1. Introduction

Soil erosion is one of the main causes of soil degradation, land loss and desertification in the world. There are many different factors of mechanical erosion; the two main factors are wind and water. Wind erosion (deflation) is lifting of small particles and its movement (transportation) to another region. Water erosion on the other hand is closely related to the amounts of rainfall, its intensity, landscape profile, soil type and the degree of vegetation cover. Soil erosion rates are expected to change in response to changes in climate for a variety of reasons. a) changes in litter cover on the ground caused by changes in both plant residue decomposition rates driven by temperature and moisture dependent soil microbial activity as well as plant biomass production rates and b) soil erosion changes due to decrease in soil organic matter concentrations in soils that lead to a soil structure that is more susceptible to erosion and increased runoff due to increased soil surface sealing and crusting. For a comprehensive description of the problematic of soil degradation and desertification caused by clear-cutting, over-grazing and over-utilization see Liebner et al. 2006 [(1)]. Improper land use in particular has contributed a great deal to soil erosion and degradation in many parts of the world (FAO 1993; UNCCD 2004) [(2-3)]. In Europe, extensive forest degradation occurred on Terra-Rossa soils in the Mediterranean, resulting in soil loss, desiccation of slopes, and transformation of lowlands into swamps. In Greece, for example, sediment transport through soil erosion amounts to 130 million t y r^{-1} nowadays (kotoulas1989) [(4)]. However, Africa and Asia are the continents most affected by desertification. In China, annual soil loss is estimated at 5.5 billion t yr^{-1} [(1)]. Deserts here are advancing at an annual rate of 10.400 km^2 [(5)], which represent about 20% of desertification worldwide. This is mainly caused by insufficient vegetation cover and water erosion on fertile top-soils. The erosion process alters the physical, chemical and microbiological properties of soil. Deprived of most of its mineralized nutrient and accumulated humus substance, it can no longer provide favorable conditions for plant growth. In northwestern China, the organic carbon content of top soils has been decreasing continuously for the last 80 years [(6)]. In order to restore vegetation in such highly degraded areas as the Loess Plateau requires the application of organic (waste) materials to first help form humus fractions so that plants can eventually grow [(7)]. But it is very difficult to compensate for lost carbon as the formation of such high-grade stable humus is very slow [(8)]. Long-term investigation of agricultural rehabilitation on degraded soils found that natural humus accumulation occurs at a rate of 0.017 to 0.023 % per year [(9)]. This means it would take 40 to 60 years to accumulate 1 % of organic carbon, which is exactly the amount that

would be needed to transform degraded areas of the Chinese Loess Plateau into productive farmland. Ecological restoration over a less extended period of time is only feasible under accelerated formation or addition of humus [(1)].

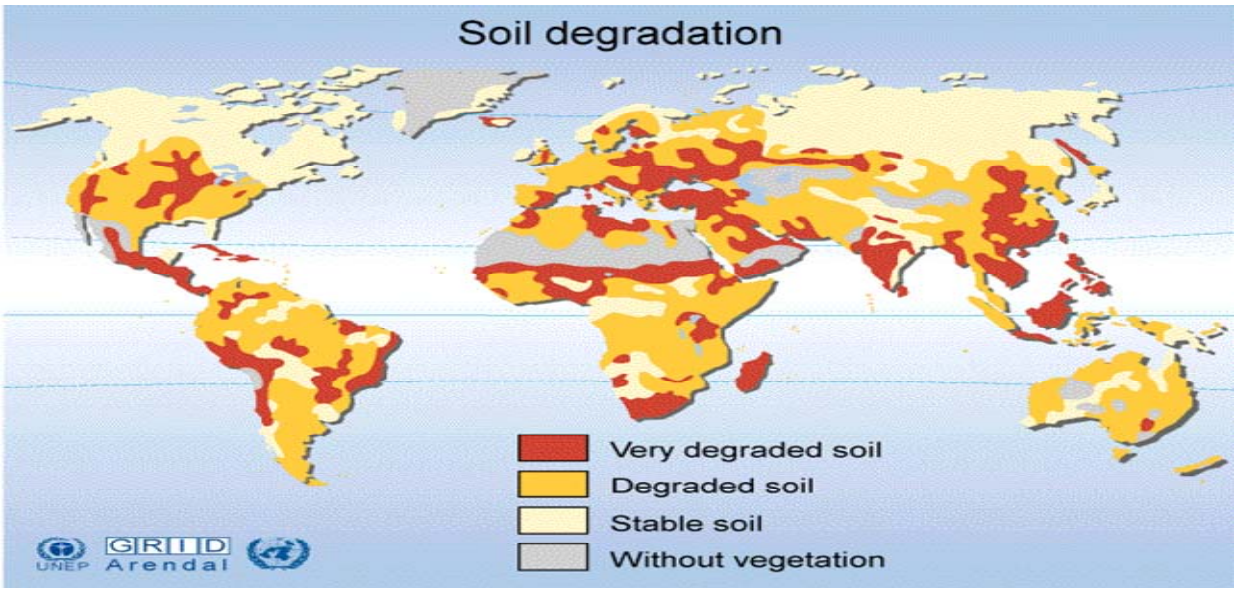


Figure 1. Soil degradation areas in all over the world [(90)].

Soil improvement by organic matter application is a quite common practice in agriculture and comprise the utilization of green manure (legumes), harvest residues, farmyard manure (dairy and beef cattle manure), poultry manure, sewage sludge, liquid manure (preferably in combination with straw), as well as different types of compost (e.g. green compost, dung compost, or slurry compost). The availability of organic matter in the desired quality and quantity is usually very problematic, especially in regions suffering from serious soil degradation or desertification [(1)]. The organic parts of harvest residues or liquid manure mineralize easily and, therefore, hardly contribute to humus formation [(9)]. Dairy and beef manure contains undigested forage and bedding, and hence higher amounts of the biopolymer lignin, which plays an important role in humus formation but decomposes very slowly in soil [(10)]. One year after application, about 25 % of the organic matter content in dairy manure is still available in the topsoil. But, assuming an agriculture soil with 2.17 % soil organic matter, 50 t ha^{-1} would be needed only to balance the carbon loss during cropping. However, most of the organic materials can not be solely applied to the soil; this is due to the low nitrogen contents of most of the materials. From soil-scientific investigations it is known that the C/N ration of organic soil amendments should be higher than (10 to 12) because otherwise the whole remaining nitrogen content of the already degraded soil would be immobilized by

microbiological growth. Hence, the application of any organic matter that hardly contains any nitrogen requires the additional application of a suitable nitrogen source.

Conventional fertilizers used as nitrogen sources, such as urea and ammonia salts are good water soluble and can therefore easily cause pollution of ground and surface water with nitrates, whose harmful effects are well known. This effect is most pronounced on sandy soils, those soil types which are mostly affected by soil degradation and erosion. Large quantities of ammonium or nitrate salts cause plasmalysis in young plants. Hence, materials with a slow-nitrogen releasing effect are most useful [(11)].

In the last two decades, many attempts have been made to synthesize slow releasing nitrogen fertilizers which yield organically bounds with nitrogen during the whole period of growth. N-Lignin plays an important role in the formation of soil organic matter during biodegradation of lignocelluloses; they give rise to precursors of humic substances which have a great influence on soil structure and fertility. In contrast to cellulose and hemicelluloses, Lignins are slowly degraded in soil because of their cross-linked structure [(12)]. N-lignin can not be leached as easily by rain fall as mineral nitrogen fertilizers because it consists of high molecular weight components. Nitrification is inhibited by fertilization with N-lignin.

Today there is a lot of interest in using technical lignins and similar ligneous materials as soil fertilizing materials as they are available in large quantities from the pulping and agricultural industries. Lignins are devoid of nitrogen and hence, they can only be used as soil improving agents after enriching them with nitrogen. This can be done using a process called oxidative ammonolysis (Ammoxidized lignins). Ammoxidation means oxidative ammmonolysis by ammonia in presence of oxygen. The N-modified products obtained from this process has unique properties as a slow nitrogen release with a slow biodegradability (long lasting organic compounds) and fertilizing efficiency with successfully soil rehabilitation applications. The nitrogen content of the N-modified lignins reported in the literature varies between 1 and 30%. During treatment of lignin with oxygen and ammonia the lignin molecule breaks into smaller parts and some reactions occur.

- Lignin becomes water-soluble and the reaction proceeds in homogeneous system.
- The content of phenolic hydroxyl groups may be increased by the cleavage of alkyl-aryl ether groups during the reaction so that the possibilities of reaction with ammonia are increased.
- The phenols which are formed by the methyl ether cleavage react with ammonia during the treatment to form various nitrogen compounds.

Concerning the nitrogen release from ammoxidation of lignin, there are two mechanisms are assumed.

- Biodegradation of the lignin matrix as a whole by means of the soil microorganisms.
- Selective chemical degradation of functional groups, for example by hydrolysis.

Hence, the different nitrogen releasing rates in soil are dependent on the nature of the chemical bonds by which nitrogen is linked to the lignin matrix. Ammoxidized lignins have already been characterized by FTIR spectroscopy and thioacidolysis by Lapierre et al. (1992) [13]. Moreover, nitrogen forming a part of complex organic structures is likely to be present in N - functionalized lignins. Recently, Potthast et al (1996) [14] reported on structural investigations of N-modified lignin by ^{15}N- NMR spectroscopy, IR spectroscopy and GC/MS. They identified aromatic nitriles, amides and urea, but no N-heterocyclic compound in the lignins.

The important questions still open nowadays are:

- How does the structure of lignin changes during oxidative ammonalysis?
- Which type of nitrogen binding forms is present in N-modified lignin?
- Does the nitrogen fixation proceeds via low molecular quinoide structures**?**

In order to find answers for these challenging questions, we studied the ammoxidation of selected technical lignins as well as ammoxidation of simple phenolic model compounds under the same conditions. Furthermore, the influence of temperature and reaction time were studied oxidation by Oxygen in 5% Sodium hydroxide (instead of ammonia) under different conditions of temperature and pressure was applied as well. Changes in the molecular structures of phenolic model compounds and selected technical lignins after Ammoxidation and/or oxidation were studied by applying different analytical techniques: GC/MS, Curie-point pyrolysis GC/MS; X-ray photoelectron spectroscopy (XPS); ^{15}N CPMAS NMR spectroscopy, elemental analysis. In addition, UV/Vis- spectroscopic measurements were performed in order to study the reaction behaviour of selected phenolic model compounds at different pH values.

2. *Objectives of the study*

Much effort has been spent over the last decades to enrich lignin with nitrogen, either by simply mixing it with mineral fertilizers or by composting it with nutrient-rich waste materials. However, these methods have not been satisfactory as nitrogen leaching remains considerable and the quantity of nitrogen incorporated into the polymeric of lignin is very small. Another way of enriching lignin with nitrogen is chemical modification. N-enrichment is possible by oxidative ammonolysis, a method first introduced by Franz and Palm (1932) [15] for N- enrichment of technical lignin. The latter is the main by-product of the pulping industry; it is characterized by structural alterations and partial degradations of the original bio-polymeric lignin structure. The reactive agents in oxidative ammonolysis are oxygen (anionic radicals) and ammonia, which are responsible for the degradation of lignin macromolecules, the cleavage of aromatic ring units, and the final incorporation of nitrogen into these structures. For high nitrogen content, oxidative ammonolysis in the past has been done exclusive at high pressures and temperatures. Products from these `` high-pressure based technologies`` contained up to 24 wt-% of nitrogen [16]. However, these lignin-based fertilizers could not compete with conventional products due to their considerable production (= energy) costs. In order to produce lignins with lower nitrogen content (5 to 6 %), C/N ratios similar to stable humus fractions (10 to 12), and better structural properties, a patented ``Ambient pressure technology`` has been developed at the Institute of Wood and Plant Chemistry, Dresden University of Technology [17].

Only little is known about the nature of nitrogen binding in N-modified lignins. In order to consider if ammoxidized ligneous materials can be used for soil improvement, detailed information regarding the mineralization behaviour and the time frames necessary for converting the organically bound nitrogen into plant-available forms are required.

No more than about 10 years ago, it was established that the majority of soil organic nitrogen has to be assigned to “some kind of amide” fraction, but not the class of hetero-aromatic nitrogen compounds as stated before. The aim of this study was to study the nature of N-binding in ammoxidized lignins and phenols by using different analytical techniques such as GC/MS, Elemental analysis, Curiepoint pyrolysis GC/MS, X-ray photoelectron Spectroscopy (XPS), and ^{15}N CPMAS NMR spectroscopy.

3. Theoretical part

3.1. Introduction

Wood is a very old raw material and has been used already several 100000 years ago as energy source, construction material or as raw material for manufacturing of tools [18]. Wood is one of the most important products of nature. It consists mainly of the three polymers cellulose, hemicellulose and lignin which are present in all woods but also a minor portion consisting of a huge variety of low molecular compounds such as extractives and salts, the proportions and chemical composition of lignin and hemicellulose differ significantly between softwoods and hardwoods, while cellulose is a uniform component of all woods.

Cellulose is the major wood component, making up approximately one half of the organic matter in both softwoods and hardwoods. It can be briefly characterized as a linear high – molecular – weight polymer built up exclusively of β- D – glucose. Because of its chemical and physical properties as well as its supramolecular structure it can fulfils its function as the main structural component of the plant cell walls.

Hemicelluloses are in close association with cellulose in the cell wall. Five neutral sugars, the hexoses, glucose, mannose, galactose, the pentose xylose and arabinose are the main constituents of the hemicelluloses. The molecular chains of hemicelluloses are much shorter than in the case of cellulose. Hardwoods contain more hemicelluloses than softwoods and the sugar composition is different.

Lignin is the third macromolecular wood component. The molecules of lignin are built up quite differently from those of the polysaccharides, as they consist of an aromatic system composed of phenyl propane units. There is more lignin in softwoods than in hardwoods and there are some structural differences between softwood and hardwood lignin. From a morphological point of view lignin is an amorphous substance located in the compound middle lamella as well as in the secondary walls. During the development of the cells lignin is incorporated as the last component into the cell walls, interpenetrating the fibrils and so strengthening the cell walls.

Minor polymeric substances: these are found in wood in small amounts as starch and peptic substances. Proteins account for at most 1% of parenchyma cells of wood, but are mainly found in the non-wooden parts of the stem, i.e. cambium and inner bark.

3.2. Lignin

3.2.1. Significance and occurrence

The term was introduced in 1819 by de Candolle and is derived from the Latin word *lignum*, meaning wood. Next to cellulose lignin is the most abundant and important polymeric organic substance in the plant world. The incorporation of lignin into the cell walls of plants gave them the chance to conquer the earth's land surface. Lignin increased the mechanical strength properties to such an extent that huge plants such as trees with heights of even more than 100 m remain upright.

Lignin is a characteristic chemical and morphological component of the tissues of higher plants such as pterodophytes and spermatophytes (gymnosperms and angiosperms), where it typically occurs in vascular tissues, specialized for liquid transport and mechanical strength (e.g. xylem). Primitive plants such as fungi, lichens and algae are not lignified [19-20]. More recent investigations on several mosses (e.g. Sphagnum magellanicum) indicate that they contain no lignin and that lignin occurrence is indeed restricted to vascular plants [21-22].

The amounts of lignin present in different plants are quite variable. While in wood species the lignin content ranges from 20 to 40% aquatic and herbaceous angiosperms as well as many monocotyledons (e.g. hors-tail speices) are less lignified [20-23-24]. Additionally the distribution of lignin within the cell wall and the lignin contents of different parts of a tree are not uniform. For example, high lignin values are characteristic for the lowest, highest and inner parts of the stem, for softwood branches, bark and compression wood. The lignin contents of needles and leaves are described inconsistently as high or low, possibly depending on their state of development [25-29].

3.2.2. Deposition of Lignin in Cell Wall.

The incorporation of the lignin within the polysaccharides cell wall frame work is generally seen as the final phase of the differentiating process of the typical secondary xylem cell. It gives the wood cell walls their characteristics with regard e.g. to strength, density or swelling properties. It was confirmed by electron spectroscopic investigations that lignin is most probably deposited initially in the cell corners when the surface enlargement of the cell is finished and just before the secondary wall 1 (S1) starts thickening. The lignification proceeds in the intercellular layer (middle lamella, ML) and the primary wall (P), starting at the tangential walls and spreading centripetally. The lignification of the compound middle lamella (ML + neighboured primary walls) continues during the differentiation of the S 1 and

S2 layers, and even until the formation of the tertiary wall (T). The lignification of the secondary wall layers proceeds slowly in a first stage but becomes more rapid after the thickening of the tertiary wall has been completed. These findings indicate a permanent lignification process throughout the whole time of cell wall differentiation, with a considerable delay to the synthesis of cellulose and polyoses. As factors influencing lignification the contents of mineral elements (mainly calcium), physiologically active compounds (e.g. auxin) and genetic factors have been assumed without definite results [30].

3.2.3. Lignin-Polysaccharide Complex

It is generally accepted today that lignin is not simply deposited between the cell wall polysaccharides, but is linked and associated with at least a certain part of them. According to Freudenberg (1968) the presence of carbohydrates is even a pre-requisite for the formation of lignin macromolecules within in the plant cell walls [19]. Nevertheless, our knowledge of the molecular and supramolecular connections between the wood cell wall components cellulose, hemicellulose and lignin is still far from settled. The phenomenon of the intimate association between the polysaccharide and lignin part of the cell wall is described by the terms lignin-polysaccharide complex (LPC) or lignin-carbohydrate complex (LCC). In a more practical sense the term describe the fact that in very different fractions isolated from wood, containing variable lignin and polysaccharide portions, the components cannot be totally separated by selective chemical treatments or special separation and purification techniques. Even in highly purified cellulose there will remain some residual hemicellulose and residual lignin. On the other hand attempts to purify a carefully isolated lignin sample failed to obtain a preparation free of polysaccharide residues. The methods of isolation, fractionation and purification are numerous, depending on the type and composition of starting material.

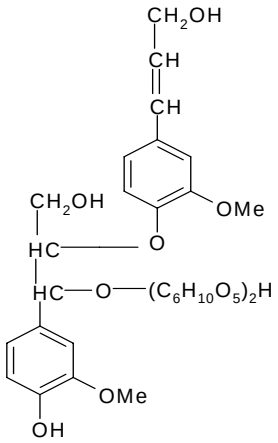
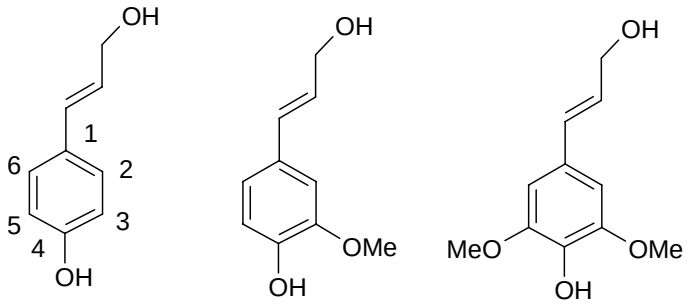


Figure 2. Linkage of sucrose to a dilignol (according to Freudenberg, Harkin 1960) [31].

3.2.4. Biosynthesis

Lignin macromolecule's biosynthesis by the plants comprises complicated biological, biochemical and chemical systems [32]. Numerous studies using radioactive carbon (^{14}C) have confirmed that the p-hydroxy-cinnamyl alcohols p-coumaryl alcohol (I), coniferyl alcohol (II) and sinapyl alcohol (III) are the primary precursors and building units of all lignins (fig. 3).



p-Coumaryl alcohol (I) Coniferyl alcohol (II) Sinapyl alcohol (III)

Figure 3 . The building units of lignin [33].

Fig. 3 gives a survey of the monomers from which the polymer lignin is formed by radical polymerization [23]. The biosynthesis of lignin starts with glucose (I) driving from photosynthesis. It is converted to shikimic acid (II) which is the most important intermediate of the so-called shikimic acid pathway. The two aromatic amino acids L-phenylalanine (IV) and L-tyrosine (V) are formed by reductive amination via prephenic acid (III) as the final compounds of that pathway. On the other hand they are the starting substances (amino acid pools) for the enzymatic phenylpropanoid metabolism (cinnamic acid pathway) leading not only to the three cinnamyl alcohols via activated cinnamic acid derivatives, but also to extractive components like flavonoids or stilbenes. The amino acids are deaminated by deaminases (phenylalanine ammonia lyase and tyrosine ammonia lyase) to their corresponding cinnamic acids (VI). The dominant further steps are successive hydroxylation (by phenolases (hydroxylases) and methylation (by O-methyltransferases) leading to p-coumaric acid (VII), caffeic acid (VIII), ferulic acid (IX), 5-hydroxy-ferulic acid (X), and sinapic acid (XI). One reason for the higher proportions of syringyl units in hardwood lignins than in softwood lignins is expected to be the higher affinity of the angiosperm 4-O-methyltransferase for 5-hydroxy-ferulic acid as compared to the respective tranferase of angiosperms. The cinnamyl alcohols (XVIII-XIX-XX) are finally formed by enzymatic activation (CoA ligase) and reduction (NADP reductase, NADP hydrogenase) of the corresponding acids via coenzyme-A thioesters (XIII-XIV) and aldehydes (XVI-XVII) [34].

