Origin of Furanic Compounds in Thermal Degradation of Cellulosic Insulating Paper

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ABSTRACT: The chemical components of cellulosic insulation (i.e., Kraft paper, cellulose, lignin, pentosans) used in electrical transformers were aged in transformer oil to determine the relative yield of furanic degradation products. The results show that the pentosans component of the paper give, by far, the highest yield of 2-furfural followed by cellulose, levoglucosan, and lignin. However, the pentosans did not produce any detectable quantities of either 5-hydroxymethyl-2-furfuraldehyde or 2-furfurol, both of which are known to be produced by the degradation of Kraft paper. α-Cellulose was found to give 3 times as much 2-furfural as levoglucosan, which is a degradation product of cellulose, suggesting another pathway to 2-furfural production from cellulose than exclusively through the commonly quoted mechanism in which levoglucosan is the intermediate. It was also found that the production of 2-furfural from levoglucosan appears to be accelerated by acidic conditions in oxidized oil. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2541–2547, 1998

Key words: cellulosic insulation; electrical transformers; transformer oil; furanic degradation products

INTRODUCTION

It was proposed that the extent of chain scission of cellulosic winding insulation in electrical transformers can be determined by measuring the concentration of specific furanic degradation products in the transformer oil.[1–3] The state of degradation of the paper determines its mechanical properties and hence its ability to effectively act as an insulator. Because the paper insulation is normally not accessible, sampling of the oil provides a convenient means to assess the condition of the paper. Furanic compounds from the paper can be quantified in the oil by HPLC.[2,4] Figure 1 shows those furanic compounds that are detectable in transformer oil that has been in contact with degraded cellulosic insulation.

Despite much work over the last decade, the origin of these furanic compounds is still not clear. Although it is accepted that they arise exclusively from the degradation of paper insulation, their precise mechanism of formation has not been fully elucidated. For instance, it has been proposed that furans come from the pentosans (five-carbon sugars) component of Kraft paper usually used in transformers.[5] Furthermore, a substantial body of literature points to levoglucosan (1,6-anhydro-β-D-glucopyranose) (LG), which is a product of the thermal degradation of cellulose, as the precursor of furanic compounds in polysaccharide degradation.

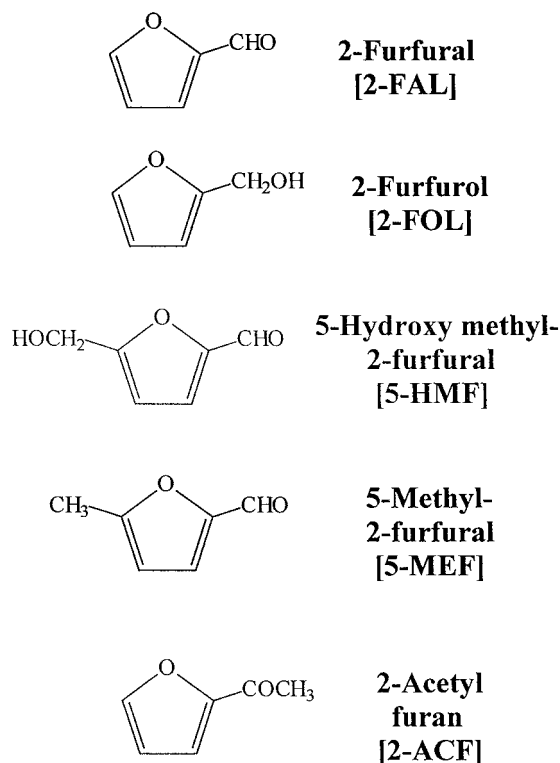It is generally recognized that the most im-

Figure 1 Furanic compounds detectable in transformer oil that has been in contact with aged cellulosic insulation.

portant step in the chain scission of cellulose is the heterolytic scission of the glycosidic linkage by intramolecular transglycolysation in a manner that is analogous to acid hydrolysis. This process results in the formation of two shorter cellulose chains, one with a short-lived resonance-stabilized glucosyl cation that gives rise, via intramolecular nucleophilic attack on O_6, to an LG end group[6,7] (see Fig. 2). Subsequently, LG formation proceeds through free chain ends; once the reaction chain is initiated, the whole chain may unzip.[7] LG can be produced at levels up to 60% at temperatures in the vicinity of 200°C. Because high concentrations of LG are possible in cellulose during heating at moderate temperatures, LG has been viewed as a major potential source of furanic compounds, for example, via the mechanism in Figure 3.[8] Furthermore, the glucosyl cation precursor to LG can also lead to furanic compounds such as 5-hydroxymethyl-2-furfuraldehyde (5-HMF) and 2-furfural (2-FAL) by the mechanism shown in Figure 4, which has been adapted from the work of Antal et al.[9]

More recently, however, a relationship has been established[1] between the rate of furan pro-

duction and the fractions of glycosidic bonds broken. This suggests that LG (which is formed by unzipping) is not involved in the main mechanism of furanic formation[10] in Kraft paper at relatively low temperatures that are typical of transformer operation between 60 and 150°C.

