Use of Paper Degradation Products for Diagnostics and Condition Assessment

Phase 2 – Identification of Marker Compounds

1017736

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Technical Update, December 2009

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PRODUCT DESCRIPTION

This report is a continuation of the Electric Power Research Institute (EPRI) report *Transformer Life Extension: Use of Paper Degradation Products for Diagnostics and Condition Assessment* (1015937). In that report, data gathered from previous research at Powertech Labs, the literature, and the databases of BC Hydro and British Columbia Transmission Company were used to establish the correlations of furanic compounds in oil with the degree of polymerization (DP_v) of insulating paper. The data were also used to estimate the end of life of a transformer and to improve transformer diagnostics. The report pointed out that 2-furaldehyde—one of the main furanic compounds—might not be the best indicator of degradation nor the DP_v of thermally upgraded paper. This report names products that are better suited as diagnostic indicators for monitoring the degradation of mixed-paper systems.

Results and Findings

Laboratory experiments were performed to identify the marker compounds for the degradation of dicyandiamide (DICY). It was observed that DICY decomposes in the presence of heat at temperatures as low as 80°C, moisture, and oxygen to form nitrogen-containing compounds. Specific nitrogen-containing compounds—including ammonia, pyrrole, and methylpyrazine—indicate the presence of decomposition products from DICY on the insulating paper. The rate of thermal decomposition of DICY was measured at different conditions in order to estimate its remaining lifetime on the paper. Even after complete depletion of DICY, the nitrogen content on the paper does not go to zero. The paper contains approximately 1% of nitrogen as other byproduct compounds, which still provides added thermal stability to the insulating paper compared to regular kraft paper.

Laboratory experiments with paper system only, oil system only, and different types of paper wrapped around copper conductor immersed in oil confirmed that the marker compounds are produced from decomposition of paper only. Marker compounds that are specific to thermal decomposition of insulating oil, insulating paper, and DICY additive were analyzed, with ammonia determined as the compound best able to estimate the amount of DICY remaining on paper. A logarithmic relationship between the concentration of ammonia in oil and DICY remaining on paper was established and used to estimate the remaining percentage of DICY and the DP_v of the paper.

This report also summarizes the development of an analytical method for monitoring the level of fault gases and marker compound(s) in the oil and headspace. This method was used to pinpoint the types of compounds in the oil that are precursors to paper degradation. A small-scale on-line monitoring system was built to continuously analyze the levels of selected marker compounds produced.

Challenges and Objectives

Currently, 2-furaldehyde is widely used as a marker of the degradation of transformer paper. Recent literature is conclusive on the existence of significant differences in the relationship between 2-furaldehyde and the DP_v during aging with the type of paper (ordinary kraft versus thermally upgraded kraft) and varying amounts of water content. Despite numerous attempts to correlate 2-furaldehyde with cellulose degradation, no satisfactory relationship has yet been established to cover the variations in in-service transformer conditions. Accordingly, the industry needs products that are better suited as diagnostic indicators for monitoring the degradation of mixed-paper systems and that are specific to the rupture of the cellulosic bonds. The amount of the marker compounds in the oil will give an indication of the DP_v of the insulating paper and the remaining life of the transformer.

Off-line analysis of furanic and other marker compounds in oil are now used as transformer diagnostic indicators on a regular basis. This approach, although convenient and widespread, presents a significant drawback: the location and time of sampling significantly influence the results. The presence of an active fault between sampling intervals could be missed—worse, the fault could progress to failure before the next scheduled sample. Also, the results between long sampling intervals might be misleading because some of the marker compounds degrade with time and temperature.

In order to overcome the limits of laboratory tests, a small-scale on-line setup attached to a portable gas chromatography with four different columns to continually detect the marker compounds was built. This setup was used to carry out research with the aim of identifying an oil-soluble chemical indicator that is specific to the rupture of the 1,4-β-glucosidic bonds of cellulose and present in the oil regardless of the type of paper. The DP_v of the paper specimens was used to establish the existence of a relationship between the amount of indicator in the oil and the fraction of glucosidic bonds ruptured.

EPRI Perspective

Detailed knowledge of the type, amount, and formation rate of decomposition products is essential for transformer diagnostics and condition assessment. The potential benefits to the utility industry are enormous, including fewer unscheduled outages or catastrophic failures through more accurate determination of the condition of transformers with mixed-paper systems. Having this predictive knowledge would also permit a shift to condition-based maintenance from costlier time-based maintenance.

Approach

This report continues Phase 1 and addresses Phases 2 and 3 of a multi-phase project. Task 1 consisted of the investigation of marker compounds from the decomposition of insulating paper and the compounds' rate of production. Task 2 involved the development of an analytical method that will accurately monitor the level of marker compounds in the oil and headspace. This information was used to determine the early stage of the degradation of insulating paper. Part of Phase 3, involving the preliminary development of an on-line monitoring system, is also covered herein.

Keywords

Cellulose degradation
Degree of polymerization (DP_v)
End-of-life of transformers
Marker compounds
On-line monitoring
Thermally upgraded cellulose paper

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

In-service transformers are subject to a combination of electrical, thermal, mechanical and environmental stresses. When these exceed their design limits, faults may develop in the form of partial discharge, arcing or hot spots resulting in the formation of fault products. Fault progression will inevitably lead to failure if the dielectric integrity is compromised. The type, magnitude and temperature of faults dictate the type, quantity and rate of formation of fault products. Detailed knowledge of product type, amount, and rate of formation is essential for condition assessment and equipment diagnosis. Of particular concern is the development of a hot spot in the paper insulation that results from overload or localized heating, as this will ultimately determine the life of the transformer. This is because the oil can be reconditioned by conventional treatment or simply replaced, but the paper degrades through an irreversible process of depolymerization.

The paper used in oil-filled power transformers is made from the Kraft process which involves delignifying wood pulp by treating with sodium hydroxide and sodium sulfate.[1] Kraft insulation paper consists of approximately 90 % cellulose, 6 % lignin and 4% hemi-cellulose. The thickness of Kraft paper insulation may vary from 30 to 120 μm and several layers are wrapped around each copper conductor to insulate each strand from the next. Cellulose is the major component of electrical grade Kraft paper and is the predominant solid insulation medium in power transformers.

Under normal operating temperatures the insulating paper electrical and mechanical properties degrade slowly with time but increase rapidly with rising operating temperature. The paper can eventually become discolored, brittle, and fragile at which point its physical and chemical properties are degraded to such an extent that it puts the electrical integrity of the equipment at risk. The presence of moisture, oxygen, copper and oil degradation products will further enhance the rate of paper degradation by initiating hydrolysis and oxidation of the cellulose.[2, 3] Therefore, it is important to find reliable and sensitive methods to monitor the condition of the paper for incipient faults, risk of failure and estimate of its remaining life. Historically, changes in the Degree of Polymerization (DP_v) of the paper have been used to estimate its condition from its new state down to extreme degrees of deterioration, and estimate expected lifetimes. However, the DP_v method is intrusive, as it requires sampling the paper from a transformer and is therefore not appropriate for continuous monitoring.

When a hot spot develops in the transformer windings, the increase in temperature causes the oil/paper insulation system to degrade and produce a variety of new compounds, including fault gases (H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, CO, CO_2), moisture, volatile (VOC) and non-volatile (NVOC) organic compounds. Compounds that originate exclusively from cellulose decomposition have been identified and include 2-furaldehyde (2-FAL) and furyl alcohol (2-FUROL) as the main products along with a number of other oil soluble furanic and non-furanic compounds at lower concentrations in addition to CO, CO_2 and moisture. Of these, 2-furaldehyde has been related to the DP_v of the paper and used as the leading indicator of the remaining life of transformers.

To increase the temperature rating of modern transformers, Kraft paper is thermally upgraded by impregnating with an additive. The additive most frequently used in thermally upgraded paper is dicyandiamide (DICY). This treatment can extend the life of paper at normal operating temperatures or allow the transformer to be safely operated at higher temperatures. The use of thermally upgraded paper has allowed transformers to be up rated from 55 °C to 65°C average winding temperature rise.

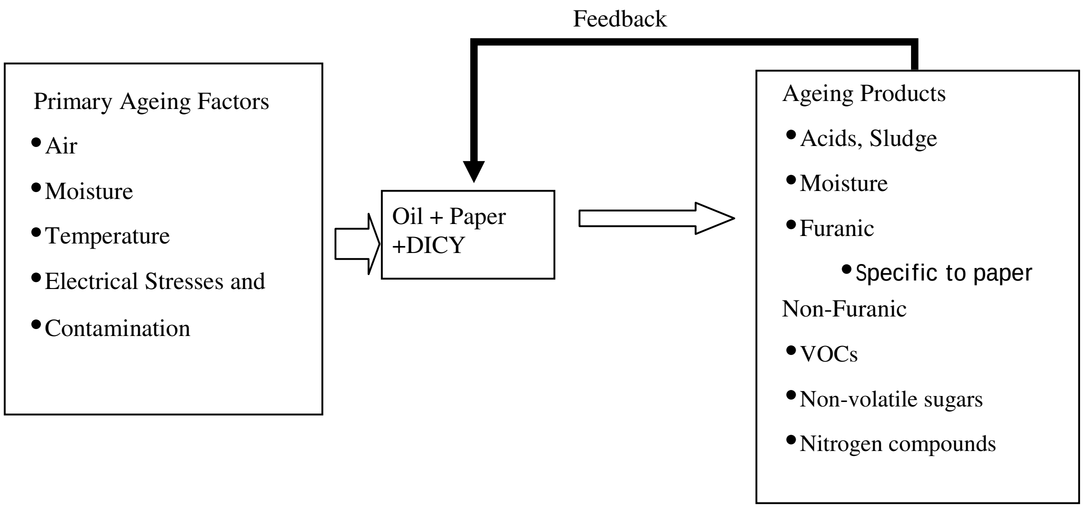
There is growing evidence suggesting that 2-furaldehyde may not be the best indicator of DP_v for thermally upgraded paper. Our own laboratory studies have shown that at a given temperature, thermally upgraded paper degrades at much slower rate than ordinary Kraft paper. Most modern transformers in North American utilities use thermally upgraded paper for the windings and Kraft paper for the remainder. For such mixed paper systems, the use of 2-furaldehyde as a marker compound for paper degradation and DP_v can be confusing or misleading. In Phase 1 of this project we addressed this issue and recommended appropriate alternatives. In Phase 2 of this project we will be investigating the presence and use of other marker compounds better suited as indicators of degradation for thermally upgraded paper and mixed paper systems and their correlation with their DP_v. To better understand the use of marker compounds for mixed paper systems it is helpful to understand the process of paper aging and degradation in a transformer.

Aging and Degradation of Insulating Paper

The environmental condition of paper will induce chemical and/or physical processes at the molecular level. These processes are the aging mechanisms. It is the chemical structure of the cellulose which provides clues to understand the aging mechanisms and aging characteristics of Kraft insulating paper. The condition and strength of the cellulose fibers themselves and the intermolecular hydrogen bonds between the cellulose chains are the most significant control factors that influence the strength of a dried sheet of paper.

From the standpoint of molecular structure, the aging of the cellulose fibers is related to the crosswise break of the inter- and intra-molecular hydrogen bonds and the lengthwise break of the molecular chains through the rupture of the 1,4-β-glucosidic bonds. Specifically, the average length of the cellulose chains is the parameter that governs the mechanical strength of the insulating papers. Such a relationship makes the viscometric degree of polymerization (DP_v) an appropriate measurement for directly assessing the progress of paper aging (20% of tensile strength corresponds to $DP_v \approx 200$). This widely used parameter by electrical power utilities gives information on the average number of β-D- glucopyranose rings per cellulose molecule. However, the DP_v measurement is impractical in the field due to the need to de-energize the transformer to extract representative paper specimens. To overcome the difficulty, it would be especially useful to identify a relationship between the cellulose DP_v and specific products dissolved in the insulating oil that is directly related to its aging. Once established, such a relationship would permit oil analyses to be used to assess the insulating paper condition of transformers in operation.

It is generally accepted that hydrolytic, oxidative and thermal degradation are the major aging mechanisms of paper insulation. Scheme 1-1 summarizes the primary aging factors for oil and insulating paper along with the aging products formed.



Scheme 1-1
Aging Factors and Mechanisms of Degradation of Paper Insulation.

Hydrolytic Degradation

This refers to the cleavage at the glucosidic linkage in the cellulose chain as shown in Figure 1-1. Cellulose is susceptible to hydrolysis by acids. Acids attack the acetal linkages and result in the breakage of the 1,4-glycosidic bonds, which will decrease the value of the degree of polymerization process. Presence of water will further increase the rate of cellulose and paper degradation.

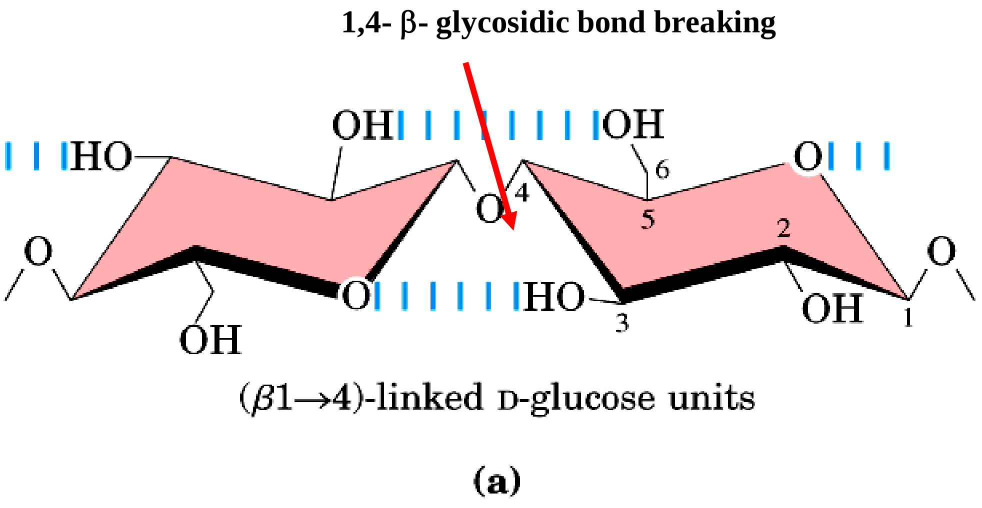


Figure 1-1
Chemical Structure of Cellulose Showing 1,4- β-Glycosidic Bond Breaking

Oxidative Degradation

Cellulose is susceptible to oxidation and oxygen will also accelerate the degradation reaction. The hydroxyl group in the cellulose molecule is the weak parts where carbonyl and carboxyl groups are formed and eventually cause secondary reactions giving chain scission. Strong oxidizing agents and/or vigorous reaction conditions can convert cellulose into CO, CO_2 and H_2O by the break up of the ring structure.

