CHAPTER-4

BIOLUBRICANTS

FROM

CELLULOSIC WASTE
1.0 Introduction

1.1 Introduction of lubrication
Lubrication is introduced between two sliding solids by adding a gaseous, liquid, or solid lubricant at the sliding interface in order to reduce friction and wear, and to carry away heat and debris generated during the sliding process. Lubrication processes can take many different forms, depending on the gross geometry of the contacting bodies, the roughness and texture of the sliding surfaces, the contacting load, the pressure and temperature, the rolling and sliding speeds, the environmental conditions, the physical and chemical properties of the lubricant, the material composition, and the properties of the near-surface layer.

1.2 Introduction of lubricants
Lubrication is simply the use of a material to improve the smoothness for movement of one surface over another; the material which is used is called a lubricant. Lubricants are usually liquids or semi-liquids, and may be solids or gases or any combination of solids, liquids, and gases. The smoothness of movement is improved by reducing friction. This is not, however, always the case, and there may be situations in which it is more important to maintain steady friction than to obtain the lowest possible friction. In addition to reducing or controlling friction, lubricants are usually expected to reduce wear and often to prevent overheating and corrosion. The lubricant is cooled upon to limit and control the friction between the components and metal to metal contact, over heating of the components, wear of the components and corrosion.

To accomplish the above functions, a good lubricant should have following properties:

- Suitable viscosity.
- Oiliness to ensure the adherence of the bearings and
loss of friction and wear when the lubrication is in the boundary region, and as a protective covering against corrosion.

- High strength to prevent the metal to metal contact and seizure under heavy load.
- Should not react with the lubricating surface.
- A low pour point to allow the flow of lubricant at low temperature to the oil pump.
- No tendency to form deposits by reacting with air, water, fuel or the products of combustion.

1.3 Classification of lubricants

1.3.1 Mineral lubricants

1.3.1.1 Fluid lubricants (Oils)

Mineral fluid lubricants are based on mineral oils. Mineral oils (petroleum oils) are products obtained from refining of crude oil. There are three types of mineral oil: paraffin, naphthenic and aromatic. Paraffin oils are produced either by hydro cracking or solvent extraction process. Most hydrocarbon molecules of paraffin oils have non-ring long-chained structure. Paraffin oils are relatively viscous and resistant to oxidation. They possess high flash point and high pour point. Paraffin oils are used for manufacturing engine oils, industrial lubricants and as processing oils in rubber, textile, and paper industries. Naphthenic oils are produced from crude oil distillates. Most hydrocarbon molecules of naphthenic oils have saturated ring structure. Naphthenic oils possess low viscosity, low flash point, low pour point and low resistance to oxidation. Naphthenic oils are used in moderate temperature applications, mainly for manufacturing transformer oils and metal working fluids. Aromatic oils are products of refining process in manufacture of paraffinic oils. Most hydrocarbon molecules of aromatic oils have non-saturated ring structure. Aromatic oils are dark and have high flash point. Aromatic oils are used for manufacturing seal compounds,
adhesives and as plasticizers in rubber and asphalt production.

1.3.1.2 Semi-fluid lubricants (greases)
Semi-fluid lubricants (greases) are produced by emulsifying oils or fats with metallic soap and water at 400-600°F (204-316°C). Typical mineral oil base grease is vaseline. Grease properties are determined by a type of oil (mineral, synthetic, vegetable, animal fat), type of soap (lithium, sodium, calcium, etc. salts of long-chained fatty acids) and additives (extra pressure, corrosion protection, anti-oxidation, etc.). Semi-fluid lubricants (greases) are used in variety applications where fluid oil is not applicable and where thick lubrication film is required: lubrication of roller bearings in railway car wheels, rolling mill bearings, steam turbines, spindles, jet engine bearings and other various machinery bearings.

1.3.1.3 Solid lubricants
Solid lubricants possess lamellar structure preventing direct contact between the sliding surfaces even at high loads. Graphite and molybdenum disulfide particles are common solid lubricants. Boron nitride, tungsten disulfide and polytetrafluorethylene (PTFE) are other solid lubricants. Solid lubricants are mainly used as additives to oils and greases. Solid lubricants are also used in form of dry powder or as constituents of coatings.

1.3.2 Synthetic lubricants
1.3.2.1 Polyalphaolefins (PAO)
Polyalphaoleins are the most popular synthetic lubricant. PAO’s chemical structure and properties are identical to those of mineral oils. Polyalphaoleins (synthetic hydrocarbons) are manufactured by polymerization of hydrocarbon molecules (alphaoleins). The process occurs in reaction of ethylene gas in presence of a metallic catalyst.
1.3.2.2 Polyglycols (PG)
Polyglycols are produced by oxidation of ethylene and propylene. The oxides are then polymerized resulting in formation of polyglycol. Polyglycols are water soluble. Polyglycols are characterized by very low coefficient of friction. They are also able to withstand high pressures without EP (extreme pressure) additives.

1.3.2.3 Ester oils
Ester oils are produced by reaction of acids and alcohols with water. Ester oils are characterized by very good high temperature and low temperature resistance.