A factor that makes studying the production of furanic compounds from Kraft paper difficult is that Kraft winding paper is a multicomponent product. The Kraft pulping process employed to manufacture electrical winding insulation paper reduces the lignin and hemicellulose content of wood by approximately 80 and 90%, respectively. The resultant paper, however, still contains between 3 and 7% lignin and 2 and 4% hemicellulose. In addition to these residues are metallic cations along with an absorbed moisture content in the range of 2−4 wt %. The amount and type of hemicellulose may be an important factor in the production of furanic compounds from cellulosic paper. Beating processes in paper manufacture distribute the hemicellulose throughout the pulp. Because hemicellulose is 3−10 times less thermally stable than cellulose, it is conceivable that furans may originate initially from pentoses in the hemicellulose such as xylan.[11]

Another factor that complicates the investigation of the formation and mechanism of furanic compounds from cellulosic insulation is the influence of water. It has been known for some time that the hydrolytic degradation of cellulose can lead to the formation of furanic compounds, particularly 2-FAL. It has been observed in operating transformers that highest rates of furfural production occur when moisture in the transformer is allowed to accumulate.[5] This suggests that hydrolysis reactions are important for the production of furanics at low temperatures. Indeed, Nevell[12] identified 2-FAL, 5-HMF, and 5-methyl-2-furfural (5-MEF) as major products of the hydrolytic degradation of cellulose in the temperature range of 100−200°C. Although water clearly promotes furanic formation, the mechanism by which this occurs is unclear. A mechanism for hydrolytic formation of 5-HMF and 2-FAL from cellulose has been proposed by Shafizadeh and Lai[8] (see Fig. 5).

Although there are some studies on the mechanism of 2-FAL formation from glucose[13] and other sugars such as D-xylose, D-fructose, and xylose,[9] there are no publications in the scientific literature on the origin and mechanism of furfural formation from the thermal degradation of cellulose.

This work evaluates the formation of furanic compounds from the constituents of Kraft paper
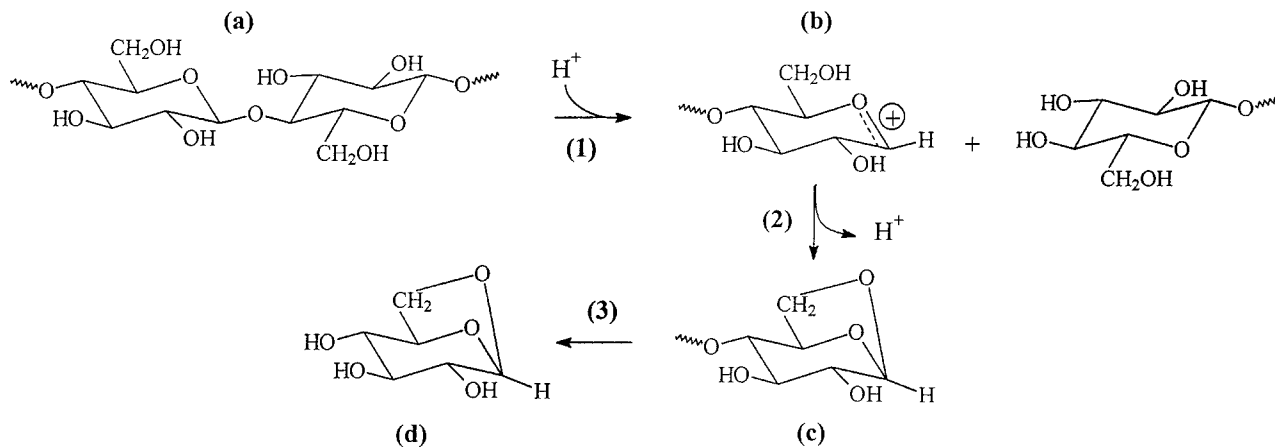
Figure 2 (a) Formation of the (b) resonance-stabilized glucosyl cation which gives (c) an LG end group via intramolecular nucleophilic attack on O_6. The LG end group can unzip from the rest of the chain by repetition of steps 1–2 to yield (d) a molecule of LG.