The glucosides must be reconverted to alcohols by β-glucosidase before the polymerization reactions (fig. 4).

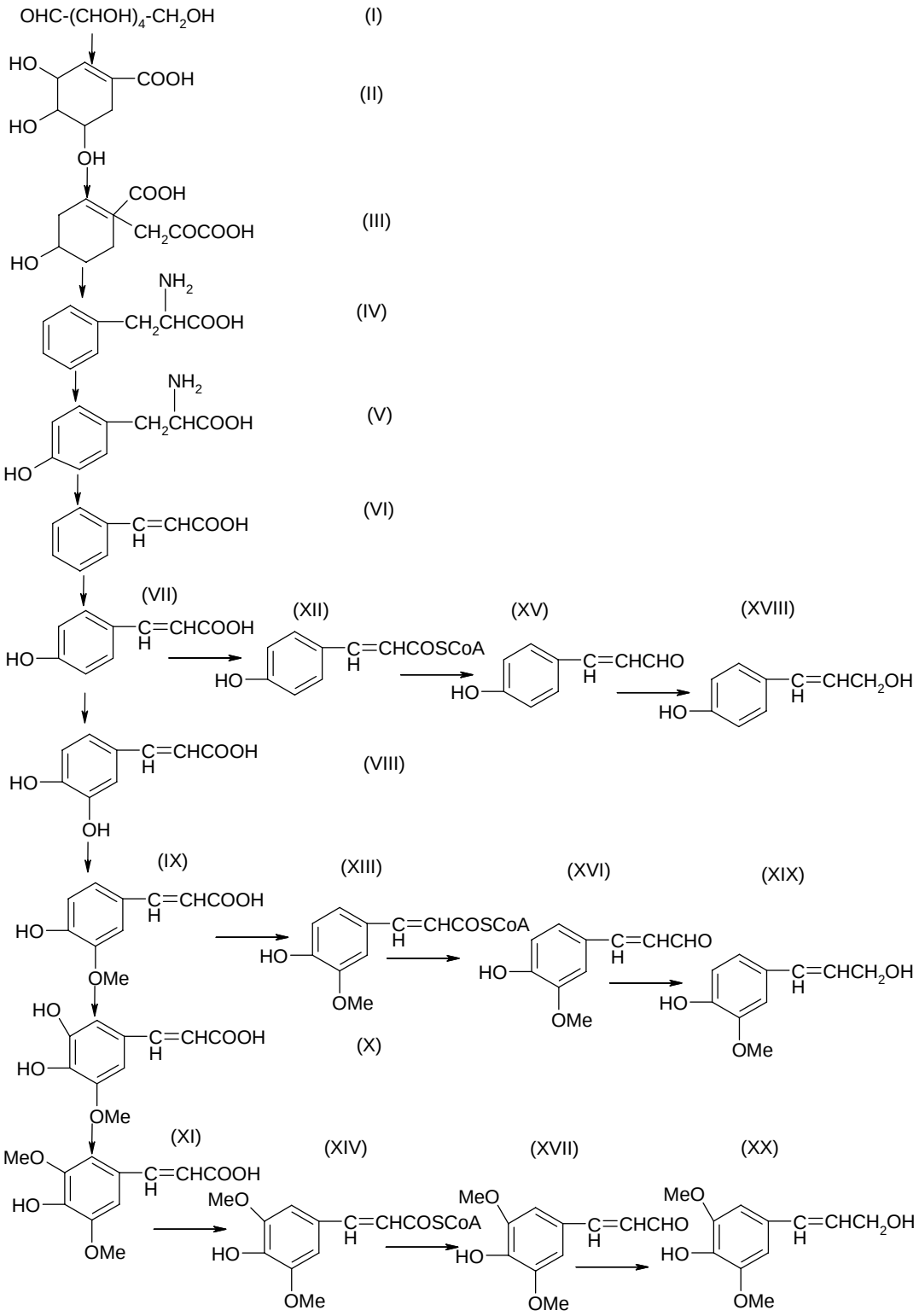


Figure 4. Metabolic pathway from glucose to phenylpropane lignin precursors.

3.2.5. Macromolecular Structure of Lignin.

Lignin is one of the most difficult natural polymers with regard to its structure and heterogeneity. The biosynthesis of lignin from the monomeric phenylpropane units can be generally described as a dehydrarogenative polymerization. The first step of the biochemical pathway for building up lignin macromolecules is the enzymatic dehydrogenation of the p-hydroxycinnamyl alcohols, yielding mesomeric ring systems with a loosened proton. Fig. 5 shows the formation of the resonance-stabilized phenoxy radicals from coniferyl alcohols by a one-electron transfer. Though the catalytic action of laccase in the presence of air or several chemical oxidation substances are able to form phenoxy radicals from cinnamyl alcohols, the most frequently suggested catalysts for initiating the polymerization reactions are cell wall peroxides in combination with hydrogen peroxide as an oxidant (peroxidise/H_2O_2-system) [35].

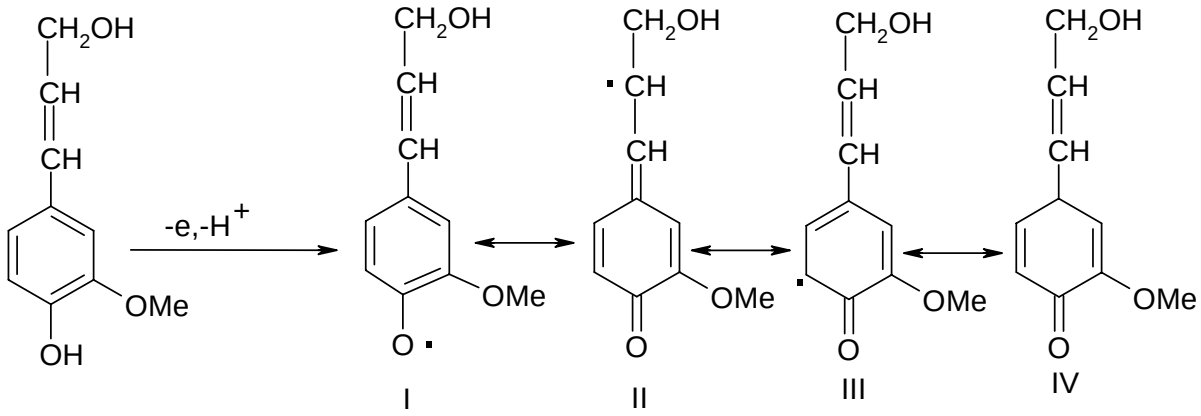


Figure 5. Enzymatic dehydrogenation of coniferyl alcohol yielding phenoxy radicals.

From quantum calculations it was deduced that all phenoxy radicals have the highest π-electron densities at the phenolic oxygen atom, thus favouring the formation of aryl ether linkages such as β-O-4 linkage, the most frequently type of bond in softwood and hardwood lignins [37]. The first step in polymerization is the formation of dimeric structures. Some prominent so-called dilignols are shown in fig. 6. The further polymerization is called ›end-wise< polymerization, involving a coupling of monolignols with the phenolic end- groups of di- or oligolignol or a coupling of two end-group radicals, yielding a branched polymer via tri-, tetra-, penta-, and oligolignols.

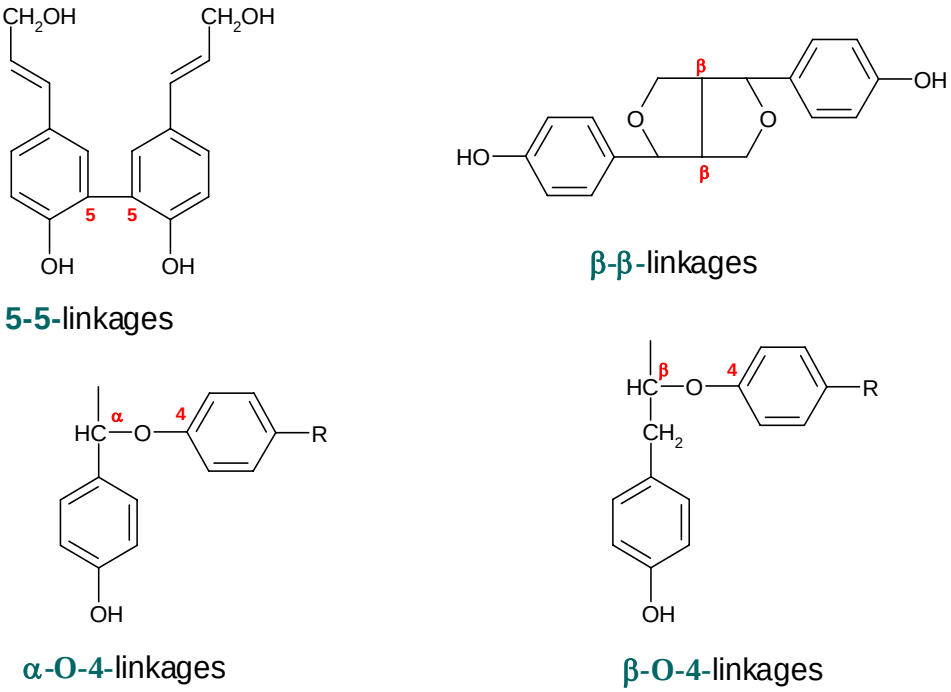
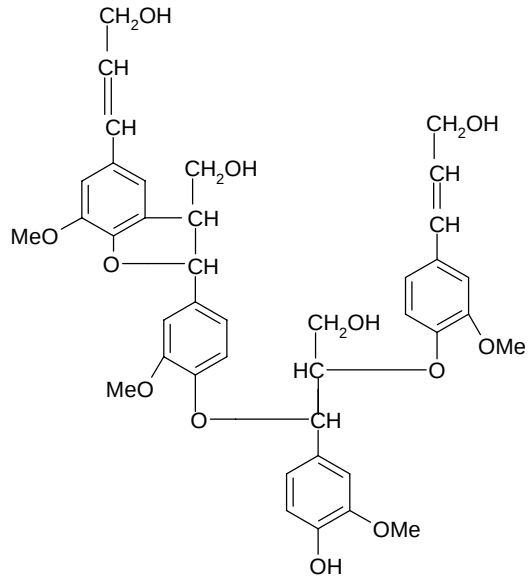
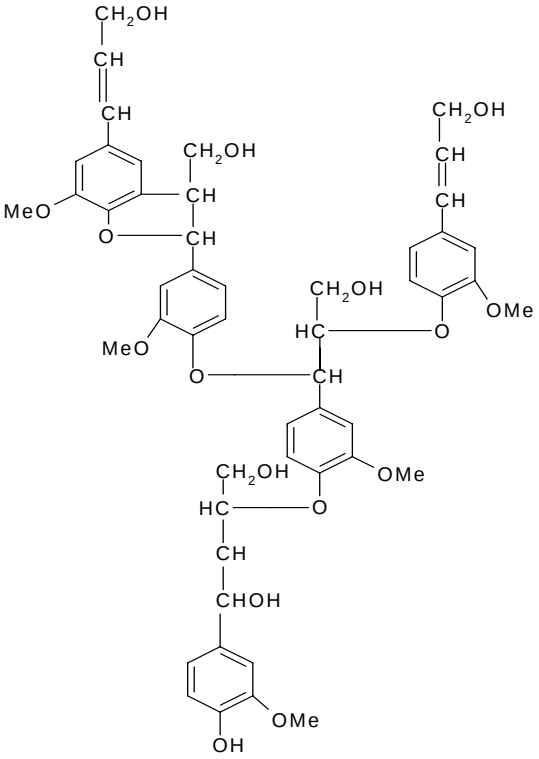


Figure 6. Selected structural sub-units of the biopolymer lignin

Figure 7 gives one example of higher structural units within the polymerization process. Summarizing the formation of lignin it is evident that these macromolecules are not formed by a genetically prescribed, regular mechanism, but by a random coupling of lignols to a non-linear polymer. The final constitution of lignin is therefore determined mostly by the reactivity and frequency of the building units involved in the polymerization. From a morphological standpoint the growing lignin molecules are forced to fill up the spaces between the performed polysaccharidic fibrillar elements of the cell wall. The incorporation of the lignin causes a de-swelling of the cell walls. Fig.7 gives two examples of higher structural units within the polymerization process. The tetralignol (guaiacylglycerol-β-coniferyl-γ-dehydrodiconiferyl ether) is formed by coupling dehydrodiconiferyl alcohol with a dimeric quinone methide. The pentalignol represents the guaiacylglycerol ether of the tetralignol.



Tetralignol



Pentalignol

Figure 7. Examples of higher lignol structures:
Tetralignol: guaiacylglycerol-β-coniferyl-γ-dehydrodiconiferyl alcohol
Pentalignol: guaiacylglycerol ether of the tetralignol.

3.2.6. Structure and Constitution of Lignin

Lignin is a large, cross-linked, racemic macromolecule with molecular masses in excess of 10,000 u. It is relatively hydrophobic and aromatic in nature. Lignin is one of the most difficult natural polymers with regard to its structure and heterogeneity. The degree of polymerization in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures which appear to repeat in a haphazard manner. Isolated lignins suffer from degradation and changing effects, impurities and the difficulty of isolating reproducible and identical lignin samples from wood. Finally it is still questionable whether carefully isolated lignins are representative of the total lignin in wood [(55)]. Many investigations were necessary to complete the picture of the principal structure of lignin as (1) degradation experiments, partly combined with tracer studies, including: ethanolysis, acidolysis, hydrogenolysis, mild hydrolysis, thioacetolysis, oxidation (2) elemental analysis, (3) determination of functional groups. Ethanolysis is the hydrolytic treatment of wood or lignin with dilute alcoholic hydrochloric acid under pressure [(56)]. Acidolysis was used for degradation by applying acidified dioxane-water mixtures (9:1) to model compounds and isolated lignin as well [(57)]. Mild hydrolysis of lignin was performed with dioxane-water mixtures (1:1) at 180 °C for 20 min or by percolation with water at 100 °C for several weeks [(58)]. Thioacetolysis is the treatment of spruce and beech wood with thioacetic acid in the presence of borontrifluoride and subsequent alkaline hydrolysis with sodium hydroxide. The oxidative degradation of lignin for structural studies must preserve the aromatic rings. Elemental analysis together with the determination of the methoxyl content gives information about the average composition of the C_9-units in lignin. Using analytical data obtained from Björkman lignin of spruce, Freudenberg (1968) described the average lignin unit with the formula $C_9H_{7.12}O_2(H_2O)_{0.40}(OCH_3)_{0..92}$, assuming the loss of approximately two hydrogen atoms and addition of 0.4 molecules of water if compared to the average elemental composition of coniferyl alcohol in softwood lignin of $C_9H_{9.1}O_2(OCH_3)_{0..92}$. The determination of functional groups such as free aliphatic and aromatic hydroxyl groups, benzyl alcohol or ether groups, carbonyl and methoxyl groups for the structural elucidation of lignin can be performed by means of numerous chemical and physical methods or combinations of both. The non-destructive physical methods include UV and IR spectroscopy as well as nuclear magnetic resonance spectroscopy (^{1}H-NMR, ^{13}C-NMR), electron spin resonance spectroscopy (ESR), and mass spectroscopy (MS), partly in combination with gas chromatography (GC-MS). As the lignin macromolecule cannot be

described by a simple combination of one or a few monomeric units by one or a few types of linkages as in the case of cellulose or hemicelluloses, lignin structure is still a matter of models. Different types of lignin have been described depending on the means of isolation [15, 16]. The first lignin model was designed by Freudenberg (1968), based on the dehydrogenative polymerization concept and fulfilling all analytical data available at that time. This scheme for spruce lignin represent 18 phenylpropane units as a section of the total molecule which was assumed to consist of more than 100 units in the native state. A small section of a lignin polymer is presented below illustrating some typical chemical linkages found in lignin.

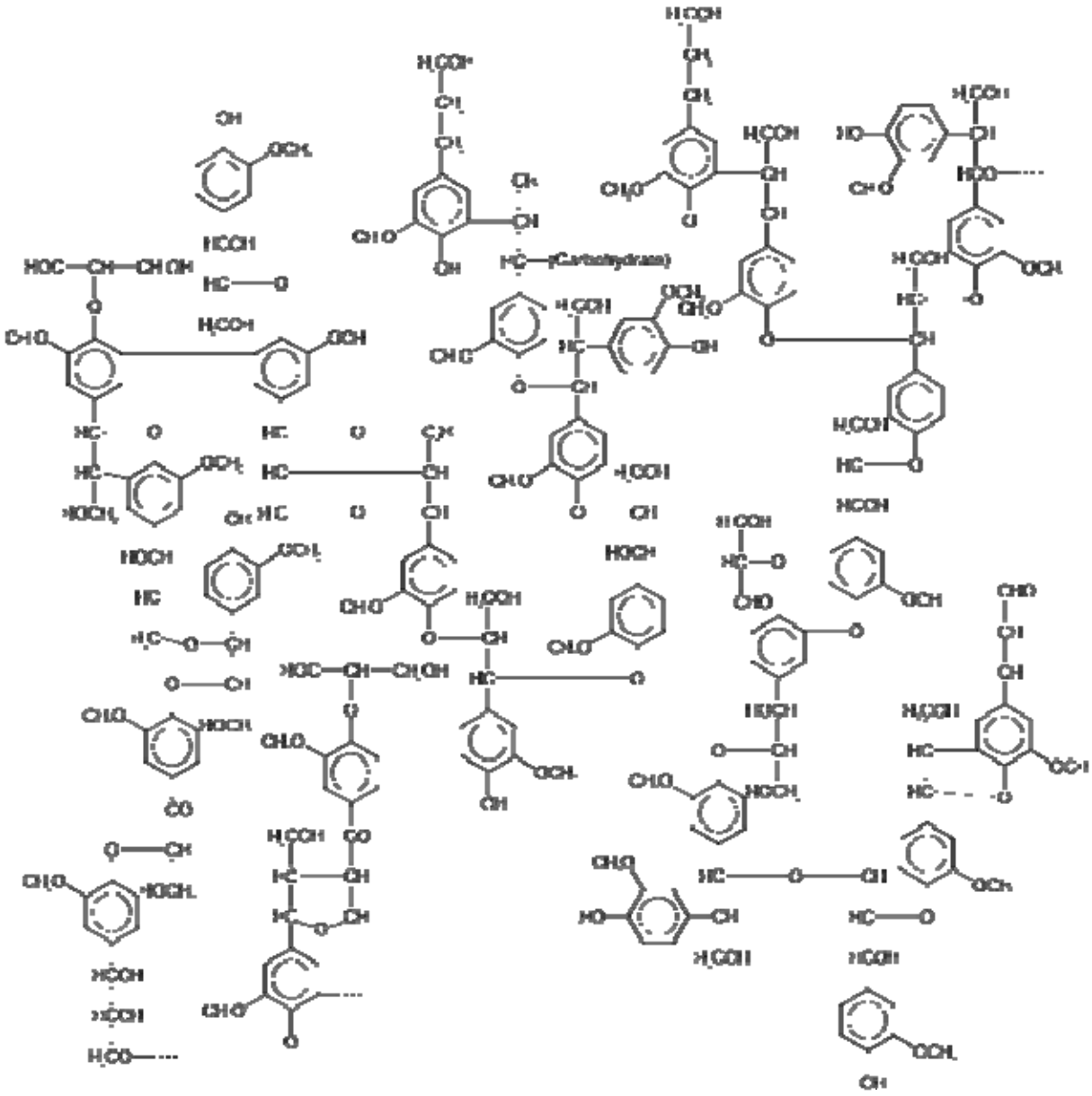


Figure 8.An example of a possible lignin structure [33].

3.2.7. Lignin isolation and Determination of the lignin content

The most important product of the chemical conversion of wood is pulp. 123 million tones of pulp were produced in 1980 on a global scale. The total consumption of paper and paperboard was 171 million tons during the same period [37]. The isolation of lignin in an unchanged form and its exact determination has not yet proved possible. All methods of isolation have the disadvantage of either fundamentally changing the native structure of lignin or releasing only parts of it relatively unchanged. Lignin isolation methods can be divided into two large groups:

1- Methods yielding lignin as residue.

2- Methods by which lignin is dissolved either without reacting with the solvent used for the extraction or by forming soluble derivatives.

Table: 1. Lignin isolation methods.

