Gassing Tendency of Natural Ester Based Transformer Oils: Low Ethane Generation in Stray Gassing Behavior

Banti Sidhiwala, T. C. S. M. Gupta

***Abstract*—**Mineral oils of naphthenic and paraffinic type are in use as insulating liquids in the transformer applications to protect solid insulation from moisture and ensures effective heat transfer/cooling. The performance of these type of oils have been proven in the field over many decades and the condition monitoring and diagnosis of transformer performance have been successfully monitored through oil properties and dissolved gas analysis methods successfully. Different types of gases can represent various types of faults that may occur due to faulty components or unfavorable operating conditions. A large amount of database has been generated in the industry for dissolved gas analysis in mineral oil-based transformer oils, and various models have been developed to predict faults and analyze data. Additionally, oil specifications and standards have been updated to include stray gassing limits that cover low-temperature faults. This modification has become an effective preventative maintenance tool that can help greatly in understanding the reasons for breakdowns of electrical insulating materials and related components. Natural esters have seen a rise in popularity in recent years due to their "green" credentials. Some of its benefits include biodegradability, a higher fire point, improvement in load capability of transformer and improved solid insulation life than mineral oils. However, the stray gassing test shows that hydrogen and hydrocarbons like methane (CH_4) and ethane (C_2H_6) show very high values which are much higher than the limits of mineral oil standards. Though the standards for these types of esters are yet to be evolved, the higher values of hydrocarbon gases that are available in the market is of concern which might be interpreted as a fault in transformer operation. The current paper focuses on developing a class of natural esters with low levels of stray gassing by American Society for Testing and Materials (ASTM) and International Electric Council (IEC) methods much lower values compared to the natural ester-based products reported in the literature. The experimental results of products are explained.

***Keywords*—**Biodegradability, fire point, dissolved gas analysis, natural ester, stray gassing.

I. Introduction

THE transformer is one of the most important links in a power generation/transmission and distribution network, and the reliability of operations depends on the smooth functioning of the transformer. Mineral oils have been used as dielectric fluids in transformers over many decades for power generation and distribution applications. The main function of the transformer/insulating oil is to provide insulation to the windings and to remove the heat generated due to heat losses resulting from alternating voltage and current within the transformer. During this process of prolonged thermal and oxidative aging, insulating fluid is subjected to various electrochemical stress resulting in many chemical byproducts. In addition, faults arising from components, layout, partial discharge, and hot spots can cause complex chemical reactions within insulating oils, leading to the hydrolysis of paper and the generation of various types of gases [1]-[3].

Synthetic esters and natural esters have been introduced in transformer applications over 30 years and 20 years, respectively. While the chemical structure of these esters is different from mineral oils, these oils offer advantages of equipment safety (higher fire points), biodegradability and extended life of solid insulation due to their high moisture retention properties and stable electric properties [4].

The use of alternate ester fluids brings in additional complex reactions due to hydrolysis, oxidation of unsaturated fatty acids and autoxidation reactions resulting in generation of hydrocarbons and other gases. However, the types of gases released are similar to dissolved gas analysis of mineral oils.

Transformers typically undergo predictive maintenance by monitoring and analyzing dissolved gases in the oil by monitoring the trends in dissolved gas analysis (DGA) program and other quality parameters such as the dielectric breakdown strength, interfacial tension, moisture content, dielectric dissipation factor (DDF), neutralization number/total acidity number, color, sludge content and the concentration of furfural and associated compounds.

Stray gassing refers to the phenomena of fault gas production from insulating fluids at normal temperatures, caused entirely by the chemical composition of the insulating liquid, and not related to the faults in the equipment under thermo-oxidative stress. Unusual gassing activity, or stray gassing, has been reported since 1970s. This gassing phenomenon has been discussed in literature since 1998. Different types of gases, including hydrogen, methane, ethane, have been noted both in sealed and breathing type of transformers.

Two approaches have been adopted by CIGRE TF 15/12.01.11 for stray gassing of a pure oil system [5].

1) At 120 °C, hydrogen and methane are shown to be the most frequent gases.
2) At 200 °C, methane and ethane have been seen to be the main gases generated.