Thermal Degradation

A number of different thermal degradation reactions are known to occur with the cellulose and paper at different temperatures. Degradation at lower temperatures (<200°C) usually refers to the normal aging of cellulosic paper. At higher temperatures (>200°C), water is lost, first from the adsorbed by the cellulose, and then by elimination from the cellulose hydroxyls. When the aging temperature is above 250°C, several competing pyrolytic reactions begin to take over. In summary, these thermal degradation reactions can be grouped into three basic classifications: the first group occurs at lower temperature and is similar to the aging reactions. Products are water, CO, CO_2 and a carbonaceous char. At higher temperatures, another reaction begins to take over which results in depolymerization of the cellulose chain and formation of anhydroglucose derivatives, volatile organic materials and tars. At still higher temperatures, more or less random bond cleavage of cellulose and intermediate decomposition products results in the formation of a variety of low molecular weight compounds. Furanic compounds are well-known intermediate decomposition products that are generated even at low temperatures (<140ºC) by the degradation of cellulose in insulation paper but not by insulation oil.

Indicators of Paper Degradation

Furans in oil

When paper degrades, the cellulose glycosidic bonds start to break apart and release glucose in the oil. Glucose is neither soluble in oil, nor stable at the operating conditions, and converts to furfurals. Furfurals refer to a whole family of furanic compounds. 2- Furaldehyde is by far the most abundant of the furanic derivatives, and the others are occasionally found in large enough concentrations to indicate significant paper degradation. High furfurals in oil indicate the cellulose and paper insulation is degrading and possibly overheating. Since the first work suggested by Burton et al. in 1984,[4] the concentration of furfurals in transformer oil has been well known to be an indicator of the extent to which the paper insulation of the windings has deteriorated.[5, 6, 7] It is generally believed that high concentrations of 2-furaldehyde, (the predominant compound) in insulating oil are a clear indication of cellulose degradation as this is the only type of material in transformers that yields this by-product. However, as shown in Phase 1 of this project the level of furanic compounds is dependent on the type of paper at the windings of the transformers. Currently there is a lack of comprehensive understanding of the key factors affecting the use of the furanic compounds as an accurate indicator of transformer end of life. Hence the end of life prediction from furanic compounds results has many deficiencies.

Dicyandiamide

The fate of the DICY additive in paper insulation of in-service transformers is not fully understood. There is a concern that it becomes depleted with time as a result of leaching by oil, reaction with moisture, products formed by oil oxidation, paper degradation, and by thermal decomposition. As the protection provided by DICY becomes depleted with time, the rate of paper decomposition will likely accelerate.

There have been numerous transformer failures that occurred previously that were attributed to the premature aging of the TUP. In some cases, laboratory analyses have confirmed the poor condition of the paper and the depletion of its DICY content. At the moment, the only way to measure the residual DICY content is to remove a sample of insulating paper and perform laboratory analysis. What is needed is a non-invasive technique for measuring the residual DICY, its effective remaining protection, and the potential onset of accelerated paper deterioration of in-service transformers. One approach is to identify specific marker compounds in the oil that are related to the residual levels of DICY in TUP.

The main objective of this project was to identify the presence of potential marker compound in oil that originated specifically from the degradation of thermally upgraded paper. Their presence and levels would be beneficial for transformer diagnostics, determining the condition of the insulating paper and estimating the remaining life of the transformer after a certain period of operation.

Other Indicators

In addition to furanic compounds, cellulose degradation generates a host of other non-furanic compounds. In a series of laboratory tests we determined the presence and identity of many of these products, some of which are specific to thermally upgraded paper. These included methanol, acetone, acetaldehyde along with low molecular weight acids, and low molecular weight sulfur compounds. Details of the work have been reported elsewhere.[8] Recent work by other researchers has indicated that methanol may be a good indicator for both Kraft and thermally upgraded paper.[9]

2

BACKGROUND

Considerable work has been done worldwide and by Powertech Labs Inc. in the area of paper aging and its relation to transformer diagnostics and condition assessment. Most research has focused on the use of furanic compounds and specially 2-furfuraldehyde and carbon oxides. As early as 1981, Tamura et al. reported a relationship between the amount of carbon oxides (CO and CO_2) in the oil and the degree of polymerization of insulating papers. The use of these gases as indicators is of limited use since they are also formed from the decomposition of oil during long-term oxidation. In 1984, Burton et.al. reported on the presence of furanic compounds in oil as specific indicators of breakdown of the paper insulation. The cumulative amount of the most abundant furan found in transformer oil -2-furaldehyde was related to the reduction of DP_v of the cellulose, both in laboratory and from in-service transformers.

To aid in furan interpretation, some researchers have developed equations to relate the furan concentration in oil with the DP_v of the paper.[10, 11] These equations have been used to predict the DP_v from the furan results. However, caution must be used as these equations generally calculate the average DPv for the entire insulation system and not the paper at the hot spot. Also most of the equations were derived from controlled laboratory experiments using regular Kraft paper and/or from transformers using non-upgraded paper. They may not be applicable to furan results from transformers with Thermally Upgraded paper or mixed paper systems, such as many of those in North America. Several studies have shown that furan levels in European transformers are higher than those in North America.[12] This may be due to the predominant use of thermally upgraded paper in North American transformers as opposed to mostly non-upgraded regular Kraft paper in European units. A review in the literature is conclusive on the existence of significant differences in the relationship between 2-FAL and DP_v during aging with the type of paper (ordinary Kraft versus TUP), and varying contents of water.[13, 14, 15]

It is apparent that the type of insulating paper (Kraft and Thermally Upgraded Paper) influences the type and amounts of products formed due to degradation and recent studies suggest that 2-furaldehyde may not be the best indicator of degradation or of the DP_v of TUP. In previous work we have detected many compounds that originated specifically from thermally upgraded paper. Our results indicated the formation of several compounds that may be more amenable to on-line monitoring. However, there is a need to fully identify and characterize which products are better suited as diagnostic indicators for monitoring the degradation of mixed (Kraft and Thermally Upgraded) paper systems. Such knowledge is necessary for more accurate estimation of the condition of the paper and detection of potential hot spots in mixed insulating paper transformers. Most of the research to date has been done at the bench scale level under controlled conditions. And although this approach is adequate for determining fundamental parameters, it lacks the sophistication of simulating actual operating conditions. What is needed then is a model based on actual transformers, which relates furans to DP_v of thermally upgraded paper and mixed paper system.

3

OBJECTIVES AND SCOPE

Objectives

The scope of this work encompassed three main objectives:

- Identify specific compounds in the oil that indicate the presence and the level of additive (dicyandiamide) in Thermally Upgraded Paper and its relation to DP.
- Identify marker compound(s) that is specific to the rupture of the cellulosic bond and that can provide credible, discernible early indications of paper degradation for on-line monitoring of transformers.
- Develop an analytical and monitoring method and evaluate appropriate sensors.

Scope

Although considerable amount of work has been carried out to relate decomposition products; mainly furanic compounds to the degree of polymerization of insulating paper, many issues still remain unresolved. These include:

- A lack of guide or interpretation algorithm that more accurately relates furanic compounds in oil to the DP_v of the paper and the remaining life of both 55 °C (Kraft Paper) and 65 °C (Thermally Upgraded Paper) rise transformers. Phase 1 of this project was aimed at developing an algorithm to use as a guide by transformer maintenance engineers and was successfully completed.
- The identification of marker compounds better suited for the determination of the condition and the DP_v of Thermally Upgraded paper and mixed paper systems.
- Lack of sensors or detection systems of key marker compounds suitable for on-line monitoring.

The method of monitoring the state of transformers by measuring relative amounts of dissolved hydrocarbons gases and chemical indicators in their insulating oil is well established. Dissolved gas analysis (DGA) has progressed to on-line monitoring. Continuous on-line monitoring allows trends on the chemical indicators concentrations to be followed for early detection of transformer faults. However, not much work has been conducted on other by-products obtained due to thermal decomposition of the insulating paper.

The project work will be carried out in phases as described below; this report will cover only Phase 2 and part of Phase 3. Work in other phases will be reported at a later date.

Phase 1: Interpretation Guide for Furanic Compounds in Oil

This phase was aimed at developing an algorithm to establish the correlation of furanic compounds to DP_v that could be used as a guide by transformer maintenance engineers and was successfully completed and published in 2008 as EPRI Report 1015937.

Phase 2: Identification of Marker Compounds

This phase is a continuation of Phase 1 and will include the identification of marker compounds that are better suited as indicators for monitoring mixed paper system degradation. In this phase, marker compounds specific to the degradation of dicyandiamide additive in TUP will be identified and correlated to the % of DICY present on paper and the DP_v of paper. This relationship will be used to estimate the remaining life of the transformer after a certain period of operation.

Also marker compounds specific to the rupture of cellulosic bonds independent of the type of paper, will also be identified along with a correlation with the DP_v of the paper in order to estimate the end of life of the transformer in a non-intrusive manner. Analytical and monitoring methods will be developed in order to accurately monitor the level of marker compounds in both oil and headspace and in order to allow identification of the types of compounds in the oil that are the precursors to the paper degradation.

Phase 3: Development of On-line Monitoring Method

Currently there are no commercially available monitoring systems suitable for on-line detection of paper degradation products. Considerable amount of research has been carried out by Powertech Labs Inc., which includes several patents related to this field of work. This proposed research will exploit and build on this knowledge and will include the development of on-line monitoring of marker compounds from paper degradation.

Phase 4: Field trials on-line monitoring

This phase is dependent on the results obtained from Phase 3. Once all the above tasks have been successfully completed, a prototype-monitoring unit will be built to monitor the target product(s). The unit will be evaluated in the laboratory for performance and then installed in the field on an in-service transformer.

4

MARKER COMPOUNDS DERIVED FROM DICYANDIAMIDE DECOMPOSITION

Introduction

As discussed in the previous section, the presence of thermally upgraded paper in a transformer will change the relationship between the amount of furans in oil and the DP_v of insulating paper. A relationship between the residual amounts of DICY in thermally upgraded and the DP_v will be very informative. However, DICY is not soluble in oil and thus cannot be used as a non-invasive method. The windings in most modern transformers are wrapped with thermally upgraded paper. It is logical to assume that the presence of decomposition product from DICY indicate excessive deterioration or a fault in the windings. Furthermore there should be a correlation among the levels of DICY decomposition products and the residual DP_v of thermally upgraded paper. Failures of the transformers insulation system most likely occur at the weakest spot-generally at a hot spot in the windings. Thus it is highly desirable to be able to distinguish the onset of fault in the windings from other locations. DICY decomposition products may also be used as indicators of winding faults.

Presently there is no means of verifying whether the aged transformer insulation still meets the thermal requirements of the standard thermally upgraded paper. No specific tests have been performed that indicate whether the insulation system is capable of handling the thermal stresses without excessive aging. The transformer owner would only learn this many years later when the transformer fails prematurely. One method to validate the thermal capability of the insulation in a power transformer is by measuring the nitrogen content of the insulation. Tests conducted before support the use of nitrogen content as a verification of the thermal capability of insulation as determined by short-term, high temperature aging tests. It was observed that low levels of nitrogen content in paper did not meet the aging criteria defined in the definition for thermally upgraded paper.

Hence, laboratory studies will be carried out with the aim of identifying chemical indicators either in the oil or headspace that are specific to the

- Residual amount of dicyandiamide (DICY) in the paper
- Correlation with DP_v of paper
- Faults in thermally upgraded paper
- Thermal decomposition of TUP and regular Kraft paper.

Once the chemical indicators have been identified and characterized, design of an on-line monitoring device will follow which will eventually be hooked up to a power transformer for real time measurement. To achieve this, the following set of experiments was carried out.

- Identification of products from thermal decomposition of DICY
- Temperature dependence of marker compounds from DICY

- Effect of temperature on residual DICY
- Correlation of other nitrogen compounds with DP_v of paper
- Other nitrogen marker compounds

Details of these experiments are given below.

Laboratory Tests

Thermal Decomposition of DICY

Preliminary studies were performed to identify marker compounds for the decomposition of dicyandiamide. Four sets of experiments were set up in 20 mL headspace vials as shown in Table 4-1. Except for the set of experiment 1, the others were done in the absence of Voltesso 35 as shown in Table 4-1. The headspace vials were heated at 150 °C for 7 days and the headspace was analyzed by GC-MS.

Table 4-1
Thermal Decomposition Products of Dicyandiamide.

Experiment	Details	Ammonia	Pyrrole	Pyrazines
1	Voltesso 35 (control)	Not observed	Not observed	Not observed
2	Dicy + Water	×		
3	Kraft Paper	Not observed	Not observed	Not observed
4	Thermally Upgraded Paper	×	×	×

Figure 4-1 and Figure 4-2 show typical Total Ion Count Mode (TIC) chromatograms of the volatile degradation products obtained from the headspace of the vials heated at 150 °C for 7 days. The potential marker compounds as identified by comparing the mass spectrum recorded at the maximum of each peak with those of the NIST MS 2002 library are listed in Table 4-3. As seen in the spectra most of the peaks eluted in the time range of 0-20 minutes are associated with nitrogen containing compounds. From the experimental results it was observed that ammonia, pyrrole and methyl pyrazines are the three main marker compounds formed from decomposition of dicyandiamide and TUP. None of these compounds were observed from the decomposition of regular Kraft paper and Voltesso 35 oil which were used as control. It is interesting to note that when dicyandiamide was heated at 150 °C for 7 days in the presence of water, only ammonia was detected. By comparison, when TUP was heated at the same temperature and for the same time interval, all three marker compounds were observed. This implies that the formation of pyrrole and pyrazines requires interaction of dicyandiamide or its decomposition products with insulating paper.

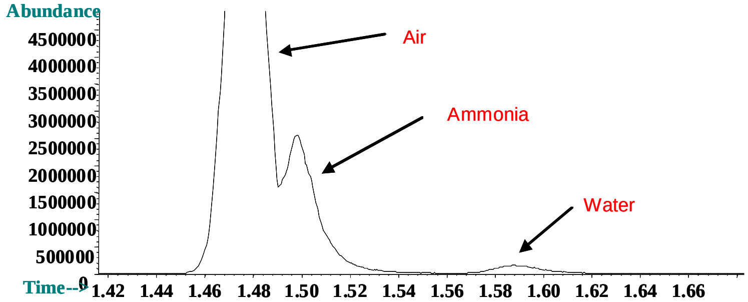


Figure 4-1
GC-MS Spectrum of the Headspace of the Vial Containing 0.1 g of Dicyandiamide Heated at 150 °C for 7 Days in the Presence of Water.