Remarks	**Treatment Lignin as residue**	**Preparation**	**References**
Acid hydrolysis of polysaccharides	H_2SO_4	Sulfuric acid lignin (Klason lignin)	Klason (1906)
Acid hydrolysis of polysaccharides	H_2SO_4/HBr	Sulfuric acid lignin(Runkel lignin)	Runkel, Wilke (1951)
Acid hydrolysis of polysaccharides	HCl	Hydrochloric acid lignin (Willstätter lignin)	Willstätter,Zechmeister (1913)
Acid hydrolysis of polysaccharides	HCl/H_2SO_4	Hydrochloric acid lignin (Halse lignin)	Halse (1924)
Acid hydrolysis of polysaccharides	HF	Hydrofluoric acid lignin	Fredenhagen, Cadenbach (1933)
Acid hydrolysis of polysaccharides	CF_3COOH	Trifluoroacetic acid lignin	Fengel et al. (1981) [38-39]
Oxidation of polysaccharides	$Na_3H_2IO_6$	Periodate lignin (Purves lignin)	Purves et al. (1947)
Hydrolysis/dissolution of polysaccharides	$NaOH/H_2SO_4/Cu(NH_3)_4(OH)_2$	Cuoxam lignin, cuproxam lignin, cuproxammonium lignin, (Freudenberg lignin)	Frudenberg et al. (1929)
	Lignin by dissolution		
No appreciable reactions between lignin and solvent	Alcohol extraction	Native lignin (Brauns lignin)	Brauns (1939)
No appreciable reactions between lignin and solvent	Vibratory milling/dioxane-water-extraction	Milled wood lignin (MWL) Björkman lignin)	Björkman (1956) [40]
No appreciable	Ball milling/H2O-	Ball-milled wood	Brownell (1965,1968)

reactions between lignin and solvent	NaSCN-$C_6H_5CH_2OH$-DMF dissolution/extraction	lignin (BMWL)	[41-42]
No appreciable reactions between lignin and solvent	Ball milling/H_2O-NaSCN-$C_6H_5CH_2OH$-DMF dissolution/extraction	Ball-milled wood lignin (BMWL)	Brownell (1965,1968) [41-42]
No appreciable reactions between lignin and solvent	Milling/enzymic treatment/solvent extraction	Cellulolytic enzyme lignin (CEL)	Pew (1957); Pew, Weyna (1962) ; Chang et al.(1975); [43] Polcin, (Bezuch (1978)
	Organosolv lignins		
Reactions between lignin and Solvent	Alcohol/HCl	Alcohol lignin	Holmberg,Runius (1925), Brauns, Hibbert (1935)
Reactions between lignin and Solvent	Dioxane/HCl	Dioxane acidolysis lignin	Storch (1936) Freudenberg, Zechmeister (1954)
Reactions between lignin and solvent	$CH_3COOH/MgCl_2$	Acetic acid lignin	Schutz, Knackstedt (1941) Brauns, Buchanan (1945)
Reactions between lignin and solvent	$HSCH_2COOH$/HCl	Thioglycolic acid lignin (TGA-L)	Holmberg (1930)
Reactions between lignin and solvent	Phenol/HCl	Phenol lignin	Clark, Brauns (1944)
Reactions between lignin and solvent	Mild hydrogenation	Hydrogenolysis lignin	Brewer et al (1948)
Reactions between lignin and Solvent	Hydrotropic solvents	Hydrotropic lignin	Traynard, Eymery (1955)
	Derivatives by inorganic reagent		
Generally technical pulping processes	Sulfite/bisulfite	Lignin sulfonates (lingo-sulfonates)	
Generally technical pulping processes	NaOH	Alkali lignin (Soda lignin)	
Generally technical pulping processes	Na_2S/NaHS	Thiolignin	
Generally technical pulping processes	NaOH/Na_2S	Kraft lignin (Sulfate lignin)	

- For origina and further early literature see references in: Brauns (1952); Brauns, Brauns (1960); Browning (1967_b); Lai, Sarkanen (1971)

During the isolation procedure the extractives must be removed to avoid the formation of condensation products with lignin. For the same reason, especially if strong mineral acids are involved in the isolation, solvents such as alcohol or acetone must be completely removed from the extracted wood. The first group of isolation methods yields so-called acid lignin's by applying sulphuric or hydrochloric acid, mixtures thereof, or other mineral acids. in the case of sulphuric acid lignins, acid concentrations between 68 and 78% (mostly 72%) are used for

the first hydrolysis stage followed by dilution steps to complete the polysaccharide treating wood with oversaturated hydrochloric acid are described as being less condensed than sulphuric acid lignins [44-45]. all lignin preparations obtained by acid hydrolysis are changed in their structure and properties, predominantly by condensation reactions [46-47]. The sulphuric acid and hydrochloric acid lignins additionally contain considerable amounts of sulphur and chlorine, respectively [48] therefore these preparations are not usable for investigating structures but are mainly applied in estimating the lignin content. Because of the disadvantages of the acid lignins several attempts have been made to obtain more carefully isolated lignins by removing the polysaccharides without acid hydrolysis. The oxidative degradation of the polysaccharide part of wood by the action of periodate ($Na_3H_2IO_6$) avoids condensation but causes some oxidative modifications of the lignin residue (periodate lignin). The dominant reaction is the oxidative conversion of sugar units to dialdehydes, thus making the polysaccharides hydrolysable with boiling water. A proposed modification of this method calls for blocking the guaiacyl groups of lignin by acetylation, thus avoiding oxidation [49].

The most important method for obtaining relatively unchanged lignin is Björkman's procedure of the vibratory milling and subsequent extraction of lignin with aqueous dioxane (milled wood lignin, MWL) [50-51-52-53-47]. In the future improved results in the field of careful lignin isolation are to be expected by the combination of mechanical, chemical and enzymatical treatments as demonstrated e.g. by Chang et al. (1975) [52] (cellulolytic enzyme lignin, CEL) and Polcin and Bezuch (1978) [53] (enzymatically isolated lignin, EIL). The former authors obtained increased yields of lignin from sweetgum (Liquidambar styractiflua) and spruce (Picea abies) by treating ball milled wood with commercial cellulose followed by a successive extraction with aqueous solutions of dioxane. A nearly complete isolation of the lignin of spruce (Picea abies), birch (Betula verrucosa) and poplar (Populus monilifera) was achieved by Polcin and Bezuch (1978) by a multistep procedure of milling, extraction and enzymatic treatment.

Organosolv lignins derived from ethanol-water delignification, which is expected to be a future pulping process [54], proved to be mostly unchanged, resembling to some extent analytical Björkman lignins [55-38-39].

A so-called autohydrolysis lignin was prepared by autohydrolysis of aspen wood meal (Populus termuloides) at 195 C° and subsequent dioxane extraction [56]. Lignin sulfonates, alkali lignin, thiolignin and sulfate lignin are lignin derivatives predominantly obtained from the waste liquors of pulping processes (technical lignin).

The determination of the lignin content is important for the wood analysis as well as for the characterization of pulps. The methods of quantitative lignin determination may be subdivided as follow:

- Direct methods, by which the lignin is determined as residue.
- Indirect methods, by which the lignin content is calculated after the determination of the polysaccharides is determined by spectrophotometric methods results from reactions of lignin with oxidizing chemicals.

3.2.8. Lignin and Lignin Derivatives: Properties and characterization

3.2.8.1. Chemical Composition and Molecular Weight

First indications regarding the origin and the chemical constitution of lignin and lignin derivatives can be obtained by elemental analysis and determination of methoxyl groups. Non-lignin components are considered by determination of ash and polysaccharide moieties. Further characteristics are the content of other functional groups (e.g. phenolic and aliphatic hydroxyl groups, carbonyl, carboxyl groups) indicating changes of lignin structure due to the isolation procedure or chemical treatments [57]. Lignin degradation or condensation reactions can also be proved by determination of the average molecular weight or size distribution [58]. Values of elemental composition and the methoxyl contents of lignins demonstrate that the carbon content of softwood lignins (60-65%) is generally higher than that of hardwood lignins (56-60%). This is due to the higher oxygen content of hardwood lignins, which is caused by their higher methoxyl content (18-22%) as compared to softwood lignins (12-16%). The nonwood lignin samples have methoxyl contents ranging between those of softwood and hardwood lignins. Acid lignins show lower methoxyl contents, probably due to the severe chemical action during isolation. Sulfur content of lignin sulfonates is much higher (6-7%) than in kraft lignins (0.2-2%). The sulfur in lignin sulfonates is bound in the sulfonate groups occurring as salts, e.g. calcium salts. Polysaccharides are a common contaminating component of isolated lignins. The amounts of residual Polysaccharides are highly dependent on the type of lignin isolation and purification, but also to some extent on the wood species. Polysaccharides in softwood lignins range on an average between (0.6-2%) lower than hardwood lignins (3-9%). A typical or average molecular weight of lignin or lignin derivatives is still a questionable matter. This is caused by several factors:

- the multiplicity of lignin isolation procedures
- degradation of the macromolecules during isolation

- condensation effects, especially under acidic condations
- the pronounced polydispersity of all solubilized lignins

As already pointed out there also no uniform values for molecular weights of technical lignins due to their heterogeneity depending on the pulping process and the influence of different purification procedures such as dialysis and ultrafiltration. The values from the literature for lignin vary between about 1000 and more than 100000 or even 10^6. The two principle solvent parameters for lignin-dissolving properties are the hydrogen bonding capacity and the cohesive energy density (Hildebrand's solubility parameter) [57]. Suitable solvents for analytical lignins isolated with organic solvents are e.g. dioxane, dimethylsulfoxide (DMSO), formamide, dimethylformamide (DMF), tetrahydrofuran (THF), pyridine, dichloroethane and ethyleneglycol-monomethlether (methyl cellosolve). Further good solvents for lignins are acetyl bromide in acetic acid and hexafluoropropanol [59]. With the exception of acid lignins, which are practically insoluble in all solvents, analytical lignins or fractions thereof may also be partially soluble in methanol, ethanol, acetone or solvent mixtures. Technical alkali lignins and lignin sulfonates are generally soluble in water, dilute alkali, salt and buffer solutions as well as in some basic and neutral polar solvents. Especially for UV spectroscopic studies the choice of a suitable solvent is restricted by the limited transmission of most of the solvents in the lower UV wavelength range.

3.2.8.2. Ultraviolet and Infrared Spectroscopic Behaviour

Ultraviolet absorption is a well-know and widely used tool for lignin identification, qualitative and qualitative determination, as well as characterization of changes in lignin structure and properties [60]. The distinct absorption of lignin in the ultraviolet range is based on its aromatic character, i.e.the sum of phenyl propane units, and on several chromophoric structural elements. The typical lignin spectrum comprises a maximum at about 280 nm followed by a slope to lower wavelengths, with amore or less pronounced shoulder in the region of 230nm. A second typical extinction maximum with a high absorptive value appears in the range between 200 and 208 nm. Nevertheless, the fine resolution of UV spectra reveals changes in the spectral behaviour caused by structural differences in lignin [61]. In contrast to softwood lignins with a maximum at about 280 nm or only slightly lower, hardwood lignins show a shift of this maximum to somewhat shorter wavelengths in the range of 275-277 nm. This fact contributes to the higher symmetry of the phenyl propane units in hardwood lignins, caused by the higher amounts of syringyl units. Additionally the absorptivities of hardwood

lignins are generally somewhat lower than those of softwood lignins, with decreasing values at increasing OCH_3/C9-ratios [62]. Infrared spectroscopy in the near IR region (wavelength range: 2.5-15 µm, wave numbers: 4000-600 cm^{-1}) is another useful physical method for characterizing lignin and lignin derivatives.

3.2.8.3. Ultrastructural Appearance

Only a few investigations are concerned with lignin structures visible in the electron microscope. Electron micrographs of fractionated lignin sulfonates show spherical shaped particles of different sizes (20-50 nm). Though even the smallest particles observed do not represent single lignin molecules, the hydrodynamic properties of soluble lignins, elucidated by viscosity, sedimentation, diffusion and relaxation experiments, support the idea that lignin appears in solution as a compact-shaped microgel (63).

3.3. Natural Lignin Degradation and Conversation into Humic Substances

Lignin plays a significant role in the carbon cycle, sequestering atmospheric carbon into the living tissues of woody perennial vegetation. Lignin is one of the most slowly decomposing components of dead vegetation, contributing a major fraction of the material that becomes humus as it decomposes. The resulting soil humus generally increases the photosynthetic productivity of plant communities growing on a site as the site transitions from disturbed mineral soil through the stages of ecological succession, by providing increased cation exchange capacity in the soil and expanding the capacity of moisture retention between flood and drought conditions. Humic substances are the most widespread and ubiquitous natural nonliving organic materials in terrestrial and aquatic environments and represent the major fraction of soil organic matter. In addition, they make up a substantial part of the fossil organic carbon incorporated into peat and low-rank coals (e.g., lignite and brown coal) Humic substances comprise a physically and chemically heterogeneous mixture of biogenic, relatively high-molecular-mass compounds with mixed aliphatic and aromatic natures. Based on solubility in acids and alkalis, they can be divided into three main fractions: humic acid (HA), which is soluble in alkali and insoluble in acid; fulvic acid (FA), which is soluble in alkali and acid; and humin, which is insoluble in both alkali and acid. Humic substances are formed by secondary synthesis reactions (humification) during the decay process and transformation of biomolecules originating from dead organisms and microbial activity. Lignin and its transformation products, as well as polyphenols and derived polymers from lower plants and microorganisms, are important starting materials in this process and provide

aromatic building blocks of high physicochemical stability [64]. Microbial degradation of humic substances—particularly of high-molecular-mass, aromatic moieties in HA and humin—is an important part of humus turnover and is therefore essential for maintaining the global carbon cycle [65] Despite this fact, little is known yet about the microorganisms which decompose and recycle humic matter. Since lignin, the complex aromatic polymer providing strength and rigidity to the cell walls and tissues of vascular plants, is a major parent material in the formation of humic substances [66], several authors studied the decomposition of natural and synthetic HA by white-rot fungi [67-72] which are the most effective lignin degraders in nature [73]. Some of these basidiomycetous fungi which colonize wood (e.g., *Phanerochaete chrysosporium*, *Trametes versicolor*, and *Nematoloma frowardii*) were shown to disintegrate high-molecular-mass HA by forming lower-molecular-mass FA and carbon dioxide (CO_2). Correlation was observed between the activity of extracellular peroxidases and HA degradation, and isolated manganese peroxidase (MnP) was even found to depolymerize and mineralize different HAs in vitro [73-75] However, since most white-rot fungi grow preferentially in compact wood (trunks, logs, branches, and stumps) and cannot compete in soil for a prolonged time [76-77]; it is doubtful whether they are involved to a large extent in humus decomposition under natural conditions [78]. In the present study, therefore, we have focused on HA degradation by a true soil-colonizing basidiomycete, *Collybia dryophila*, which is a very common species in European and North American woodlands and grows in different layers of forest litter from both coniferous and deciduous trees [79- 81].

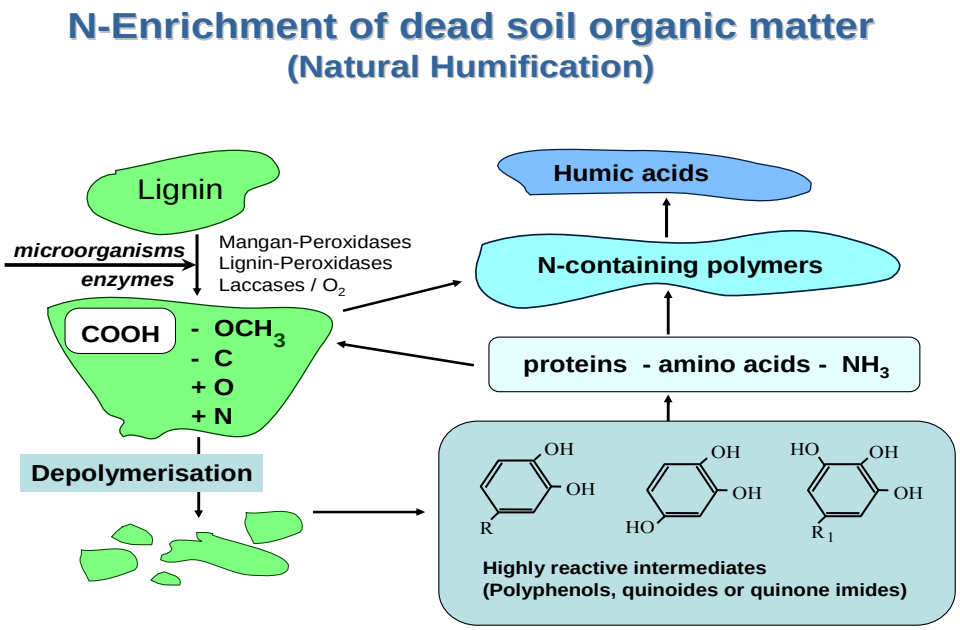


Figure 9. Scheme of the natural humification process [82].

3.4. Artificial Humification by Ammoxidation of Lignins

Modern day, high density agriculture operations, including tillage, irrigation, fertilization and multiple cropping, deplete organic matter in the soil, and most importantly, the humus component of soil organic matter. Organic matter is divided into two main categories, organic residues and stable soil humus. Stable soil humus, a small percentage of total soil organic matter, is the end product of organic matter decomposition when performed under anaerobic, or oxygen free, conditions, beneath the soil surface. The resulting organic structures can be hundreds of years old and are considered as slow renewable resource. Soil scientists tell us that stable soil humus categorized into three distinct fractions, 50 percent humans, 10 percent fulvic acids and 40 percent humic acid. Soil productivity is enhanced when these components are found in abundance as they are in naturally high organic soils. Humic and fulvic acids are the more ``soil active`` fractions of stable soil humus. These structures have the potential to influence a number of reactions in the soil, enhancing the soil's performance, including cation exchange capacity, soil structure stability, water retention, microorganism activity and the buffering capacity of the solution. Even a slight reduction in actual humus can dramatically reduce soil productivity, increasing the demands for fertilizers to simply maintain the same level of productivity. Nutrient uptake in plant roots is virtually impossible in the absence of soil humus. It is assumed (polyphenol theory) that humus formation proceeds via the formation of highly reactive quinoide intermediates (fig. 9).

Ammoxidation of lignins is a complex process due to the macromolecular structure and multi-functionality of lignin. Correspondingly, a multitude of reaction products can be obtained depending on process parameters and educts.

The percentage of free and etherified phenolic OH groups is decisive for reaction behavior. In the presence of free, unetherified phenolic OH groups, reactive quinone methides can be formed in alkaline medium which react further to ortho- or paraquinoide structures. A nucleophilic attack at the α-C atom is difficult because the formation of quinone methides leads to increased electron density at this site. As a result, the original phenyl propane structure remains unchanged [14-16]. Reactive quinone plays an important role in N-modification. Quinone imides can be formed in the presence of ammonia or amines, which can further react to N-rich polymers depending on reaction conditions. Another reaction pathway is the formation of bicarboxylic acids by oxidative ring cleavage and the formation of the corresponding ammonia salts, amines, and imines (Fig. 10). In contrast to non-

etherified phenolic groups, lignin structures with etherified phenolic OH groups cannot form quinone methides; this mainly because of the lower electron density at the α-C atom, which makes a nucleophilic substitution at this site easier. Etherified phenolic structures are transformed into aliphatic and benzoic amides or ammonia salts of carboxylic acids. Under strong reaction conditions, aromatic nitriles can be formed too. Also, methoxyquinone are released, which can react to form quinone imides and the corresponding nitrogen containing compounds (Fig. 11).

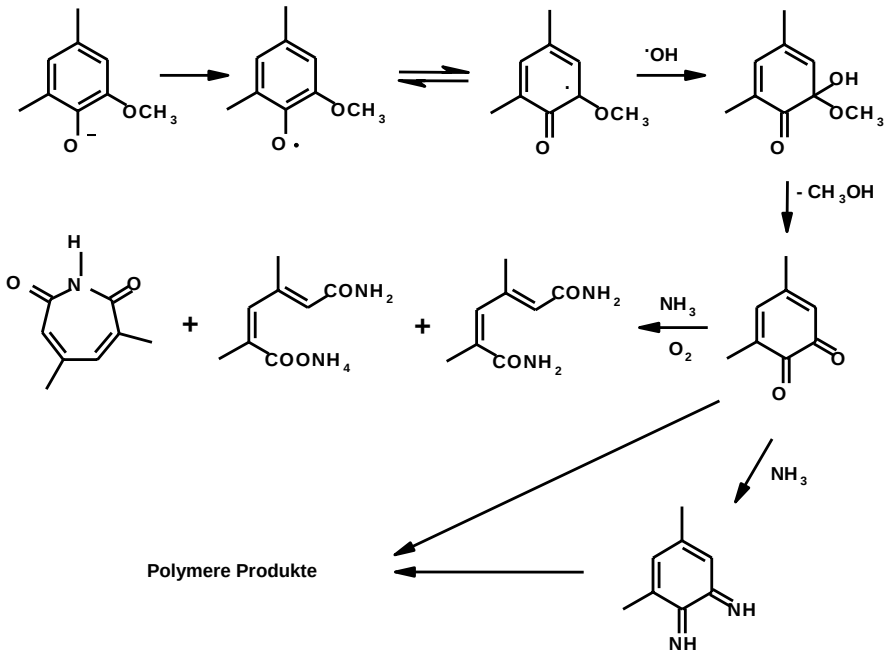


Figure 10. Oxidative ammonolysis of lignin structures containing free phenolic OH groups (Gierer) [14].

