

Survey on Structure-Property relationship of Vegetable esters

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In the current scenario, mineral oil is mostly used in correlation with Kraft paper (insulation paper) as the dielectric medium in most of the transformers. The raising concerns on environment, lack of petroleum reserves and disposal problems with used mineral oils has motivated researchers to focus on biodegradable and renewable insulating fluids. The search for new insulating fluids is guided by factors such as environmental requirements and other safety and economic considerations. Vegetable-oil based transformer fluids meet most of the above criteria. Hence, a lot of research has been taken up in the field of Bio-based dielectric fluids over past few decades. Their performance as dielectric fluid is on par with mineral oils to a greater extent. However, they fail to meet some of the requirements. This paper reviews the properties of water content, kinematic viscosity, pour point, ageing and oxidation stability that have to be enhanced, and furnishes their correlation with the chemical structure of the oils based on unsaturation, side chains and carbon count. Finally, the structural modifications that can be carried out for upgrading its properties are discussed, providing an insight to performance enhancing additives.

Keywords: Vegetable esters, insulating fluids, structure property analysis, bio-degradable oil.

1.0 INTRODUCTION

Transformer oil acts as an insulating and cooling medium in transformers. The insulating oil fills up pores in fibrous insulation, the gaps between the coil conductors, the spacing between the windings and the tank, thus increasing dielectric strength of liquid insulator. Transformer in operation generates heat in windings, and this is transferred to the oil. The oil is then cooled through radiators and circulated back[1]. In transformers, mineral oil has been widely used as a coolant and as an insulator for over a century. However, due to its depleting sources, sustainable production of transformer fluid is being hotly debated worldwide. It is also acknowledged that mineral oil primarily produced from petroleum products, have several drawbacks such as, non-biodegradability, low flash point, non-renewability

and could cause a serious problem to biosphere due to their spillage and land filling problem after end of the life of oil [2].

The above mentioned concerns have increased the attention to look for alternate, which can be produced from materials available abundantly in nature and potentially offer greater opportunities in the long run. This gave rise to use of silicon oils as an alternative and provided an added advantage of low flammability along with the excellent dielectric properties. However, the solution was short lived as silicon oil proved very expensive and non-biodegradable.

This paved the way towards usage of synthetic and natural esters as an alternative to the conventional mineral oil. Due to the utility interest, research efforts started in mid 90s to develop a fully

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biodegradable insulating fluid. Vegetable oil was considered as the most likely candidate for the production of fully biodegradable insulation medium for transformers and allied electrical equipments. Vegetable oils are available in plenty as a natural resource, obtained from plant seeds and flowers. They offset all the main risks associated with common mineral oil, such as high flammability and environmental impact. Vegetable oils have superior properties than mineral oils, viz., high biodegradability, low toxicity, high flash points, high fire points, provide lower flammability and it is considered more environmental friendly[3]. In addition, these vegetable oils absorb more moisture compared to mineral oils whilst maintaining their insulation properties. Only recently transformer-

grade vegetable oils have been commercialized and have become available for the usage in low rating transformers successfully. Some of the commercialized vegetable esters as insulating oil are BIOTEMP, Envirotemp FR3 and MideleN[4].

However, vegetable oils are associated with some of the major drawbacks such as high pour point, high kinematic viscosity, low oxidation stability and poor ageing as shown in table 1. To overcome these limitations, there is a need to possess the knowledge on chemical structure and composition of these oils and relate to their influence on the above properties. With this information, the process of production, refining and blending ratios of fatty acids can be established to meet the requirements of transformer fluids.

TABLE 1
PROPERTY COMPARISON BETWEEN MINERAL OIL AND VEGETABLE ESTERS [5-7].

Properties	Mineral oil	Vegetable esters	International Standards
Chemical type	Hydrocarbon	Esters	-
Appearance	Colorless-Light yellow	Colorless-Light yellow	ISO 2049
Break Down Voltage, kV	30-85	82-97	IEC 60156
Dissipation factor at 25°C, at 100°C,	0.05 max	0.25	ASTM D924
	0.3 max	1.00	
Dielectric Constant at 25°C	2.2	3.1	IEC 60247
Specific resistance at 25°C, ohm.cm	10 ¹⁴ -10 ¹⁵	10 ¹⁴	ASTM D1169
Water Content, ppm	10-25	50-100	ASTM D1533
Kinematic Viscosity at i) 0°C, cSt ii) 40°C, cSt iii) 100°C, cSt	<76	77-143	ASTM D445
	3-16	16-37	
	2-2.5	4-8	
Density at 20°C, g/cm ³	0.83-0.89	0.87-0.92	ASTM D1298
Flash point, °C	100-170	315-328	ASTM D92
Fire point, °C	110-185	350-360	ASTM D92
Pour point, °C	-30 to -60	-19 to -33	ASTM D97
Interfacial Tension, dynes/cm	40-45	25	ASTM D971
Total Acid Number, mg KOH/g	<0.03	0.04	ASTM D974
Biodegradability, CEC-L-33 (21 days), %	30	97-99	ASTM D7044-15