All insulating oils tend to produce "stray gases" in service, in

B. Sidhiwala is M.Tech Chemical Engineer from Dharmsinh Desai University, Gujarat, India. He is working with APAR Industries Ltd., Mumbai, India (e-mail: banti.sidhiwala@apar.com).

TCSM Gupta is PhD in refining chemistry from Indian Institute of Petroleum, Dehradun, India, working with APAR Industries Limited, India (corresponding author, e-mail: tcsm.gupta@apar.com).

various amounts and patterns depending on the oil used. Stray gassing of oil has been defined by CIGRE as "the formation of gases in electrical insulating oils heated at relatively low temperatures of 90 to 200 °C" [6]. Stray Gassing is due to the chemical instability of oil molecules after they have been submitted to refining procedures, such as for example hydrogen treatment to remove impurities and undesirable chemical structures in mineral oils. Such treatments may oversaturate the hydrocarbon chains of mineral oil with hydrogen, which is then released as H_2 gas, together with some C_2H_6 and CH_4, when the oil is heated at various Stray Gassing temperatures, or is in contact with oxygen. It has been inferred that, even when the transformers are not energized, predominance of such stray gassing activity has been noticed [7].

The gases from stray gassing have not been shown to be harmful to the equipment, and usually level off over time. However, a prior knowledge/information of the stray gassing data will guide users to distinguish between genuine fault conditions in electrical equipment and stray gasses.

Though the gassing behavior of natural esters is found to be similar to mineral oils, the testing of in-service natural esters over the last two decades have reported high levels of ethane in literature without any apparent faults reported in the operating units [8].

Though, DGA has been accepted as a reliable tool for detecting early signals of faults and any abnormality in transformer condition monitoring, the most common evaluation schemes may fail to distinguish between stray gassing and certain types of fault gases leading to misinterpretation. It is thus advantageous to have a method for characterizing stray gassing behavior (under thermo-oxidative stress). Such stray gassing information should be taken into account when selecting an oil for equipment, so that it is useful in interpreting the DGA data as and when performed [9].

II. Stray Gassing Tendency in Mineral Oils

Mineral insulating oil is made up of hydrocarbon molecules with various functional groups (CH, CH_2, and CH_3) that are paraffinic, naphthenic and aromatic in nature. Mineral oil degradation during power transformer operation can result in the formation of gaseous molecules as a result of a variety of reactions, including primary decomposition, free radicals, and other secondary chemical reactions. When only a single hydrogen atom remains in a trace amount of a degraded hydrocarbon, it can react with the secondary atom to form a hydrogen molecule (H_2), as shown in (1):

$$H\cdot + \cdot H \rightarrow H_2 \tag{1}$$

Additionally, when atomic hydrogen combines with the methyl group's free radicals, the covalent connections between the carbon atoms in the aromatic structure may break, as mentioned in (2) & (3):

$$H_3C\cdot + \cdot H \rightarrow CH_4 \tag{2}$$

$$H_3C\cdot + \cdot CH_3 \rightarrow C_2H_6 \tag{3}$$

A few gases (H_2) have a possibility of forming at lower temperatures, whereas others (CH_4, C_2H_6, C_2H_2, and C_2H_4) only form at higher temperatures. Insulating paper and pressboard are made of cellulose molecules that are joined by glucose molecules; the length of the glucose chain determines the mechanical strength of the material. These cellulose molecules contain various groups (CO, CH_2 and CH), among which the C-O bond is weaker and can lead to the generation of gases at temperatures below 100 °C. At higher temperatures, the insulating paper can lead to the formation of CO_2. Apart from the gases mentioned above, the oxygen and hydrogen present in transformer oil are not affected by electrical malfunctions. The level of CO and CO_2 gases produced is determined by the amount of oxygen in the oil, but the opposite of this drop in O_2 content in oil commonly causes an anomalous rise in operating temperature of transformer. As a result, the volume of gas generation can be used to determine the severity of defects, and the concentration of various gases can be related to a particular failure mode or electrical faults inside the transformer [10].

The industry introduced new dielectric fluids derived from alternative natural sources of seed oils in the 1990s. The primary reasons for using natural ester-based dielectric fluids are environmental benefits due to excellent biodegradability, fire safety due to high fire points, and other potential electrical benefits such as less moisture impact on the dielectric strength of paper insulation and preservation of insulation system in transformers for reliability.

