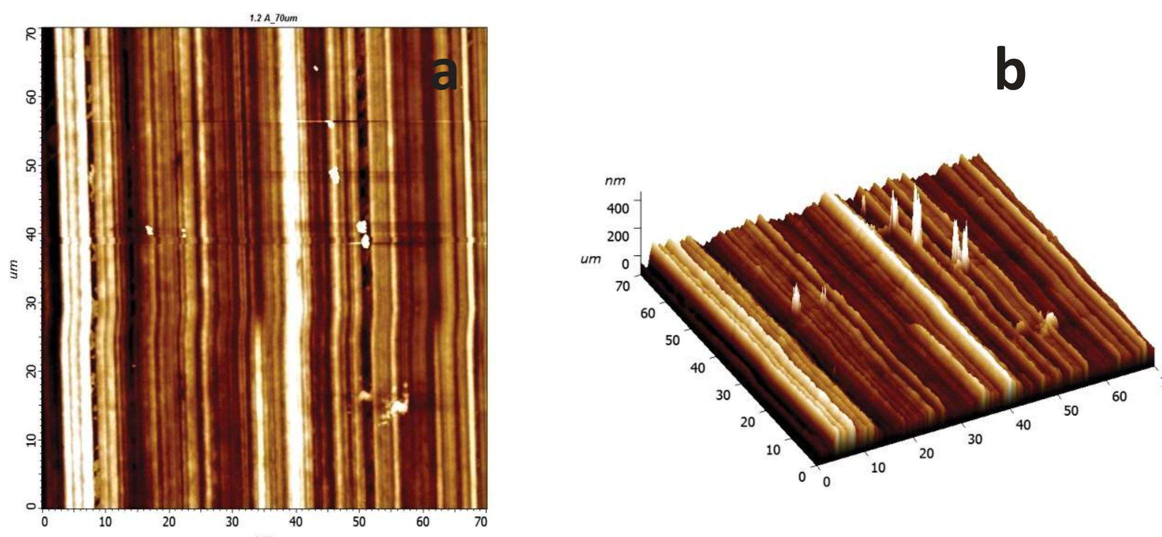

Figure 4.13. AFM roughness topography of the worn surface tested with raw cottonseed oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

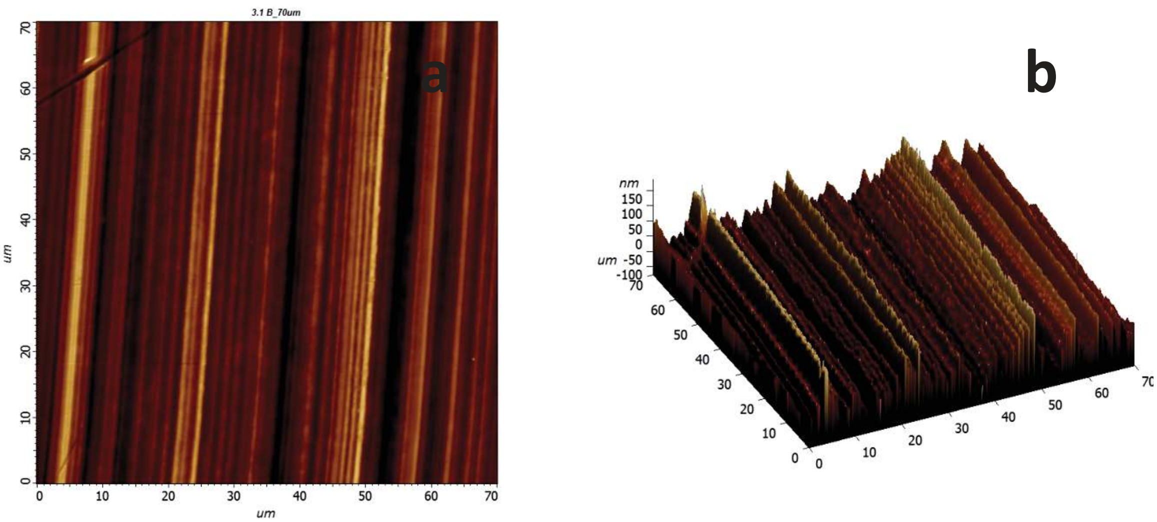

Figure 4.14. AFM roughness topography of the worn surface tested with raw olive oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