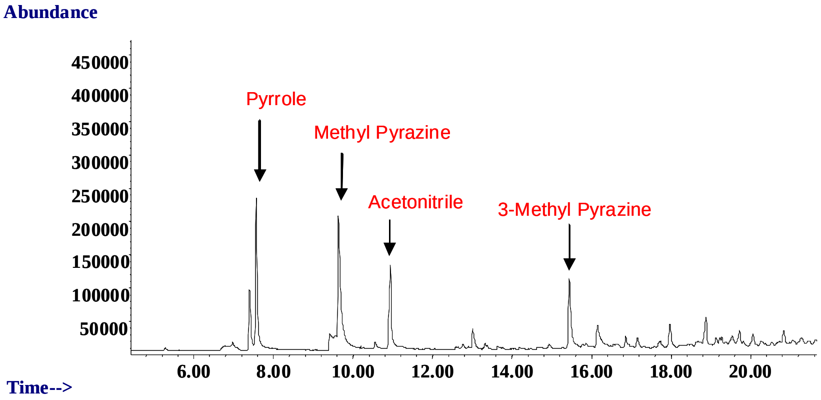
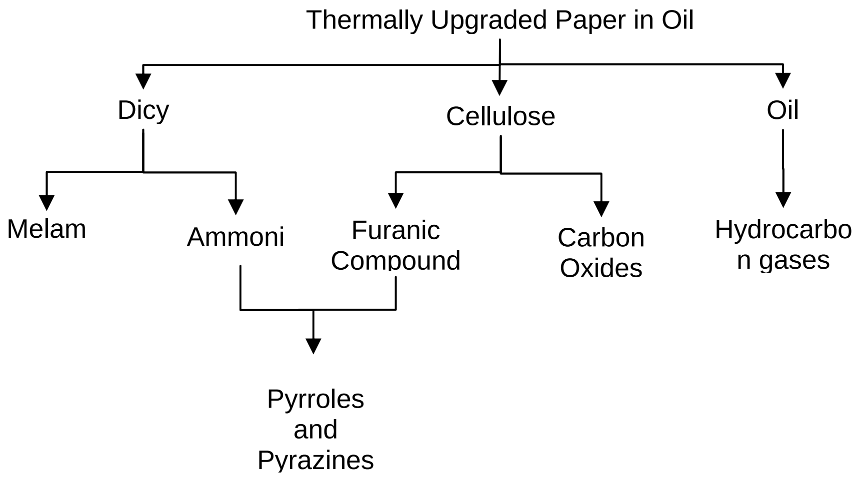


Figure 4-2
GC-MS Spectrum of the Headspace of the Vial Containing 0.1 g of TUP.

Note: Ammonia was also produced in this reaction but it is off the scale of the graph.

Mechanism of Decomposition

The mechanism through which pyrrole and pyrazines are formed when TUP is decomposed in the presence of heat and moisture is shown in Scheme 4-1. The three main components in a transformer that are prone to thermal decomposition are cellulose, dicyandiamide (if thermally upgraded paper is used) and oil. Dicyandiamide decomposes in the presence of water to give melam and ammonia. Cellulose decomposes to give furanic compounds and carbon oxides (carbon monoxide and carbon dioxide) and oil decomposes to give hydrocarbon gases. Pyrroles and pyrazines seem to be formed by the interaction of furanic compounds with the ammonia as shown in literature.



Scheme 4-1
Proposed Mechanism for Thermal Degradation of TUP in Oil

Temperature Dependence of Marker Compounds from DICY

Experimental section

A set of bench scale experiments was set up to determine the rate of formation of the marker compounds identified above as a function of temperature. Table 4-2 shows the content of each vial that was heated separately at the temperature of 140, 160, 180 and 200°C for 24 hours. The vials were then removed from the oven, allowed to cool down to room temperature, then analyzed by Headspace/GC-MS.

Table 4-2
Materials Used to Determine Temperature Dependence DICY Marker Compounds

Groups	Contents of Headspace Vials
1	1 g of Regular Kraft Paper
2	1 g of Thermally Upgraded Paper
3	1 g of Regular Kraft Paper + 1 g of Unused Voltesso 35 Oil
4	1 g of Thermally Upgraded Paper + 1 g of Unused Voltesso 35 of Oil

Results and Discussion

Table 4-3 shows a list of volatile compounds formed by the degradation of insulating paper and dicyandiamide on the paper. The common compounds formed by decomposition of both TUP and regular Kraft paper are 2-furaldehyde and furfuryl alcohol. However, nitrogen containing compounds, namely ammonia, pyrrole and methyl pyrazines are formed only from the degradation of thermally upgraded insulating paper. At the specific conditions reported here, the level of furfuryl alcohol produced in TUP is higher than that observed from regular Kraft paper and the level of 2-furaldehyde is lower in TUP. These observations have been previously reported in the literature and have been explicitly detailed in Phase 1 of this project.

Low molecular weight compounds such as acetone was also observed, however acetone is obtained from both the decomposition of paper and oil, with paper being the main source. This makes acetone a good screening compound but not a good marker compound for the decomposition of paper. As expected the rate of production of marker compounds increases with temperature as shown in Figure 4-3. More details about the rate of production of marker compounds and the relationship with the DP_v of paper are addressed in Chapter 5.

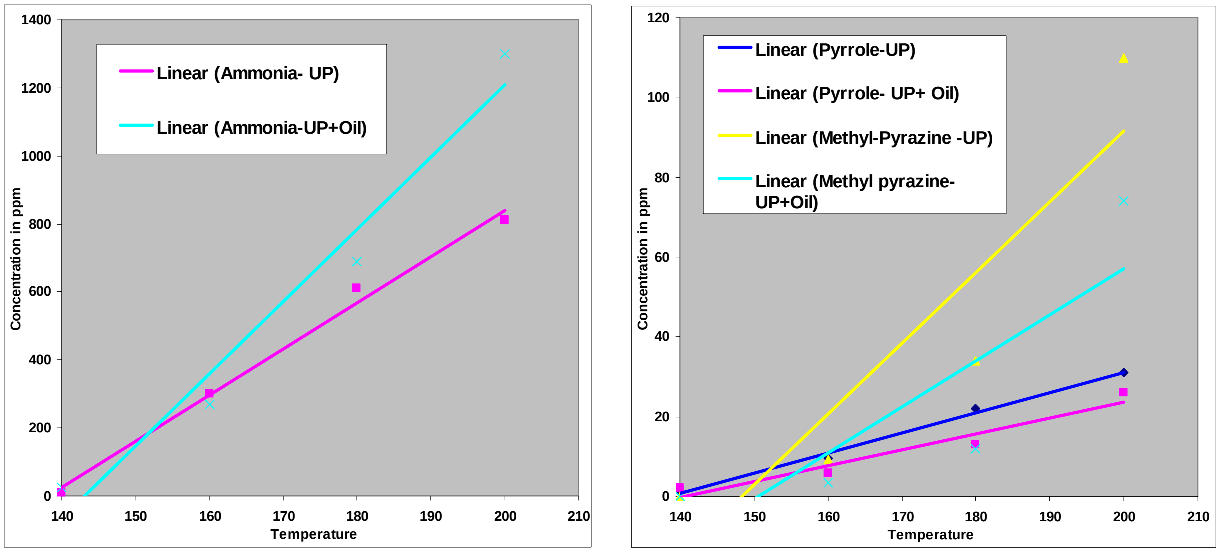


Figure 4-3
Relationship between Potential Marker Compounds and Temperature.

Table 4-3
List of Potential Indicators for Paper Degradation Products from Various Sources

Compounds	Kraft Paper				Upgraded Paper				Kraft Paper + Oil				Upgraded Paper + Oil			
	140	160	180	200	140	160	180	200	140	160	180	200	140	160	180	200
Ammonia	0	0	0	0	8.8	300	610	810	0	0	0	0	26	270	690	1300
Acetone	0.7	3.3	12	64	2.9	5	10	22	1.3	6.8	16	36	2.1	5.9	14	31
Pyrrole	0	0	0	0	1.4	9.6	22	31	0	0	0	0	2	5.9	13	26
Methyl Pyrazine	0	0	0	0	0	9.4	34	110	0	0	0	0	0	3.5	12	71
2-Furaldehyde	0	24	210	700	0	0	0	0	0	16	45	190	0	0	0	0
Furfuryl Alcohol	0	0	17	0	0	74	140	130	0	0	0	12	0	13	24	83

Rate of Degradation of Dicyandiamide (DICY)

While the aging experiment was underway, additional tests were carried out in order to estimate the rate of degradation of DICY on insulating paper and the rate of formation of marker compounds from DICY decomposition. Additional testing was carried out to gather information on the nitrogen content on the paper and how well the paper is protected after complete depletion of DICY. To do this, four key parameters were measured during the aging process namely:

- DICY content of the paper
- Total Nitrogen Content of the paper
- Degree of Polymerization of the paper
- Rate of production of identified marker compounds.

Experimental

Materials

Insulating oil - Unused Voltesso 35, heated at 105°C and vacuum dried
Thermally Upgraded Paper- wrapped around copper conductor of 1 cm width, 0.2 cm thickness and 5 cm length was used. The paper contained 7% by weight of water and 3.5 % DICY.
Copper conductor- each 5 cm long conductor weighed 10 g out of which 9.75 g was copper and 0.25 g was paper. The copper conductor was slightly bent so that it does not lie flat in the container.

Round metal cans were used as test containers in which thermal aging was performed. The test containers (32) were set up following the details in Table 4-4. Each test vessel contained:

- 0.13 L of clean Voltesso 35 oil
- 1 g of paper weight (4 × 0.25 g)
- 0.13 L of headspace (36 mg of O_2 in the headspace)

This ratio of materials was taken from a paper reported by Thomas Prevost.[16]

For dry paper, the containers containing the copper wrapped with paper were oven dried at 105 °C. The containers were removed from the oven one at a time and 130 mL of degassed oil was added and then sealed immediately with airtight lids. Once the containers were put assembled, they were placed in convection ovens at the pre-set temperatures of 90, 110, 120 and 140°C for different number of days as shown in Table 4-4.

Table 4-4
Experimental Details of Set Up for Rate of Decomposition of Dicyandiamide

	Heating Temperature for Dry Paper in Air				Heating Temperature for Wet Paper in Air			
Days	140°C	120 °C	110 °C	90 °C	140 °C	120 °C	110 °C	90 °C
0.1	x	x	x	x	x	x	x	x
14	x	x			x	x		
28	x		x	x	x		x	x
42	x	x			x	x		
56			x	x			x	x
70		x				x		
84			x	x			x	x

Analytical Procedures

Paper degradation was monitored by measuring the change in the Degree of Polymerization (DP_v) as per ASTM 4233. The moisture content of the paper was determined by Karl Fischer titration as per ASTM D3277.

DICY content of the paper was determining by using an in-house method developed at Powertech Labs Inc. The paper was extracted with methanol and the infrared absorption of the extract at 2198 cm^{-1} due to the DICY content was determined by FTIR. The IR absorbance from a methanol extract of untreated paper aged under the same conditions was used for background subtraction.

The total nitrogen content was obtained by elemental analysis.

Results and Discussion

DICY Content

The results of residual DICY content in paper as a function of aging time and temperature are shown in Figure 4-4. We can see that the DICY content of the paper decreases rapidly with time and temperature. However, as we can see from Figure 4-5, DICY decomposition with temperature follows a typical Arrhenius function. This implies that other factors in addition to temperature play a minor role in the decomposition process. Also at the same conditions, the DICY level of “wet” paper decreased more rapidly than that of the dry paper.

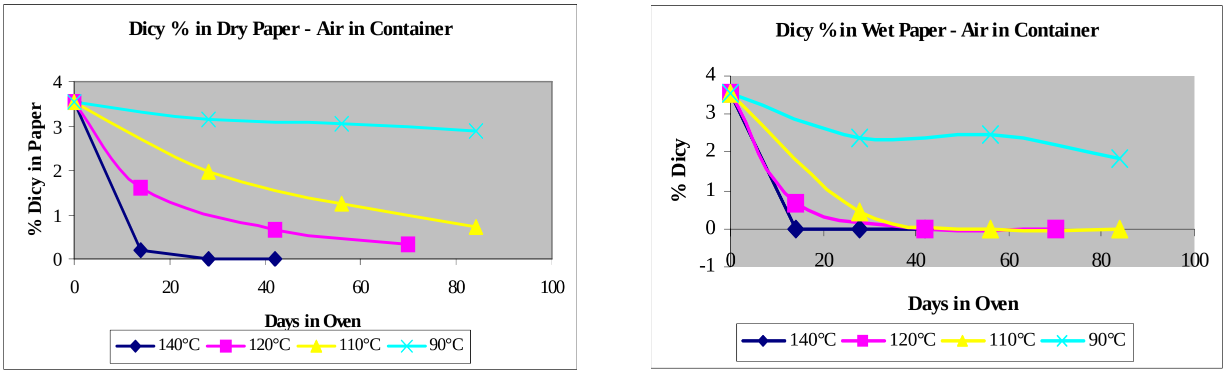


Figure 4-4
Effect of Temperature on DICY content in Wet and Dry Insulating Paper

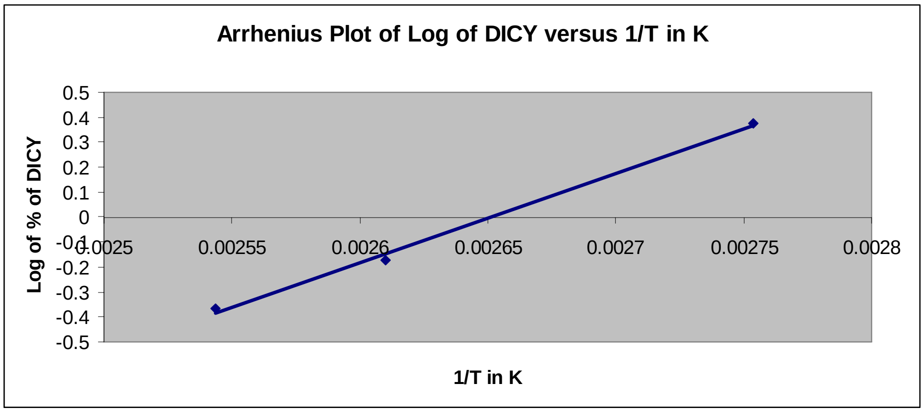


Figure 4-5
Arrhenius Plot of Log % of DICY versus 1/T.

Figure 4-6 shows the relationship between DICY content, DP_v and nitrogen content of the paper as a function of aging time and temperature. We note that the decrease of DICY follows the decrease in the DP_v. During the aging period, there is an initial sharp decrease in the $DP_{v,}$ the total nitrogen content, and the levels of DICY present in the insulating paper, and then stabilize. Similar trends are observed at both temperatures. A linear relationship is also observed between the degree of polymerization and the % of nitrogen on paper as shown in Figure 4-7.

It is worthwhile noting that the nitrogen content of paper does not follow the depletion of DICY. Figure 4-6 shows that the nitrogen content on the paper after DICY is completely depleted is still around 1 %. This indicates that DICY decomposes to other nitrogen containing compounds that remain in the paper and still provide thermal stability.