1.3.2.4 Silicones
Silicones are a group of inorganic polymers, molecules of which represent a backbone structure built from repeated chemical units (monomers) containing Si=O moieties. Two organic groups are attached to each Si=O moiety: e.g methyl+methyl (\(\text{CH}_3\)\_2), methyl+phenyl (\(\text{CH}_3 + \text{C}_6\text{H}_5\)), phenyl+phenyl (\(\text{C}_6\text{H}_5\)_2). The most popular silicone is polydimethylsiloxane (PDMS). Its monomer is (\(\text{CH}_3\)\_2SiO). PDMS is produced from silicon and methylchloride. Other examples of silicones are polymethylphenylsiloxane and polydiphenylsiloxane. Viscosity of silicones depends on the length of the polymer molecules and on the degree of their cross-linking. Short non-cross-linked molecules make fluid silicone. Long cross-linked molecules result in elastomer silicone. Silicone lubricants (oils and greases) are characterized by broad temperature range: -100°F to +570°F (-73°C to 300°C).

1.3.3 Vegetable lubricants
Vegetable lubricants are based on soybean, corn, castor, canola, cotton seed and rape seed oils. Vegetable oils are environmentally friendly alternative to mineral oils since they are biodegradable.
Lubrication properties of vegetable base oils are identical to those of mineral oils. The main disadvantages of vegetable lubricants are their low oxidation and temperature stabilities.

1.3.4 Animal lubricants
Animal lubricants are produced from the animals’ fat. There are two main animal fats: hard fats (stearin) and soft fats (lard). Animal fats are mainly used for manufacturing greases.

1.4 Application of Lubricants
Efficient operation of machinery largely depends not only on the lubricant selected but also on its method of application. Lubricants formerly were applied by hand, but modern machinery requires exact methods that can be precisely controlled. For most machinery, different methods of lubrication and types of lubricants must be employed for different parts. In an automobile, for example, the chassis is lubricated with grease, the manual transmission and rear-axle housings are filled with heavy oil, the automatic transmission is lubricated with special-grade light oil, wheel bearings are packed with grease that has a thickener composed of long fibres, and the crankcase oil that lubricates engine parts is lightweight, free-flowing oil(1).

1.5 Introduction of biolubricants
Mostly in the last two decades, lubricant customers are aware of the negative effects that traditional lubricants exert on the environment and, therefore, are demanding new green products able to reduce this impact. In addition to this, the increase in the use of eco-friendly materials has been promoted as a result of strict government regulation that some countries are adding in their legislation (2). Infact, the use of biodegradable lubricants is not an innovative idea (i.e. 4000 B.C natural fats were used for cart wheels lubrication). Lately bio lubricants are of increasing
importance for different applications like engines, gears and transmission (2).

Standard lubricating greases formulation are gel colloidal suspension in which suitable thickener, usually a metallic soap is disperses in a mineral or synthetic oil, both components considered non-biodegradable materials. Obviously, the generalised use of this formulation for different application incorporates parts of these products into the environment, thus increasing pollution and destroying natural resources (3). The first step made to produce a friendlier lubricating grease formulation was the replacement of the mineral oil the main component (70-95%, w/w) by a vegetable one (4). Using vegetable oil in the lubricant formulation reduces environmental pollution, since it is highly biodegradable (5). Vegetable oils have many other advantages, such as low toxicity, low evaporation, high load carrying abilities, naturally multi grade, good solver power for additives, etc. On the contrary, these raw materials also have the disadvantages such as low temperature performance, low oxidation stability and high cost (6).

However complete biodegradable lubricating grease will imply not only the replacement of the mineral oil by a suitable vegetable one, but also using natural thickeners, which can suitably play the role of traditional metallic soaps or polyureas. Numbers of researchers have reported oil substitution satisfactorily (7), and some products are being sold as biodegradable greases, although they still contain a non biodegradable thickener agent in their formulations.

In a study (8), different gels like cellulosic derivatives suspension in a castor oil medium where proposed as potential substitute of lubricating greases for some application. Cellulosic derivatives present some advantages as lubricating grease thickeners. They are biodegradable biopolymers obtained from the most abundant natural polymer (9) and on the other hand they can provide suitable rheological properties to these formulations (10) in
particular, the use of ethyl cellulose combined with other cellulose derivatives, i.e. methyl cellulose or α cellulose, yields gel-like dispersion with acceptable thermal, rheological and mechanical proprieties. The term oleo gel was used according to the definition proposed by (11) for solid like gels attending to the dynamic rheological properties, which otherwise fits the rheological response of traditional lubricating greases. The role of ethyl cellulose, by increasing oil viscosity, is essential to impart long term physical stability to these oleogels (8). Moreover, some standard mechanical stability tests, usually performed on lubricating greases, were carried out in order to evaluate the suitability of these oleogels for lubricant applications. Consequently, the main objective of the present work was to test graft copolymers derived from grafting of waste cellulose as thickeners for lubricants, which combined with suitable vegetables oils would yield biodegradable greases with appropriate performance.
2.0 Present Work

This chapter describes the separation of cellulose from cellulose rich biomass. Cellulosic waste was grafted with different monomers namely BMA and MMA. Grafted copolymers were used to formulate biolubricants using waste vegetable oils (Used Cottonseed oil and Waste DCO stand oil).
3.0 Review of Literature.

Khullar R et al have reported grafting of acrylonitrile on to cellulosic material derived from bamboo (12).