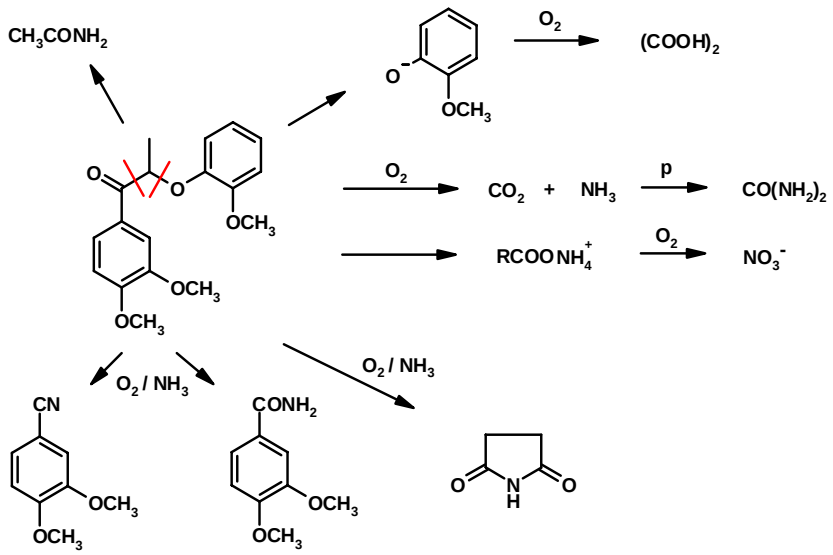


Figure 11. Oxidative ammonolysis of lignin structures containing etherified phenolic groups[14]

There is evidence from a couple of studies that the formation of natural humus precede via a step-wise degradation of the lignin macromolecule and the formation of highly reactive quinoide intermediates (fig. 12). The essential reactions that transform the lignin polymer, such as demethoxylation, demethylation, formation of quinones, oxidation of aliphatic side-chains, cleavage of aromatic ring system, and nitrogen enrichment, also occur naturally in soils [83].

Therefore, we studied not only the ammoxidation of technical lignins but also a couple such lignin-derived low-molecular phenolic compounds. Figure 12 illustrate the relationship between phenolic intermediates and the formation of humic acids [82]. By highly reactive quinoide intermediates the humic acids were proceeds formed.

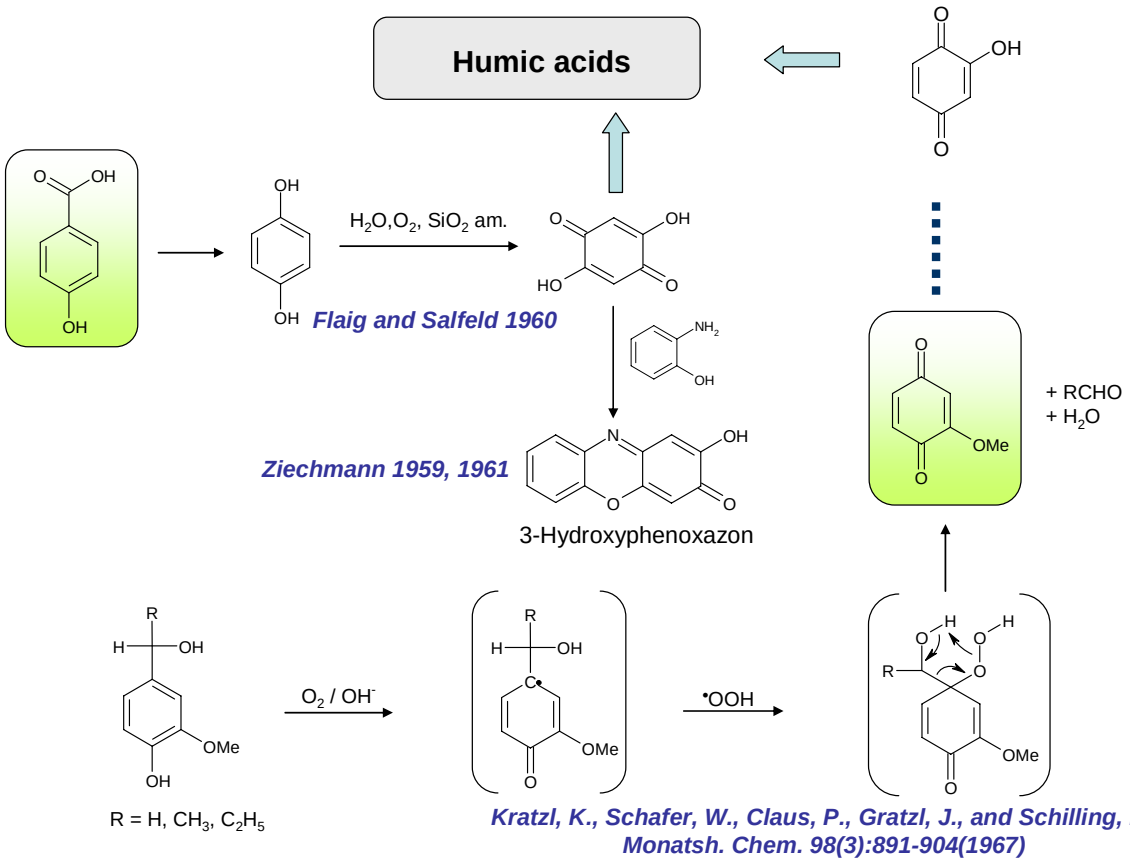


Figure 12. Relationship between phenolic intermediates and the formation of humic acids [82].

Comprehensive field studies on utilization of ammoxidized lignins and ligneous materials for soil rehabilitation revealed that especially in those countries which suffer seriously from soil erosion and unfavorable climatic conditions, this type of organic nitrogen fertilizer is of great

interest. N-lignin contains a high portion of organically bound nitrogen. This factor is important since mineralization of this fraction is usually much slower then the release of nitrogen from ammonia groups. Due to the low solubility, slow mineralization of the main portion of nitrogen and the polymeric character, N-lignins are not leached out by heavy rainfall. The resistance is against drought or frost by the physiologically active components in N-lignin. The mineralization process that converts N-modified lignin to different stable substance that is humus feeds the soil population of micro-organisms and other creatures, thus maintaining high and healthy levels of soil life. N-modified lignin is a colloidal substance, and increases the soil's cation exchange capacity, hence its ability to store nutrients by chelation as can clay particles; thus while these nutrient cations are accessible to plants, they are held in the soil safe from leaching away by rain or irrigation.

3.5. Artificial and Natural Humification in comparison

Ammoxidation of organic matter containing lignin structures can thus be described as accelerated natural humification; the processes that naturally take place in topsoil (starting from dead organic matter) are merely transferred into a special reactor, using ligneous raw or even waste materials from the pulping industry (technical lignin). Differences in the molecular structure of the two products may result from the different groups of the substances involved in their reaction cycles.

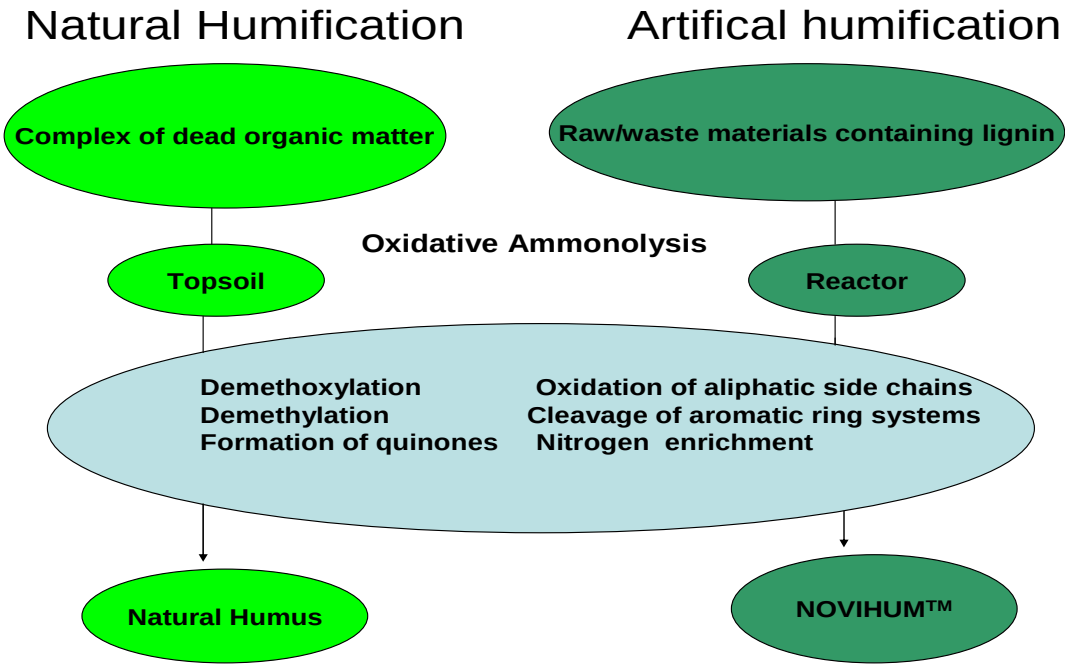


Figure 13. Oxidative ammonolysis as the main principle for natural and artificial humus formation [82]

Natural humification always affects the organic matter as a whole (e.g. lignin, cellulose, hemicellulose, protein, fats, sugars and resins). In contrast, lignite contains higher percentage of non-reactive condensed structures and less functional groups in consequence of the preceding coalification process [84].

On comparison with its natural equivalent, the novel artificial humus, registered under the trademark NOVIHUM™, showed similar elements contents, percentage of different nitrogen bonding forms, types and amounts of functional groups, as well as certain physical properties (Tab. 2).

Tabel: 2. Comparison between natural and novel artificial humus

Data sources: Katzur et al. (2002b)

Humus Type	Total Nitrogen (%)	Ammonia Nitrogen (% of total N)	Amide Nitrogen (% of total N)	S.o.b. Nitrogen[a] (% of total N)
NOVIHUM™	5.8 - 6	31.2 - 33	11.6 - 13	57.1 - 59
Natural humus	1 - 5	10 - 25	21 - 45	~ 50
	Total Carbon (%)	OCH3 Groups (%)	CEC ($mmol_c\ kg^{-1}$)	Molecular Weight ($g\ mol^{-1}$)
NOVIHUM™	65.8 - 68	2.9 - 3	547 - 650	$> 10^4$
Natural humus	41 - 62	0.9 – 1.8	1800 - 3000	$10^4 - 2 * 10^5$

[a] S.o.b. = strongly organically bound nitrogen

The results obtained for different soil physical and soil chemical conditions, as well as different plant species provide that NOVIHUM™ is able to stimulate plant growth and to supply nitrogen to the plants over a distinctly longer period of time than common fertilizers [85]. This is mostly due to the fact that NOVIHUM™ contains different nitrogen bonding forms deriving from oxidative ammonolysis.

Flaig and Söchtig (1973) [86] were the first to assess oxidative ammonolysis of lignins under artificial or forced humification with an eye to the distinct properties of the resulting products. They found that the nitrogen incorporated was hydrolysable and plant-available at different points in time. [87- 88] classified the nitrogen bonds into three types:

- Ammonia groups (short-term plant-available),
- Amide groups (mid-term plant-available),
- Strong organically bound nitrogen groups (long-term plant-available).

The time-differentiated mineralization of the three nitrogen bonding forms can be considered beneficial because:

- The total nitrogen content of the N-modified products can be more completely exploited than that of mineral fertilizers, which are an economic gain as such but will also lead to higher plant yield over several growth periods [16- 85- 89].
- Nutrient leaching into the groundwater is reduced; especially in sandy soils [85-89].The application of artificial humus is environmentally friendly.

The high percentage of stable humus fractions gives NOVIHUM^{TM} the status of a nutrient accumulator, which can be recharged on demand. Due to the multitude of functional groups and the high specific surface, the novel products has cationic exchange capacities of 547 –650 $mmol_c\ kg^{-1}$ in its dry matter, which is 30 to 50 % of the CEC values of soil organic matter (1800-3000 $mmol_c\ kg^{-1}$).

4. Materials and Methods

4.1. Materials and general techniques

The most of chemicals (Methoxybenzoquinone, Acetamide, Urea, Ammoinum oxalate and $^{15}NH_4OH$) were obtained from commercial suppliers (Sigma-Aldrich) and used without further purification. All solvents were purified and dried. Deionized water was used for all aqueous extractions and for all aqueous solutions. Yields refer to organic and aqueous phases after being completely dried. For removal of solvents a Büchi rotavapor was used. Solids were dried in a dessicator. Column chromatography was performed on silica gel G_{60} (40–63 μm). Melting points, determined on a kofler-type micro hot stage with Reichert-Biovar microscope, are uncorrected.

4.2. Wet-chemical analysis

Reactions were monitored by thin layer chromatography (TLC) on silica gel 60 plates (5 x 10 cm, 0.25 mm). Spots were detected under UV light at 254 nm and 366 nm as well as by staining with a solution of visualization reagent or by means of Dragendorff's reagent. The latter is a solution that is commonly used for detecting nitrogeneous compounds on which the reagent gives an orange colored precipitate .

- *Preparation of 5% $^{14}NH_4OH$ solution*

Nitrogen exists as two stable isotopes, ^{14}N (abundance 99.63 percent) and ^{15}N (abundance 0.37 percent). The isotope ^{13}N is not stable and has a life time 9.9 min. 5% $^{14}NH_4OH$ solution was prepared by adding 5 ml of 25% $^{14}NH_4OH$ to 20 ml of deionized water.

- *Preparation of 5% $^{15}NH_4OH$ solution*

0.8 ml of 6 N 100 % $^{15}NH_4OH$ solution was placed in a 100 ml volumetric flask and filled up to the mark with 5% aqueous $^{14}NH_4OH$ solution.

4.3. Instrumental analysis

4.3.1. GC/MS

Was performed using a GC 6890N / MSD 5973B bench-top instrument (Agilent Technologies). Separation of the compounds were achieved using a fused silica HP- 5ms

(30m, 0.25mm, 25μm), a helium column flow of 0.9 ml/min, an oven programme starting with 100°C (5 min), then 10°C/min to 280°C (20 min), and an auxiliary temperature programme starting at 280°C (14 min). Inlet was operated in split mode (25:1) at 280°C. Ionization was performed in EI mode at 70 eV, 230°C, and 1.5. 10^{-5} Torr. MSDCHEM Station (evaluation of chromatograms), NIST 2003 Mass Spectra Library.

4.3.2. Elemental analysis

Were performed at the microanalytical laboratory of the Institute of Physical Chemistry at the University of Vienna and are reported in percent atomic abundance.

4.3.3. *Ultraviolet-visible spectroscopy*

Ultraviolet-visible spectrophotometry (UV/ VIS) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

4.3.4. X-ray photoelectron spectroscopy *(XPS)*

Experiment was measured by using VG ESCALAB 220i XL with Mg kα- radiation (12 kV, 20 mA). The overview measurements were measured in sutible energy condition 50 eV and the signal spectra N 1s, C 1s and O 1s in 10 eV. The measurements were corrected by (1.3 ect.: 1. 8 eV) for C 1s for aromatic system C-H and the electron binding energy (E_B) = 284.8 eV. The solutions energy of spectrometers was 0. 8 eV (the kinetic energy value of Ag $3d_{5/2}$ – line for suitable energy was 10 eV). Individual spectra were measured by general program analysis for XPS UNIFIT 2008.

4.3.5. ^{15}N CPMAS NMR

Solid state cross-polarization magic angel spinning (CPMAS) spectroscopy was performed using a BRUKER AVANCE 400WB spectrometer (9.4 T) using CP/MAS probe with 7 mm ZrO_2 rotors. Resonance frequency, sample rotation frequency, and recycle delay time were 40.55 MHz, 5 kHz, and 0.5 s, respectively. ^{15}N chemical shifts are referred to neat liquid nitro methane d = 0 ppm and were determined using $^{15}NH_4$ $^{15}NO_3$ as external standard (PhD thesis of Luvuyo Tyhoda).

Contact time for cross-polarisation τ= 250μs
Spin-lattice relaxation time D1= 500ms

Rotation frequency νR= 4 kHz
Number of scans 200.00

4.3.6. Curiepoint pyrolysis GC/MS

Was performed using a Fischer Curiepoint pyrolyzer CPP-40 connected to an Agilent GC/MS system (HP 6890, HP 5973). Samples of 150 µg each were pyrolyzed at 600°C using Fecralloy^{TM} vessels. Separation was achieved by means of a HP-5 ms column.

4.4. Visible and Ultraviolet Spectroscopy of phenolic model compounds

Ultraviolet-visible spectroscopy (UV/ VIS) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound.
The Beer-Lambert law states that the absorbance of a solution is directly proportional to the solution's concentration. Thus UV/VIS spectroscopy can be used to determine the concentration of a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

Stock solutions of different phenols were prepared by dissolving 250 mg of the perticular compounds in 10 ml of methanol. Buffer solutions for adjusting the pH of the phenol solutions to 7, 8, 9, 10 and 11 were prepared according table 3.
Table: 3. Ingredients of the different buffer solutions.

Buffers solutions	Contents
Buffer pH 7	50 ml of 0.1 M KH_2PO_4 + 29.1 ml 0.1 M NaOH
Buffer pH 8	50 ml of 0.025 M $Na_2B_4O_7$*10 H_2O + 21 ml 0.1 M HCl
Buffer pH 9	50 ml of 0.025 M $Na_2B_4O_7$*10 H_2O + 4.6 ml 0.1 M HCl
Buffer pH 10	50 ml of 0.05 M $NaHCO_3$ + 10.7 ml 0.1 M NaOH
Buffer pH 11	50 ml of 0.05 M Na_2HPO_4 + 4.1 ml 0.1 M NaOH

After determing the maximum absorbance for the particular phenols 200 µ of the stock solution was dissolved in 1.8 ml of each buffer solution (pH 7, 8, 9, 10 and 11). Starting from adding the buffers, the adsorbance at $A_{\lambda max}$ was measured after 0, 5, 10, 30 and 60 min under continued stirring which was only stopped a few seconds before the measurement started.

4.5. Ammoxidation of Phenolic model compounds.

Table 4: Sample labels of the aqueous (aq.ph.) and organic phases (org.ph.) of ammoxidized phenolic model compounds (1g phenolic model compound, 20ml of 5% NH_4OH, 3h, 2bar O_2, 100°C)

Reactants (phenols)	**Sample labels**
Hydroquinone	A/^{14}N/aq.ph and A/^{14}N/org.ph
4-Methyl catechol	B/^{14}N/aq.ph and B/^{14}N/org.ph
2-Methoxy-4-methyl phenol	C/^{14}N/aq.ph and C/^{14}N/org.ph
Catechol	D/^{14}N/aq.ph and D/^{14}N/org.ph
Methoxyhydroquinone	E/^{14}N/aq.ph and E/^{14}N/org.ph
2-Methoxy phenol	F/^{14}N/aq.ph and F/^{14}N/org.ph

4.5.1. General Procedure of ammoxidation:

1 g of the corresponding phenolic model compound was dissolved in 20ml of 5% $^{14}NH_4OH$ and the solution was placed in a glass vessel inside a stainless steel autoclave. After sealing and pressurizing the autoclave with oxygen (quality 5.0, Linde Austria) up to 2 bar, the mixture was stirred at 100°C for three hours. The reaction mixture was then cooled down to room temperature, and two phases - an organic and an aqueous one -, were obtained by ethyl acetate extraction in the separation funnel. The organic phase was dried over Na_2SO_4, filtrated and evaporated.

Prior to TLC analysis, the dry “organic phase” was dissolved in ethyl acetate, and an eluent mixture consisting of 50% ethyl acetate and 50% of hexane was used.

The aqueous phase was dried in Petri dishes for two days at least. Prior to TLC analysis, a small quantity of the dry “aqueous phase” was dissolved in DMSO, and a DCM/methanol mixture (5:1 v/v) was used as an eluent.

GC/MS measurements of the organic phase were performed on 20 mg samples dissolved in 0.5 ml of ethyl acetate.