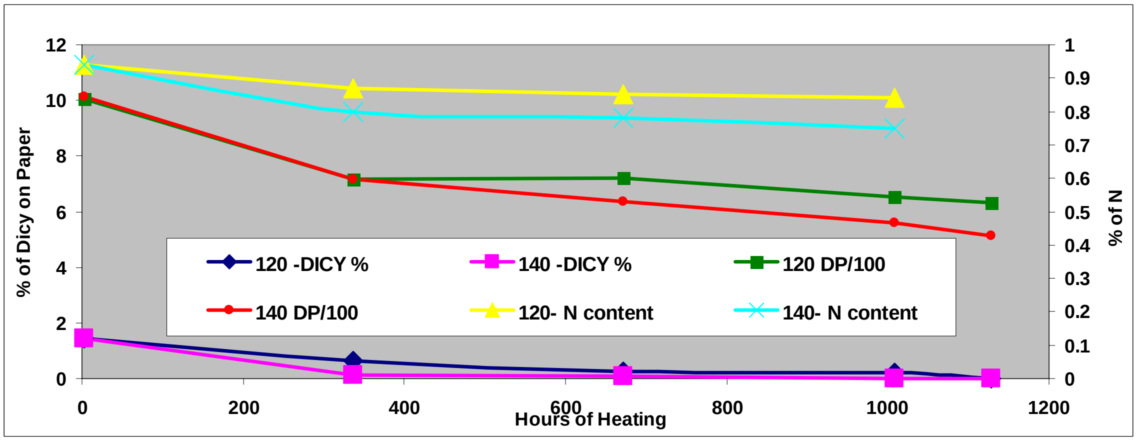


Figure 4-6
Effect of Aging of Insulating Paper at Different Temperatures on all Measured Parameters

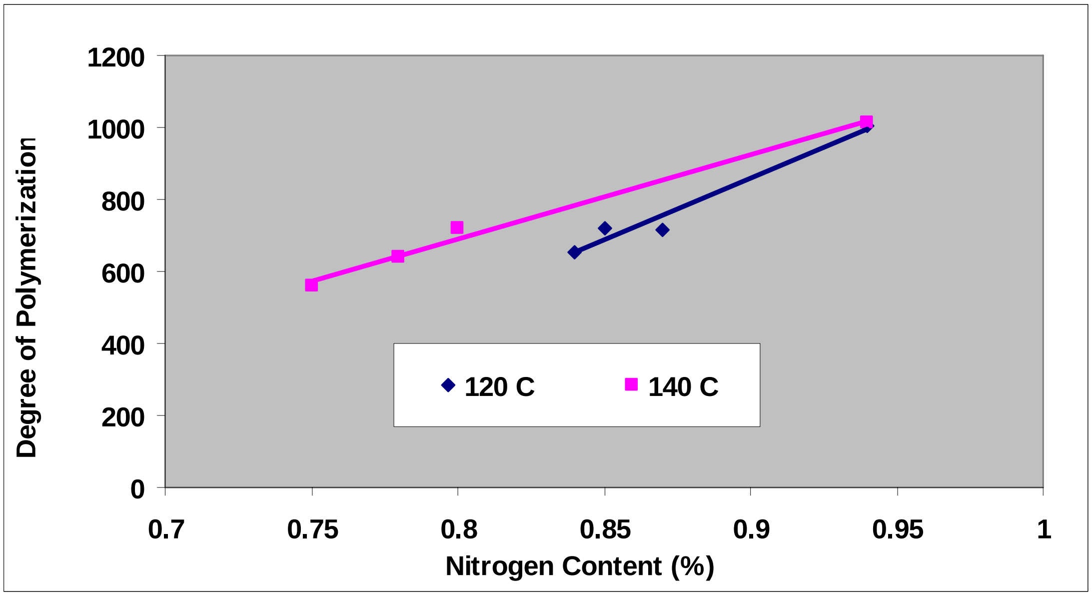


Figure 4-7
Relationship between Degree of Polymerization and Nitrogen Content.

Life Expectancy of Dicyandiamide

The life expectancy of Dicyandiamide on insulating TUP is summarized in Table 4-5. It shows that water increases the rate of decomposition of DICY and that dry paper has a longer life expectancy than wet paper. For power transformers operating at 90°C or lower and kept dry, it will take one year for the DICY content in the paper to be depleted, but only 6 months if the system is wet. If the power transformer operates at a higher temperature, the DICY in the insulating paper will be depleted between 1-6 months.

Table 4-5
Life Expectancy of DICY

Temperature	Water in Paper	Time for Dicy content in Paper to Fall to <0.5%
Above 110°C	Wet Paper	<1 month
90°C	Wet Paper	6 months
Above 120°C	Dry Paper	< 1 month
120°C	Dry Paper	2 months
110°C	Dry Paper	3 months
90°C	Dry Paper	1 year

Nitrogen Content of Paper

As shown in Figure 4-6, the decrease in the nitrogen content on the paper is not that drastic compared to the decrease in the DICY content. It was observed that even though DICY is completely depleted from the paper, there was an average of 1 % of nitrogen content on the paper and the only source of the nitrogen is from the degradation of DICY. From literature, DICY is known to break down at a quite moderate temperature of 80°C. Hence, the nitrogen content on the paper can be associated with the DICY being hydrothermally decomposed to other nitrogen containing compounds that have either adsorbed onto the surface or have chemically reacted with the active sites on the paper after the decomposition of DICY.

Previous research has shown that DICY decomposes hydrothermally to give nitrogen containing compounds such as ammonia, guanylurea, guanidine, urea and melamine. Ammonia, melamine and guanidine have been observed from dimethyl disulphoxide extract of the paper using Gas-Chromatography-Mass Spectroscopy. The nitrogenous compounds formed give some stability to the paper. As shown in Figure 4-6 above, with the leveling of the total nitrogen content coming from guanidine and melamine, no drastic change in the DP_v is observed.

Ammonia as an Indicator of DICY Decomposition

As shown above, the lifetime of the additive dicyandiamide on TUP ranges from 6 months to 1 year depending on the operating conditions of the transformers. As demonstrated in Phase 1 of this project, the presence of dicyandiamide as additive on the insulating paper alters the type and the amount of paper degradation products formed especially furanic compounds. Hence it is important to identify nitrogen containing marker compounds that are soluble in oil and can act as an indicator to estimate the level of DICY remaining on the paper. From the list of nitrogen compounds formed from the decomposition of DICY, ammonia was selected as a potential candidate since it was more soluble in the oil than other nitrogen containing compounds.

The concentration of ammonia dissolved in oil from thermal decomposition of DICY in Thermally Upgraded paper in each tin container was measured. This was determined from the headspace of the oil using GC-MS. Figure 4-8 shows that ammonia production with time of aging is linear up to complete depletion of DICY and remains constant afterwards.

A drastic drop is observed in the level of ammonia at the higher temperature of 140 °C and this is associated with a leak in the tin containers after being heated for a long lapse of time. Once

DICY is completely decomposed into other nitrogen containing compounds, the level of ammonia produced remains constant. This indicates that the nitrogen containing compounds produced on DICY decomposition do not decompose into ammonia in the presence of heat and moisture. A constant increase in the level of ammonia will be indicative of the presence of DICY. Upon the complete consumption of DICY the ammonia level stays consistent unless there is a leak or being consumed in other side reactions. Hence, ammonia can be used as a marker compound for the presence of DICY on the insulating paper. However, this relationship is followed in the absence of other influencing factors such as a leakage, oil change, and reclamation of oil. An increase of 20°C in temperature doubles the rate of production of ammonia as shown in Figure 4-8.

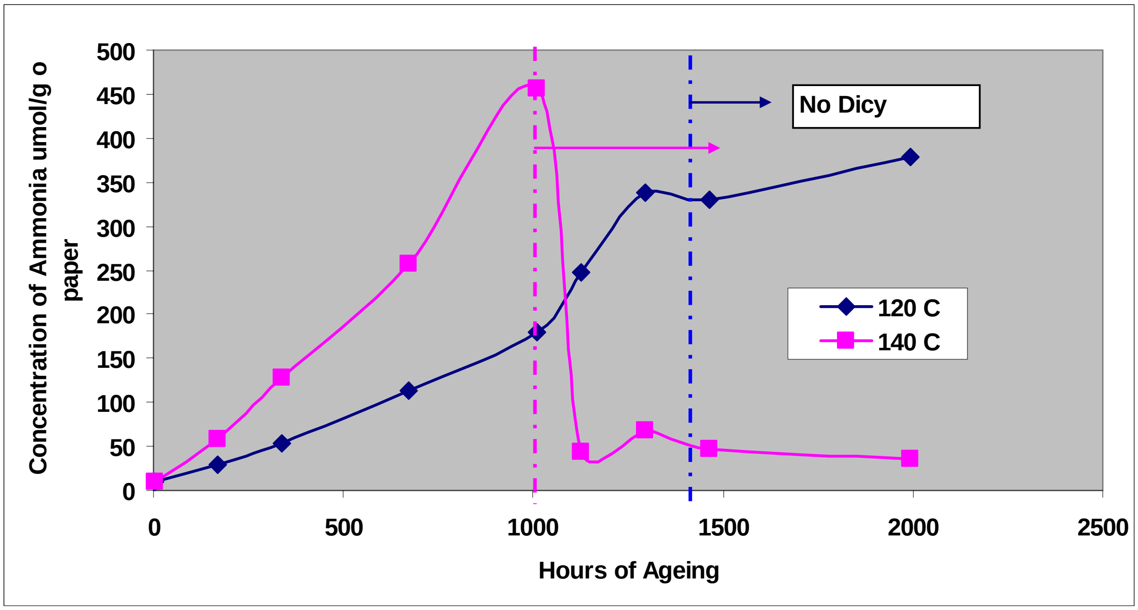


Figure 4-8
Amount of Ammonia Produced with Respect to Hours of Aging of Insulating Paper.

The amount of ammonia produced can be used as a non-intrusive marker compound to measure the level of DICY present on the insulating paper and the degree of polymerization of insulating paper. Figure 4-9 shows a logarithmic relationship (Equation 4-1 and Equation 4-2) between the % of dicyandiamide remaining on insulating paper and the level (in µmol) of ammonia released per g of paper until complete depletion of dicyandiamide. There is no significant difference between these two equations suggesting that the amount of ammonia produced is independent of temperature; however, the rate of ammonia production is dependent on temperature. After the depletion of dicyandiamide, the level of ammonia remains constant in the oil unless there is a leak leading to a drop in the level of ammonia.

$$\% \text{ of DICY remaining} = -0.9782 \text{ Lg [Ammonia]} + 2.3392$$

Equation 4-1
Relationship between % of DICY and Concentration of Ammonia at 120 °C.

$$\% \text{ of DICY remaining} = -0.0.8417 \text{ Lg [Ammonia]} + 2.0496$$

Equation 4-2
Relationship between % of DICY and Concentration of Ammonia at 140°C.

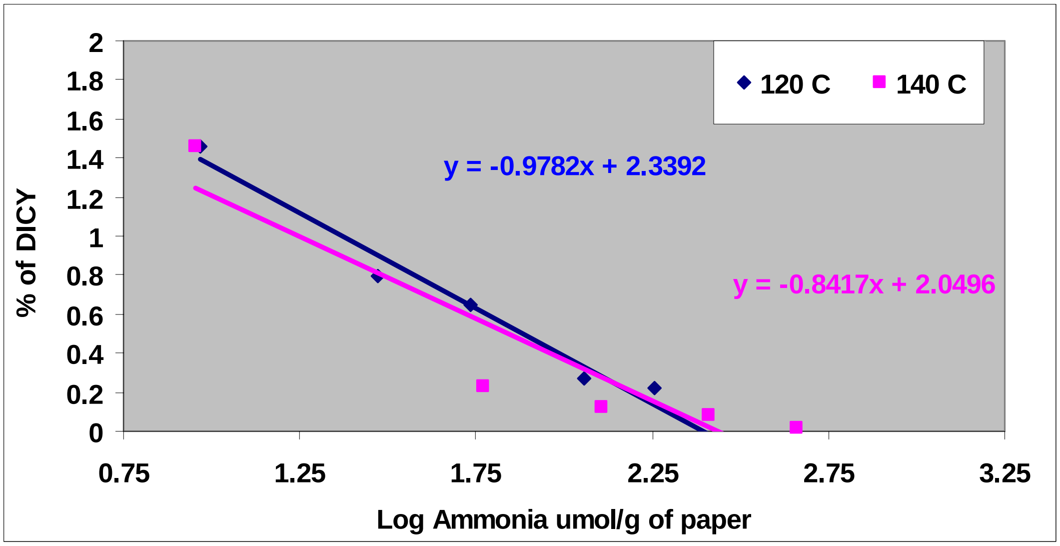


Figure 4-9
Relationship between Concentrations of Ammonia and % of DICY Left on TUP.

A logarithmic relationship was also identified between the degree of polymerization and the concentration of ammonia independent of the temperature as shown in Figure 4-10 below. Hence, if the concentration of ammonia in μmol per gram of paper is known the average degree of polymerization of the insulating paper can be calculated using the logarithmic Equation 4-3 and Equation 4-4 without having to de-energize the transformer to take a paper sample for DP_v measurement. Again, these two equations are not significantly different indicating the independence of this relationship on temperature.

$$DP_v = -246.12 \text{ Lg [Ammonia]} + 1199.3$$

Equation 4-3
Relationship between Concentration of Ammonia and Degree of Polymerization at 120°C.

$$DP_{v\,=} -257.25 \text{ Lg [Ammonia]} + 1225.9$$

Equation 4-4
Relationship between Concentration of Ammonia and Degree of Polymerization at 140°C.

However, this method is reliable only if the oil is tested for ammonia on a regular basis thus eliminating false result due to leaks of ammonia. Once the level of ammonia remains constant, indicating that complete depleting of dicyandiamide, or there is a drop due to leakage, this logarithmic relationship between concentration of ammonia and DP_v is no more applicable and reliable.