III. Stray Gassing Tendency in Natural Ester Fluids

Review of literature on in-service ester liquids reveals high level of ethane generation without any fault activity which can be attributed to the difference of basic chemical features of mineral oils and ester fluids. Mineral oils constitute of hydrocarbon with paraffinic, naphthenic and aromatic carbons with varied carbon chain length. In case of natural esters, the principle functional groups are ester and acids (fatty acids) with paraffinic carbon chain of seventeen carbons as the basic back bone with multiple double bonds. Depending upon the origin of natural ester source the typical fatty acids palmitic, stearic, oleic, linoleic and linolenic acid contents as represented in Table I vary of which oleic, linoleic and linolenic acids play significant role in the chemical and oxidative behavior of the oils [11].

TABLE I
Fatty Acid Composition (%) of Some Natural Ester Liquids

Source	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Grape seed	8	4	15	73	< 1
Peanut	11	2	48	32	< 1
HOSUN	< 3	< 3	> 91	≤ 2	< 0.2
Walnut	11	5	28	51	5
Soybean	11	4	24	54	7
Rape Seed	4	2	62	22	10
Flax Seed	3	7	21	16	53

Production of predominant quantities of alkanes, specifically ethane in natural esters is based on the oxidation of unsaturated fatty acid constituent in the oil follow two oxidation mechanism pathways; formation of hydro-peroxides by autoxidation and by singlet oxygen reaction. At elevated temperatures, autoxidation reactions are more rapid in the presence of polyunsaturated fatty acids whereas the singlet oxidation pathway mechanism is in the presence of photosensitive species present in the oil and the exposure of oil to light. The former mechanism may be predominant in the current insulating oil applications and type and constituents in the oils will play predominant role in generation of ethane [12]. Thus, to address the concerns of generation of gases under normal operating conditions and with the advent of changing refining technologies for producing mineral oils and alternate ester fluids, methods have been standardized simulating the operating conditions and thermal and oxidative aging in the presence of copper with and without oxygen have been introduced.

The ASTM D7150 method is designed to include thermal and oxidative conditions retaining the time duration whereas the method given in IEC 60296 is designed at lower operating temperature and lesser duration of time. These test methods describe the procedures to determine the gassing characteristics due to thermal stress of insulating liquids specifically and without the influence of other electrical apparatus materials or electrical stresses.

Stray gassing limit for mineral oils deployed in special applications in IEC 60296 is set as 50 µl/l of hydrogen (H_2), 50 µl/l of methane (CH_4), and 50 µl/l of ethane (C_2H_6). If the oils meet these specifications, then they are considered as "Non-Stray Gassing Type". However, in the case of ASTM D 7150, the duration of testing is longer (164 hours instead of 48 hours) and the temperature is set at 120 °C instead of 105 °C and though there is no set limit specified for gases, the test conditions are closer to an oxidation test as per Method C of IEC 61125.

IV. Experimental Section

In the current paper, High Oleic Sunflower oil (HOSUN) based ester fluid has been developed and evaluated for stray gassing behavior along with soybean, sunflower based insulating fluid and mineral oil-based transformer oil according to ASTM D7150 and IEC 60296 standards [13], [14]. The objective of the study is to study the behavior of oils under various test conditions and to understand the predominant mechanism. ASTM D7150 specifies two sample preparation methods (method A & B) for stray gassing tests. This paper focuses on Method A. In Method A, the oil is filtered through a mixed cellulose ester filter. Duplicate samples of the oil are purged with air zero (and other duplicate samples with nitrogen) for 30 minutes. The oil samples are sparged with two gases to simulate the various types of oil preservation systems used in transformers, namely free-breathing and in contact with oxygen (air zero) and sealed (nitrogen). Duplicate samples are then placed in a glass syringe, and then aged at 120 °C for 164 hours. After the aging period, the samples are removed from the oven, cooled to ambient temperature and then subjected to dissolve gas analysis. Similarly, for stray gassing evaluation as per IEC 60296 method for 48 hours at 105 °C with and without copper. The details of ATSM D7150 (Method A) & IEC 60296 are mentioned in Table II. IEC 60599 and IEC 60567 standards are used to interpret the absolute values of the stray gases in natural ester fluids for ASTM D7150 method and IEC 60296 respectively.