2.0 VEGETABLE OILS

Vegetable oils are triglycerides of fatty acids generally extracted from plants. Vegetable oils mostly consist of natural esters of fatty acids. Brief information on the ratios is provided in table 2. The chemical structure

of natural esters is based on a glycerol backbone, to which three naturally occurring fatty acid

groups (saturated and unsaturated) are bonded and the structure of various fatty acids are presented in Figure 1.

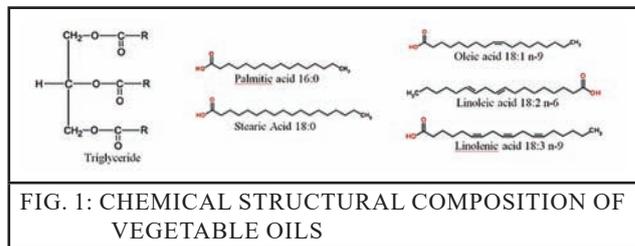
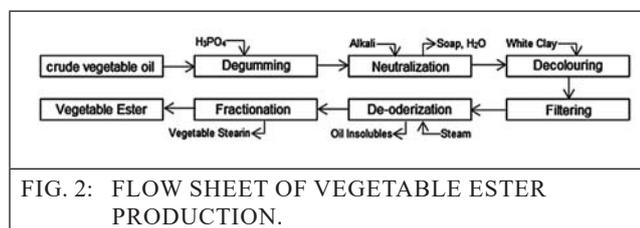


TABLE 2
COMPOSITION OF VEGETABLE OILS WITH FATTY ACID RATIOS (WT %)[9].

Oils	Saturated acids		Unsaturated acids			Other acids	Un-saturation
	Palmitic acid	Steric acid	Oleic acid	Linoleic acid	Linolenic Acid		
Castor oil	1%	1%	3%	4%	<1%	93% (Ricinoleic acid:90%)	97%
Canola oil	4%	2%	56%	26%	10%	2%	92%
Sunflower oil	6%	4%	29%	60%	<1%	1%	89%
Olive oil	10%	2%	78%	7%	1%	2%	86%
Soybean oil	10%	4%	23%	51%	4%	5%	81%
Palm oil	44%	4%	40%	10%	<1%	5%	50%
Coconut oil	9%	2%	7%	2%	<1%	80% (Lauric acid: 50%)	9%

2.1. Processing of Vegetable Esters

The oil can be extracted from the seeds through mechanical extraction where the seeds are compressed forcing the oil matter out of the seeds or through solvent extraction process where a solvent (hexane or petroleum ether) is used to remove the oil content from the seeds, followed by fractionation to obtain the oil. It is observed that the later process is very efficient. After the oil is extracted, it is subjected to further refining processes to meet the required criteria of insulating fluids. The complete process of refining vegetable oils is presented in Figure 2. The oil is degummed to remove any impurities, followed by neutralization to remove free fatty acids. The oil is then bleached to further removal of other impurities. Final filtration is carried out to remove any oil insolubles present.



2.2. Structure-Property Relationship

2.2a. Water content

Water or moisture in the oil can be present in two forms, dissolved water and free water. Dissolved water is when the water molecules are bonded/ adhered to the slightly polar parts of the oil molecules. Water in this form does not attribute to major changes in the dielectric properties of the oil. With the saturation of dissolved water content, the water is then present in the form of free water which greatly hinders the dielectric properties of oil. The saturation value of water in vegetable oils is found to be higher (around 1000ppm) than that of mineral oils (about 60ppm) [10]. This massive variation in water solubility of vegetable esters can be explained using the structure of oil molecules. The vegetable oils which primarily consist of triglycerides, have comparatively higher polar sites found at the oxygen end of ester bonds which allows the water to adhere to the oil molecules through Hydrogen bonding and Van der Waal forces. [11] On the other hand the

lack of polar sites in the mineral oil structure is the reason why the value of water solubility is observed to be low.