(i.e., cellulose, lignin, and pentosans), as well as from LG heated individually in transformer mineral oil.

EXPERIMENTAL

Materials

Cellulose powder, lignin (a by-product of the Kraft process), and pentosans were obtained from Aldrich. The cellulose powder was a high purity grade consisting mainly of α-cellulose and containing no pentosans or lignin. LG was obtained from Sigma Pharmaceuticals. Mineral oil (a standard Esso grade, P60) and high-grade naphthenic transformer oil (Nynas 10GB), both of which are used in electrical transformers, were chosen as the media for the aging experiments.
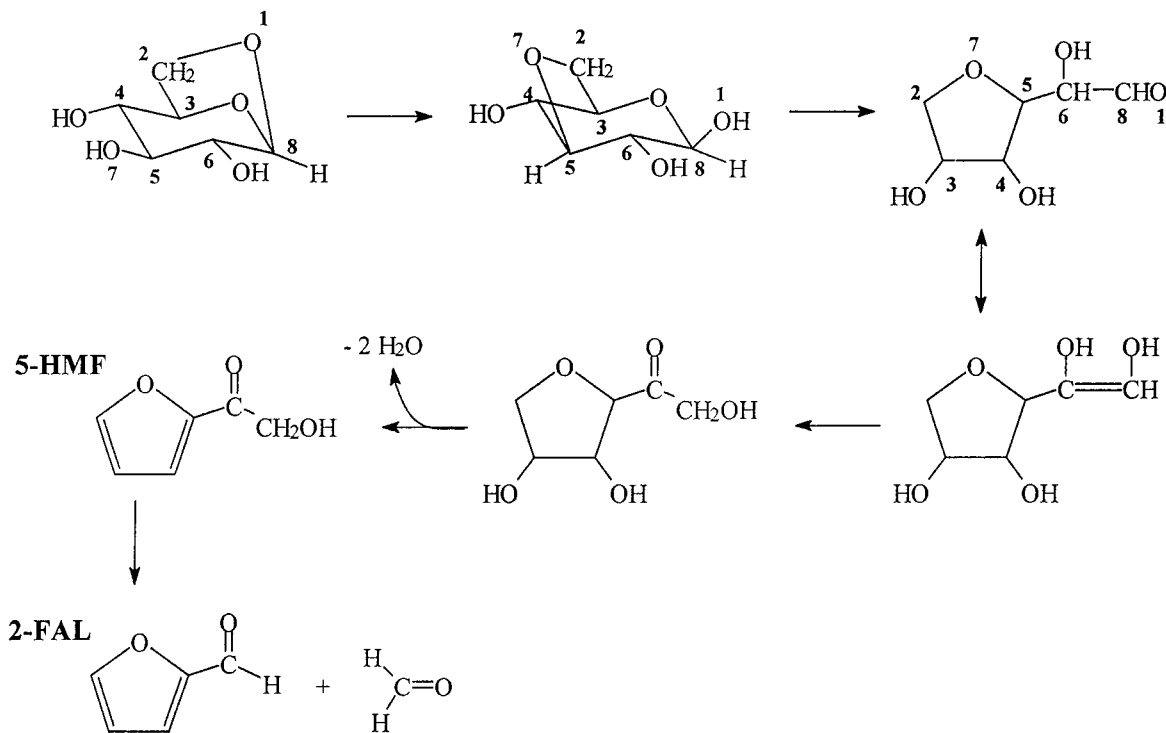