Sanchez R, et al have reported thermal and mechanical characterization of cellulosic derivatives based on oleo gels potentially applicable as biolubricating greases influent of ethyl cellulose molecular weight (13).

Sanchez R et al have reported rheological and mechanical properties of oleo gels based on castor oil and cellulosic derivatives potentially applicable as biolubricating greases and influences of cellulosic derivative’s concentration ratio (14).

Sanchez R et al have reported gel like dispersions based on cellulosic derivatives and castor oil applicable as biodegradable lubricating greases (15).

Kanazawa H and Suzuki M have reported chemical modification of cotton fibre & grafting of methyl methacrylate on to cotton fibres with CeIV salt (16).
4.0 Materials and Method.

Cellulosic wastes used were extracted from Rice husk waste, purified in our laboratory using well-known process. Waste oils (Used Cottonseed oil and Waste DCO stand oil) were obtained from M/S. Sukhadia Garbaddas Bapuji, Anand and Doshi and sons, Anand. Both oils were used as it is without any treatment or modifications. N-butyl methacrylate, methyl methacrylate, ceric ammonium nitrate, methanol and Sodium lauryl sulphate (sodium dodecyl sulphate) were procured from Dutt Enterprise, manufactured by Samir tech chemicals, Vadodara. All materials were used as such without any further purification.

4.1 Pre-treatment to agriculture waste.

Rice husk waste is cleaned dried to less then 1% moisture content using a hot air oven drier at 100°C (± 5°C) for 24 hrs. Then it is milled to uniform size. Cellulosic wastes were mixed with 1.25 % (m/m) sulphuric acid solution in water, boiled for 30 min under reflux, filtered with linen cloth under vacuum. Residue is further mixed with 1.25 % (m/m) Sodium Hydroxide solution in water, boiled for 30 min under reflux, filtered with linen cloth under vacuum, washed with water to make it free from alkali. Residue there off obtained is dried in oven at 100 (± 5°C) for three hours until moisture comes less then 1 %.

4.2 Grafting of cellulose with BMA.

100 ml methanol was stirred in a 500 ml capacity round bottom flask fitted with stirring assembly, Nitrogen purging and with reflux condenser. 10 gm cellulose rich waste was added slowly to methanol under constant stirring. Temperature was maintained at 50-55°C for 15 minutes. After 15 min of stirring under 50-55°C temperature, 1 gm ceric ammonium nitrate was added to the mixture. Stirring was continued for 30 min further at 50-55°C
temperature. 10 ml BMA solution was added very slowly for 2 hours at same temperature with stirring. After completion of addition of BMA, mixture was allowed to stir for 8 hours with temperature maintained at 50-55° C. After the reaction was over, the reaction mixture was filtered and washed with distilled water several times and weighed. The material thus obtained was washed with dimethyl formamide, to remove homopolymer formed. It was than dried under vacuum oven at 50 °C for 48 hours and weighed. The dry product thus obtained was characterised by FTIR.

4.3 Grafting of cellulose with MMA

100 ml methanol was stirred in a 500 ml capacity round bottom flask fitted with stirring assembly, Nitrogen purging and with reflux condenser. 10 gm cellulose rich waste was added to methanol under constant stirring. Temperature was maintained at 50-55° C for 15 minutes. After 15 min of stirring under 50-52° C temperature 1 gm ceric ammonium nitrate was added to the mixture. Stirring was continued for 30 min further at 50-52°C temperature. 10 ml MMA solution was added very slowly for 2.5 hours at same temperature with stirring. After completion of addition of MMA, mixture was allowed to stir for 8 hours with temperature maintained at 50-52° C. After the reaction was over, the reaction mixture was filtered and washed with distilled water several times and several times and weighed. The material thus obtained was washed with dimethyl formamide, to remove homopolymer formed. It was than dried under vacuum oven at 50°C for 48 hours and weighed. The dry product thus obtained was characterised by FTIR.
Table – 1: Code of grafted copolymers synthesised from Cellulosic wastes.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Name of Cellulosic waste</th>
<th>Monomer Used</th>
<th>Code of grafted copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rice husk waste cellulose.</td>
<td>n-Butyl Methacrylate (BMA)</td>
<td>RBMA</td>
</tr>
<tr>
<td>2.</td>
<td>Rice husk waste cellulose.</td>
<td>Methyl Methacrylate (MMA)</td>
<td>RMMA</td>
</tr>
</tbody>
</table>

4.4 Analysis of grafted copolymers

4.4.1 Fourier transmission infrared spectroscopy (FTIR)

Fourier transmission infrared spectroscopy was used for scanning of grafted Cellulosic waste in the range of 4000-400 cm⁻¹ in KBr (Spectrochem AR grade). KBr was first fused, powdered and dried hot air oven under vacuum. The absence of moisture in dried KBr pellet was checked by scanning IR spectra of dried KBr. Dried KBr was used for the preparation of Pellet samples.