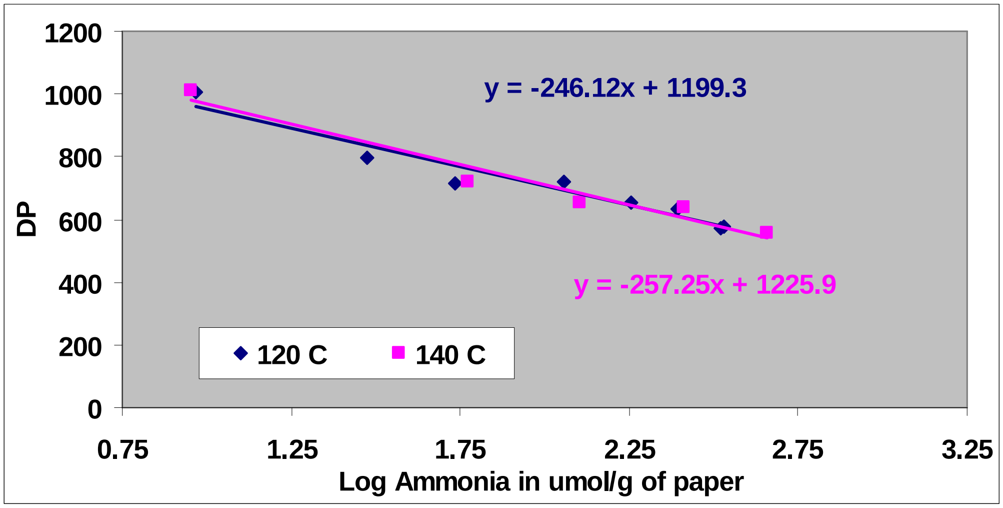


Figure 4-10
Relationship between Concentration of Ammonia and Degree of Polymerization of Insulating Paper.

Other Nitrogen Containing Marker Compounds

As discussed earlier, pyrrole and methyl pyrazines might prove to be useful as potential markers for the decomposition of TUP. Pyrrole and methyl pyrazines are not obtained by the sole decomposition of DICY but by the combination of decomposition of insulating paper and DICY or DICY degradation products. To be useful as a marker, a compound should be chemically stable, it should be soluble in the insulating oil and it should remain in the oil for extended periods of time. A set of experiments were undertaken to evaluate the suitability of pyrrole and methyl pyrazine as indicators of degradation of TUP.

Volatility and Stability of Pyrrole and Methyl Pyrazine

To determine the volatility and stability of pyrrole and methyl pyrazine, laboratory experiments were carried out with 125 mL paint cans containing oil and paper heated in an oven for ten days at two different temperatures, 70 and 140°C. Some of the cans were vented with a small puncture in the lid while others were sealed. Oil samples were analyzed by headspace GC-MS to determine the residual concentrations of the two marker compounds.

As shown in Table 4-6 at 140°C, 89 % of the pyrrole in the vented container is lost with only 11 % of it remaining in the oil, whereas for methyl pyrazine 70 % of it remains in the oil. At 70 °C, not much of the pyrrole and the methyl pyrazines are lost with 80 and 90 % remaining in the oil respectively. Hence it is shown here that most of the pyrrole is lost at high temperature either by decomposition to other nitrogen compounds or just by venting. Hence this shows that pyrrole is not a stable enough compound to be used as a quantitative marker for the degradation of Thermally Upgraded Paper as it suffers from thermal instability as well as having too high volatility. However, its presence indicates that there is a hot spot currently occurring.

Methyl pyrazine on the other hand did not degrade or get lost at the higher temperatures and warrants further investigation as a marker compound for monitoring the degradation of TUP.

Table 4-6
Comparison of Retention of Volatile Compounds in Sealed versus Vented Containers

	Pyrrole	Methyl Pyrazine
140 °C sealed tin container	680, 000	1,250,000
140 °C vented tin container	75,000	880,000
% remaining in oil	**11**	**70**
70°C sealed tin container	1,840,000	1,120,000
70°C vented tin container	1,480,000	1,040,000
% remaining in oil	**80**	**93**

Analysis of Pyrrole and Methyl Pyrazine

A number of laboratory techniques were used to try and quantify the levels of these compounds in oil. These techniques include GC-MS. and HPLC. Headspace analysis and methanol extraction techniques were also evaluated. Most of the analyses performed in this report were headspace analysis using GC-MS. As shown in Figure 4-3, we can see that in general, higher temperatures and longer times generate more pyrrole and methyl pyrazine. However, this is not always true since presumably some of the pyrrole and methyl pyrazines are lost with time.

We have also carried out the analysis of pyrrole and methyl pyrazines on routine oil samples from in-service transformers containing Thermally Upgraded Paper. To date we have not detected any significant amounts of these products. This may be due to several reasons namely due to:

- Low operating temperatures of the transformers in question
- Loss of pyrrole and pyrazines due to leakage
- Complete depletion of DICY. The level of pyrrole and pyrazine produced are dependent on the amount of DICY present since the DICY or DICY decomposition products react with the paper decomposition products to make the pyrrole and methyl pyrazine. On complete depletion of the DICY the level of pyrrole and pyrazines decreases due to leakage or reaction with other by-products. This is shown later on in Chapter 5.

5

MARKER COMPOUNDS FROM CELLULOSE

In the previous section we identified several potential marker nitrogen containing compounds specific to thermally upgraded paper. Although these compounds could be correlated to the extent of degradation of thermally upgraded paper and its DP_v, they originated from the DICY additive rather that the paper itself. Their correlation to the condition of paper is indirect and may be misleading because of existing conditions that effect DICY but not the paper. Work carried out in this section was intended to investigate the presence of paper degradation products in oil as potential marker compound(s) specific to the rupture of the cellulosic bond independent of the type of insulation paper (Kraft or Thermally Upgraded Paper) used. In this way, the amount of the marker compound in the oil will give an indication of the DP_v of the insulating paper and the remaining life of the transformer.

Experimental Set up

A test cell for the accelerated aging of paper in oil was designed and built suitable for the monitoring of decomposition products both in the oil and the headspace. The assembled cell is shown in Figure 5-1. The cell consisted of a glass chamber and a demountable aluminum top chamber. The top chamber was fitted with a sample port for the headspace, one for oil phase, and two others for venting and purging. It was also fitted with electrical feedthroughs and thermocouple sensors. A magnetic stir bar was introduced in the aging cell for even heat distribution.

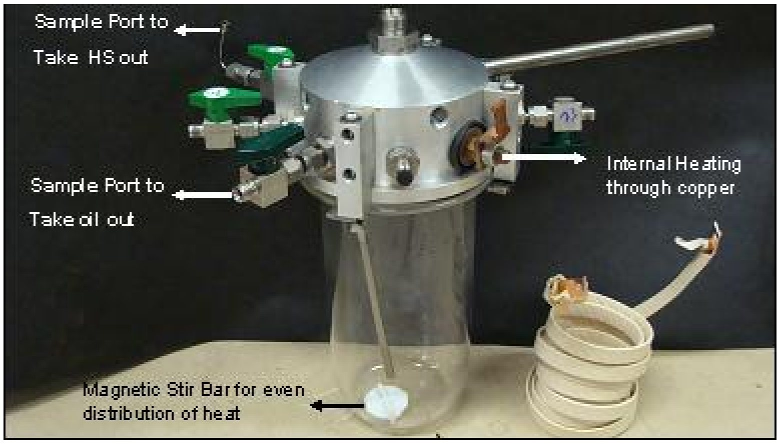


Figure 5-1
Paper Aging Test Cell with Internal Heating of Insulating Paper.

The insulating paper was heated internally through the coils and the temperature of the oil at the coil was recorded. Each test cell contained 2.5 m of copper wire wrapped with either regular Kraft paper or Thermally Upgraded paper to give 12.5 g of paper wrapped around the copper conductor. It also contained 850 mL of unused Voltesso 35 oil, making the ratio of oil to paper to be 60:1. Before starting the experiment, the paper was dried in the oven at 105°C for 1 hour. The oil was also dried and degassed prior to use. The aging cell was internally heated with the temperature at the coil maintained at 140°C and the temperature of the oil at 130°C. Three aging test were carried out, one with only new Voltesso oil as a control, one with Voltesso oil and Kraft paper around the copper windings and the last one with Voltesso oil and Thermally Upgraded paper at the windings.

Analysis of Marker Compounds

Samples of headspace gas and oil were removed periodically and analyzed for the presence of new compounds resulting from paper/oil degradation. Gas samples from the headspace were analyzed by direct injection into a gas chromatograph set up for DGA or in a gas chromatograph-mass spectrometer (GC-MS) unit. The oil samples (10g) were extracted with 1mL of methanol and analyzed for furanic and other non volatile marker compounds by High Performance Liquid Chromatography (HPLC) and GC-MS. Analysis for volatile marker compounds in oil was carried out by headspace analysis by GC-MS. This was done by heating 10 g of the oil to 120°C for 30 minutes and then allowing them to equilibrate before analyzing the headspace gas using GC-MS.

Results and Discussion:

Identification of Compounds with Potential Diagnostic Significance

A list of paper degradation by-products from paper in oil that accelerate aging experiments is detailed in Table 5-1. They were identified from headspace and oil extract analysis by comparing the mass spectrum recorded at the maximum of each peak with those from the NIST MS 2002 library. With the exception of ammonia, dimethyl disulfide and methane thiol, the early eluting peaks are associated with low-molecular weight volatile organic compounds. These molecules have already been reported in the pyrolysates of pure cellulose.[17, 18, 19] The proposed mechanism to account for their presence involves the formation by chain scission of carbonium ions that may decompose irreversibly to form unsaturated products containing aldehyde and enol groups.[20] These products may produce volatile carbonyl compounds as identified in Table 5-1 below. Higher molecular weight carbonyl compounds are also identified in the decomposition of paper including furanic compounds.

In order to eliminate products obtained from the decomposition of oil only as marker compounds for paper decomposition, the same experiment was carried out with Voltesso 35 oil in the test cell as a control. The compounds identified in the headspace and methanol extract of an oil sample from the control experiments are highlighted in red in Table 5-1. It is evident that oil oxidation can contribute to a certain extent to some of the detected paper degradation by-products. A peak showing 90 % match with 2-methyl-2-propanol was seen to be associated only with the aging of the oil. After examining the mass spectrum for co-elution and confirming the peak identity by injecting pure compounds, acetone, methanol, ammonia, pyrrole and methyl pyrazine were retained for further testing. The interference of the oil aging over the use of these molecules for estimating the paper damage was also evaluated.

Nitrogen containing compounds namely ammonia, pyrrole and methyl pyrazines have already been discussed in Chapter 4. Acetone and methanol were potentially better marker compounds since their production was independent of the type of paper that was used at the windings. As explained before, ammonia was obtained by the decomposition of DICY and pyrrole and methyl pyrazines on the hand was obtained by the decomposition of only Thermally Upgraded Paper.

Table 5-1
List of Key Compounds Identified from Paper Decomposition.

Compounds	Thermally Upgraded Paper	Kraft Paper
Acetyldehyde	×	×
Ammonia	×	
Dimethyl Disulfide	×	×
Methane thiol	×	×
Furan	×	×
2-Methyl-2-propanol	×	×
Acetone	×	×
Acetic Acid	×	×
Butanal	×	×
2-Butanone	×	×
Methanol	×	×
Ethanol	×	×
Water	×	×
1-Butanol	×	×
2,5-Dimethyl Furan	×	×
Formic acid	×	×
Propanoic acid	×	×
Pyrrole	×	
Methyl Pyrazine	×	
Dimethyl Pyrazine	×	
2-Furaldehyde	×	×
2-Furfurylalcohol	×	×
2,6-Di-tert-butyl-p-cresol	×	×
Other Furanic compounds	×	×

Stability of Potential Marker Compounds

The stability of the potential marker compounds with time was assessed at temperatures that could be found in open breathing transformers where the oil is in contact to the atmosphere through a conservator. This oxidative condition was achieved by filling the headspace (21 mL vials) with 9 mL of oil solutions containing potential marker compounds namely 3 ppm of methanol and 2.5 ppm of acetone.

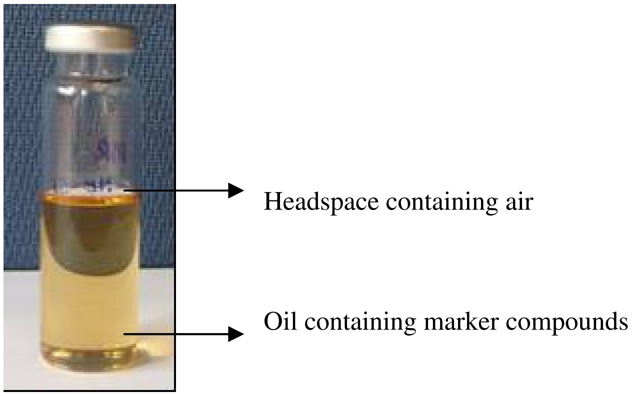


Figure 5-2
Set Up for Measuring Stability of Potential Marker Compounds.

The experiments were set up at four different temperatures for different aging time as shown in Table 5-2 below. The concentrations of methanol and acetone were measured by headspace analysis using GC-QUAD instrument. The results are shown in Figure 5-3. The results indicate that within experimental variability measured with duplicate cells, the concentration of methanol and acetone remained reasonably constant for over 1000 h test duration at 70 and 90°C heating. However, at higher temperatures (110°C), acetone increases rapidly after an induction period of about 400 h, showing an increase of 1.1 µg/kg of oil/h. At 120 °C, following an induction period of 200 it increases even more rapidly at a rate of 5.12 µg/kg of oil/h. On the other hand methanol shows a slight decrease with increasing temperature.

Table 5-2
Experimental Set-Up for Measuring the Stability of Potential Marker Compounds

Hours of Heating	Temperature °C			
	70	90	110	120
3	☒	☒	☒	☒
168	☒	☒	☒	☒
336	☒	☒	☒	☒
672	☒	☒	☒	☒
1008	☒	☒	☒	☒

From tests carried out with blank oil samples, it can be deduced that the appearance of acetone could essentially be attributed to the oxidation of oil components. Indeed the increase in rate of 1.1µg/kg of oil/h and 5.12µg/kg of oil/h measured at 110°C and 120°C respectively, accounts for the values noted in the solution. Hence, at high temperatures, oil oxidation contributes significantly to the generation of acetone, making this compound unsuitable as a marker compound for the decomposition of paper.

On the other hand, a measurable decrease in the concentration of methanol is observed at 120 °C for longer hours as shown in Figure 5-3. This decrease may be attributed to leaks through the vial septum or a reduction in the gas-oil partitioning coefficient of methanol with temperature. Hence appropriate gas partitioning should be used in order to correct for this loss in concentration of polar compounds such as methanol.