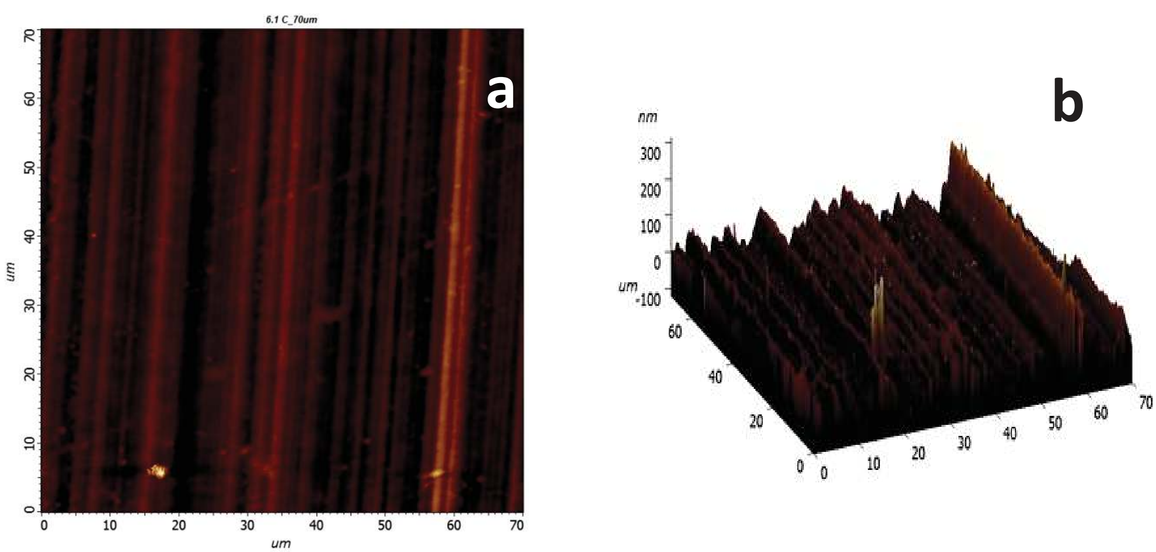

Figure 4.15. AFM roughness topography of the worn surface tested with raw sesame oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

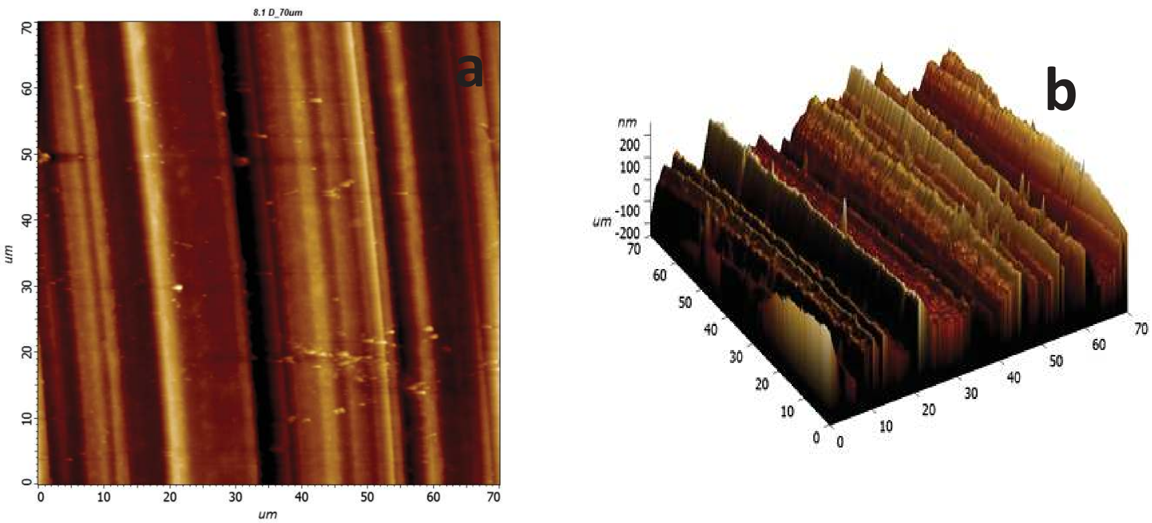

Figure 4.16. AFM roughness topography of the worn surface tested with raw neemseed oil (load 392N, speed 1200 rpm for 1h) showing (a) 2-dimensional and (b) 3-dimensional view.