A mixture of 1 mg of pure dried sample and 100 mg KBr powder was ground in a mortar pestle for about 10 minutes. The resulting mixture was placed in the sample dye. It was placed in hydraulic vacuumed press machine and compressed at high pressure about 5-10 tons for making the transparent pellet. Remove the pellet holder, discard the pellet, return die and pellet holder to the desiccators (64). The IR spectrum of this transparent pellet was scanned by FTIR Spectroscopy, Spectrum GX, Perkin Elmer, series-200, USA.
4.4.2 Grafting parameters

4.4.2.1 Percent total conversion (% Ct)

It shows the total increase in rate of cellulose after the grafting process.

\[ \% \text{ Ct} = \frac{\text{wt of polymer grafted} + \text{wt. of homo polymer}}{\text{Weight of monomer charged}} \times 100 \]

4.4.2.2 Percentage grafting (% G)

It shows the weight percentage of polymer actually grafted on cellulose.

\[ \% \text{ G} = \frac{\text{weight of polymer grafted}}{\text{Initial weight of substrate}} \times 100 \]

4.4.2.3 Percent grafting efficiency ( % GE)

It is the efficiency in percentage of a polymer to graft on cellulose under given set of condition.

\[ \% \text{ GE} = \frac{\text{weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{weight of homopolymer}} \times 100 \]

4.5 Preparation of Biolubricant from grafted co-polymer and waste oils

10 gm dried RBMA was blended with 50 gm waste oils (used cottonseed oil and Waste DCO stand oil) individually at 150 °C along with 1 gm Sodium lauryl sulphate (SLS), resulting mixture was stirred for 1 hour to get uniformity. In the same manner 10 gm dried RMMA was blended with 50 gm waste oils (used cottonseed oil and Waste DCO stand oil) individually at 150 °C along with 1 gm Sodium lauryl sulphate(SLS), resulting mixture
was stirred for 1 hour to get uniformity. Prepared lubricants were employed for various performance and characterisation analysis (as mentioned in table no.:3)

Table – 2: Code of biolubricants formulated using grafted copolymers and waste oils

<table>
<thead>
<tr>
<th>Sr. no.:</th>
<th>Code of grafted copolymer</th>
<th>Waste oil used</th>
<th>Code of biolubricant.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RBMA</td>
<td>Used cottonseed oil</td>
<td>RBMAC</td>
</tr>
<tr>
<td>2.</td>
<td>RBMA</td>
<td>Waste DCO stand oil</td>
<td>RBMAD</td>
</tr>
<tr>
<td>3.</td>
<td>RMMA</td>
<td>Used cottonseed oil</td>
<td>RMMAC</td>
</tr>
<tr>
<td>4.</td>
<td>RMMA</td>
<td>Waste DCO stand oil</td>
<td>RMMAD</td>
</tr>
</tbody>
</table>

4.6 Analysis of biolubricants

4.6.1 Determination of thermal stability (TGA) (17)

4.6.1.1 Procedure

7.0 mg sample was taken in sample pan and was placed in instrument. Analysis was conducted in the temperature range of 50 to 550 °C at a heating rate of 10°C/min. Nitrogen gas was used to provide inert atmosphere. TGA graph was generated by thermo Gravimetric Analyser, Model: Pyris -1 TGA, Perkin Elmer, USA.

4.6.2 Determination of kinematic viscosity ,Cst at 40 °C (18)

4.6.2.1 Procedure

100 gm biolubricants were taken for the determination. The temperature of the water bath was maintained at 40°C. Viscometer having designation BS/IP/RF No 6 was used for the determination of the kinematic viscosity of the biolubricants prepared. When the temperature of the water bath was reached at 40°C, viscometer was placed in the bath so that the upper filing mark was about 3 cm below the surface of the bath liquid and the capillary was
vertical as judged by a plumb line observed in two directions at right angles. 100 gm of biolubricant sample was taken into a 100 ml beaker and was kept into a water bath at 40°C. Temperature of sample was maintained at 40°C, sample was taken out and sufficient quantity of the filtered sample was poured into the filing tube to a point just above the upper filling mark. The sample was allowed to flow freely to the lower mark of the bulb “C”. When the sample was reached to the lower mark of the bulb “C”, immediately the stopwatch was started and the time was recorded in seconds, up to which the sample reached to the upper mark of the bulb “C”. Total time for the flow was recorded.

4.6.2.2 Calculation for kinematic viscosity at 40°C:

Kinematic viscosity = stopwatch reading × factor.

Where,

f= factor of viscometer. (Factor was taken as per certificate provided by viscometer manufacturer/ calibrator).

4.6.3 Determination of kinematic viscosity, Cst at 100 °C (18)

4.6.3.1 Procedure:

100 gm biolubricants were taken for the determination. The temperature of the water bath was maintained at 100°C. Viscometer having designation BS/IP/RF No 4 was used for the determination of the kinematic viscosity of the biolubricants prepared. When the temperature of the water bath was reached at 100°C, viscometer was placed in the bath so that the upper filing mark was about 3 cm below the surface of the bath liquid and the capillary was vertical as judged by a plumb line observed in two directions at right angles. 100 gm of biolubricant sample was taken into a 100 ml beaker and was kept into a water bath at 100°C. Temperature of sample was maintained at 100°C, sample was taken out and sufficient quantity of the filtered sample was
poured in to the filing tube to a point just above the upper filing mark. The sample was allowed to flow freely to the lower mark of the bulb “C”. When the sample was reached to the lower mark of the bulb “C”, immediately the stopwatch was started and the time was recorded in seconds, up to which the sample reached to the upper mark of the bulb “C”. Total time for the flow was recorded.