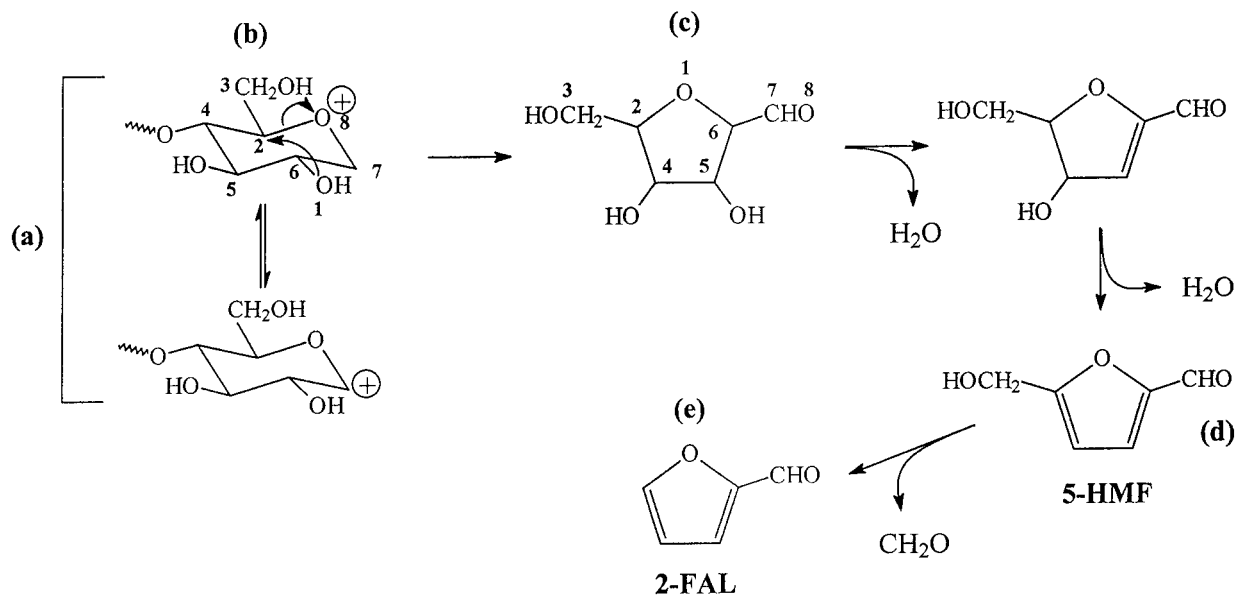**Figure 3** Production of 5-HMF and 2-FAL from LG.[8]

Figure 4 Mechanism of production of 5-HMF and 2-FAL from the (a) resonance-stabilized glucosyl cation by attack of the (b) hydroxyl group on C_2 onto C_5 to give (c) ring contraction and the furanic precursor. Two consecutive water elimination steps give (d) 5-HMF and elimination of formaldehyde ultimately gives (e) 2-FAL. Adapted from Antal et al.[9]

Aging and Furanics Analysis

Glass test vials (height, 8 cm; diameter, 5 cm; volume, 150 mL) with narrow necks (diameter, 1 cm) were used. All glassware was thoroughly cleaned with water and then acetone and dried at 100°C. The oil (100 mL) was carefully introduced into the vessel via a funnel with a long stem. The glass vials were sealed at the narrow neck using a flame torch. Duplicate samples of either cellulose or lignin or pentosans (0.5 g) and LG (0.3 g) in 100 mL of oil were prepared. Samples of LG alone in either an air or nitrogen atmosphere were also prepared. The vials were heated at 130°C for 1 week.

Furanic compounds were extracted from the oil using methanol and analyzed by HPLC using the CIGRE method 15.01.03 (CIGRE). This technique allows the quantification of five common furanic derivatives of Kraft paper (Fig. 1).

FTIR Analysis

LG was dissolved in methanol and cast onto KBr disks. The solvent was allowed to evaporate (2 days, ambient conditions), and the disks were examined by FTIR with a Perkin–Elmer System 2000 instrument by coadding 16 scans with a resolution of 4 cm^{-1}.

RESULTS

Figure 6 is a representative chromatogram of the furanic compounds detected in oil containing LG heated for 1 week at 130°C.

Cellulose

The results in Table I show that cellulose may be the main source of 5-HMF and the second major source of 2-FAL in Kraft paper. All five furanic compounds normally detected in Kraft paper were also detected in the cellulose powder.