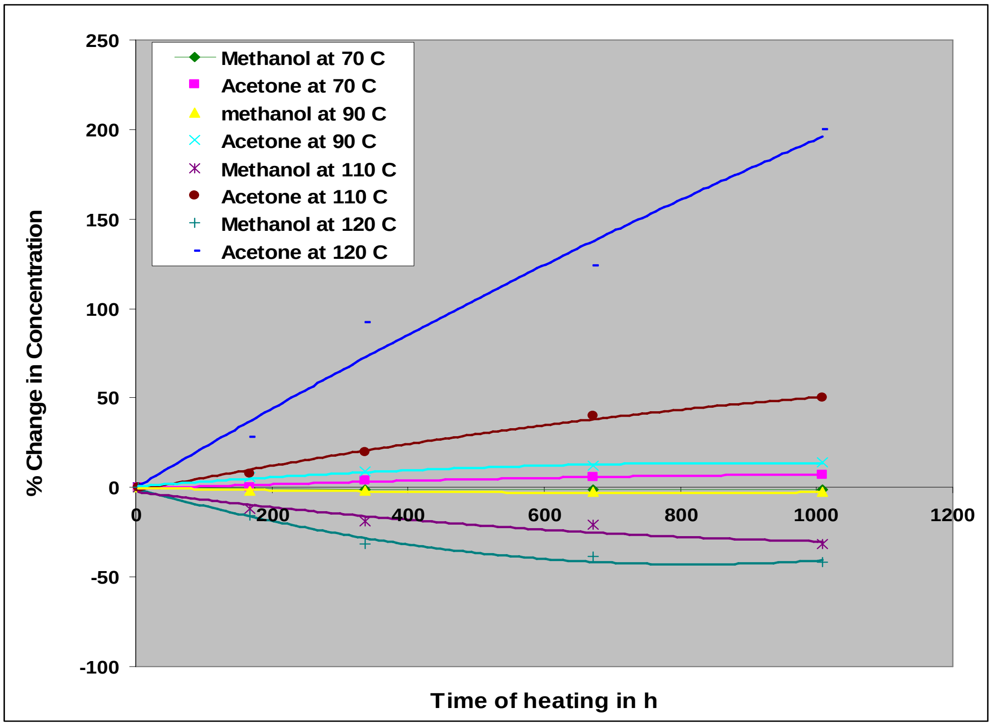


Figure 5-3
Stability of Potential Marker Compounds with Time at Different Temperatures

Origin of Methanol

It is essential to verify that methanol as a potential marker is being generated by the decomposition of ∝-cellulose rather than the secondary paper constituents. A study performed previously[21] suggests that methanol is mainly produced from ∝-cellulose and more specifically from the rupture of the 1,4-glycosidic bonds. Through this study it was shown that at least one molecule of methanol is generated each time a 1,4-glycosidic bond is ruptured, independent of the type of paper being used. This was contrary to what was obtained when 2-furaldehyde was used as a marker compound since very low amount of 2-furaldehyde are detected in transformers with Thermally Upgraded Paper. One possible explanation for the low levels of 2-furaldehyde in oil has been reported as the reaction of 2-furaldehyde with dicyandiamide, the additive used in Thermally Upgraded Paper to form other compounds.

Rate of Formation of Methanol and Acetone

The same experimental set up and analytical methods described on page 4-3 were used to identify the rate of formation of methanol and acetone

Results and Discussions

The amount of potential marker compounds obtained from accelerated aging experiments at 120 and 140 °C are summarized in Table 5-3 and Table 5-4. Typical results of the change in degree of polymerization (expressed in terms of $(1/DP_t-1/DP_0) * 1000$, where DP_t is the degree of polymerization at time t and DP_0 is the initial degree of polymerization) for the two different temperatures as a function of time is shown in Figure 5-4.

Table 5-3
Amount of Marker Compounds Produced When TUP Is Heated at 120°C.

Hours of Heating	Dicy (%)	Dp_v	Water (ppm)	Acetone (ppm)	Methanol (ppm)	Ammonia (ppm)	Pyrrole (ppm)
3	1.46	1006	3	0	0.08	1.79	0
168	0.80	789	5	0.08	1.62	5.71	0.91
336	0.64	715	8	1.07	2.19	10.42	1.43
672	0.27	695	11	2.72	2.67	21.80	2.06
1008	0.22	655	17	2.57	3.91	34.67	2.39
1128	0	632	41	3.43	4.23	47.68	3.28
1296	0	576	42	3.12	5.02	65.04	1.94
1464	0	553	32	1.93	4.15	63.52	2.77

Table 5-4
Amount of Marker Compounds Produced When TUP Is Heated at 140°C.

Hours of Heating	Dicy %	Dp	Water (ppm)	Acetone (ppm)	Methanol (ppm)	Ammonia (ppm)	Pyrrole (ppm)
3	1.46	1012	2	0.04	0.22	1.17	0.28
168	0.23	718	8	2.16	2.56	11.34	1.40
336	0.12	656	10	2.68	3.63	24.53	2.73
672	0.09	638	11	3.63	4.57	49.55	4.03
1008	0.02	558	24	4.91	5.77	87.79	5.41
1128	0	512	55	4.22	7.46	8.25	6.85
1296	0	430	45	3.15	8.20	13.19	6.59
1464	0	411	55	3.64	9.97	8.99	3.57

A fairly good linearity[22] is observed between the two isotherms as shown in Figure 5-4 which appears to be a result of the scission of the 1,4-β-glycosidic bonds of the cellulose. A slight deviation from linearity is also observed at the beginning (Figure 5-4, right) and can be associated to the "weak bonds" that could be natural in origin to the cellulose as detailed by other authors.[23, 24, 25] With respect to time the pseudo- first order reaction moves to a higher order suggesting that the rupture of the “weak bonds” is now extended over more ordered domains. However, in general this relation shows a good linearity over the two different temperatures, confirming that the overall degradation process is dominated by a given mechanism. Most importantly, the rate at which DP_v decreases does not change after the depleting on DICY suggesting that the other nitrogenous compounds formed due to thermal decomposition of DICY provides similar or some sort of stability to the paper.

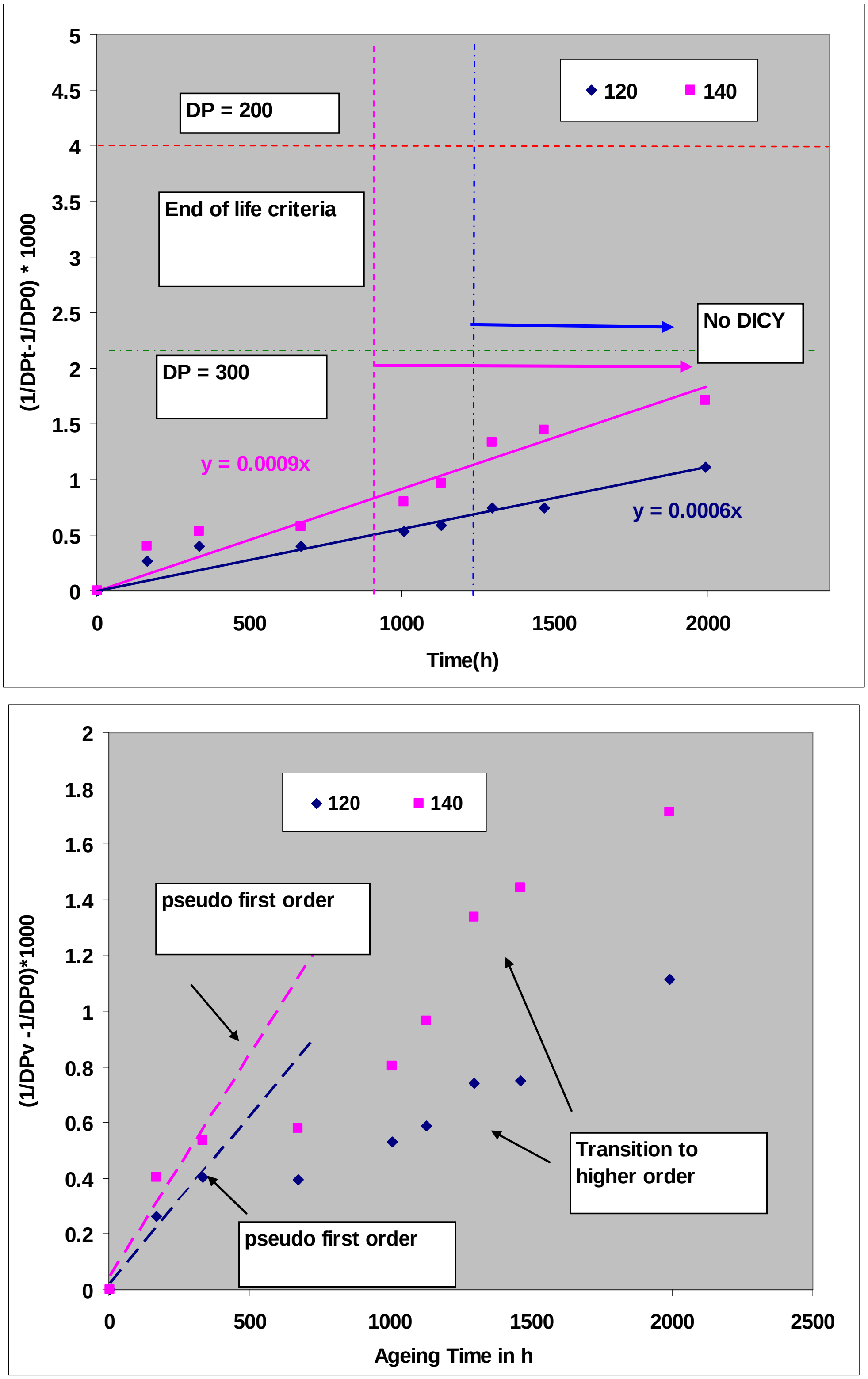


Figure 5-4
Relationship between Degree of Polymerization and Time of Aging.

Acetone and Methanol as Marker Compounds

Both acetone and methanol were identified as potential marker compounds during the experiments. However, acetone cannot be used as a marker compound since the rate of production of acetone is not reliable. As shown in Figure 5-5 as a drop in concentration can be observed due to either reaction of acetone with other polar compounds present or leakage. The other reason why acetone cannot be used as a marker compound is because it is produced by the thermal decomposition of both paper and oil.

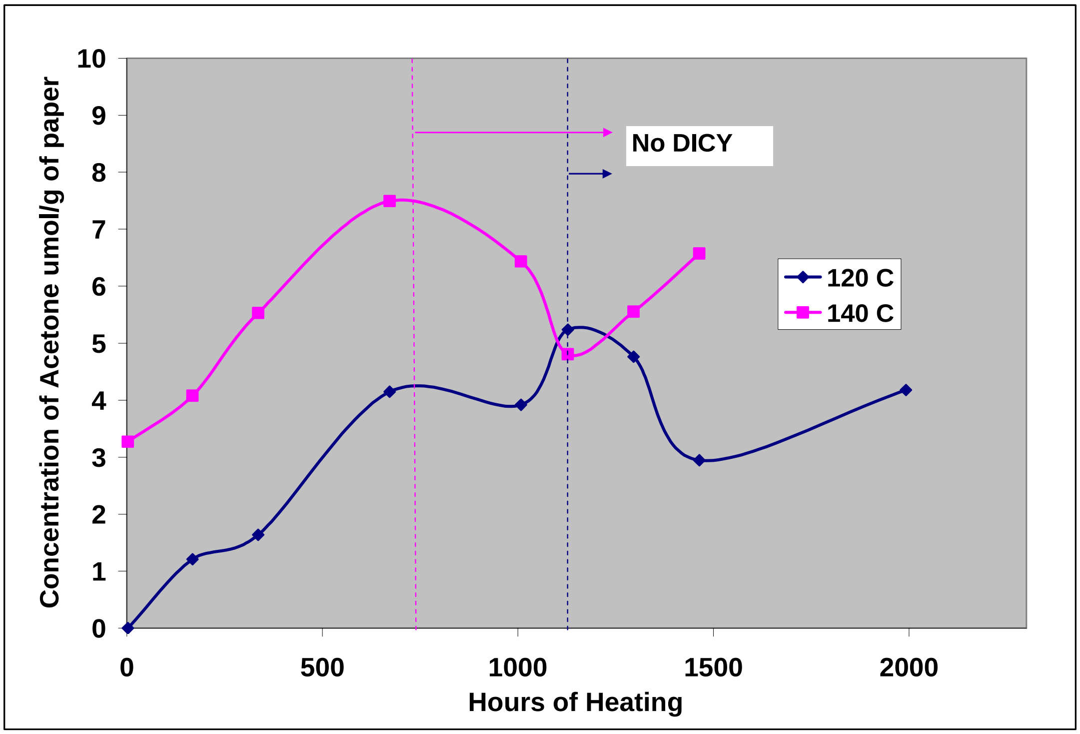


Figure 5-5
Rate of Acetone Production.

Typical examples of methanol production at two temperatures with time for the two paper/oil systems are illustrated in Figure 5-6. A linear relationship exists for the concentration of methanol produced with time even after the complete depletion of dicyandiamide. There is a leveling of concentration with time, as illustrated in Figure 5-6 (right), suggesting that the reaction is shifting to a higher order. Equation 5-1 and Equation 5-2 describe the relationship between the concentration of methanol (in µmol per g of insulating paper) and the degree of polymerization. It shows it to be independent of the temperature and there is no great deviation from linearity even after complete depletion of DICY as shown in Figure 5-7 (left). It was also observed that the rate of production of methanol doubles with an increase of 20°C in temperature. The same relationship was also measured for acetone.

$$DP_v = -27.2\ [\text{Methanol}] + 944.35$$

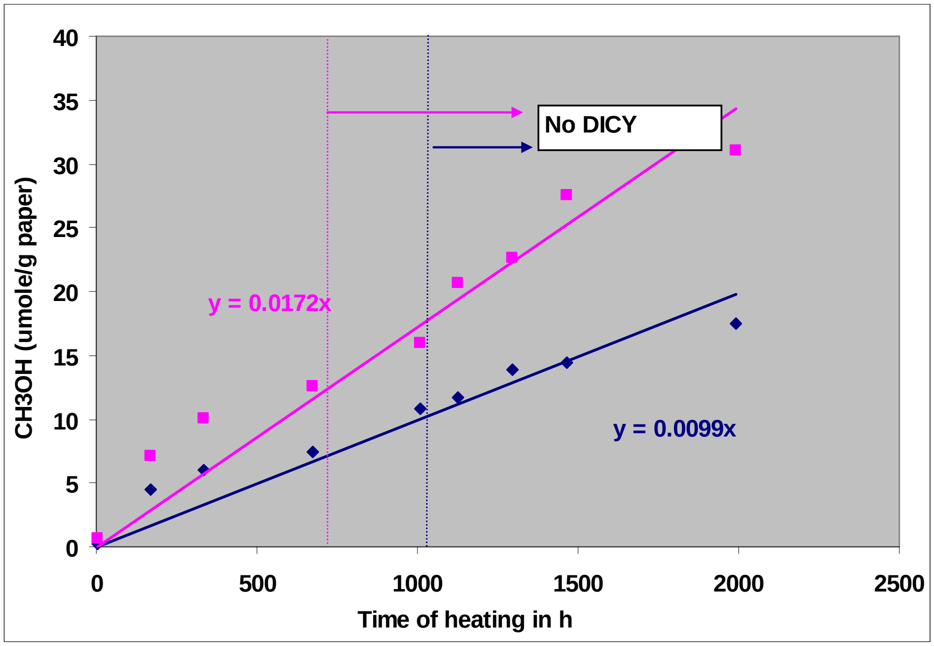
Equation 5-1
Relationship between DP_v and Concentration of Methanol at 120 °C.

$$DP_v = -19.04\ [\text{Methanol}] + 902.23$$

Equation 5-2
Relationship between DP_v and Concentration of Methanol at 140 °C.