Vegetable esters can also increase the thermal stability of solid insulator present in electrical equipment, as they remove moisture from solid insulation more effectively when compared to mineral oil thus allowing increased equipment life [7].

2.2b. Kinematic viscosity

Viscosity of an insulating liquid affects the ability to transfer heat by conduction. Conduction cooling is major heat removal mechanism in transformers. The higher viscosity would be expected to result in poor cooling within the transformer. But the vegetable esters are found to have higher specific heat than mineral oil, which balances the efficiency of cooling [12].

Kinematic viscosity of vegetable esters can vary with chain length of the fatty acid (increases with increase in the fatty acid chain length). The kinematic viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds, branching. The presence of different functional groups also influence the kinematic viscosity of the esters. This explains the high viscosity of castor oil whose major composition is ricinoleic acid (Figure 3) which contains an -OH group in the carbon chain. The -OH groups of two molecules bond with each other and resulting in higher shear rate and thus high viscosity. Further, the nature of oxygenated moieties influences the kinematic viscosity in the order of $\text{COOH} \approx \text{C-OH} > \text{COOCH}_3 \approx \text{CO} > \text{C-O-C} > \text{no oxygen}$ [13].

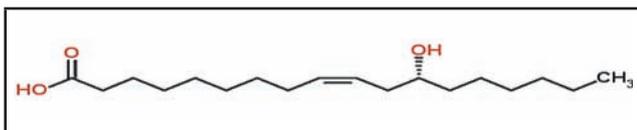


FIG. 3: STRUCTURE OF RICINOLEIC ACID WITH -OH GROUP THAT INCREASES THE VISCOSITY OF OIL EXPONENTIALLY.

Due to the above factors, vegetable esters exhibit higher kinematic viscosity when compared to mineral oils. To meet the desired values for operation, modification in the structure of vegetable esters have to be done either at the stage of processing the oil or proper selection of fatty acids and composition of saturated and unsaturated compounds.

2.2c. Pour point

Pour point is the temperature at which transformer oil just flows under the prescribed conditions. Pour point is a useful measure to know how insulating fluid performs at low temperature, particularly when it is required to cold start a transformer at very low temperature conditions. Vegetable oils have higher pour point than mineral oils typically in the range -15 to -25°C . Pour point of natural ester increases with increase in the saturation level of hydrocarbons. This can be clearly observed in case of coconut oil which consists of about 90% saturated compounds and has a pour point of around 20°C . It is also observed that higher molecular weight is associated with higher pour point. On the contraire more branching in hydrocarbon chain, more -OH groups and cis-type unsaturation is linked with lower pour point. However, it has been reported that cold start of the transformer with natural ester is achieved even at temperatures lower than its pour point. Some reports show cold starts up to -30°C . For further lowering the pour point of vegetable esters, oil blends as well as pour point depressants are added [3].

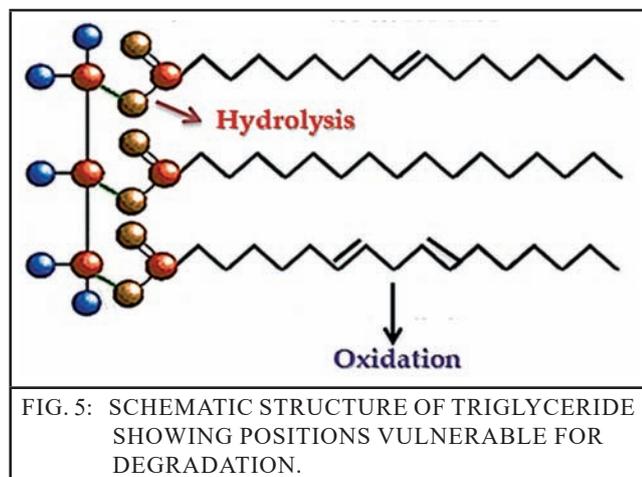
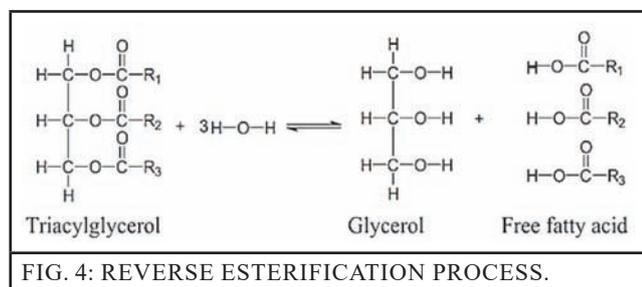
2.2d. Ageing and oxidation stability

The performance of transformer fluid over time is an important parameter to be studied. The ageing process of vegetable oils can be described by the oxidation of the unsaturated bonds (carbon-carbon double bonds) of vegetable oil under thermal stress. Three processes occur, i.e hydrolytic scission, oxidation and oxidative polymerization [3], [14].