Pentosans

The degradation of pentosans in oil produces considerable amounts of 2-FAL at almost 4 times more than that produced by cellulose powder under the same conditions. It can be seen from the data in Table I that the degradation of pentosans does not produce detectable quantities of 5-HMF. This is consistent with the fact that 5-HMF is usually produced as a degradation product of hexoses (six-carbon sugar) such as glucose, while 2-FAL is commercially produced by the acid hydrolysis of pentosans. Furthermore, Kato and Ko-
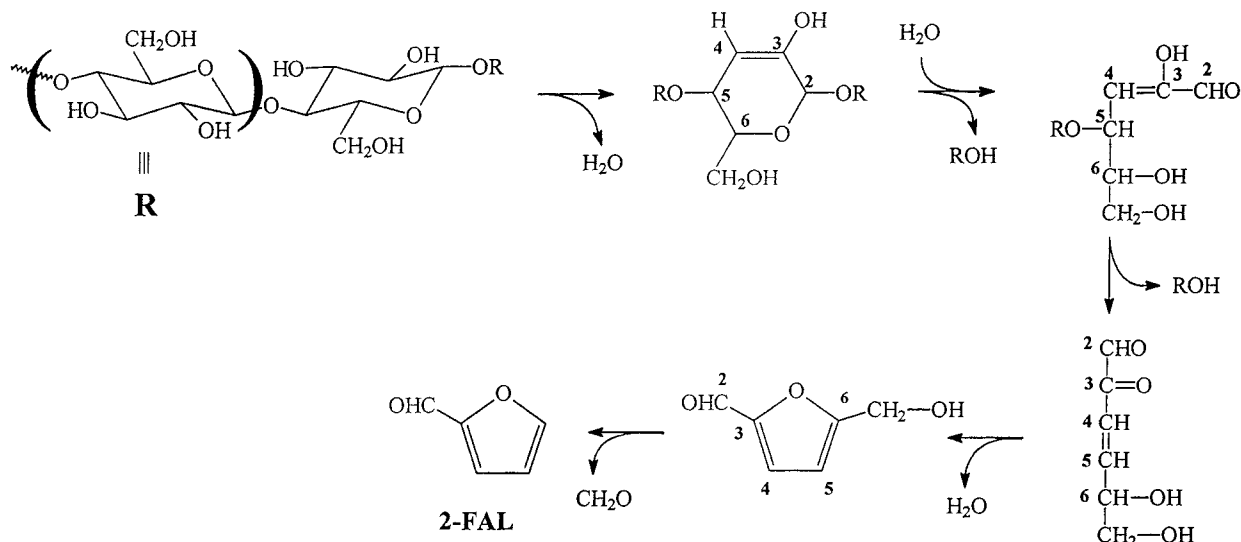
Figure 5 Production of 5-HMF and 2-FAL from acid-catalyzed, hydrolytic thermal degradation of cellulose; R represents the cellulose chain. Adapted from Shafizadeh and Lai.[8]

morita reported that 5-HMF can thermally decompose by losing formaldehyde to give 2-FAL.[14]

LG

The major furanic product from LG decomposition in mineral oil is 2-FAL. This is followed by 2-furfurol (2-FOL) and 5-HMF. 5-MEF is formed at one level of magnitude lower than 2-FAL. Similar results are reported by Shafizadeh and Lai[8] who found that LG pyrolyzed under nitrogen produced 0.9% 2-FAL and 0.1% 5-MEF. They also showed

Figure 6 Sample HPLC chromatogram of the furanic compounds from LG detected in mineral oil.

by radiochemical labelling that 100% of the 2-FAL is formed by a series of rearrangement and elimination reactions involving the C-2 of the anhydropyranose ring of cellulose (as in Fig. 3).

Lignin

Lignin produces negligible furanic compounds after heating at 130°C. Indeed, lignin is composed of phenylpropane groups that cannot give furanic compounds at these temperatures. The contribution of lignin to the production of furans from Kraft paper is therefore minimal.
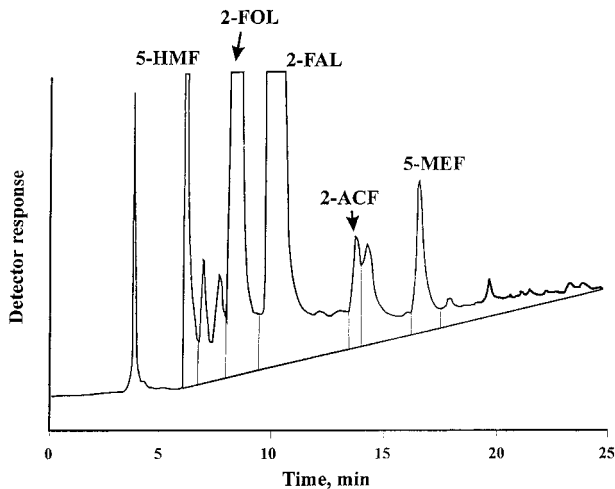
LG Heated in Air and Nitrogen in Absence of Oil

LG was heated at 130°C in both air and nitrogen atmospheres, and the IR spectral changes were recorded. Both samples underwent chemical modification that was revealed by modification of the IR spectrum; however, there was no difference observed between the inert and oxidizing atmospheres, suggesting the thermal degradation involved no free radical processes and a relative resistance of LG to thermal oxidation.