4.6.3.2 Calculation for kinematic viscosity at 100°C:

Kinematic viscosity = stopwatch reading × factor.
Where,
f= factor of viscometer. (Factor was taken as per certificate provided by viscometer manufacturer/ calibrator).

4.6.4 Determination of Viscosity Index (19)

4.6.4.1 Procedure:
The kinematic viscosity at 100°C was recorded. The value of “L” from table 17-B, D2270 pg. no. 938 against the kinematic viscosity at 100°C was derived. The kinematic viscosity at 40°C was recorded. The value of “D” from chart in 17-B, D2270 pg. N. 938 was recorded.

4.6.4.2 Calculation:
Viscosity Index = \((L - U) \times 100/D\).
Where,
L = value derived from table in 17-B, D2270 pg. no. 938 from viscosity at 100°C of an biolubricant whose viscosity index is to be calculated. (It is viscosity at 40 deg C (100 deg F) of an biolubricant of VI = 0 having same viscosity at 100 deg C (210 def F) as the biolubricant whose Viscosity index is to be calculated.
U = kinematic viscosity at 40°C in cst.
H = value derived from table in 17-B, D2270 pg. no. 938 from viscosity at 100°C of an biolubricant whose viscosity index is to be calculated. (It is viscosity at 40 deg C (100 deg
F) of an biolubricant of VI = 100 having same viscosity at 100 deg C (210 def F) as the biolubricant whose Viscosity index is to be calculated

\[ D = (L - H), \text{ record the value from chart in 17-B, D2270 pg.no.938} \]

### 4.6.5 Determination of Copper Corrosion Strip Test (20)

#### 4.6.5.1 Preparation of Strips.

- **Mechanical Cleaning of Strips:** The copper strips were cleaned by rubbing with No.0 fine steel wool, followed by rubbing with lintless paper and washing with ASTM grease analysis naptha. The strips were dried with lint less paper and then bend midway between the ends to form an angel of approximately 45 degree.

- **Chemical Cleaning of Strips:** The strips were wiped with a clean cloth to remove surface and then bend midway between the ends to form an angel of approximate 45 degree. The strips were immersed in 100 ml of the sulphuric-nitric acid mixture at 40±1°C, for total of 15 to 20 seconds after chemical activity begins as evidenced by the noticeable formation of oxides of nitrogen. The strips were rinsed for approximately 20 sec (until free of acid) in running tap water and then were immersed for 60 sec at room temperature in 100 ml of the dichromate cleaning solution. The strips were washed in a sufficient numbers of changes of distilled water (200 ml of water for each wash) until they were free from acid or free chromate ion, which was evidenced by no colour change of blue litmus paper and no yellow colour in the last wash water. After washing the strips were dried and cleaned with filter paper to remove excess surface moisture. The strips were then dried in hot air oven.
at 60°C. Only those strips which were entirely free from stain were used.

4.6.5.2 Procedure.

4 gm of the Biolubricants were placed in each of two glass sample dishes and insert a copper strip on edge into the grease in each dish so that approximately one half of the strips were immersed. The dishes were placed on the bottom trays of the dish holder and placed in the cylinder chamber. The cylinder chamber was assembled& placed in the bath at 100°C, The temperature was observed and recorded. The glass test dishes were removed from the cylinder chamber, and the strips were washed with grease analysis naptha, the copper strips were dried carefully with blotting lintless paper. The copper strips were examined for any evidence of discolouration, etching or corrosion.

4.6.5.3 Interpretation of Result.

Report the sample as passing the test if the appearance of the test strips matches, or is better than, that of the comparison standard.

4.6.6 Determination of Water Content (21)

4.6.6.1 Standardization of Karl Fischer Reagent:

50 ml of specially dried methanol was taken in a clean dry titration flask. Stopper was inserted and magnetic stirrer was adjusted to give a smooth stirring. Burette was filled with karl fischer reagent. Electrodes were immersed in titration flask and instrument was started. As addition was governed by instrument it self we have taken care to watch it carefully. When end point reaches buzzer of instrument was started and addition was stoped by instrument. Burette reading was recorded. To the solution in the titration flask 10μl of water was added by using a 10μl of micro syringe, and titration was carried out to end point.
4.6.6.1.1 Calculation.

Calculate the water equivalence of the Karl Fischer reagent as follows.

\[ F = \frac{W}{T} \]

Where,

- \( F \) = water equivalence of Karl Fischer reagent, in mg/ml.
- \( W \) = \( \mu l \) of water added.
- \( T \) = ml of reagent required for titration of the added water.

4.6.6.2 Procedure:

0.2gm the biolubricants were taken to titration flask. Titration flask was stoppered immediately to prevent absorption of moisture from the atmosphere. Titration was started by using Karl Fischer reagent from burette. Titration was done by instrument once we have started it. Burette reading was record at the end point. (75)

4.6.6.3 Calculation:

Water content = \( B.R \times F / W \times 10 \).

Where,

- \( F \) = water equivalence of Karl Fischer reagent, in mg/ml.
- \( W \) = weight of sample.