Curiepoint pyrolysis GC/MS was performed at 600°C on 200µg samples which were placed in a Fecralloy^{TM} vessel.

4. 5. 2. Derivatization for GC/MS

Due to the high polarity (-OH and –COOH groups), the oxidized aqueous phases of the oxidized or ammoxidized phenolic model compounds or lignins could neither be directly analysed with GC/MS nor separated by means of column chromatography. Amongst the different derivatization procedures acetylation, methylation, and silylation are obviously the most common ones. Hence, all of the three methods have been applied.

4.5.2.1. Silylation

Silylation by BSTFA is the most widely used derivatization technique. Nearly all functional groups which present a problem in gas chromatographic separation (hydroxyl, carboxylic acid and amine) can be derivatized by silylation reagents. It involves the replacement of an acidic hydrogen on the compound with a trialkylsilyl group, for example, -$SiMe_3$. The derivatives are generally less polar, more volatile and more thermally stable. 20 mg of aqueous phase was dissolved in 0.5 ml of EE and 0.1 ml of BSTFA was added. The mixture was heated to 70°C for 12hours.

4.5.2.2. Acetylation of the aqueous phases.

The term acetylation refers to the introducing of an acetyl group (resulting in an acetoxy group) into a compound which consists of one, active hydrogen atom at least. Acetic anhydride is commonly used as an acetylating agent. In the current study, the aqueous phases were acetylated under both, acidic and alkaline conditions.

4.5.2.2.1. Acetylation aqueous phase under acidic conditions.

Table 5: Sample labels of the acetylated aqueous phase of ammoxidized hydroquinone in acidic medium (0.25 g aqueous phase of ammoxidized hydroquinone).

Reactants	**Sample labels**
Aqueous phase of Ammoxidized hydroquinone	Acidic acytelated/A/^{14}N/aq.ph

In 100 ml round flask, the aqueous phases of ammoxidized hydroquinone was dissolved in 5 ml of a mixture consisting of equal volumes of acetic anhydride and sulphuric acid and stirred overnight at 40°C. Afterwards the reaction mixture was neutralized (pH= 7) by adding saturated aqueous $NaHCO_3$ solution in an ice bath. The reaction mixture was extracted three times with ethyl acetate and the combined organic phases were then washed with saturated solution of NaCl (brine). The organic phase was dried over $MgSO_4$, and then filtrated and rotated. For TLC analysis, the crude product was dissolved in EE. After the first run using Ethyl acetate 2:1 hexane as an eluent, the spots were further separated by using DCM 5:1 methanol as a second eluent.

4.5.1.2.2. Acetylation of the aqueous phases under alkaline conditions

Table 6: Sample labels of the acetylated aqueous phase of of ammoxidized phenolic model compounds in alkaline medium.

Reactants	**Sample labels**
hydroquinone	Alkaline acytelated/A/^{14}N/aq.ph
4-methyl catechol	Alkaline acytelated/B/^{14}N/aq.ph
catechol	Alkaline acytelated/D/^{14}N/aq.ph

In 100 ml round flask, 250 mg of the aqueous phases ammoxidized of selected phenolic model compounds were dissolved in 6 ml of a mixture consisting of equal volumes of acetic anhydride and pyridine and stirred overnight at 40°C. The reaction mixture was neutralized by adding saturated aqueous $NaHCO_3$ solution in an ice bath. The reaction mixture was extracted three times with ethyl acetate and the combined organic phases were then washed with saturated solution of NaCl (brine). The organic phase was dried over $MgSO_4$, and then filtrated and rotated. For TLC analysis, the crude product was dissolved in EE. After the first run using Ethyl acetate 2:1 hexane as an eluent, the spots were further separated by using DCM 5:1 methanol as a second eluent.

4.5.2. Column chromatographic conditions

4.5.2.1. Column chromatography separation for acetylated 4-methyl catechol

The TLC and GC/MS results revealed that acetylation under alkaline conditions gave fewer compounds than under acidic conditions. Hence, column chromatographic separation was performed on the reaction mixture which was obtained under alkaline conditions.

0.14 g of the product which was obtained from the aqueous phase of ammoxidized 4-methyl catechol by acetylation under alkaline conditions was completely dissolved in EE. In the column chromatography, first and second separation was obtained by using EE 4: 1 hexane as eluent. Afterword the third separation and fourth one were obtained by using a mixture of DCM 5:1 Methanol and characterized... Finally, Methanol was used and could indicate the fifth separation. TLC and GC/MS were performed for all different compounds as well.

4.5.2.2. Column chromatography separation for acetylated catechol

0.94 mg of the product which was obtained from the aqueous phase of ammoxidized catechol by acetylation under alkaline conditions was completely dissolved in EE. Column chromatography yielded five separated compounds. TLC and GC/MS were performed for all different compounds as well.

4.5.4. Ammoxidation of Phenolic model compounds using ^{15}N labelled NH_4OH.

Table 7: Sample labels of the aqueous and organic phases of ammoxidized phenolic model compounds (20ml of 5% $^{15}NH_4OH$, 1g of phenolic model compound, 3h reaction time, 2bar O_2, 100°C)

Reactants	**Sample labels**
Hydroquinone	A/^{15}N/aq.ph and A/^{15}N/org.ph
4-Methyl catechol	B/^{15}N/aq.ph and B/^{15}N/org.ph
2-Methoxy-4-methyl Phenol	C/^{15}N/aq.ph and C/^{15}N/org.ph
Catechol	D/^{15}N/aq.ph and D/^{15}N/org.ph
Methoxyhydroquinone	E/^{15}N/aq.ph and E/^{15}N/org.ph
2-Methoxy phenol	F/^{15}N/aq.ph and F/^{15}N/org.ph
Methoxybenzoquinone	G/^{15}N/aq.ph and G/^{15}N/org.ph

The reaction was carried out under the same conditions as described in chapter 4.4.

4.6. Oxidation of Phenolic model compounds.

Table 8: Sample labels of the aqueous and organic phases of oxidized phenolic model compounds (20 ml of 5% NaOH, 1g of phenolic model compounds if not otherwise indicated, 3h reaction time, 2bar O_2, 100°C);

Reactants	Sample labels
Hydroquinone	A/ NaOH /aq.ph and A/ NaOH /org.ph
4-Methyl catechol	B/ NaOH /aq.ph and B/ NaOH /org.ph
2-Methoxy-4-methyl Phenol	C/ NaOH /aq.ph and C/ NaOH /org.ph
Catechol	D/ NaOH /aq.ph and D/ NaOH /org.ph
Methoxyhydroquinone	E/ NaOH /aq.ph and E/ NaOH /org.ph
2-Methoxy phenol	F/ NaOH /aq.ph and F/ NaOH /org.ph
50 mg of Apocynol	Apocynol/ NaOH /aq.ph and org. ph/100°C
25 mg of Apocynol	Apocynol/ NaOH /aq.ph and org. ph/25°C

The reaction was carried out under the same conditions as described in chapter 4.4. Oxidation of Apocynol was performed at two different temperatures (100°C and 25°C).

Methylation of oxidized aqueous phases compounds.

Methylation is another derivatization procedure for replacing active protons of hydroxy, carboxyl, amine or amide groups by methyl groups. This is commonly performed using electrophilic methyl sources such as iodo methane; dimethyl sulphate and dimethyl carbonate which easily undergo SN^2 type nuclophilic substitution reactions.

Table 9: Sample labels of the methylated aqueous phases of oxidized phenolic model compounds.

Reactants	Sample labels
0,1g of Hydroquinone aqueous phase + 5 ml DMSO + 1 ml MeI + 0,2g NaOH.	Methylated/A/ NaOH /aq.ph
0,05g of 4-Methyl catechol aqueous phase + 5 ml DMSO + 0, 5 ml MeI + 0,1g NaOH.	Methylated/B/ NaOH /aq.ph
0,025g of 2-Methoxy-4-methylphenol aqueous phase + 5 ml DMSO + 0, 25 ml MeI + 0,05g NaOH.	Methylated/C/ NaOH /aq.ph
0,025g of Catechol aqueous phase + 5 ml DMSO + 0, 25 ml MeI + 0,05g NaOH.	Methylated/D/ NaOH /aq.ph
0,05g of Methoxyhydroquinone aqueous phase + 5 ml DMSO + 0, 5 ml MeI + 0, 1 g NaOH.	Methylated/E/ NaOH /aq.ph
0,02g of 2-Methoxy phenol aqueous phase + 5 ml	Methylated/F/ NaOH /aq.ph

DMSO + 0, 25 ml MeI + 0, 05 g NaOH.	
8 mg of Apocynol aqueous phase + 5 ml DMSO + 0, 1 ml MeI + 0, 02 g NaOH.	Methylated/Apocynol/NaOH/aq.ph /100°C
5 mg of Apocynol aqueous phase 25°C + 5 ml DMSO + 0, 1 ml MeI + 0, 02 g NaOH.	Methylated/Apocynol/NaOH/aq.ph/25°C

Soild sodium hydroxide (amounts *cf*. tab. 8) was placed in a dry 100 ml round bottom flask and a solution of the particular aqueous phase of the ammoxidized phenolic model compound in 5 ml of DMSO was added. Methyl iodide was added dropwise under stirring and cooling with an external ice bath over a time period of 8 min. After adding 10ml of each, chloroform and water the organic the mixture was transferred into a separation funnel were mixture was exttracted several times with chloroform. The combined organic phases were washed 4 times with deionized water, dried over $MgSO_4$, and then filtrated and rotated.

4.7. Ammoxidation of 2,5-Dihydroxy-1,4-benzoquinone with 5% aqueous NH_4OH and ^{15}N-labelled 5% aqueous NH_4OH at different temperature and pressure.

Table 10: Sample labels of the aqueous and organic phases of ammoxidized 2,5-dihydroxy-1,4-benzoquinone (1g was dissolved in 20 ml of 5% $^{14}NH_4OH$ and 5% $^{15}NH_4OH$, 3h, 2bar O_2, 100°C; 25°C and ambient pressure)

Reactants / conditions	**Sample labels**
$^{14}NH_4OH$ / 100°C	H/^{14}N/aq.ph and H/^{14}N/org. ph
$^{15}NH_4OH$ / 100°C	H/^{15}N/aq.ph/100°C and H/^{15}N/org.ph/ 100°C
$^{15}NH_4OH$ / 25°C	H/^{15}N/aq.ph/25°C and H/^{15}N/org.ph/25°C
$^{15}NH_4OH$ / 25°C and ambient pressure	H/^{15}N/aq.ph/ambient pressure and 25°C; H/^{15}N/org.ph/ambient pressure and 25°C

1 g of 2,5-Dihydroxy-1, 4-benzoquinone was dissolved in 20 ml of a 5% aqueous NH_4OH solution which was enriched with ^{15}N-labelled $^{15}NH_4OH$ as described in chaper 4.4. The reaction vessel was pressurized with 2bar of O_2 and the mixture was stirred at 100°C for three hours. After cooling down the reaction mixture was extracted 4 times with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtrated and rotated. The remaining aqueous phases were air-dried in a hood and further dried in a desiccator over P_2O_5. A small amount of a violett solid which precipitated during the evaporation at the wall of the round

bottom flask (experiment 3 hours, 2 bar O_2 and 100C° only) was separated (for labelling cf. next chapter) and subjected to further studies.

4.7.1. Methylation of the aqueous and insoluble organic phase of ammoxidized 2,5-dihydroxy-1,4-benzoquinone.

Table 11: Sample labels of the methylated fractions of ammoxidized 2,5-dihydroxy-1,4-benzoquinone

Reactants	Sample labels
0.1 g of aqueous phase + 5 ml DMSO + 0.2 g NaOH + 0.1 ml MeI	Methylated/H/^{14}N/aq. ph
5 mg of violet organic phase + 5 ml DMSO + 0.01 g NaOH + 0.05 ml MeI	Methylated/H/^{14}N/violet org. ph

Methylation was performed as described in chapter 4.6.1.

4.7.2. Acetylation of the aqueous phase of ammoxidized 2,5-dihydroxy-1,4-benzoquinone under alkaline conditions

Table 12: Sample labels of the acetylated aqueous phase of ammoxidized 2,5-dihydroxy-1,4-benzoquinone in alkaline medium.

Reactants	Sample labels
0, 1 g of Ammoxidized hydroquinone aqueous phase + 5 ml of acetic anhydride + 5 ml of pyridine.	Alkaline acytelated/H/^{14}N/aq.ph

Acetylation was performed as described in chapter 4.4.1.2.2.

4.8. Oxidation of 2,5-Dihydroxy-1,4-benzoquinone.

Table 13: Sample labels of the aqueous and organic phases of oxidized 2,5-dihydroxy-1,4-benzoquinone (1g was dissolved in 20ml of 5% NaOH, 2bar O_2, 3h at 100°C and 25°C, respectively).

Reactants / conditions	Sample labels
NaOH/100°C	H/ NaOH /aq.ph/100°C and H/ NaOH /org. ph/100°C
NaOH/25°C	H/ NaOH /aq.ph/25°C and H/ NaOH /org. ph/25°C

Oxidation was performed as described in chapter 4.6. (100°C and 25°C).

4.9. Ammoxidation vs. oxidation of methoxyhydroquinone.

Methoxy hydroquinone was oxidized and ammoxidized under identical conditions except that ammonia hydroxide was used instead of sodium hydroxide in the case of ammoxidation. The reaction was carried out by dissolving 1g of methoxy hydroquinone in 20 ml of 5% aqueous ammonia hydroxide solution (ammoxidation) or 20 ml of 10^{-3} M aqueous sodium hydroxide solution (oxidation). The reaction vessel was pressurized with 2bar of O_2 and the mixture was stirred at 100°C for three hours. After cooling down the reaction mixture was extracted 4 times with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtrated and evaporated. The remaining aqueous phases were air-dried in a hood and further dried in a desiccator over P_2O_5. The yields of the organic and aqueous phase were detemined. GC/MS was performed for the two phases as well.

4.9.1. Methylation of ammoxidized methoxy hydroquinone (2 h, 2 bar O_2 and 100C°).

Methylation was performed as described in chapter 4.7.1.

4.9.2. Acetylation of ammoxidized methoxy hydroquinone (2 h, 2 bar O_2 and 100C°).

Acetylation was performed as described under alkaline conditions in chapter 4.4.1.2.2.

4.9.3. Column chromatographic separation of acetylated ammoxidized methoxyhydroquinone.

0.1 g of Acetylated ammoxidized Methoxy hydroquinone was complete dissolved in EE. A glas column (diameter / length 50 cm) was filled with 10 g of silica gel. The gel was covered with a 2mm thick layer of quertz sand. Separation of the acetylated reaction mixture was achieved by using ethyl acetate 2: 1 hexane and Dichloromethane5:1 Methanol as eluents.

Table 14: Sample labels of the column chromatographic seperation of acetylated ammoxidized methoxyhydroquinone.

Eluents	**Fraction 1**	**Fraction 2**	**Fraction 3**	**Fraction 4**
EE 2: 1 hexane	Fraction1/acetylated ammoxidized methoxyhydroquinone	Fraction2/acetylated ammoxidized methoxyhydroquinone		
DCM 5:1 MeOH			Fraction3/acetylated ammoxidized methoxyhydroquinone	Fraction4/acetylated ammoxidized methoxyhydroquine

4.10. Ammoxidation of technical lignins.

4.10.1. Ammoxidation of Indulin AT ™ (Kraft lignin)

1 g of Indulin AT was dissolved in 20 ml of 5 %aqueous NH_4OH and the solution was placed in an autoclave. The reaction vessel was then pressurized with 2bar of O_2 and the mixture was stirred at 100°C for three hours. The reaction mixture was air-dried in **a** petri dish for two days and further dried in a desiccator over P_2O_5.

4.10.2. Amoxidation of Indulin AT™ (Kraft lignin) with ^{15}N-labelled 5% aqueous NH_4OH.

1 g of Indulin AT was dissolved in 20 ml of a 5% aqueous NH_4OH solution which was enriched with ^{15}N-enriched NH_4OH as described in chaper 4.5. Ammoxidation and work-up was carried out as described in 4.10.1.

4.10.2.1. Reduction reactions on Ammoxidized indulin AT™.

The idea of the reduction reactions were: From the XPS and the CPMAS NMR results there is some evidence that most of the nitrogen seems to be bound in amide-type bonds (big resonance signal at -260 to -280 ppm). If this broad peak results from amides the peak should be shifted or even disappear after reducing the amides. Two common reduction reactions were employed a) reduction with Zn/HCl and b) reduction with sodium hypobromide.

4.10.2.1.1. Reduction by Zn/HCl

In a three-necked flask a mixture of 20 g Zinc granules, 0.9 g of ammoxidized Indulin AT and 150 ml of deionized water were refluxed for 15 minutes. 65 ml of 37 % HCl were added dropwise and the reaction mixture was stirred overnight. After cooling the mixture was filtratedand neutralised with 360 ml of 1 M aqueous NaOH solution (white PPT contained). Organic phase was extracted several times with alltogether 300 ml of diethyl ether, and the combined ether extracts were dried over KOH granules. Evaporation gave 0, 07 g of a yellow solid compound (stabilizer). The brownish filter residue was washed several times with 5% HCl and subsequently with water in order to remove $ZnCl_2$ / HCl until the washings were free of chlorine. Yield of the dried filter residue was 63 g.

4.10.2.1.2. Reduction by sodium hypobromide

In 1000 ml round flask, 20 g of NaOH was dissolved in 150 ml distillation water and stirred in ice bath. 0, 52 ml of bromine was dropped, and then 0.5 g of Ammoxidized indulin. The ice bath was removed and the reaction mixture stirred for 30 min at room temperature. The reaction mixture was heated to 60°C and stirred for 25 min in oil bath. For nitrogen passing through the system, the reaction mixture was refluxed 104°C for 30 min. cooling in room temperature "brownish solution obtained". 450 ml of 37 % HCl was added "neutralization" till pH 7, the colour turned into dark yellow and white ppt was contaminated. Filtration (was very difficult) and then washing by water till no chlorine "tested by silver nitrate".**The yield (brown dust) = 50 mg.** N^{15}- NMR solid state**,** Peaks of amide and Urea were disappeared. May be Urea was reduced into ammonia and some gases. Amides were reduced into amine compounds. To confirm this result we have reduced Urea and amide.

4.10.2.1.3. Reduction of Urea by Sodium hypobromide

1 g of urea was dissolved in 83 ml of aqueous NaOBr dropwise under stirring and cooling in a 100 ml round bottom flask. The ice bath was then removed and the reaction mixture was stirred at room temperature for 25 min and at 60C° for another 30 min. The reaction mixture was finally refluxed for 30 min. After cooling, the reaction mixture was neutralized with 1M HCl, and then rotated. The yield = 18, 79 g (white crystals). The complet yield was dissolved in 40 ml of ethanol. Afterword the solution was filtrated and rotated. The yield = 0, 28 g.

4.10.2.1.4. Reduction of Acetamide by Sodium hypobromide

1 g of acetamide was dissolved in 83 ml of aqueous NaOBr dropwise under stirring and cooling in a 100 ml round bottom flask. The ice bath was then removed and the reaction mixture was stirred at room temperature for 25 min and at 60C° for another 30 min. The reaction mixture was finally refluxed for 30 min. After cooling, the reaction mixture was neutralized with 1M HCl, and then rotated. The yield = 26 g (white crystals). The complet yield was dissolved in 40 ml of ethanol. Afterword the solution was filtrated and rotated. The yield = 0, 84 g.

4.10.3. Amoxidation of Indulin AT with ^{15}N-labelled 5% aqueous NH_4OH and sodium hydroxid.

1 g of Indulin AT and 0.8 g sodium hydroxide were dissolved in 20 ml of 5 % aqueous ammonia hydroxide which was enriched with ^{15}N as described in chapter 4.5. After

transferring the mixture into an autoclave the reaction vessel was pressurized at 2 bar oxygen and the mixture was stirred at 100°C for three hours. After cooling the reaction mixture was air-dried in a petri dish and further dried in a desiccator over P_2O_5. Yield was 2 g. N^{15}- NMR spectroscopy: 100 mg of ammoxidized Indulin AT was dissolved in 5% NaOD (not completely soluble) and filtrated prior to the measurement.

4.11. Ammoxidation of lignite with 5% aqueous NH_4OH.

1 g of Lignite was dissolved in 20 ml of 5 %aqueous NH_4OH and the solution was placed in an autoclave. The reaction vessel was then pressurized with 2bar of O_2 and the mixture was stirred at 100°C for three hours. The reaction mixture was air-dried in **a** petri dish for two days and further dried in a desiccator over P_2O_5. The yield was 1 g.

4.12. Elemental Analysis: Carbon, Hydrogen and Nitrogen.

The composition of a compound is often expressed in terms of the weight percent of each element in the compound. Elemental analysis is an analytical technique that enables the determination of the amounts of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). The elemental analysis of a compound is particularly useful in determining the empirical formula of the compound. Different samples for (CHN) analysis were performed by burning the ammoxidized samples. The Ammoxidized aqueous phases were typically wrapped in a tin capsule and inserted into a furnace held at 1200^{o}C.