The sample changes from a white crystalline solid to a brown glassy residue. One study reported that significant uncatalyzed polymerization of LG can occur when it is heated under nitrogen, even at relatively low temperatures.[13] Such polymerization reactions may explain some of the

Table I Furanics Yield in Mineral Oil at 130°C for 1 Week (ppm)

	2-FAL	5-HMF	2-FOL	5-MEF	2-ACF
Cellulose[a]	176	15.5	14	12	5
Pentosans[a]	600	ND	ND	4	2
Lignin[a]	1.1	0.4	1.1	0.2	1
Levoglucosan[b]	28	12	14	0.8	0.2

2-ACF, 2-acetylfuran; ND, not detected.
[a] 0.5 g.
[b] 0.3 g.

changes in the LG spectrum because the oxygen bridge in LG would be converted to a glucosidic bond. The temperature used in this experiment should not induce fragmentation of the LG into volatiles because LG reportedly undergoes appreciable exothermic decomposition between 224 and 314°C.[15]

DISCUSSION

Comparison of the relative production of 2-FAL from both LG and pure cellulose shows that on an equal weight basis, the cellulose in mineral oil gives 3 times as much 2-FAL as does LG. This suggests that there must be other pathways to 2-FAL production in cellulose than exclusively through the LG intermediate route, which implies intramolecular rearrangement and elimination reactions with and without ring cleavage, respectively.[4,9] In addition, there is also a route suggested by Shafizadeh and Lai[8] that involves acid-catalyzed, hydrolytic thermal degradation (Fig. 5).

The amount of 2-FAL formed from LG in mineral oil is 1 order of magnitude larger than the corresponding amount formed in naphthenic oil (see Fig. 7). This can be related to the greater oxidizability of the oil medium and the effect that acidic residues (as produced from oil oxidation) have on the rate of furfural production. Indeed, IR examination of the carbonyl region of the oils after the heating experiment shows that naphthenic oils are more resistant to thermal oxidation than straight-chain mineral oils. Furthermore, it has been demonstrated that under acid-catalyzed thermal degradation conditions, 3 times more 2-FAL is produced than under neutral conditions.[8] It is significant to note that the industrial production of 2-FAL from D-xylose employs temperatures in the 160–280°C range, a sulfuric acid catalyst, and residence times of a few minutes.[9]

CONCLUSIONS

The propensity for 2-FAL production upon heating at 130°C in oil follows the trend pentosans ≫ cellulose > LG ≫ lignin and 5-HMF production follows the trend cellulose > LG ≫ lignin > pentosans.

Cellulose yields 3 times as much 2-FAL as does LG, suggesting that there are other pathways to 2-FAL production in cellulose at temperatures less than 130°C than exclusively through the LG intermediate route.

Pentosans produce considerable amounts of 2-FAL on heating but do not give any detectable 5-HMF or 2-FOL.

There is evidence to suggest that the production of furfural from LG is accelerated by acidic conditions in oxidized oil because 2-FAL is detected in significantly higher quantities in mineral oil than in naphthenic oil. The yield of 5-HMF from LG is the same in both mineral and naphthenic oil, indicating that its production is not significantly affected by oxidation of the oil.

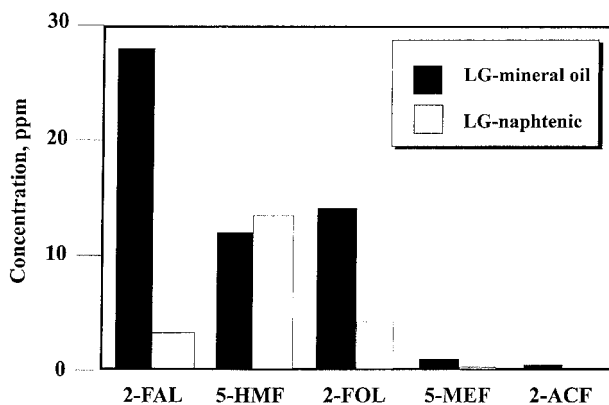Lignin (from the Kraft process) produces negligible furanics as a result of heating in mineral oil.

Figure 7 Bar graph showing the yield of furanic compounds from LG in mineral and naphthenic oils.

Degradation of LG at 130°C is likely to occur through an ionic molecular mechanism because an air or nitrogen atmosphere has no effect.

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