4.6.6 Determination of Density gm/cm\(^3\) @ 15 °C (22)

4.6.7.1 Procedure:

Pyknometer of 50ml capacity was weighed to the nearest 0.5mg. The Pyknometer was filled with the sample. The Pyknometer and its content were heated to 40°C by immersing Pyknometer up to its neck in the constant temperature bath. The Pyknometer was kept at this temperature in the bath for 20 minutes. When the temperature was constant, the dry capillary stopper was firmly inserted. The Pyknometer was removed from the bath. The
Pyknometer and contents were cooled to room temperature. All traces of samples and water were removed from the exterior surface of Pyknometer by wiping it with a clean lint free cloth. Pyknometer abd contents were weighed.

Density = weight of content / Vol of pyknometer.

4.6.7.2 Note
Give correction to determine density at 15 °C from ASTM D1250 80 Vol III Table 53 B

4.6.8 Determination of loss on drying
4.6.8.1 Procedure:
5 gm of material was weighed in tared aluminium dish having diameter 50 mm & depth of about 40 mm. The dish was placed in an air oven maintained at 100±5°C and dried for 2 hours. Dish was placed in desiccator, cooled & weighed. Drying was repeated until constant weight was obtained. Loss on drying(LOD) was reported as estimate of moisture content.(38)

4.6.8.2 Calculation:
\[ \% \text{ Moisture} = \frac{100(M_1 - M_2)}{M_1 - M} \]

Where,
M₂= Weigh of dish with material after drying.
M₁= Weigh of dish with material before drying.
M= Weight of empty dish.
4.6.9 Determination of sodium content (24)

4.6.9.1 Procedure:
Biolubricant solution was prepared by taking 2 g of prepared biolubricant in silica crucible. Material was ignited in muffle furnace for 2 hours at 550±20°C. Silica crucible was taken out and cooled. Mass was digested in concentrated 5 N HCl by boiling on hot plate. The solution thus obtained was diluted to 250 ml in volumetric flask with Milli Q Water. Sample solution aspirated directly in to flame photometer. Standard concentration series of sodium was prepared using sodium standard solution of 5 to 50 μg/ml Na with 5 μg/ml Na difference in concentration series. Same series was aspirated for calibration of flame photometer for sodium.

4.6.9.2 Calculation:

Sodium mg/kg = flame photometer reading × dilution factor × first dilution/weight of sample.

4.6.10 Determination of potassium content (25).

4.6.10.1 Procedure:
Biolubricant solution was prepared by taking 2 g of biolubricant in silica crucible. Material was ignited in muffle furnace for 2 hours at 550±20°C. Silica crucible was taken out and cooled. Mass was digested in concentrated 5 N HCl by boiling on hot plate. The solution thus obtained was diluted to 250 ml in volumetric flask with Milli Q Water. Sample solution aspirated directly in to flame photometer. Standard concentration series of potassium was prepared using potassium standard solution of 5 to 50 μg/ml K with 5 μg/ml K difference in concentration series. Same series was aspirated for calibration of flame photometer for potassium.
4.6.10.2 Calculation:
Potassium, mg/kg = flame photometer reading × dilution factor × first dilution/weight of sample.

4.6.11 Determination of calcium content (26)

4.6.11.1 Procedure:
Biolubricant solution was prepared by taking 2 g of biolubricant in silica crucible. Material was ignited in muffle furnace for 2 hours at 550±20°C. Silica crucible was taken out and cooled. Mass was digested in concentrated 5 N HCl by boiling on hot plate. The solution thus obtained was diluted to 250 ml in volumetric flask with Milli Q Water. Sample solution aspirated directly in to flame photometer. Standard concentration series of calcium was prepared using calcium standard solution of 15 to 50 μg/ml Ca with 5 μg/ml Ca difference in concentration series. Same series was aspirated for calibration of flame photometer for calcium.

4.6.11.2 Calculation:
Calcium, mg/kg = flame photometer reading × dilution factor × first dilution/weight of sample.

4.6.12 Determination of lithium content.

4.6.12.1 Procedure:
Biolubricant solution was prepared by taking 2 g of biolubricant in silica crucible. Material was ignited in muffle furnace for 2 hours at 550±20°C. Silica crucible was taken out and cooled. Mass was digested in concentrated 5 N HCl by boiling on hot plate. The solution thus obtained was diluted to 250 ml in volumetric flask with Milli Q Water. Sample solution aspirated directly in to flame photometer. Standard concentration series of Lithium was prepared using calcium standard solution of 5 to 50 μg/ml Li with
5 μg/ml Li difference in concentration series. Same series was aspirated for calibration of flame photometer for lithium

4.6.12.2 Calculation:

Lithium, mg/kg = flame photometer reading × dilution factor × first dilution/weight of sample.
5.0 Results and discussion

5.1 Results

5.1.1 FTIR of Cellulose and Grafted copolymers

![FTIR of Cellulose and Grafted copolymers](image)
Chapter – 4 Biolubricants from cellulosic waste

ISTAR, SICART, Sardar Patel University, V.V.Nagar 183
5.1.1.1 FTIR Overlays of Cellulose to RBMA/RMMA
5.1.2 TGA of Biolubricants

**TGA of RBMAC**

**TGA of RBMAD**
5.1.3 Results of grafting parameter

Table: 03 Results of grafting parameter

<table>
<thead>
<tr>
<th>Graft copolymer code</th>
<th>% Ct</th>
<th>% G</th>
<th>% GE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBMA</td>
<td>114.71</td>
<td>199.30</td>
<td>82.79</td>
</tr>
<tr>
<td>RMMA</td>
<td>126.53</td>
<td>219.32</td>
<td>82.49</td>
</tr>
</tbody>
</table>