5. Results and Discussion

5.1. Ultraviolet-Visible Spectroscopy of phenols.

In the present study a couple of different simple phenoles and benzoquinones were used as model compounds to shed more light onto the reaction behavior and the pathways of nitrogen incorporation of technical lignins upon ammonoxidation.

As the formation of phenol anion radicals is supposed to be one of the key initial steps for subsequent demethoxylation, formation of quinoids and quinone imins, cleavage of aliphatic side chains and even cleavage of aromatic rings, the reactivity of the different phenolic and quinoide model compounds was studied at different pH values. For that purpose, the adsorption maxima of all model compounds were determined at pH 7, 8, 9, 10, and 11. After that, oxygen was introduced by vigorously stirring the solutions and the shift of the adsorption maxima and the increase of the adsorbance was measured.

5.1.1. Methoxyhydroquinoine

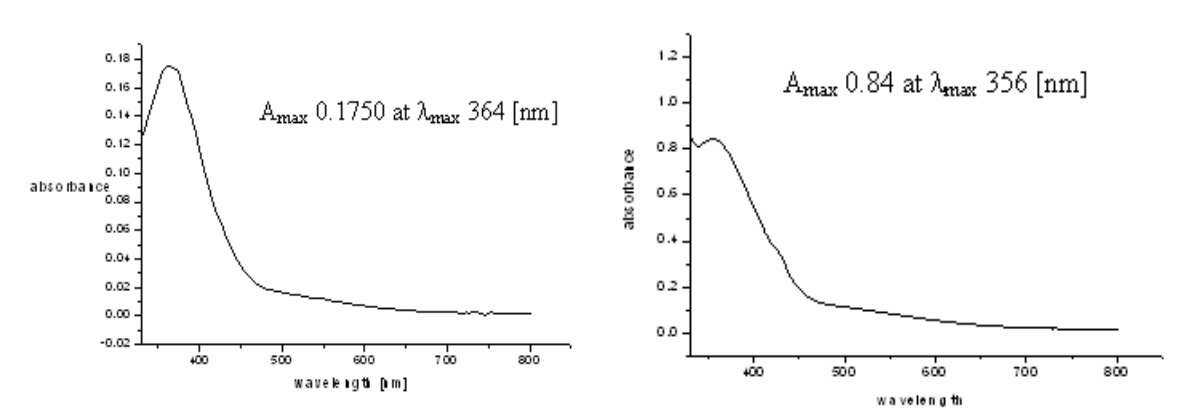
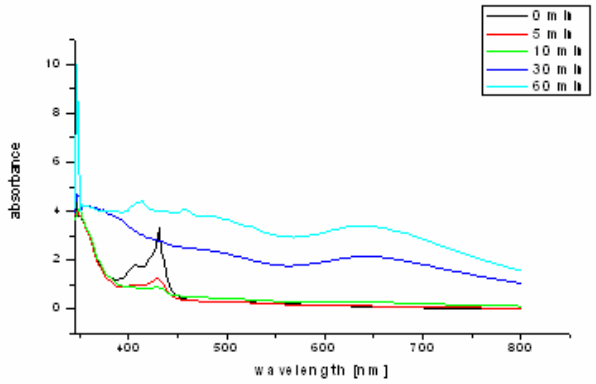
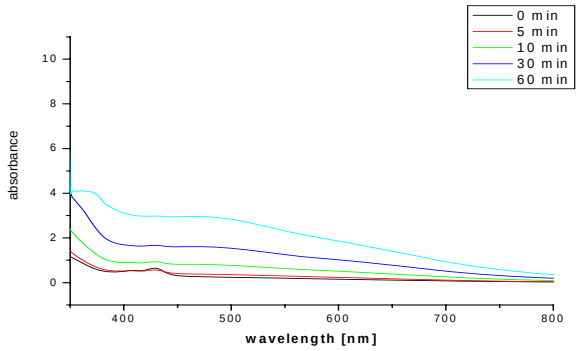


Figure14. Spectra of methoxyhydroquinone in water and buffer Solution pH 8 from left to right.



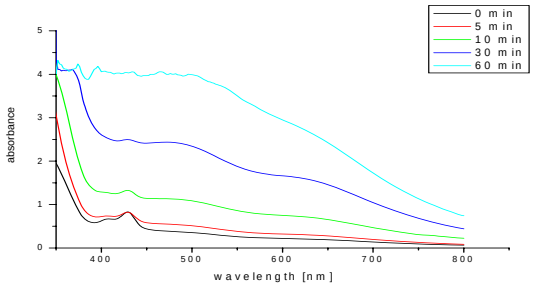
time	λ_{max} [nm]	A_{max}
0 min	432	3.30
5 min	432	1.21
10 min	432	0.87
30 min	432	3.78
60 min	458	4.07

Figure 15. Spectra of methoxyhydroquinone in buffer Solution pH 7 at different times (0, 5, 10, 30 and 60min) with data table.

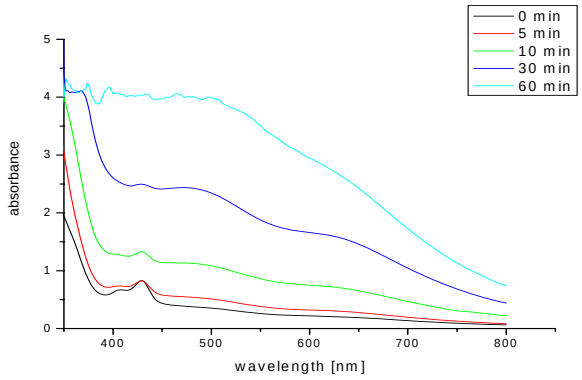


time	λ_{max} [nm]	A_{max}
0 min	428	0.54
5 min	428	0.55
10 min	428	0.93
30 min	428	1.66
60 min	428	2.97

Figure 16. Spectra of methoxyhydroquinone in buffer pH 9 solution at different times (0, 5, 10, 30 and 60 min) with data table.

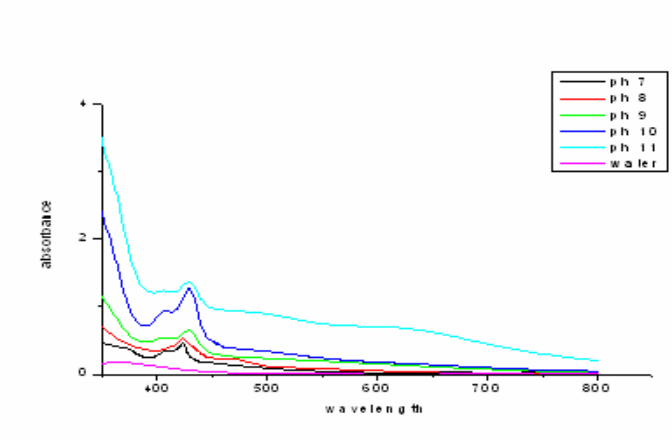


time	λ_{max} [nm]	A_{max}
0 min	430	0.82
5 min	430	0.84
10 min	428	1.68
30 min	424	2.66
60 min	426	4.16



time	λ_{max} [nm]	A_{max}
0 min	430	0.82
5 min	428	0.82
10 min	428	1.32
30 min	428	2.49
60 min	434	4.05

Figure 17. Spectra of methoxyhydroquinone in buffer solution pH 10 and pH 11at different Times (0, 5, 10, 30 and 60 min) with tables respectively.



pH	λ_{max} [nm]	A_{max}
water	364	0.17
pH 7	432	0.61
pH 8	354	0.63
pH 9	428	0.75
pH 10	430	1.26
pH 11	430	1.36

Figure 18. Spectra of methoxyhydroquinone in different buffers solutions pH 7, 8, 9, 10, 11 and water with table of data.

5.1.2. 2,5-Dihydroxy-1,4-benzoquinone

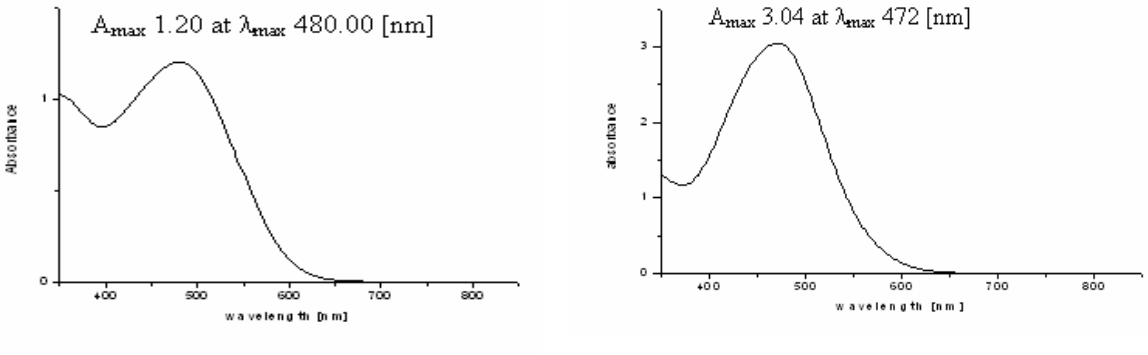
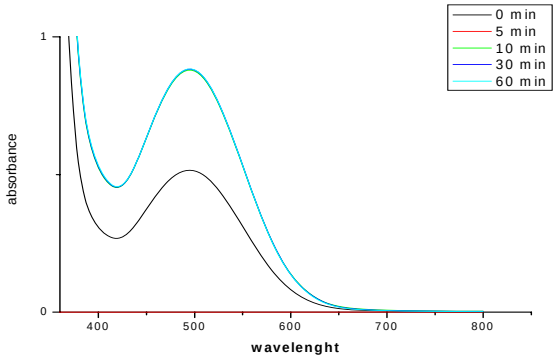
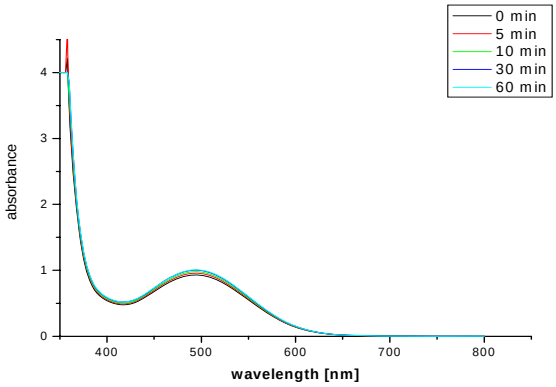


Figure 19. Spectra of 2,5-dihydroxy-1,4-benzoquinone in water and buffer solution pH 8 from left to right.

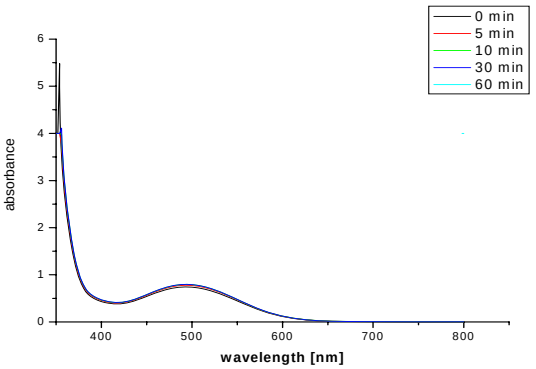


time	λ_{max} [nm]	A_{max}
0 min	494	0.51
5 min	494	0.88
10 min	494	0.88
30 min	428	0.88
60 min	434	0.88

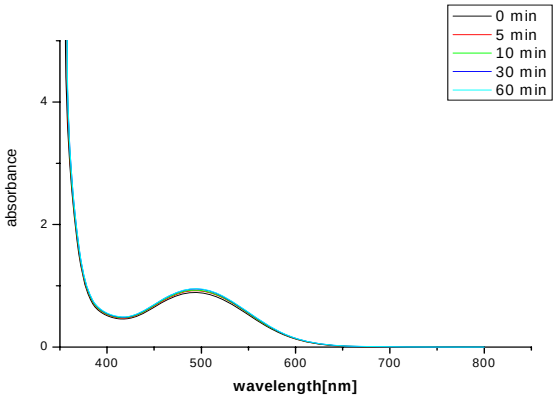
Figure 20. Spectra of 2,5-dihydroxy-1,4-benzoquinone in buffer Solution pH 7 at different times (0, 5, 10, 30 and 60 min) with table of data.



time	λ_{max} [nm]	A_{max}
0 min	494	0.93
5 min	494	0.95
10 min	494	0.97
30 min	494	1.00
60 min	494	1.02

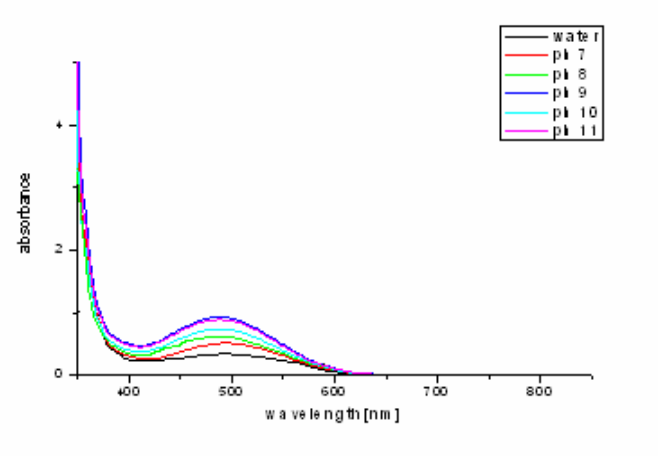


time	λ_{max} [nm]	A_{max}
0 min	494	0.74
5 min	494	0.77
10 min	494	0.79
30 min	494	0.79
60 min	494	0.79



time	λ_{max} [nm]	A_{max}
0 min	494	0.89
5 min	494	0.92
10 min	494	0.93
30 min	494	0.94
60 min	494	0.95

Figure 21. Spectra of 2,5-dihydroxy-1,4-benzoquinone in buffer Solution pH 9, pH 10 and pH 11 at different times (0, 5, 10, 30 and 60 min) with data tables respectively.



pH	λ_{max} [nm]	A_{max}
Water	480	0.35
pH 7	494	0.51
pH 8	472	0.65
pH 9	488	0.93
pH10	488	0.74
pH 11	488	0.89

Figure 22. Spectra of 2,5-dihydroxy-1,4-benzoquinone in in different buffers solutions pH 7, 8, 9, 10, 11 and water with data table.

5.1.3. 4-Methylcatechol

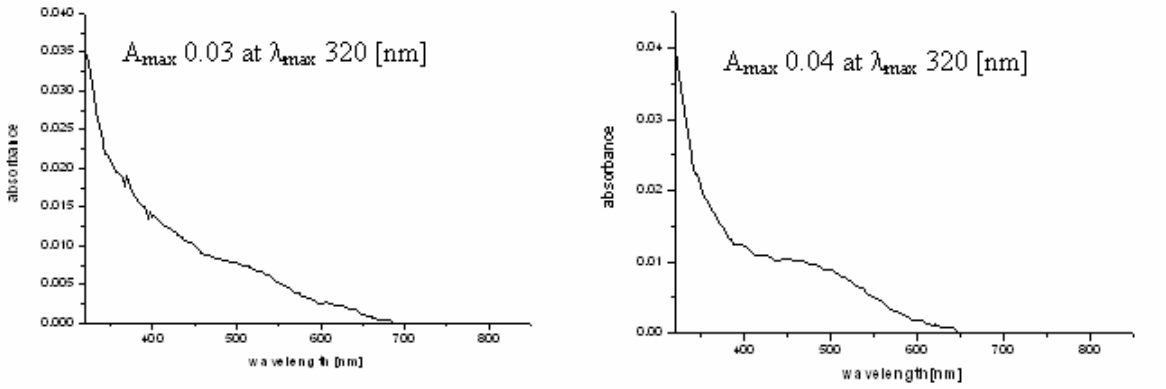
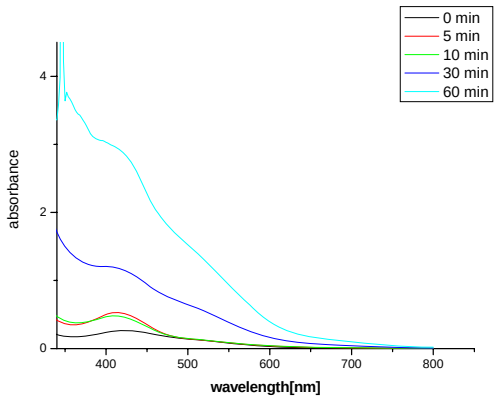
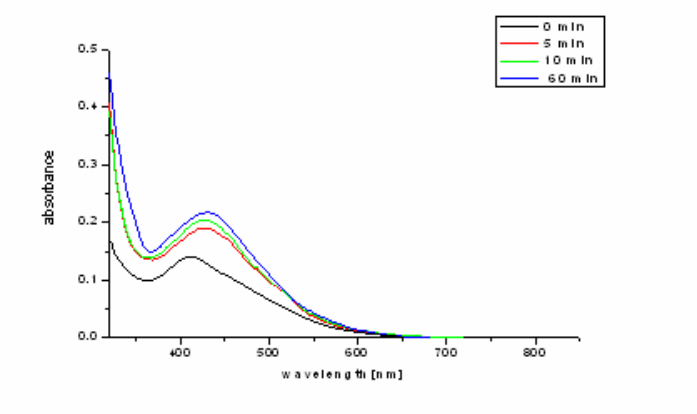


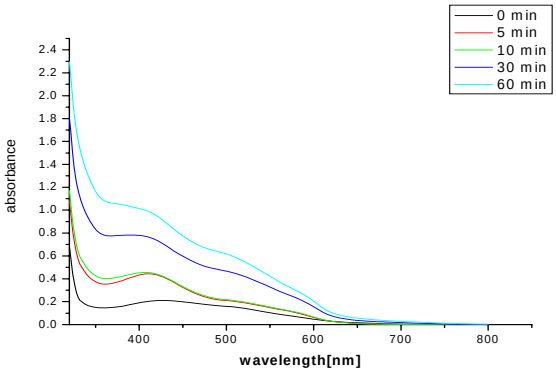
Figure 32. Spectra of 4-methylcatechol in water and buffer Solution pH 8 from left to right.



time	λ_{max} [nm]	A_{max}
0 min	422	0.26
5 min	412	0.53
10 min	412	0.48
30 min	412	1.18
60 min	412	2.95

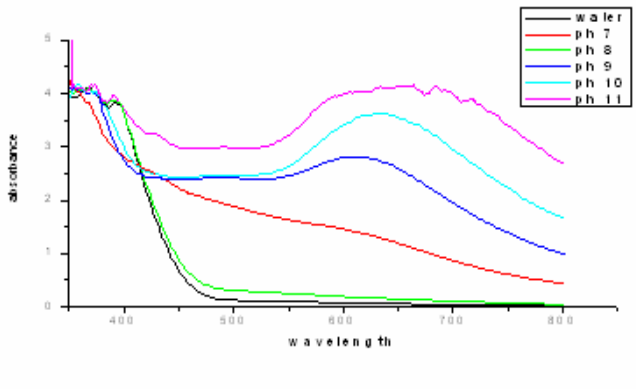


time	λ_{max} [nm]	A_{max}
0 min	422	0.12
5 min	422	0.18
10 min	422	0.20
60 min	422	0.22



time	λ_{max} [nm]	A_{max}
0 min	426	0.21
5 min	410	0.44
10 min	410	0.46
30 min	390	0.78
60 min	320	2.29

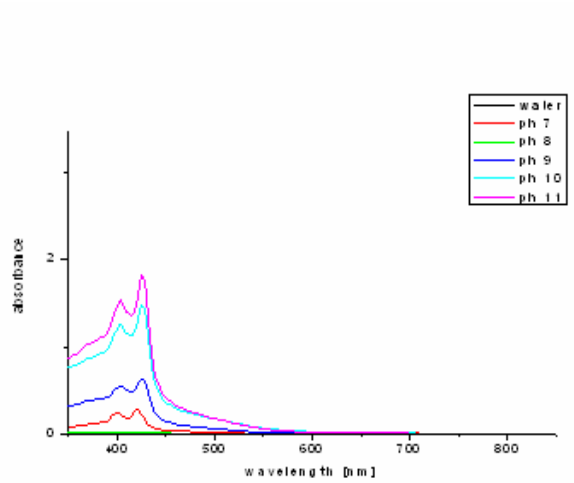
Figure 24. Spectra of 4-methylcatechol in buffers Solution pH 7, pH 9 and pH 10 measuring at different Times (0, 5, 10, 30 and 60 min) with tables of data respectively.



pH	λ_{max} [nm]	A_{max}
Water	386	0.111
pH 7	636	1.98
pH 8	636	0.161
pH 9	636	2.58
pH 10	614	3.62
pH 11	632	4.12

Figure 25. Spectra of 4-methylcatechol in different buffers solution pH 7, 8, 9, 10, 11 and water with table of data.