2.2d (i) Hydrolysis:

Hydrolysis is the reverse esterification reaction as represented by Figure 5. Under the influence of water, incomplete ester molecules and free fatty acids emerge. The ester molecules are disconnected at their C-O-bonds as shown in Figure 4.

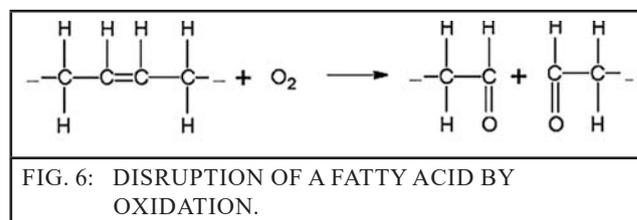
Since the free fatty acids themselves accelerate the process of hydrolysis, it is also called an autocatalytic reaction. Further acceleration occurs when water content, oil temperature, or percentage of dissolved metals increase. As the consequence of the hydrolysis, total acid number increases.



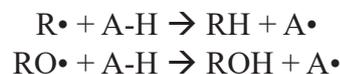
2.2d (ii) Oxidation:

In the presence of oxygen, it appears that in natural ester based insulating fluids the occurrence of oxidative rancidity is directly related to the presence of fatty acids. This mechanism happens when oxygen from the air reacts with esters double bonds as shown in Figure 6 [3], [15]. With the increase in unsaturation content, the resonance between the double bonds push the oxidation rates even further. The process of oxidation is through free radical reaction yielding peroxides and hydrogen peroxide as primary products.

These compounds, due to their instability go through a series of reactions, yielding volatile components such as aldehydes and ketones (secondary products). The reactivity is higher as the number of unsaturation in the chemical chain increases.



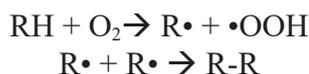
Molecules capable of reducing or inhibiting oxidation reaction of other molecules are known as antioxidants. Oxidation inhibitors or antioxidants play a vital role as reducing agent, free radical scavenger, singlet oxygen scavenger and chelator. An important class of oxidation inhibitors contains phenolic compounds such as butylated hydroxy-anisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and propylgallate. The mechanism of antioxidant activity is as shown below:



The oxidation stability can be increased with decrease in the unsaturation levels of fatty acids. This can be brought about with the help of hydrogenation process during refining to remove the unsaturation.

2.2d (iii). Oxidative Polymerization:

The oxygen from air attacks the double bonds present in ester structure and with the formation of peroxides as the major product, long chain carbon structure with free radicals are also produced. These free radicals undergo polymerization and a long chain hydrocarbon is formed. This results in increase of viscosity. Increase in viscosity is associated with decline in the rate of heat dissipation from the windings thus reducing the efficiency of the transformer. The following reaction illustrates the polymerization reaction in the presence of oxygen and catalyst.



The effects of ageing on the insulating properties of vegetable ester are being discussed in table 3,

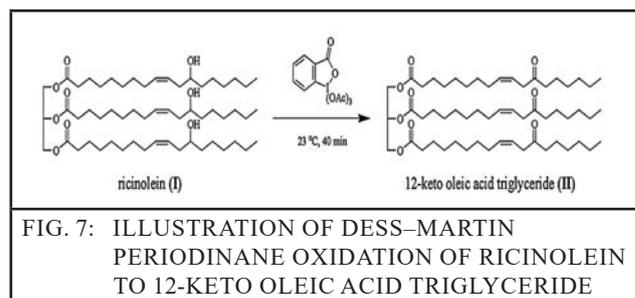
in comparison with the mineral oil properties. The results pertain to an ageing test conducted under presence of air, with catalyst materials for a period of 1440 hrs.