5.1.4 Results of analysis of biolubricants

TABLE: 04 Analyses of biolubricants

<table>
<thead>
<tr>
<th>Test</th>
<th>RBMAC</th>
<th>RBMAD</th>
<th>RMMAC</th>
<th>RMMAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature stability</td>
<td>93.25 % stable up to 250°C</td>
<td>96.79 % stable up to 250°C</td>
<td>95.26 % stable up to 250°C</td>
<td>96.57 % stable up to 250°C</td>
</tr>
<tr>
<td>Kinematics Viscosity @ 40 deg C Cst</td>
<td>910.00</td>
<td>859.00</td>
<td>939.00</td>
<td>950.00</td>
</tr>
<tr>
<td>Kinematics Viscosity @ 100 deg C Cst</td>
<td>106.00</td>
<td>126.00</td>
<td>130.00</td>
<td>119.00</td>
</tr>
<tr>
<td>VI</td>
<td>214.32</td>
<td>253.46</td>
<td>247.08</td>
<td>229.34</td>
</tr>
<tr>
<td>Copper Corrosion strip test</td>
<td>Passes the test</td>
<td>Passes the test</td>
<td>Passes the test</td>
<td>Passes the test</td>
</tr>
<tr>
<td>% Water (K.F)</td>
<td>6.80</td>
<td>5.23</td>
<td>5.92</td>
<td>4.63</td>
</tr>
<tr>
<td>Density @ 15 deg C gm/cc</td>
<td>01.0551</td>
<td>01.0239</td>
<td>01.1113</td>
<td>01.1267</td>
</tr>
<tr>
<td>% loss on drying @ 100</td>
<td>7.88</td>
<td>5.46</td>
<td>7.02</td>
<td>5.60</td>
</tr>
<tr>
<td>+/- 5 deg C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Sodium mg/kg</td>
<td>39121.00</td>
<td>37890.00</td>
<td>42189.13</td>
<td>39665.64</td>
</tr>
<tr>
<td>Potassium mg/kg</td>
<td>11370.18</td>
<td>11758.33</td>
<td>11541.14</td>
<td>11452.11</td>
</tr>
<tr>
<td>Calcium mg/kg</td>
<td>413.92</td>
<td>487.57</td>
<td>590.19</td>
<td>592.26</td>
</tr>
<tr>
<td>Lithium mg/kg</td>
<td>4.91</td>
<td>5.12</td>
<td>3.97</td>
<td>3.78</td>
</tr>
</tbody>
</table>

5.2. Discussion of Experimental

5.2.1 Discussion of pre-treatment of Cellulosic agriculture waste.

Cellulosic waste collected was given pre-treatment to remove dust and dirt. Material was pulverised to reduce particle size and to increase the surface area. Cellulosic waste was containing crude fibre (cellulose, hemicellulose and lignin), pectines, carbohydrates, starch, polysaccharides, fat, proteins and minerals were treated with sulphuric acid and than with sodium hydroxide solution to remove pectines, carbohydrates, starch, polysaccharides, fat, proteins and minerals by hydrolysis and dissolution. The fibrous mass is obtained after treatment which is indication of separation of mixture of cellulose, hemicellulose from biomass.

5.2.2 Discussion of Grafting of Cellulose with BMA and MMA

Grafting of cellulosic waste was done using methanol as solvent. Ceric ammonium nitrate is used as initiator in copolymerisation. Ceric ion exclusively participate in the formation of active cites on the cellulose (27,28). The mixture was soaked by heating it to 50-55 °C for 30 min. soaking time allows ceric solution to defuse in to cellulose fiber prior to grafting reaction there by allowing initiation
of free radicals on the cellulose by oxidation with Ce^{IV} ions \((29, 30)\). Monomer was added to the resulting mixture under stirring at very slow rate of addition to obtain maximum site of cellulose for the polymerisation prepared by soaking of Cellulosic waste with ceric ammonium nitrate. Above 55 °C temperature radical termination reaction might be accelerated leading to decrease of graft yield. \((31)\) Hence the reaction temperature was kept below 55 °C. The mixture was stirred for 8 hours at same temperature conditions. The increase in grafting site in the initial stages of reaction due to high rate of ceric ion participation in the formation of reactive site at the cellulose back bone \((32)\).

### 5.2.3 Discussion of FTIR of Graft Copolymers

The FTIR Spectra of grafted copolymers were recorded. In the FTIR spectra of both grafted copolymers \((BMA/MMA)\) the characteristic bands at 1729 cm\(^{-1}\) corresponds to carbonyl group(-C=O) which confirms the grafting of acrylate monomers on to the cellulose. 3342cm\(^{-1}\)Corroponds to hydroxyls of cellulose and peaks between 1000 and 1100 cm\(^{-1}\) are due to glycosidic linkage of cellulose.

**Discussion of FTIR overlays of Cellulose to RBMA/RMMA**

FTIR overlays evidentially confirms the grafting acrylate monomers on to the cellulose by presence of peak at 1729 cm\(^{-1}\) corresponds to carbonyl group(-C=O), peaks between 1000 and 1100 cm\(^{-1}\) are due to glycosidic linkage of cellulose as they are in FTIR of cellulose.