4.3. Evaluation of antifriction performance

The mean coefficient of friction (COF) values for different biolubricants presented in Table 4.5. The operating condition was same as an antiwear test to examine the friction behavior. The mean COF of sunflower, and rapeseed oil has shown lower values as compared to the rest of the biolubricants. However, olive, castor and neemseed oil have shown the COF at the similar level. One can say that the rate of tribo-film formation for these oils is similar. Also, it demonstrates that there is no direct proportional relation between COF and WSD variation for the explored oils in our study. In simple words, it can say that WSD was minimum for the additive-free cottonseed oil (as in antiwear test), but COF was not lowest as expected. The friction is assumed to be in direct proportion to wear variation. It means high wear causes higher friction. In our investigation, cottonseed oil showed highest mean COF (i.e. 0.0888) while rapeseed and sunflower showed lower COF. It can be speculated that apart from the fatty acid composition there are other two factors which may be responsible for such antifriction results. First, the rate of the formation of tribo-film during sliding and second, the stability of the film under higher applied test load. Therefore, one can say that rapid and stable tribo-film formation rate improves the tribological property significantly. Furthermore, the calculated friction factor and Sommerfeld number (Appendix-B) for the base oils also confirm the system is working in boundary lubrication regime.

Table 4.5. Summary of mean coefficient of friction for different biolubricants.

Base oil	COF (Avg.)	Standard Deviation (σ)
Castor	0.078	0.0037
Sunflower	0.0628	0.0022
Rapeseed	0.0656	0.0006
Olive	0.0767	0.0029
Neemseed	0.0784	0.0036
Sesame	0.0856	0.0019
Cottonseed	0.0888	0.0027

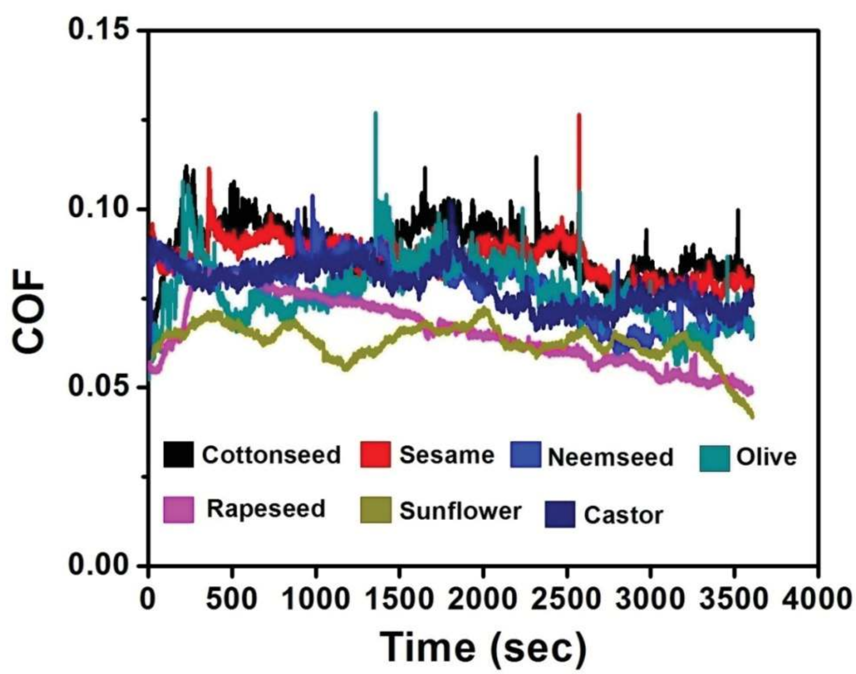

Figure 4.17. Variation in coefficient of friction for different biolubricants tested at load 392N, speed 1200 rpm for 1h.

The obtained COF results indicate that rapeseed and sunflower have potential to form protective film rapidly as compared to the rest of the biolubricants. Also, the film thickness and its stability may not be constant throughout the test run. Therefore, the tribo-film characteristics entirely depend upon oil physical properties.

Figure 4.17 depicts the variation in the COF of the test run for different biolubricants. The close observation of the trend reveals that, except for castor oil, the friction increases just after the start of the test thereafter decreases or remains constant, it is an indication of the wear-in period. Castor oil shows decreasing trend, probably the castor oil has high viscosity (0.28 N-s/m^2) and lubricity as compared to the other oils (Table 3.1). Therefore, the metal to metal contact is low and castor oil self-capable to keeping the asperities away.

4.4. Thermal stability of the biolubricants

Thermogravimetric curves for all the selected raw biolubricants (without additive) presented in Figure 4.18. It exhibits the thermal decomposition profiles for different biolubricants were almost similar but the difference at the beginning of decomposition temperature (called as onset temperature; T_{onset}).

Table 4.6. The initial decomposition temperature of the biolubricants.