As in the case of scissions as shown in Figure 5-7, some deviations from the linearity are noticeable; however, the overall relationship shows good linearity over the two temperatures. It is interesting to note that methanol production is virtually linear with number of scissions regardless of the depletion of DICY as shown in Figure 5-7. The slope of the linear relations for the TUP to the number of scissions is also independent of temperature. The results compiled for Figure 5-7 were used to calculate the number of scissions per β-D-glucopyranose unit as well as the ratio of [Methanol]/[Scissions] and is tabulated in **Error! Reference source not found.**.

For the test results done here, the statistical production of up to 2 molecules of methanol for every scission were attributed. This differs from what is reported by Jalbert et. al,[21] which showed a ratio of 1:1 for methanol molecule for number of scissions as detailed in **Error! Reference source not found.** (Appendix Section).



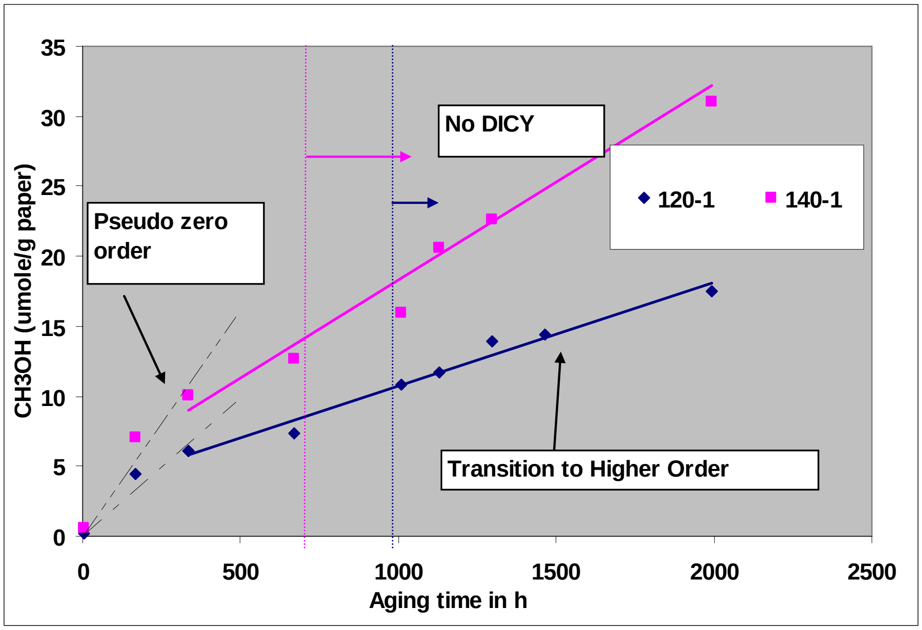


Figure 5-6
Typical Examples of the Increase of the Methanol Concentration in Oil with Time

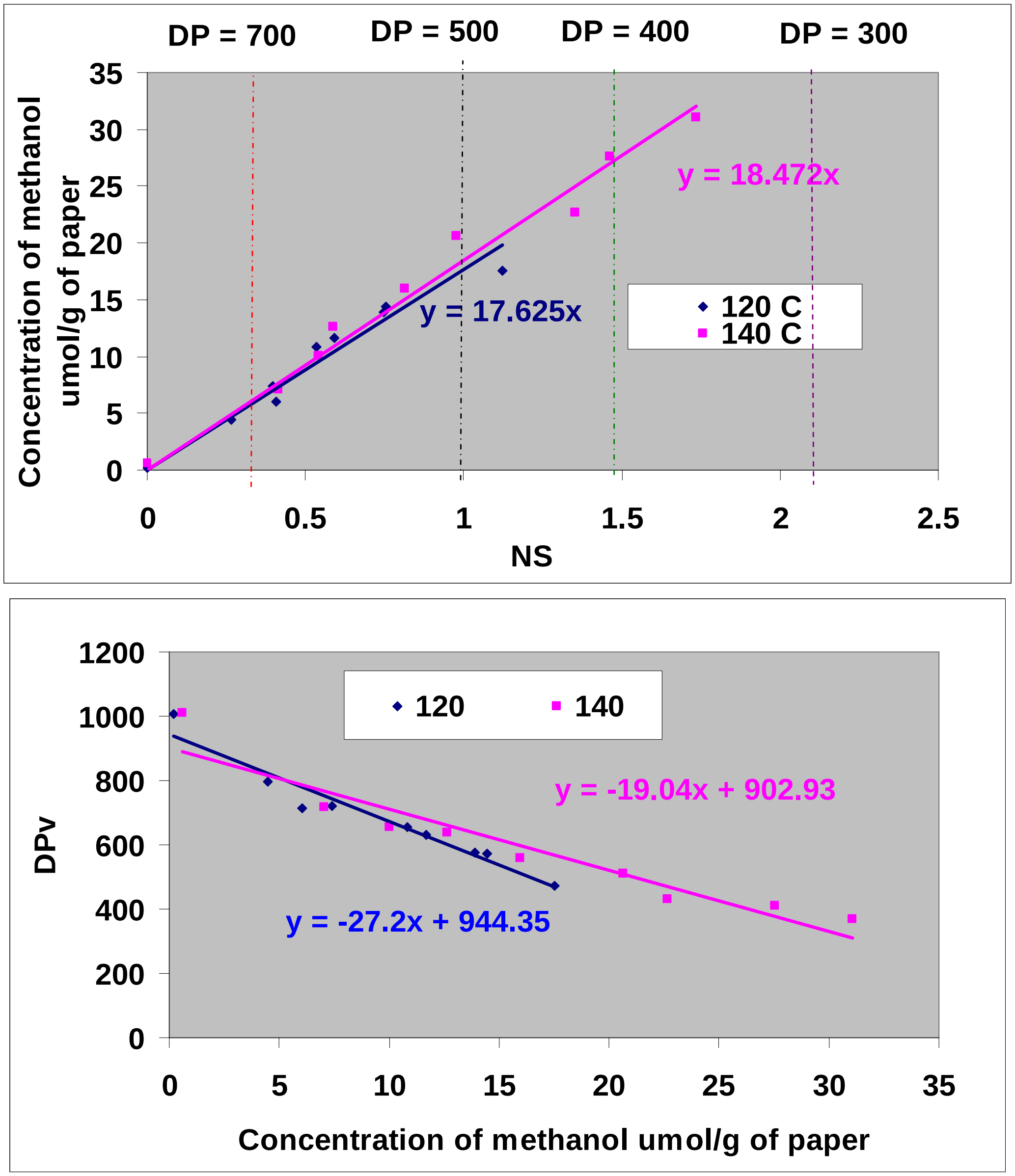


Figure 5-7
Relationship between DP_v, Concentration of Methanol and Number of Chain Scission.

6

ON-LINE MONITORING OF MARKER COMPOUNDS - PRELIMINARY STUDIES

The long term goal is to develop a unit for on-line monitoring of key marker compounds from paper degradation. Work in this section was undertaken to develop the analytical and monitoring methods that will

- Show proof of concept
- Accurately monitor the level of marker compounds identified in both oil and headspace
- Allow the online identification of the types of compounds in the oil that are precursors to the paper degradation.

Experimental Set-up

The on-line monitoring unit consisted of:

- a test vessel for controlled accelerated aging of oil and paper,
- a gas separating unit to isolate marker compounds from the oil and
- an analysis unit for measuring the concentrations of the marker compounds.

The test vessel consisted of a stainless container of 1.8 L capacity fitted with aluminum top and sealed with a Viton O-ring. The unassembled components are shown in Figure 6-1 and the assembled unit is shown in Scheme 6-1. The aluminum top was fitted with inlet and outlet ports and valves for oil sampling, and thermocouples to measure the temperature of the oil.

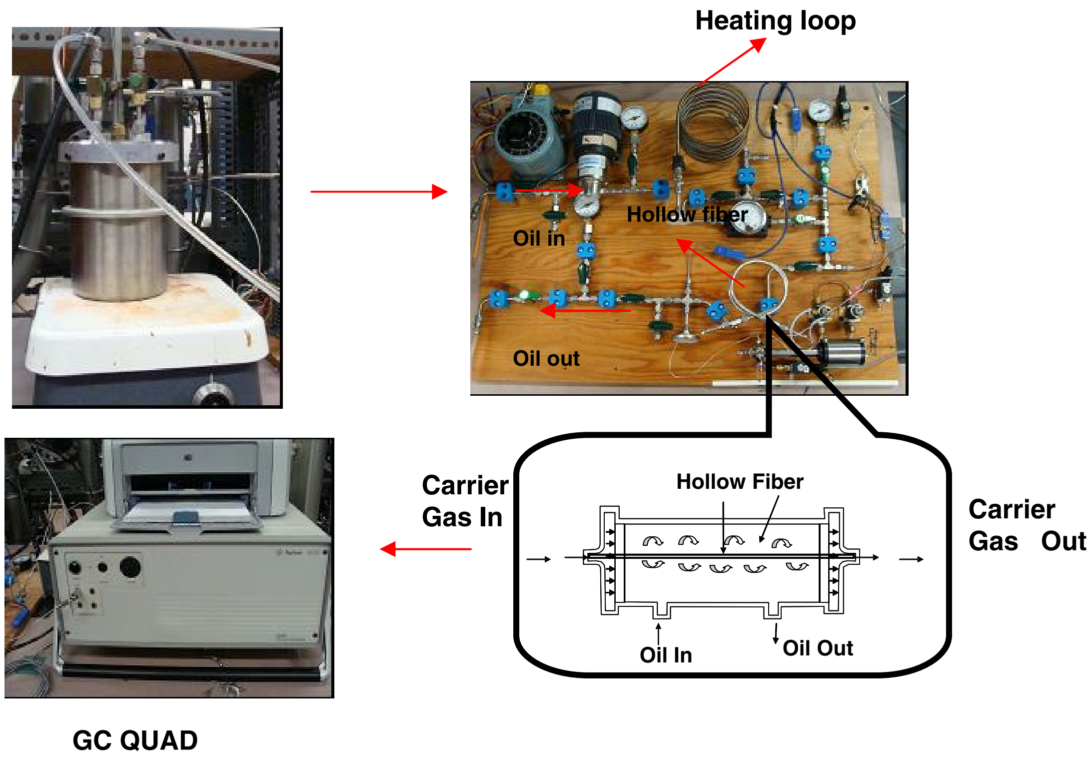
The test vessel contained 870 g of unused Voltesso 35 oil (approximately 1.0 L) and thermally upgraded paper wrapped around copper conductor in 14 turns of 2 layers wrapped around a 3.5 inch diameter block. A total of 21 g of thermally upgraded paper was present in the test vessel, giving a ratio of 1:40 of paper to oil.

A pump was used to circulate oil continuously from the test vessel through the on-line set up for gas extraction as shown in Scheme 6-1. The oil flowed from the test vessel through a heating loop maintained at constant temperature. A thermocouple attached at the end of the heating loop continuously recorded the temperature of the oil. The oil then flowed through a gas extraction loop that contained a gas permeable hollow fiber as detailed in Scheme 6-1. The oil flow rate through the gas extraction loop was adjusted to allow equilibration of the volatile compounds from the liquid oil phase to the vapor phase. The volatile compounds permeating through the hollow fiber were transferred using inert gas to the injection port of a micro gas chromatograph with four channels (GC-QUAD) to measure the level of marker compounds produced. The temperature at the hollow fiber was also recorded using a thermocouple. This temperature is important to correct for the partition coefficient needed to calculate concentrations of marker compounds in the oil.

Figure 6-1
Stainless Steel Vessel Used to Age Insulating Paper.

Test Procedure

The paper wrapped conductor was dried by placing it in the open vessel and heating at 70 °C overnight followed by heating at 105°C for 20 minutes. Unused Voltesso 35 oil was vacuum degassed then dried and transferred to the test vessel. The test vessel was sealed and heated at 100 °C then allowed to cool to room temperature thus allowing the moisture in the oil and paper to redistribute. The vessel was then purged with nitrogen for 10 minutes and sealed at 1 atmosphere. The initial sample of oil was collected and the moisture level of the oil was noted at 2.42 ppm.



Scheme 6-1
Unit for Online Monitoring of Marker Compounds from Insulating Paper Degradation.

In order to reduce heat loss, the test vessel was wrapped with glass wool, and then heated externally using a heating plate to 150°C for a total of 52 hours. There was a temperature gradient when the oil was heated externally. The average temperature at which the oil and the insulating paper were heated was 140°C. Once a total of 52 h of heating elapsed, the test cell was opened oil and paper samples removed and the degree of polymerization of the paper and the amount of DICY remaining on the paper were measured.

Partition Coefficients of Marker Compounds

Variation of transformer load with time induces the changes in the winding and the oil temperature. As the oil/headspace and paper/oil partition coefficients are dependent on temperature, thermal cycling leads to the migration of the fault compounds between the oil, paper and the headspace as the system approaches an equilibrium state. In order to understand the overall dynamics of the migration of marker compounds from the oil in the hollow fiber, it is necessary to investigate the migration between only two contacting phases (oil and the headspace of the hollow fiber).

To observe the dynamic partition between the oil and the hollow fiber with temperature, a standard oil solution containing the different marker compounds were passed through the online set up as shown in Scheme 6-1. The temperature of the oil was altered by heating at the loop and the partition coefficient of the marker compounds was calculated. When the oil was pumped out of the testing vessel through the gas extraction set up a drop in temperature of the oil was observed. The oil was heated at the heating loop to keep a constant temperature at the loop. The partition coefficients measured were used to calculate the concentration of the marker compounds present in oil.

A linear relationship was observed between the partition coefficients of the marker compounds and the temperature with an increase in partition coefficient with an increase in temperature as shown in Figure 6-2. These partition coefficients were used for the online determination of the marker compounds.

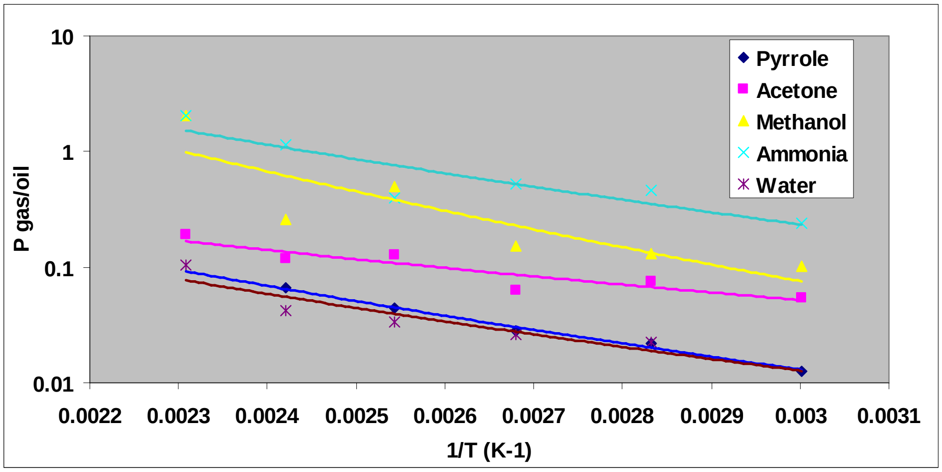


Figure 6-2
Partition Coefficients of Marker Compounds at Different Temperatures.