TABLE II
STRAY GASSING METHOD COMPARISON

	ASTM D7150 (Method A)	IEC 60296
Duration	164 h ± 15 min.	48 h ± 0.5 h
Temperature, °C	120 °C ± 2 °C	105 °C ± 2 °C
Filter process	A Mixed cellulose ester filter of 1 to 1.2 µm pore size	-
Copper surface area	-	9.6 cm^2 to 10 cm^2
Sparge	Flow rate: 200 ml/min. 1) 30 min ± 3 min with dry air 2) 30 min ± 3 min with dry N_2	-
Oil volume for testing	25 ml of insulating oil in 30 ml syringe 40 ml of insulating oil in 50 ml syringe	50 ml to 60 ml of oil with copper and without copper in 100 ml glass syringe
Oil analysis	ASTM D 3612 / IEC 60599	IEC 60567

V. Results and Discussion

The results on hydrogen and hydrocarbon gases (CH_4, C_2H_6) for all the samples according to IEC 60296 method are presented in Table III. In all the three test conditions of inert, oxidative and catalytic oxidative test conditions, the HOSUN based oil showed very low levels hydrocarbon gases generation compared to other natural ester fluids and at par with mineral oils meeting the criteria of "non-stray gassing" as per the IEC 60296 stray gassing limit of mineral oils.

TABLE III
HYDROCARBON GASES GENERATION IN STRAY GASSING TEST (IEC 60296), AGING @105°C FOR 48 H

Sample	Condition	H_2	CH_4	C_2H_6
Mineral oil	Air purged	1.5	1.2	1.4
Soybean oil	Air purged	31.2	ND	188.2
Sunflower oil	Air purged	16.4	ND	245.6
HOSUN	Air purged	49.1	3.6	3
Mineral oil	N_2 purged	2.7	<1	1.4
Soybean oil	N_2 purged	139.8	1.9	237.5
Sunflower oil	N_2 purged	7.7	ND	182.6
HOSUN	N_2 purged	31.6	2.9	15.2
Mineral oil	Air purged+ copper	3.9	1.2	1.7
Soybean oil	Air purged+ copper	38.4	ND	160.9
Sunflower oil	Air purged+ copper	24.4	ND	239.4
HOSUN	Air purged+ copper	45.2	2.6	3
Mineral oil	N_2 purged+ copper	ND	<1	ND
Soybean oil	N_2 purged+ copper	36.8	ND	223.6
Sunflower oil	N_2 purged+ copper	4.6	ND	207.2
HOSUN	N_2 purged+ copper	18.6	2.6	12.1

Values are in µl/l, ND- Not Detected

From the results presented in Table IV, as per ASTM D 7150 method A, the hydrocarbons generated in case of HOSUN are much lower and comparable to mineral oils.

According to the results, it is evident that the HOSUN based ester insulating fluid shows extremely low thermo-oxidative reaction resulting very low hydrocarbon generation which further consolidates that the chemical constituents play significant role in formulating a product with very low gassing behavior and such dielectric fluid generates extremely low stray gases than the sunflower and soybean oil in majority conditions and very similar to the mineral oil gases.

TABLE IV
STRAY GASSING (ASTM D7150), AGING @120°C FOR 164 H

Sample	Condition	H_2	CH_4	C_2H_6
Mineral oil	Air purged	66.5	4	4.9
Sunflower	Air purged	516	5.6	5598
Soybean	Air purged	GEL	GEL	GEL
HOSUN	Air purged	613	7.8	27
Mineral Oil	N_2 purged	30.7	14.9	22.3
Sunflower	N_2 purged	360	41	958
Soybean	N_2 purged	145	ND	14
HOSUN	N_2 purged	71.5	10	19.6

Values are in µl/l, ND- Not Detected, GEL – gel formation due to oxidative polymerization.

VI. CONCLUSIONS

It is possible to develop a product by careful selection of natural ester source. HOSUN based ester insulating fluid has high oleic content and very low linoleic and linolenic acid contents resulting in low ethane generation in stray gassing tests which are similar to mineral oils.