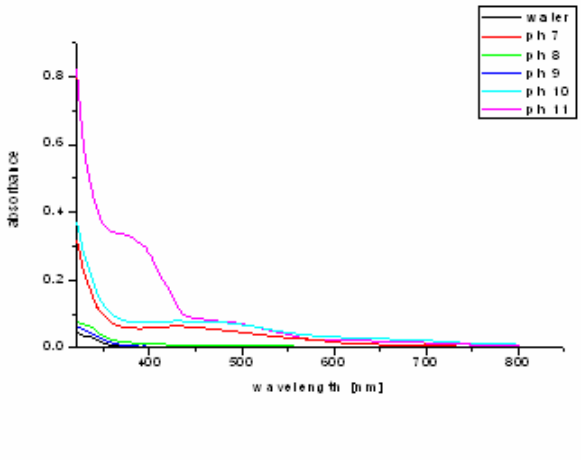
5.1.4. Hydroquinone



pH	λ_{max} [nm]	A_{max}
Water	428	0.005
pH 7	428	0.31
pH 8	428	0.01
pH 9	428	0.56
pH10	428	1.89
pH 11	428	1.91

Figure 26. Spectra of hydroquinone in different buffers solution pH 7, 8, 9, 10, 11 and water with table of data.

5.1.5. Catechol



pH	λ_{max} [nm]	A_{max}
Water	----------	----------
pH 7	394	0.91
pH 8	----------	---------
pH 9	----------	---------
pH10	394	1.00
pH 11	394	1.27

Figure 27. Spectra of catechol in different buffers solution pH 7, 8, 9, 10, 11 and water with table of data.

From the Ultraviolet-visible spectroscopy all phenols showed increasing absorbance at increasing time and pH. Methoxyhydroquinone was the most reactive one; it has the highest absorbance value. Catechol was less reactive and gave low absorbance value. Genarly quinones were reactive than other phenols. At pH 11 for all phenols were the highest absorbance and reactivity.

5.2. Ammoxidation of phenols and lignins.

5.2.1. Introduction

Oxidative ammonolysis is a complex process due to the macromolecular structure and multi-functionality of lignin. Correspondingly, a multitude of reaction products can be obtained depending on process parameters and educts. **Most** Lignins and Phenols are soluble in 5% aqueous ammonium hydroxide solution at room temperature mainly due to the formation of phenolate ions. Only a few strongly condensed lignins such as Kraft lignin Indulin AT showed certain resistancy upon dissolution. However, all materials were completely soluble at longer stirring.

Almost all ammoxidation reaction were carried out at 100°C and 2bar oxygen, using a solution of 1g of the particular lignin or phenolic model compound in 20ml of 5% aqueous NH_4OH solution and a reaction time of three hours.Comprehensive studies of lignin ammoxidation have shown that that the kinetics of lignin solublization follow a peseudo-first order reaction law during the whole reaction period. In ammoxidation reaction, it is possible that radical reactions appreciably contribute to lignin and phenols oxidation, while nitrogen incorporation should mostly occur via nuclophilic reactions. Ammonia as a nucleophile could attack carbonyl groups or quinoide structures with possible substitution of methoxyl groups by oxygen.

As radical reactions requires usually higher activation energies compared to nuclophilic reactions, ammoxidation under moderate reaction conditions (100°C, 2bar oxygen) should mainly give nucleophilic substitution rather then radical reactions.

Amongst the many different reaction sites the irregular polymer lignin has, the percentages of free phenolic and etherified groups play an important role regarding the type and distribution of reaction products and nitrogen binding forms.

In case of the free phenolic groups it is assumed that the basic step in ammoxidation is the formation of phenolic oxygen anionic radicals which are formed under alkaline conditions. The radical is supposed to become stabilized by formation of quinone methide structures which exhibit different electrophilic reaction centers.

The introduction of nitrogen in organic linkages is only occurring when both, oxygen and ammonia are present. Nitrogen incorporation into lignin and phenols occurs predominantly via the formation of quinone methids, O-demethylation and oxidative cleavage of aromatic rings.

The objective of the present work was to study the structural changes in lignins and phenolic model compounds caused by ammoxidation under comparatively mild reaction conditions. Ammoxidized compounds have been characterized by different analytical methods. It was established that nitrogen is present partly as ammonia salts, but it is mainly incorporated in the form of amides, aromatic nitriles, amines and urea.

5.2.2. GC/MS results

All crude reaction products from the ammoxidation of the phenolic model compounds were extracted with ethyl acetate yielding the "organic phase". The residues are referred to as "aqueous phase". All of the aqueous phases were subjected to different derivatization procedures such as silylation, acetylation, and methylation in order to convert them into more lipophilic compounds which were then analysed by means of GC/MS. Thin layer chromatography (TLC) and the results of the GC/MS analysis of the silylated, methylated or acetylated aqueous phase and the organic phases reveal that the organic phases consisted in most cases of the educts whereas the the reaction products were usually insoluble in ethyl acetate and remained in the aqueous phase.

5.2.2.1. Hydroquinone

Table.16. GC/MS results of ammoxidized Hydroquinone and its derivatives.

		Hydroquinone/^{14}N/aqu.ph/silylated	
Retention time	**Relative percentage**	**Name of compound**	**probability**
9.22 min	10%	1,2-Bis(trimethylsiloxy)ethane m/z = 206 [M^+], 191 [M - CH_3]$^+$, 149 [M - C_2H_5CO]$^+$, 147 [M - $CH_2OC_2H_5$]$^+$.	83%
10.86 min	3%	Silane, (1-cyclohexen-1-yloxy)trimethyl- m/z = 170 [M^+], 155 [M - CH_3]$^+$, 142 [M –CO]$^+$,127 [M - CH_3CO]$^+$	97%
11.11 min	3%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	86%
12.39 min	20%	Ethanedioic acid, bis(trimethylsilyl) ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	90%
14.01 min	10%	**Urea, N,N' -bis(trimethylsilyl)** m/z = 204 [M^+], 189 [M - CH_3]$^+$, 171 [M - CH_3 and H_2O]$^+$	96%

14.65 min	15%	Trimethylsilyl ether of glycerol m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	90%
16.34 min	30%	Silane, [1,4-phenylenebis(oxy)]bis[trimethyl m/z = 254 [M^+], 239 [M - CH_3]$^+$, 112 [M – 2(trimethyl-silane]$^+$	96%
17.52 min	5%	Malic acid, tris(trimethylsilyl) ester m/z = 350 [M^+], 335 [M - CH_3]$^+$, 307 [M - CH_3CO]$^+$	94%
20.83 min	2%	Benzoic acid, 2,5-bis(trimethylsiloxy)-, trimethylsilyl ester m/z = 370 [M^+], 355 [M - CH_3]$^+$, 303 [M - C_2H_5CO]$^+$	91%
20.90 min	2%	Silanamine, N-[(17á)-3,17-bis[(trimethylsilyl)oxy]estra-1,3,5 m/z = 431 [M^+], 416 [M - CH_3]$^+$, 289 [M – 2(trimethyl-silane]$^+$	49%

Hydroquinone/14N /org.ph/in EE

Retention time	**Relative percentage**	**Name of compound**	**probability**
14.59 min	100%	Hydroquinone m/z = 110 [M^+], 109 [M-H]$^+$, 108 [M-2H]$^+$, 81 [M-C_2H_5]$^+$, 53 [M-C_4H_5]$^+$	95%

Acetylation/ Hydroquinone/^{14}N /aqu.ph in acidic conditions

Retention time	**Relative percentage**	**Name of compound**	**probability**
9.25 min	15%	Diacetamide m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	86%
9.71 min	3%	1,2-Ethanediol, diacetate m/z = 146 [M^+], 104 [M - CH_3CO]$^+$	53%
15.57 min	2%	Triacetin m/z = 218 [M^+], 203[M - CH_3]$^+$	50%
16.93 min	80%	Hydroquinone, acetylated m/z = 194 [M^+], 179 [M - CH_3]$^+$, 152 [M - CH_3CO]$^+$	91%

Acetylation/ Hydroquinone/^{14}N /aqu.ph in alkaline conditions

Retention time	**Relative percentage**	**Name of compound**	**probability**
7.76 min	2%	1,1-Ethanediol, diacetate m/z = 146 [M^+], 104 [M - CH_3CO]$^+$	56%
8.91 min	5%	Diacetamide m/z = 101 [M^+], 86 [M-CH_3]$^+$, 73 [M-CO]$^+$	86%
16.54 min	13%	1-Benzyl-3-hydroxypyrrolidine m/z = 177 [M^+], 149 [M –CO]$^+$	37%
16.90 min	80%	Hydroquinone, acetylated m/z = 194 [M^+], 179 [M - CH_3]$^+$, 152 [M - CH_3CO]$^+$	91%

The results provided in table 16 clearly show that the organic phase after ammoxidation consists of only hydroquinone. Aqueous phase after silylation obtain many peaks at different retention times. The most important compounds were Urea. Glycerol, Amine and different salts of organic acids have different molecoular weights. Acytelation aqueous phase after ammoxidation in acidic and alkaline conditions have amide and the most was acetylated hydroquinone. From these results, the nitrogenous compounds were few.

5.2.2.2. 4-Methylcatechol

Table: 17. GC/MS results of ammoxidized 4-methylcatechol and its derivatives.

		4-methylcatechol /^{14}N/org.ph in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		4-methylcatechol	
14.76 min	100%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 107 [M - OH]$^+$	96%
		4-methylcatechol /^{14}N/aqu.ph/silylated	
Retention time	**Relative percentage**	**Name of compound**	**Probability**
		Acetamide, 2,2,2-trifluoro-N,N-bis(trimethylsilyl)	
6.57 min	10%	m/z = 257 [M^+], 242 [M - CH_3]$^+$, 197 [M - $3CH_3$]$^+$	96%
7.03 min	2%	1,2-Bis(trimethylsilyl)-4-methylbenzene (silylated 4-methyl catechol) m/z = 236 [M^+], 221 [M - CH_3]$^+$, 219 [M - OH]$^+$	40%
		Ethanedioic acid, bis(trimethylsilyl) ester	
7.30 min	2%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	64%
		Acetamide, 2,2,2-trifluoro-N-(trimethylsilyl)	
7.52 min	20%	m/z = 185 [M^+], 170 [M - CH_3]$^+$, 115 [M – (trimethyl-silane]$^+$	25%
		Disiloxane, hexamethyl	
9.24 min	15%	m/z = 162 [M^+], 147 [M - CH_3]$^+$,	64%
		Malonic acid, bis(2-trimethylsilylethyl ester	
9.54 min	3%	m/z = 304 [M^+], 289 [M - CH_3]$^+$, 237 [M - C_2H_5CO]$^+$	38%
		Ethanedioic acid, bis(trimethylsilyl) ester	
12.39 min	10%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	91%
		Urea, N,N'-bis(trimethylsilyl	
14.01 min	15%	m/z = 204 [M^+], 189 [M - CH_3]$^+$, 171 [M - CH_3 and H_2O]$^+$	96%
		Trimethylsilyl ether of glycerol	
14.63 min	15%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	91%
		Butanedioic acid, methyl-, bis(trimethylsilyl) ester	
15.31 min	3%	m/z = 276 [M^+], 261 [M - CH_3]$^+$, 233 [M - CH_3CO]$^+$	53%
		Oleamide, N-trimethylsilyl	
26.63 min	5%	m/z = 353 [M^+], 337 [M - CH_3]$^+$, 324 [M - C_2H_5]$^+$	91%
		Acetylated /4-methylcatechol /^{14}N /aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Acetamide, N-(3-methyl-2-oxobutyl	
8.87 min	2%	m/z = 143 [M^+], 128 [M - CH_3]$^+$, 100 [M - CH_3CO]$^+$	25%
		Diacetamide	
8.94 min	3%	m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	58%
		2,3-Dimethyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione	
14.39 min	5%	m/z = 240 [M^+], 225 [M - CH_3]$^+$, 210 [M - $2CH_3$]$^+$	64%
		1,2-Benzenediol, diacetate	
16.01 min	10%	m/z = 194 [M^+], 179 [M - CH_3]$^+$, 177 [M - OH]$^+$	91%
		1-Methyl-3,5-diisopropoxybenzene or Phenol, 2-methoxy-, acetate 166	
17.33 min	80%	m/z = 208 [M^+], 193 [M - CH_3]$^+$, 178 [M - $2CH_3$]$^+$	78%

It is evident from the pyrogram that the organic phase after ammoxidation contains only 4-methylcatechol. Aqueous phase after silylation obtain many peaks at different retention times. The most important compounds were Acetamide, Urea, Glycerol and different salts of organic

acids have different molecoular weights. Acytelation aqueous phase after ammoxidation in alkaline conditions contains amides compounds with acetylated 4-methylcatechol.

Acetylated aqueous phase was separated by column chromatography. The separation was not completely; partially separation was obtained (more than one compound in every separation).

Table: 18. Column separation results of acetylated aqueous phase ammoxidized 4-methylcatechol.

		Fraction 1/ acetylated /4-methylcatechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Benzaldehyde	
8.87 min	10%	m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	96%
		Acetamide, N,N-diethyl-	
9.96 min	1%	m/z = 115 [M^+], 100 [M - CH_3]$^+$, 86 [M – CH_2CH_3]$^+$	74%
		Benzyl Alcohol	
10.44 min	4%	m/z = 108 [M^+], 91 [M - OH]$^+$, 77 [M – CH_2OH]$^+$	98%
		Acetic acid, phenylmethyl ester	
12.84 min	2%	m/z = 150 [M^+], 135 [M - CH_3]$^+$, 107 [M –CH_3CO]$^+$	97%
		Ethanone, 2-ethoxy-1,2-diphenyl-	
13.84 min	3%	m/z = 240 [M^+], 225 [M - CH_3]$^+$, 211 [M –CH_3CH_2]$^+$	90%
		1,2-Benzenediol, diacetate	
15.98 min	20%	m/z = 194 [M^+], 179 [M - CH_3]$^+$, 177 [M - OH]$^+$	91%
		Phenol, 4-methyl-, acetate	
17.31 min	70%	m/z = 166 [M^+], 151 [M - CH_3]$^+$, 149 [M - OH]$^+$	90%
		Fraction 2/ acetylated /4-methylcatechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**propability**
		Diacetamide	
9.01 min	10%	m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	80%
		Acetamide, N,N-diethyl	
9.80 min	15%	m/z = 115 [M^+], 100 [M - CH_3]$^+$, 86 [M – CH_2CH_3]$^+$	91%
		Benzyl Alcohol	
10.50 min	70%	m/z = 108 [M^+], 91 [M - OH]$^+$, 77 [M – CH_2OH]$^+$	97%
		Acetic acid, phenylmethyl ester	
12.82 min	5%	m/z = 150 [M^+], 135 [M - CH_3]$^+$, 107 [M –CH_3CO]$^+$	98%
		Fraction 3/ acetylated /4-methylcatechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**propability**
		2-(Diethylamino)acetonitrile	
7.81 min	15%	m/z = 112 [M^+], 97 [M - CH_3]$^+$, 82 [M - $2CH_3$]$^+$	64%
		Benzoic acid, 2,4-dimethoxy-, methyl ester	
8.37 min	5%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M –CH_3CO]$^+$	27%
		Formamide, N,N-diethyl	
8.48 min	30%	m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	60%
		Benzaldehyde	
8.90 min	50%	m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	94%
		Fraction 4/ acetylated /4-methylcatechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**propability**
		Benzoic acid, 2,4-dimethoxy-, methyl ester	
8.37 min	25%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M –CH_3CO]$^+$	27%
		Benzaldehyde	
8.90 min	25%	m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	87%
10.83 min	50%	Phthalic acid, di(3,4-dimethylphenyl) ester	35%

		m/z = 375 [M^+], 360 [M - CH_3]$^+$, 345 [M –2CH_3]$^+$	
		Fraction 5/ acetylated /4-methylcatechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**propability**
8.37 min	20%	Benzoic acid, 2,4-dimethoxy-, methyl ester m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M –CH_3CO]$^+$	27%
10.83 min	80%	Phthalic acid, di(3,4-dimethylphenyl) ester m/z = 375 [M^+], 360 [M - CH_3]$^+$, 345 [M –2CH_3]$^+$	35%

There is some evidence from the pyrograms that every fraction has more than one compound as mentioned above, for the first fraction the most is 4-Methylphenol acetate, the second fraction is Benzyl Alcohol, the third fraction contains main peak at retention time 8.904 min Benzaldehyde, the fourth fraction obtains also Benzaldehyde; Phthalic acid, di(3,4-dimethylphenyl) ester and The fifth separation was the same compounds.

5.2.2.3. 2-Methoxy-4-methylphenol

Table: 19. GC/MS results of ammoxidized 2-Methoxy-4-methylphenol and its derivatives.

		2-Methoxy-4-methylphenol /^{14}N/org.ph in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
13.41 min	100%	2-Methoxy-4-methylphenol m/z = 138 [M^+], 123 [M - CH_3]$^+$, 107[M –CH_3O]$^+$	97%
		2-Methoxy-4-methylphenol /^{14}N /aq.ph in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
11.14 min	3%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	90%
11.39 min	2%	Acetic acid, [(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 220 [M^+], 205 [M - CH_3]$^+$, 190 [M –2CH_3]$^+$	62%
13.55 min	5%	Propanedioic acid, bis(trimethylsilyl) ester	87%
14.65 min	15%	Trimethylsilyl ether of glycerol m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	91%
15.31 min	5%	Butanedioic acid, methyl-, bis(trimethylsilyl) ester m/z = 276 [M^+], 261 [M - CH_3]$^+$, 233 [M - CH_3CO]$^+$	78%
24.47 min	70%	3,3'-Dimethyl-1'-hydroxy-5,8-dimethoxy-2,2'-binaphthalene-1,4,5',8'-tetrone m/z = 418 [M^+], 403 [M - CH_3]$^+$, 375 [M - CH_3CO]$^+$	60%

Organic phase after ammoxidation is only 2-Methoxy-4-methylphenol. Aqueous phase after silylation obtains many peaks at different retention times. The main is 3,3'-Dimethyl-1'-hydroxy-5,8-dimethoxy-2,2'-binaphthalene-1,4,5',8'-tetrone, Glycerol and little of different organic acids.

5.2.2.4. Catechol

Table: 20. GC/MS results of ammoxidized Catechol and its derivatives.

		Catechol/^{14}N/org.ph in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
13.44 min	100%	1,2-Benzenediol (Catechol) m/z = 110 [M^+], 21 [M – H_2O]$^+$, 81 [M - HCO]$^+$	90%
		Catechol/^{14}N /aq.ph in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
11.13 min	5%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	64%
13.03 min	10%	Hexanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 276 [M^+], 261 [M - CH_3]$^+$, 233 [M - CH_3CO]$^+$	50%
14.65 min	5%	Trimethylsilyl ether of glycerol m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	52%
15.23 min	80%	Silane, [1,2-phenylenebis(oxy)]bis[trimethyl- (silylated Catechol) m/z = 254 [M^+], 239 [M - CH_3]$^+$, 142 [M - 2(trimethyl-silane]$^+$	96%
		Acetylation / Catechol/^{14}N /aq.ph	
Retention time	**Relative percentage**	**Name of compound**	**probability**
8.95 min	5%	Diacetamide m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	86%
13.91 min	15%	Catechol Monoacetate m/z = 152 [M^+], 137 [M - CH_3]$^+$, 109 [M - CH_3CO]$^+$	78%
16.05 min	80%	1,2-Benzenediol, diacetate m/z = 194 [M^+], 179 [M - CH_3]$^+$, 151 [M - CH_3CO]$^+$	91%

The pyrogram reveals that the organic phase after ammoxidation is only Catechol. Aqueous phase after silylation contains many peaks at different retention times. The main compounds are Silane, [1,2-phenylenebis(oxy)]bis-trimethyl (silylated Catechol), Glycerol and different organic acids salts,. Aqueous phase after acetylation have many peaks at different retention times (Benzenediol-1,2-diacetate, diacetamide and catechol monoacetate).

Acetylated aqueous phase were separated by column chromatography. The separation was not completely; partially separation was obtained (more than one compound in every separation).

Table: 21. Column separation results of acetylated aqueous phase ammoxidized catechol.