Results and Discussion

The marker compounds identified with the thermal decomposition of insulating paper and oil were methanol, acetone, ammonia and pyrrole. A linear increase in the amount of these marker compounds was observed with respect to time as shown in Figure 6-3. The rate of production of the marker compounds are different with ammonia being the highest followed by methanol, acetone and then pyrrole.

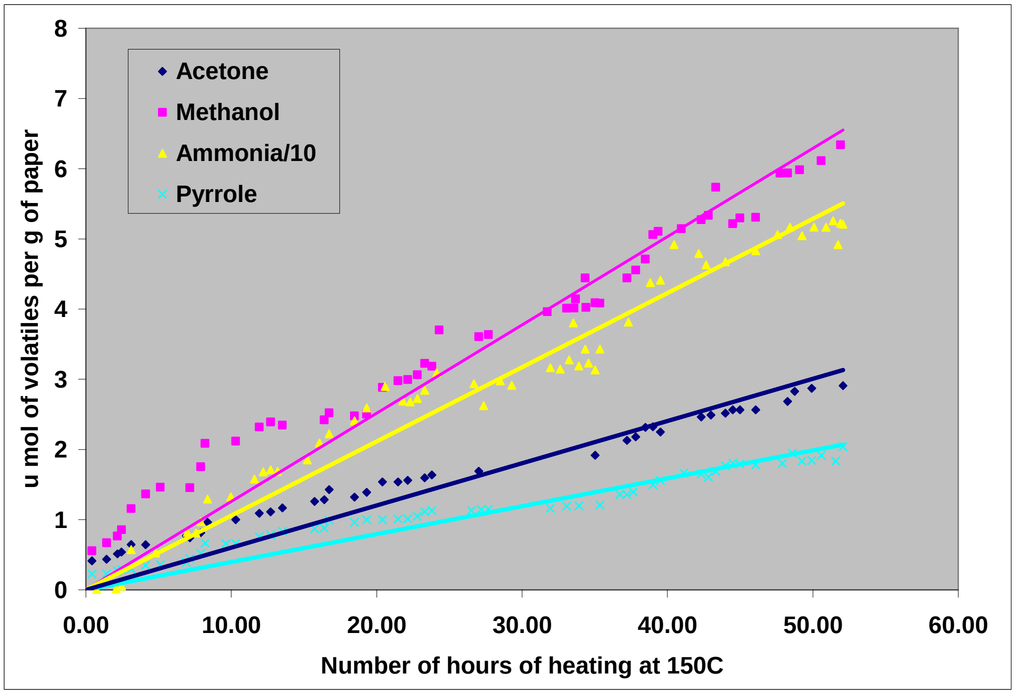


Figure 6-3
Linear Relationship between Concentration of Marker Compounds and Hours of Heating.

After 52 hours of heating, a sample of paper was taken out and the degree of polymerization of the paper and the % of DICY remaining on the paper were measured and compared to the values obtained using Equation 4-1 to Equation 5-2 as shown in Table 6-1. Better accuracy was observed when the concentration of methanol was used to calculate the degree of polymerization. An error of about ±1.5% was obtained with methanol compared to ±1.2-2.1 % with ammonia as the marker compound. However, it should be noted that after 52 h of heating at 140°C there is no complete depletion of DICY, so ammonia can also be used as an indicator to calculate the $DP_{v.}$ Using the concentration of ammonia, the % of DICY present on paper was also calculated and an error range of 1.2-1.6% was observed.

These results show that the equations derived during these experiments were reliable to calculate the degree of polymerization of paper using methanol or ammonia as marker compounds.

Table 6-1
Comparison Table of Observed and Calculated Degree of Polymerization and DICY Content.

Compounds	Conc. (umol/g of paper)	Equations	Temp. (°C)	Calculated Value	Measured Value	% Error
Methanol	6.34	DP = -27.2 [Methanol] + 944.35	140	DP = 772	DP = 768	0.5
	6.34	DP =-19.07 [Methanol] + 902.23	120 C	DP = 781	DP = 768	1.7
Ammonia	52.08	DP = -257.25 Lg [NH3] + 1225.9	140 C	DP = 784	DP = 768	2.1
	52.08	DP = -246.12 Lg [NH3] + 1199.3	120 C	DP = 777	DP = 768	1.2
	52.08	DICY = -0.8417 Lg [NH3] + 2.0496	140 C	DICY = 0.60	DICY = 0.61	1.6
	52.08	DICY = -0.9782 Lg [NH3] + 2.3392	120 C	DICY = 0.66	DICY = 0.61	7.6

7

CONCLUSIONS AND FUTURE WORK

Conclusions

Marker compounds form Dicyandiamide

Based on laboratory experiments to date, the following conclusions can be derived. Dicyandiamide decomposes at a temperature as low as 80 °C in the presence of oxygen and moisture to give nitrogen compounds such as ammonia, urea, guanidines and melams. Water increases the rate of decomposition of dicyandiamide and reduces its life expectancy. The residual level of DICY on thermally upgraded paper can be related to its DP_v; however, this is not practical as a sample of paper will be required. The decomposition products from DICY are also effective at providing thermal protection of the paper and a good correlation between total nitrogen content of paper and its DP was observed.

Ammonia

Among the nitrogen containing compounds, ammonia is soluble in oil and can be readily detected from the oil or headspace by gas chromatography. The production of ammonia from decomposition of DICY on paper increases linearly with time, until complete depletion of DICY and then remains constant. A logarithmic relationship was identified between the concentrations of ammonia and degree of polymerization of thermally upgraded paper before complete depletion of DICY. This relationship can be used to calculate the degree of polymerization of paper without having to de-energize the transformer to take paper sample.

A logarithmic relationship was also identified between the concentration of ammonia and the level of DICY on paper. This relationship can be used to identify the amount of DICY remaining on the paper. Commercially available sensors that can detect ammonia in the range of 0-100 ppm are available and have the potential for low cost on-line monitoring.

Other Nitrogen Compounds

Other nitrogen containing compounds such as pyrrole and methyl pyrazines were also identified; pyrrole was found to have high volatility and not ideal as a marker compounds for thermally upgraded paper. In addition, the level of pyrrole and methyl pyrazine was found to be dependent on the presence of DICY and ammonia. Once DICY is depleted, the level of pyrrole and methyl pyrazine remains constant if not decreases due to leaks or decomposition.

Marker Compounds from Cellulose

Marker compounds specific to the rupture of cellulosic bonds were identified and a relationship between the concentration of the marker compound and the degree of polymerization of the insulating paper was derived. The two key marker compounds identified were acetone and methanol. There is a linear dependence on the production of acetone with DICY content on the paper. However, acetone is also produced from insulating oil at moderate concentrations compared to insulating paper. Hence, acetone may be used as a screening compound for hot spots but not as a specific marker compound for paper decomposition.

Methanol was the other marker compound identified. It is obtained by sole decomposition of cellulose and a linear relationship was observed between the concentration of methanol and the degree of polymerization independent of temperature and dicyandiamide content. A linear relationship between the degree of polymerization and the concentration of methanol was also observed and can be used as a nonintrusive technique to estimate the DP_v of the paper.

On-Line Monitoring of Marker Compounds

A laboratory system was set up capable of on-line monitoring of the marker compounds from thermally upgraded paper. This was used to identify the key marker compounds and monitor their rate of formation during controlled accelerated oil/paper aging experiments. This set up was used to double check the accuracy of the equations derived and was used to calculate the remaining DP_v of insulating paper which resulted into a 2% error range.

Future Work

•*Phase 3: Development of On-line Monitoring*

Phase 3 of this work will include two main tasks namely

- The sensor acquisition and evaluation

  A state of the art review will be conducted to assess the current knowledge and developments in the field and to identify available and emerging sensors and monitoring techniques suitable for our application as needed. This will then be evaluated with the target compounds and typical operating conditions for selectivity, sensitivity and detection limits.

- Equipment design and simulations of faults.

  Laboratory equipment will be designed and build to represent fault conditions as encountered in transformers. For this purpose, existing equipments, model transformers test chamber and other equipments from previous work as shown in Figure 7-1 will be made available in conjunction with selected or adopted specific sensors. The goal is to determine the suitability of the sensors to detect and monitor the target fault products.

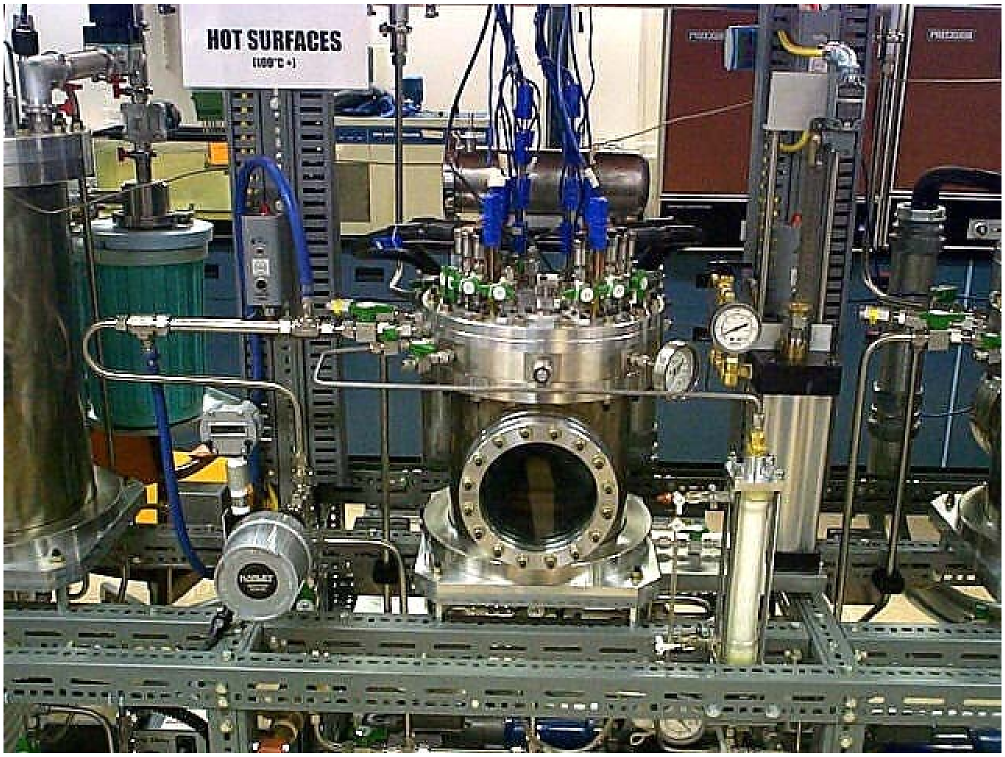


Figure 7-1
Model Transformer Test Chamber

- *Phase 4: Field Trials of On-line Monitoring*

This phase is dependent on the results obtained from phases 3. Once all those tasks have been successfully completed, a prototype-monitoring unit will be built to monitor the target fault product. The unit will be evaluated in the laboratory for performance. An attempt will be made to install the prototype-monitoring unit in the field on an in-service transformer. The tasks will include:

- Prototype Design and Evaluation

  This will consist of designing, building and lab evaluation of a prototype on-line monitoring system capable of monitoring the candidate marker compounds. It is anticipated that a membrane oil/gas-separating module will be used in conjunction with a specific sensor or detection system. The unit's performance will be evaluated for several parameters, including: response, specificity, detection limit, and interference from other products, ease of use potential for field applications.

- Field Trials

  Once the prototype unit has been evaluated in the lab, the unit will be installed on an in-service transformer at a selected location. The unit will be used to monitor the candidate marker compounds in the oil and relate their amounts and generation rate with the operating conditions of the transformer.

A
APPENDIX

Table A-1
Comparison between Methanol Production and Scissions for Paper Degradation.

Temp-hours of heating	DP	Number of chains initially	NS=(DPi/(Dpf-1)	Number of chains in the tin cans	Methanol (ppm) in oil	methanol in oil in ug	Scissions umol/g	[methanol] umol/g	methanol/scissions
120-3	1006	2.70855E-19	0	4.79961E+18	0.07467	8.58705	0	0.206419471	0
120-168	796	2.71E-19	0.264	4.79962E+18	1.61579	185.81585	3.23	4.466727163	1.380276264
120-336	715	2.71E-19	0.407	4.79962E+18	2.18832	251.6568	4.99	6.049442308	1.211744935
120-672	720	2.71E-19	0.397	4.79962E+18	2.67213	307.29495	4.872	7.386897837	1.516042502
120-1008	655	2.71E-19	0.536	4.79962E+18	3.91344	450.0456	6.573	10.81840385	1.645811884
120-1128	632	2.71E-19	0.592	4.79962E+18	4.22448	485.8152	7.259	11.67825	1.608814846
120-1296	576	2.71E-19	0.747	4.79962E+18	5.02272	577.6128	9.157	13.88492308	1.516283213
120-1464	574	2.71E-19	0.753	4.79962E+18	5.2236	600.714	9.232	14.44024038	1.564175177
120-1992	474	2.71E-19	1.122	4.79962E+18	6.3336	728.364	13.767	17.50875	1.271758568
140-3	1012	2.72E-19	0	4.77099E+18	0.22305	25.65075	0	0.616604567	0
140-168	718	2.72E-19	0.409	4.77099E+18	2.555935	293.932525	4.993	7.065685697	1.415131445
140-336	656	2.72E-19	0.543	4.77099E+18	3.631235	417.592025	6.617	10.03826983	1.516973729
140-672	638	2.72E-19	0.586	4.77099E+18	4.56528	525.0072	7.148	12.62036538	1.765575762
140-1008	558	2.72E-19	0.814	4.77099E+18	5.76839	663.36485	9.921	15.94627043	1.607321759
140-1128	512	2.72E-19	0.977	4.77099E+18	7.46084	857.9966	11.908	20.62491827	1.732038517
140-1296	430	2.72E-19	1.35	4.77099E+18	8.19559	942.49285	16.504	22.65607813	1.372762975
140-1464	411	2.72E-19	1.463	4.77099E+18	9.96902	1146.4373	17.831	27.55858894	1.54557356
140-1992	370	2.72E-19	1.735	4.77099E+18	11.2352	1292.048	21.158	31.05884615	1.467970629

B
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