### 5.2.4 Discussion of Preparation of Biolubricants from grafted copolymer and waste oils

Different waste oils (Used cottonseed oil and Waste DCO oil) were selected with respect to their non commercial value. Both oils are of different fatty acid profile. Oils were stirred with grafted copolymers for 1 hour at 150 °C using SLS as Emulsifier, so that
oil gets absorbed in graft polymers. Temperature was raised to give maximum penetration of oil in graft polymers. The resulting mixture is gel like lubricant can be used as grease.

5.3 Discussion of Results of Analysis of biolubricants

5.3.1 Discussion of Thermal Stability

The thermal stability was estimated with the help of TGA. TGA of RBMAC and RBMAD shows more than 93% stability up to 250 °C and up to 350 °C more than 50% thermally stable and even in case of RBMAD is more than 70% stable at 350 °C. This makes it useful in lubricating low speed bearings. Almost same results are obtained in RMMAC and in RMMAD. All biolubricants shows usefulness up to 250 °C, both TGA shows almost complete decomposition at 550 °C this indicates the prevention of use of both biolubricants in high temperature applications.

5.3.2 Discussion Of Kinematic Viscosity @ 40 °C

Kinematic viscosity was measured by IP/BP viscometer at 40°C using constant temperature water bath. Kinematic viscosity of RBMAD is more recorded than RBMAC and same findings are for RMMAD and RMMAC. This is because of higher viscosity of DCO stand oil than used cottonseed oil. Higher the viscosity betters the lubrication. Also higher viscosity at 40 °C will sustain its viscosity at 100 °C yielding better Viscosity index which is indicator of performance of lubricant on temperature range.

5.3.3 Discussion of Kinematic Viscosity @ 100 °C

Kinematic viscosity @ 100 °C was recorded between 106 to 130 cst (mm²/s) lowest is recorded for RMMAD and highest is for RBMAC. Use of used cottonseed oil gives thermals stability to biolubricants as oil is having more percentage of higher chain fatty acids with
unsaturations which upon thermal change convert to saturated fatty acids and gives stability to lubricants.

5.3.4 Discussions of viscosity index

Viscosity index of all biolubricants shows more than 200 which indicate its working range in thermally unstable environment.

5.3.5 Discussions of Copper Corrosion Strip Test

All biolubricants passes the test. This is an evidence of safe to use the lubricants in corrosive environment as they do not contribute any property which leads corrosion to host metal on which it is applied.

5.3.6 Discussion of Water content

Water content of all biolubricants varies from 4.63 to 6.80 RMMAD is having less water content than RMMAC which is because of use of Dehydrated Castor Oil(used DCO oil) which is free of water.

5.3.7 Discussion of Density gm/cm$^3$.

Density of all biolubricants is reported above 1.0000 gm/cm$^3$, as all lubricants are derived from Cellulosic waste.

5.3.8 Discussion of Loss on drying.

Loss on drying of all biolubricants indicates the water content and loss on drying are almost same so there are no volatiles which may lose during the usage.

5.3.9 Discussion on Sodium content mg/kg

Process involves the use of sodium lauryl sulphate (sodium dodecyl sulphate) for the formulation of biolubricants hence sodium content of all lubricants are very high. These helps in utilizing excess oil to be converted in alkali soap during usage which will increase lubricity of lubricants.
5.3.10 Discussion on Potassium content mg/kg

Potassium content of all biolubricants are very from 11370 to 11758 mg/kg which is due to the use of natural source of Cellulosic waste as potassium is an abundant element in plant sources. Higher potassium concentration helps in maintaining consistency of lubricants.

5.3.11 Discussion on Calcium content mg/kg

Calcium mg/kg varies from 413 to 592 mg/kg in all biolubricants. Less quantity of calcium prevents precipitation and fast drying of lubricants on application site.

5.3.12 Discussion on Lithium content mg/kg

Lithium mg/kg is very negligible has no effect on any performance of biolubricants.
6.0 Conclusion

Waste vegetable oils can be successfully used as a base oils to formulate biolubricants (Semi-solid grease). Graft copolymers of waste cellulose using MMA and BMA as grafting monomers were used as thickeners for biolubricants. Biolubricants exhibits competitive performance properties. Use of waste and natural materials for such value added application can give a technical and logical solution for replacement of traditional petrochemicals based raw materials.
7.0 Reference

5. Stempfel E.M, NLGT spokesman, 68, 8-23 (1998)
17. SICART/INST/OP/004
18. IS 1448(25):1992
19. ASTM 2270-77
21. ASTM 1744-64
22. IS 1448(32):1970
23. IS 1448:1992
24. AOAC 966.16 18th ed.
25. AOAC 965.30 18th ed.
26. AOAC 944.03 18th ed.
28. Gupta. S ,chemical modification of cassia occidentalis seeds gum
Ph.D thesis forest research institute dehradun, 181-191 (2005 )
31. Kulkarni A.Y , Mehta P.C, j. of app. polymer sci.,12, 1321-
1342 (1968)
32. Heikal S.O, Elkalyubi S.F, j of applied Polymer Sci., 27, 3027-
3041 (1982)