PROPERTIES	Vegetable Ester		Mineral Oil		International standard
	New	Aged	New	Aged	
Color Number	0.5	2.5	0.5	4.5	ASTM D1500
Total Acid Number (mg KOH/g)	0.02	0.23	0.05	0.22	ASTM D664
Kinematic Viscosity (mm ² /s) at 40°C	34	2250	9	<20	ASTM D445
Dielectric Dissipation Factor	0.00195	0.033	0.00011	0.000388	ASTM D924
Break Down Voltage (kV)	88	89	71	36	ASTM D1816

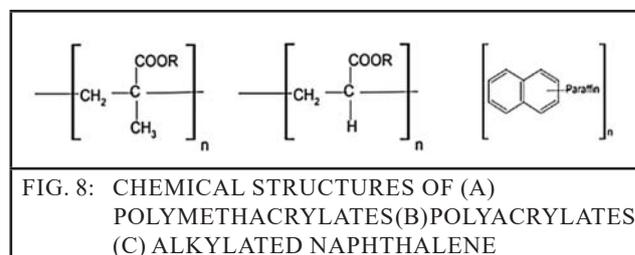
3.0 CURRENT RESEARCH SCENARIO

Presently, some vegetable esters are used as dielectric fluids in smaller transformers. A good deal of research is being carried out to rule out the above mentioned limitations of vegetable esters as transformer fluids. Two major paths have been considered to upgrade the properties of oils, firstly regarding the production, refining techniques of vegetable esters and secondly, through the usage of property enhancing additives.

The viscosity of the oil can be modified by altering the structure of vegetable esters as per our requirements. An additional step of hydrogenation that was added to the process of refining to reduce unsaturation showed significant reduction in kinematic viscosity. The rate of hydrogenation must also be optimized such that other properties like pour point aren't affected by the sudden decline in unsaturation[17]. Also Sai Ba, et al. [18] showed that the viscosity booming – OH group in ricinoleic acid can be converted to a ketone group using Dess–Martin periodinane as illustrated in Figure 7. The above modification was observed to bring down the kinematic viscosity to a great extent with the elimination of hydroxyl group.

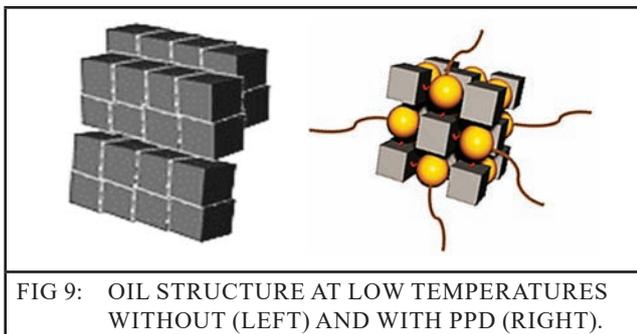


Pour point depressants (PPD) are used to bring down the pour point of the insulating fluids. The PPDs are mainly polymeric species such as Polymeth acrylates, Polyacrylates and Alkalated naphthalene as represented in Figure 8[19].



The usage of PPD's provides good results in lowering pour points. The structural changes brought in by the usage of PPD are illustrated in Figure 9. Unfortunately the PPDs used are majorly non-biodegradable. Hence, they must be

used in specific quantities to enhance pour point but also keeping in mind the consequence of non-biodegradability.



4.0 CHALLENGES AND TECHNICAL DIFFICULTIES

The research in the field of natural esters as an alternative to mineral oil is still in its mid stages with numerous challenges to be solved. The properties and limitations of vegetable esters restrict its usage in larger transformers. Retro filling transformers with natural esters have also been reported but, complete usage of natural esters in larger transformers is yet to be brought into large scale action. Further, structure of transformer itself has to be modified for usage of natural esters as transformer fluid.

The internal faults of the transformer can be correlated when mineral oil is used as the dielectric fluid based on the gases present in oil by Dissolved Gas Analysis (DGA) technique. However, in case of natural esters, specific correlations are yet to be established due to the lack of data base. Some research shows that most of the correlations remain same but complete correlations have not been drawn yet.

5.0 CONCLUSION

- Vegetable oil as transformer oil plays a vital role in helping the world to resolve the environmental issues.
- Knowledge on their chemical structure and its impact on the properties have to be gained and modification in their structure results in improving Oxidation stability, viscosity and Pour point for the end use.

- Vegetable esters with modifications in their chemical structure meet the requirements of transformer utility.
- High water solubility of vegetable esters is explained by the presence of polar group on triglyceride towards which water molecules are attracted.
- The presence of long chain, unsaturation and oxygen rich functional groups explains the high kinematic viscosity associated with natural esters.
- The chemical structure of triglycerides and its composition explains the high pour point that is observed with natural esters. The use of PPDs for improving the pour point has been accounted.
- Finally the correlation between structures, composition of oil and oxidation stability of the oils have been studied. The mechanism of antioxidant activity has been reported.

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