Base oil	**T_{onset} (°C)**
Neemseed	291
Olive	301
sesame	309
Cottonseed	320
Sunflower	398
Castor	432
Rapeseed	417

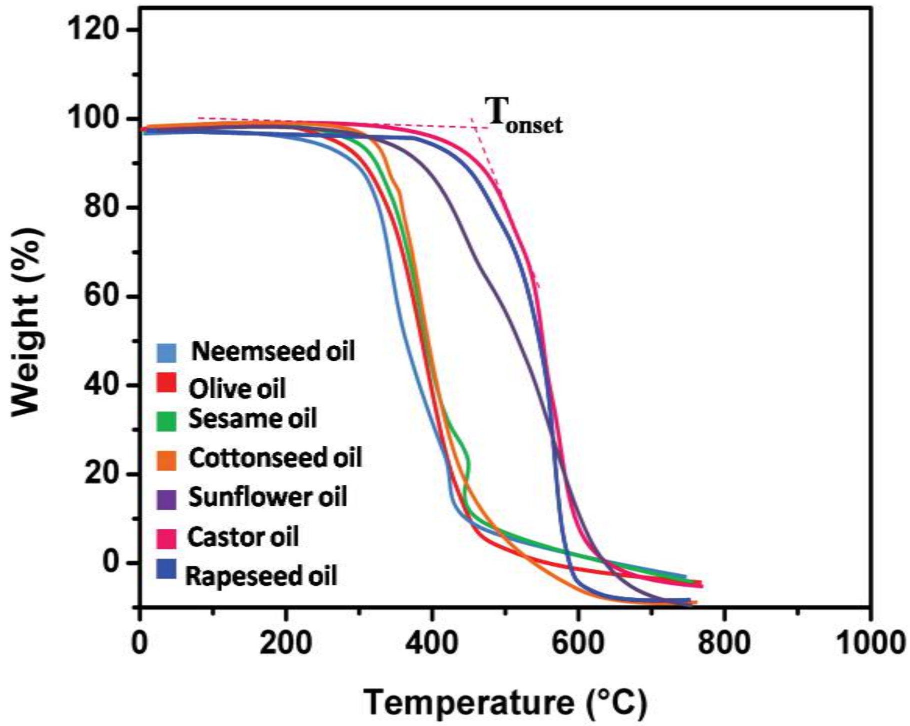

Figure 4.18. TGA curve for different biolubricants to estimate decomposition temperature.

It is also noticed that in few cases (i.e, rapeseed, sunflower and cottonseed) some negative weight % present in the Figure 4.18. It may be due to the presence of residues in the base oil. Therefore, residues present in the oil might have caused the incomplete combustion and shown negative trend in the curve.

Table 4.6 represents the summary of T_{onset} temperature. A plateau may observe for all the biolubricants between 200 to 300°C ranges, indicating no thermal effect on oil structure. The lowest decomposition temperature was obtained for neemseed oil while highest for castor oil (Table 4.6). Castor, rapeseed and sunflower oil exhibits start of decomposition at approximately 400°C temperature or higher. The stability order obtained from TGA analysis was; Castor > Rapeseed > Sunflower > Cottonseed > Sesame > Olive > Neemseed.

It reveals that castor oil was less susceptible to degradation with the temperature than other oils. Moreover, the end of decomposition range varied from approx. 430 to 650°C for different raw biolubricants. It can be identified in Figure 4.18 by the sudden change from inclined to nearly horizontal and further up to the asymptotic value. The end of decomposition was maximum for the sunflower oil thereafter castor oil, while neemseed decomposed earliest. TGA results correlated with the results of GC-MS with the oil composition. It is fascinating that TGA results show the good agreement with the GC-MS fatty acid composition results. It also shows that C18:1 and C18:2 contents in the biolubricants have a critical role in thermal properties variation.

4.5. Summary of the chapter

The chemical compositions of the all explored biolubricants have shown distinct characteristics of antiwear and antifriction performance. The biolubricants have shown the WSD in the range from 759.8 (min.) to 906.4 µm (max.) and mean COF values from 0.0628 to 0.0888. Rapeseed and sunflower oil have shown lower friction values as compared to cottonseed, neemseed, castor, olive, and sesame oil. However, on considering the friction trend with castor oil it can presume that rapid film formation rate than other oils. In this study, the behavior of COF was varying with the different biolubricants tested, however no specific trend was observed between the viscosity and COF.

Based on the obtained friction and WSD results, thermal decomposition properties, formation and stability of the protective films; the rapeseed, sunflower, and castor oils have chosen for the further investigation.