- The results of stray gassing tests can be used to create a thermal stress-related gassing fingerprint.
- The stray gassing baseline is low and the HOSUN oils are not stray gassing type and there is no need of adjusting the base line for the gases detected during standard DGA tests to differentiate between stray gassing activity and classic transformer faults.
- The HOSUN is good alternative option that generates extremely low stray gassing compared to other conventional natural esters similar to mineral oils.

REFERENCES

[1] X. Zhang, E. Gockenbach, "Asset-Management of Transformers Based on condition Monitoring and Standards Diagnosis", IEEE Electrical Insulation Mag., Vol. 24, No. 4, 2008, 26-40.
[2] M. Duval, A. dePablo, "Interpretation of Gas-In-Oil Analysis Using New IEC Publication 60599 and IEC TC 10 Databases", IEEE Electrical Insulation Mag., Vol. 17, No. 2, 2001, 41.
[3] M. Duval, "Dissolved Gas Analysis: It Can Save Your Transformer", IEEE Electrical Insulation Mag., Vol. 24, No. 4, 1989, 22-27.
[4] M. Phoshoko, "Predictive maintenance of transformers through stray gassing studies", Powertech Transformers, 2017.
[5] I. Höhlein, "Unusual Cases of Gassing in Transformers in Service", IEEE Electrical Insulation Magazine, Vol.22, No.1, 2006.
[6] Cigre D1.01/A2.11_296: Recent Development in DGA Interpretation, June-2006.
[7] M. Duval, T. Heizmann, "Identification of stray gassing of Inhibited and Uninhibited Mineral Oils in Transformers", Energies, 2020.
[8] M. Lahbrook, H. Al-Amin, R. Martin, "Natural ester and synthetic ester fluids, applications and maintenance, 10th Jordan International Electrical and Electronics Engineering Conference", 2017.
[9] S.J. Han, T. Gaglio, X. Zhang, "Aging performance of natural ester based dielectric fluids for transformer system", 21st international conference on electricity distribution, June 2011.
[10] A. J. Amalanathan, R. Sarathi, M. Zdanowski, R. Vinu and Z. Nadolny, "Review on Gassing Tendency of Different Insulating Fluids towards Transformer Applications", *Energies* 2023, *16*(1), 488.
[11] D. Hanson, K. Li, J. plascencia, C. beauchemin, J. Luksich, A. Lemm, "Understanding Dissolved Gas Analysis of Ester Fluids- part 1: stray gas production under normal operating conditions", Siemens Transformer Conference, 2010.
[12] D. Hanson, K. Li, J. plascencia, C. beauchemin, J. Luksich, A. Lemm, C. Claiborne, D. Cherry, G. Frimpong, R. Martin, "Understanding Dissolved Gas Analysis of Ester Liquids: an Updated Review of Gas Generated in Ester Liquid by Stray Gassing, Thermal Decomposition and Electrical Discharge", Electrical Insulation Conference (EIC), Montréal, Qc, Canada, 2016, 19-22.
[13] ASTM D7150 – 13, "Determination of Gassing Characteristics of Insulating Liquids under Thermal Stress".
[14] IEC 60296:2020, "Fluids for electrotechnical applications – Mineral insulating oils for electrical equipment".

Banti Sidhiwala obtained his M.Tech Chemical Engineering from Dharmsinh Desai University, Gujarat, India in 2015 and Bachelor of Chemical Engineering from G.H.Patel College of Engineering and Technology, Gujarat, India 2013. He has about 8 years of experience in fields of Dielectric fluids, lubricants in the area of Product development.

T.C.S.M. Gupta obtained his Ph.D in refining chemistry from Indian Institute of Petroleum, Dehradun, India in 1992 and Master's in chemistry from University of Roorkee, India. He has about 31 years of experience in fields of dielectric fluids, lubricants, additives in the areas of product development/quality and Business development. Currently he is working with APAR Industries Ltd, India as Sr. Vice President. Dr. Gupta has presented/co-authored more than 50 papers and filed 4 Indian patents. He is Vice President of NLGI. India Chapter, Board Member of Asian Lubricant Industry Association, Singapore, Life Member of Tribology Society of India.