		Fraction 1/ acetylated /Catechol /^{14}N aqu.ph	
Retention time	**Relative percentage**	**Name of compound**	**probability**
8.92 min	1%	Benzaldehyde m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	95%
9.83 min	1%	Acetamide, N,N-diethyl- m/z = 115 [M^+], 90 [M - CHO]$^+$	91%
10.16 min	1%	Benzoxazole m/z = 119 [M^+], 100 [M - CH_3]$^+$,	93%

		Acetic acid, phenylmethyl ester	
12.86 min	1%	m/z = 150 $[M^+]$, 135 $[M - CH_3]^+$, 107 $[M - CH_3CO]^+$	95%
		Catechol Monoacetate	
14.12 min	5%	m/z = 152 $[M^+]$, 137 $[M - CH_3]^+$, 109 $[M - CH_3CO]^+$	68%
		1,2-Benzenediol, diacetate	
16.21 min	89%	m/z = 194 $[M^+]$, 179 $[M - CH_3]^+$, 151 $[M - CH_3CO]^+$	91%
		1,2,3-Benzenetriol, triacetate	
19.76 min	1%	m/z = 252 $[M^+]$, 237 $[M - CH_3]^+$, 209 $[M - CH_3CO]^+$	86%
		1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	
21.71 min	1%	m/z = 278 $[M^+]$, 263 $[M - CH_3]^+$, 248 $[M - 2CH_3]^+$	87%

Fraction 2/ acetylated /Catechol /^{14}N aqu.ph

Retention time	**Relative percentage**	**Name of compound**	**probability**
		Diacetamide	
8.97 min	4%	m/z = 101 $[M^+]$, 86 $[M - CH_3]^+$, 73 $[M –CO]^+$	78%
		Acetamide, N,N-diethyl	
9.84 min	1%	m/z = 115 $[M^+]$, 90 $[M - CHO]^+$	91%
		Benzyl Alcohol	
10.49 min	5%	m/z = 108 $[M^+]$, 91 $[M - OH]^+$, 77 $[M – CH_2OH]^+$	97%
		1,2-Benzenediol, diacetate	
15.99 min	90%	m/z = 194 $[M^+]$, 179 $[M - CH_3]^+$, 151 $[M - CH_3CO]^+$	91%

Fraction 3/ acetylated /Catechol /^{14}N aqu.ph

Retention time	**Relative percentage**	**Name of compound**	**probability**
		Diacetamide	
9.32 min	90%	m/z = 101 $[M^+]$, 86 $[M - CH_3]^+$, 73 $[M –CO]^+$	83%
		1,2-Benzenediol, diacetate	
16.02 min	10%	m/z = 194 $[M^+]$, 179 $[M - CH_3]^+$, 151 $[M - CH_3CO]^+$	95%

Fraction 4/ acetylated /Catechol /^{14}N aqu.ph

Retention time	**Relative percentage**	**Name of compound**	**probability**
		Acetamide, N,N-diethyl	
9.95 min	5%	m/z = 115 $[M^+]$, 90 $[M - CHO]^+$	91%
		1,2-Benzenediol (Catechol)	
13.40 min	50%	m/z = 110 $[M^+]$, 21 $[M – H_2O]^+$, 81 $[M - HCO]^+$	95%
		1,2-Benzenediol, diacetate	
13.91 min	45%	m/z = 194 $[M^+]$, 179 $[M - CH_3]^+$, 151 $[M - CH_3CO]^+$	78%

Every fraction obtains more than one compound as mentioned above, for first and second fraction the main is 1,2-Benzenediol. Third fraction and fourth contained mainly diacetamide.

5.2.2.5. Methoxyhydroquinone

Table: 22 GC/MS results of ammoxidized Methoxyhydroquinone and its derivatives.

Methoxyhydroquinone/^{14}N/org.ph in EE

Retention time	**Relative percentage**	**Name of compound**	**probability**
		1,4-Benzenediol, 2-methoxy (Methoxyhydroquinone)	
16.51 min	100%	m/z = 140 $[M^+]$, 125 $[M - CH_3]^+$, 109 $[M - CH_3O]^+$	75%

Methoxyhydroquinone/^{14}N /aq.ph in EE+BSTFA

Retention time	**Relative percentage**	**Name of compound**	**probability**

		Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.14 min	25%	m/z = 218 [M^+], 203 [M - CH_3]$^+$, 188 [M - 2CH_3]$^+$	78%
		Trimethylsilyl ether of glycerol	
14.65 min	15%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	90%
		Urea, N,N'-bis(trimethylsilyl)	
15.32 min	60%	m/z = 204 [M^+], 189 [M - CH_3]$^+$, 171 [M - CH_3 and H_2O]$^+$	30%

Acetylation / Methoxyhydroquinone/^{14}N /aq.ph

Retention time	Relative percentage	Name of compound	probability
		Diacetamide	
8.93 min	25%	m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	87%
		Propanoic acid, 2-oxo-, ethyl ester	
10.25 min	5%	m/z = 130 [M^+], 115 [M - CH_3]$^+$, 100 [M - 2CH_3]$^+$	30%
		1,1,2-Triacetoxyethane	
13.96 min	5%	m/z = 204 [M^+], 189 [M - CH_3]$^+$, 161 [M - CH_3CO]$^+$	78%
		1,4-Benzenediol, diacetate	
16.98 min	5%	m/z = 194 [M^+], 179 [M - CH_3]$^+$, 151 [M - CH_3CO]$^+$	91%
		Phenol, 3,4-dimethoxy-, acetate	
17.72 min	5%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	70%
		1,4-Benzenediol, 2-methoxy-, diacetate	
19.12 min	15%	m/z = 224 [M^+], 209 [M - CH_3]$^+$, 181 [M - CH_3CO]$^+$	95%
		2,2',5,5'-Tetramethoxybiphenyl	
25.85 min	40%	m/z = 274 [M^+], 259 [M - CH_3]$^+$, 231 [M - CH_3CO]$^+$	40%

Organic phase after ammoxidation contained only Methoxyhydroquinone. Ammoxidised aqueous phase after silylation obtained different compounds at different retention times as follow: Urea-N,N'-bis(trimethylsilyl), Propanoic acid, 2-[(trimethylsilyl)oxy]-trimethylsilyl ester and Trimethylsilyl ether of glycerol. Acetylated ammoxidized aqueous phase obtained different compounds as 2,2',5,5'-Tetramethoxybiphenyl, Diacetamide and different organic acids salts.

Acetylated aqueous phases were separated by column chromatography. The separation was not completely; partially separation was obtained (more than one compound in every separation).

Table: 23. Column separation results of acetylated aqueous phase ammoxidized Metoxyhydroquinone.

Fraction 1/ acetylated /Methoxyhydroquinone /^{14}N aqu.ph

Retention time	Relative percentage	Name of compound	probability
		Diacetamide	
9.06 min	5%	m/z = 101 [M^+], 86 [M - CH_3]$^+$, 73 [M –CO]$^+$	78%
		Benzyl Alcohol	
10.52 min	3%	m/z = 108 [M^+], 91 [M – OH]$^+$, 77 [M – CH_2OH]$^+$	93%
		1,1,2-Triacetoxyethane	
13.93 min	2%	m/z = 204 [M^+], 189 [M – CH_3]$^+$, 161 [M – CH_3CO]$^+$	90%
		Benzyl Morphiline	
16.57 min	70%	m/z = 177 [M^+], 160 [M –OH]$^+$,	80%
		1,4-Benzenediol, diacetate	
16.96 min	5%	m/z = 194 [M^+], 179 [M - CH_3]$^+$, 151 [M - CH_3CO]$^+$	60%

		1,4-Benzenediol, 2-methoxy-, diacetate	
19.13 min	2%	m/z = 224 [M^+], 209 [M - CH_3]$^+$, 181 [M - CH_3CO]$^+$	96%
		2,2',5,5'-Tetramethoxybiphenyl	
25.85min	5%	m/z = 274 [M^+], 259 [M - CH_3]$^+$, 231 [M - CH_3CO]$^+$	60%
		1,2-Benzenedicarboxylic acid, diisooctyl ester	
27.72 min	3%	m/z = 390 [M^+], 375 [M - CH_3]$^+$, 361 [M – CH_2CH_3]$^+$	58%

Fraction 2/ acetylated /Methoxyhydroquinone /^{14}N aqu.ph

Retention time	Relative percentage	Name of compound	probability
		Benzene, isocyanato	
8.89 min	50%	m/z = 119 [M^+], 91 [M - CO]$^+$, 77 [M - CNO]$^+$	94%
		Aniline	
9.29 min	35%	m/z = 93 [M^+], 77 [M - NH_2]$^+$	95%
		Acetamide, N,N-diethyl	
9.85 min	10%	m/z = 115 [M^+], 90 [M - CHO]$^+$	91%
		N,N-Diethylpropionamide	
11.52 min	5%	m/z = 129 [M^+], 114 [M - CH_3]$^+$, 100 [M - CH_2CH_3]$^+$	80%

Fraction 3/ acetylated /Methoxyhydroquinone /^{14}N aqu.ph

Retention time	Relative percentage	Name of compound	probability
		Benzaldehyde	
8.95 min	50%	m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	96%
		Benzyl Alcohol	
10.50 min	40%	m/z = 108 [M^+], 91 [M - OH]$^+$, 77 [M – CH_2OH]$^+$	97%
		Benzaldehyde dimethyl acetal	
11.927 min	7%	m/z = 152 [M^+], 137 [M - CH_3]$^+$, 109 [M - CH_3CO]$^+$	95%
		Acetic acid, phenylmethyl ester	
12.821 min	3%	m/z = 150 [M^+], 135 [M - CH_3]$^+$, 91 [M - CH_3COO]$^+$	97%

First fraction contained mainly of Benzyl morphiline and little amounts of Diacetamide, Benzyl Alcohol, 1,1,2-Triacetoxyethane, 2-methoxy-1,4-Benzenedioldiacetate and 2,2',5,5'-Tetramethoxybiphenyl. Second fraction consist of Benzene isocyanato, Aniline, Acetamide-N,N-diethyl and N,N-Diethylpropionamide. Third fraction obtained Benzaldehyde, benzyl alcohol, Benzaldehyde dimethyl acetal and Acetic acid phenylmethyl ester. Fourth separation was stabilizeronly.

5.2.2.6. 2-Methoxy phenol

Table: 24. GC/MS results of ammoxidized 2-Methoxy phenol.

2-Methoxy phenol /^{14}N/org.ph in EE

Retention time	Relative percentage	Name of compound	probability
		2-Methoxy phenol	
11.56 min	100%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	96%

2-Methoxy phenol /^{14}N /aq.ph in EE+BSTFA

Retention time	Relative percentage	Name of compound	probability
		Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.14 min	10%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	68%
		Acetic acid, [(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.41 min	2%	m/z = 220 [M^+], 205 [M - CH_3]$^+$, 190 [M –2CH_3]$^+$	10%

		Propanedioic acid, bis(trimethylsilyl) ester	
13.55 min	70%	m/z = 248 [M^+], 233 [M - CH_3]$^+$, 174 [M – trimethyl-silane]$^+$	97%
		Trimethylsilyl ether of glycerol	
14.65 min	8%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	74%
		Ethanimidic acid, N-(trimethylsilyl)-, trimethyl ester	
17.55 min	5%	m/z = 203 [M^+], 108 [M - CH_3]$^+$, 129 [M – trimethyl-silane]$^+$	43%
		Benzoic acid, 3-methoxy-4-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
20.68 min	5%	m/z = 312 [M^+], 297 [M - CH_3]$^+$, 282 [M - 2CH_3]$^+$	95%

Ammoxidized organic phase is only 2-Methoxy phenol. Ammoxidized aqueous phase after silylation contains different compounds, Propanedioic acid-bis(trimethylsilyl) ester is the mainly contents with different amounts of Propanoic acid-2-[(trimethylsilyl)oxy]-trimethylsilyl ester, Acetic acid-[(trimethylsilyl)oxy]-trimethylsilyl ester, Trimethylsilyl ether of glycerol, Ethanimidic acid-N-(trimethylsilyl)-trimethyl ester and Benzoic acid-3-methoxy-4-[(trimethylsilyl)oxy]- trimethylsilyl ester.

5.2.2.7. 2,5-Dihydroxy-1,4-benzoquinone

Table: 25. GC/MS results of ammoxidized 2,5-Dihydroxy-1,4-benzoquinone.

2,5-Dihydroxy-1,4-benzoquinone/^{15}N/org.ph/100C°/ violet organic layer in EE+BSTFA			
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Trimethylsilyl ether of glycerol	
14.62 min	2%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	93%
		2,5-di (trimethylsilyl) benzoquinone	
21.13 min	10%	m/z = 284 [M^+], 269 [M - CH_3]$^+$, 254 [M - 2CH_3]$^+$	94%
		2,5-Dihydroxybenzyl alcohol, tris(O-trimethylsilyl)-	
22.07 min	5%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 327 [M – CH_2CH_3]$^+$	60%
		Hexadecanoic acid, trimethylsilyl ester	
23.38 min	2%	m/z = 328 [M^+], 313 [M - CH_3]$^+$, 299 [M – CH_2CH_3]$^+$	97%
		9,12-Octadecadienoic acid (Z,Z)-, trimethylsilyl ester	
24.89 min	1%	m/z = 352 [M^+], 337 [M - CH_3]$^+$, 309 [M – $CH_2CH_2CH_3$]$^+$	99%
		Octadecanoic acid, trimethylsilyl ester	
25.16 min	2%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 313 [M – $CH_2CH_2CH_3$]$^+$	99%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.46 min	3%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M – CH_2CH_3]$^+$	98%
		Silylated di hydroxybenzohyroquinone	
27.57 min	80%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 413 [M – trimethyl-silane]$^+$	9%
2,5-Dihydroxy-1,4-benzoquinone/^{15}N /org.ph/100C°/ soluble organic layer in EE			
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Benzaldehyde	
8.93 min	5%	m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	94%
		Phenol, 2-methoxy-	
11.53 min	10%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	95%
		Phenol, 2-methoxy-4-methyl-	
13.29 min	30%	m/z = 138 [M^+], 123 [M - CH_3]$^+$, 107 [M –CH_3O]$^+$	97%
25.70 min	35%	4H-1-Benzopyran-4-one, 3,5-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)	

		-7-methoxy m/z = 330 [M^+], 313 [M - OH]$^+$, 299 [M –CH_3O]$^+$	
		2,2',5,5'-Tetramethoxybiphenyl	
26.70 min	20%	m/z = 274 [M^+], 259 [M - CH_3]$^+$, 231 [M - CH_3CO]$^+$	53%
		2,5-Dihydroxy-1,4-benzoquinone/^{15}N /aq.ph/ 100C°/ in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Ethanimidic acid, N-(trimethylsilyl)-, trimethylsilyl ester	
8.52 min	5%	m/z = 203 [M^+], 188 [M - CH_3]$^+$, 132 [M – trimethyl-silane]$^+$	68%
		1,2-Bis(trimethylsiloxy)ethane	
9.20 min	1%	m/z = 206 [M^+], 194 [M - CH_3]$^+$, 179 [M - 2CH_3]$^+$	67%
		Butanedioic acid, bis(trimethylsilyl) ester	
10.61 min	2%	m/z = 262 [M^+], 247 [M - CH_3]$^+$, 191 [M – trimethyl-silane]$^+$	43%
		Urea, N,N'-bis(trimethylsilyl)-	
14.22 min	3%	m/z = 204 [M^+], 189 [M - CH_3]$^+$, 171 [M - CH_3 and H_2O]$^+$	40%
		Benzoic acid, 2,4,5-tris[(trimethylsilyl)oxy]-, propyl ester	
21.67 min	5%	m/z = 428 [M^+], 413 [M - CH_3]$^+$, 329 [M – CH_2CH_3]$^+$	72%
		2,5-Dihydroxybenzyl alcohol, tris(O-trimethylsilyl)-	
22.07 min	5%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 313 [M – $CH_2CH_2CH_3$]$^+$	60%
		Benzoic acid, 2,4,5-tris[(trimethylsilyl)oxy]-, propyl ester	
22.72 min	60%	m/z = 428 [M^+], 413 [M - CH_3]$^+$, 357 [M – trimethyl-silane]$^+$	60%
		Silylated di hydroxybenzohyroquinone	
22.93 min	20%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 413 [M – trimethyl-silane]$^+$	9%
		2,5-Dihydroxy-1,4-benzoquinone/^{15}N /org.ph/ 25C°/ in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Butanoic acid, 3-oxo-, ethyl ester	
8.61 min	100%	m/z = 130 [M^+], 115 [M - CH_3]$^+$, 101 [M – CH_2CH_3]$^+$	91%
		2,5-Dihydroxy-1,4-benzoquinone/^{15}N /aq.ph/25C°/ in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Trisiloxane, octamethyl	
7.04 min	3%	m/z = 236 [M^+], 220 [M - O]$^+$, 204 [M –CH_3OH]$^+$	90%
		1,2-Bis(trimethylsiloxy)ethane	
9.28 min	1%	m/z = 206 [M^+], 194 [M - CH_3]$^+$, 179 [M - 2CH_3]$^+$	78%
		2-Furancarboxylic acid, trimethylsilyl ester	
12.36 min	1%	m/z = 184 [M^+], 169 [M - CH_3]$^+$, 139 [M - 3CH_3]$^+$	97%
		Benzoic acid trimethylsilyl ester	
14.11 min	5%	m/z = 194 [M^+], 179 [M - CH_3]$^+$, 135 [M - $OCOCH_3$]$^+$	97%
		Trimethylsilyl ether of glycerol	
14.62 min	3%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	91%
		4-Pyrimidinamine, 5-methyl-N-(trimethylsilyl)-2-[(trimethylsilyl)oxy	
18.37 min	2%	m/z = 269 [M^+], 254 [M - CH_3]$^+$	83%
		Estra-1,3,5(10)-trien-17-one, 2,3-bis[(trimethylsilyl)oxy	
20.72 min	15%	m/z = 430 [M^+], 415 [M - CH_3]$^+$,400 [M - 2CH_3]$^+$	91%
		Benzoic acid, 2,4,5-tris[(trimethylsilyl)oxy]-, propyl ester	
22.72 min	20%	m/z = 428 [M^+], 413 [M - CH_3]$^+$, 357 [M – trimethyl-silane]$^+$	60%
		Hexadecanoic acid, trimethylsilyl ester	
23.36 min	15%	m/z = 328 [M^+], 313 [M - CH_3]$^+$, 299 [M – CH_2CH_3]$^+$	99%
		Octadecanoic acid, trimethylsilyl ester	
25.14 min	10%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 313 [M – $CH_2CH_2CH_3$]$^+$	99%
		Silylated benzohyroquinone	
27.75 min	25%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 413 [M – trimethyl-silane]$^+$	9%
		2,5-Dihydroxy-1,4-benzoquinone/^{15}N /aq.ph/25C°/ in DMSO+BSTFA	
Retention	**Relative**	**Name of compound**	**probability**

time	percentage		
		Acetophenone, 2'-(trimethylsiloxy	
14.73 min	40%	m/z = 208 $[M^+]$, 193 $[M - CH_3]^+$, 178 $[M - 2CH_3]^+$	40%
		Silane, [[(17á)-2,4-dimethoxyestra-1,3,5(10)-triene-3,17-diyl]bis (oxy)]bis[trimethyl-	
22.80 min	60%	m/z = 476 $[M^+]$, 461 $[M - CH_3]^+$, 445 $[M - OCH_3]^+$	

2,5-Dihydroxy-1,4-benzoquinone/^{15}N /aq.ph/25C°/ambient pressure/ in EE

Retention time	Relative percentage	Name of compound	probability
		Butanoic acid, 3-oxo-, ethyl ester	
8.65 min	100%	m/z = 130 $[M^+]$, 115 $[M - CH_3]^+$, 101 $[M - CH_2CH_3]^+$	91%

2,5-Dihydroxy-1,4-benzoquinone/^{15}N /aq.ph/25C°/ ambient pressure/ in EE+BSTFA

Retention time	Relative percentage	Name of compound	probability
		Trisiloxane, octamethyl	
7.06 min	5%	m/z = 236 $[M^+]$, 220 $[M - O]^+$, 204 $[M - CH_3OH]^+$	90%
		1,2-Bis(trimethylsiloxy)ethane	
11.08 min	5%	m/z = 206 $[M^+]$, 194 $[M - CH_3]^+$, 179 $[M - 2CH_3]^+$	86%
		2-Furancarboxylic acid, trimethylsilyl ester	
12.36 min	2%	m/z = 184 $[M^+]$, 169 $[M - CH_3]^+$, 139 $[M - 3CH_3]^+$	94%
		Benzoic acid trimethylsilyl ester	
14.10 min	3%	m/z = 194 $[M^+]$, 179 $[M - CH_3]^+$, 135 $[M - OCOCH_3]^+$	97%
		Trimethylsilyl ether of glycerol	
14.62 min	5%	m/z = 308 $[M^+]$, 219 [M - tetramethyl-silane]$^+$	91%
		4-Pyrimidinamine, 5-methyl-N-(trimethylsilyl)-2-[(trimethylsilyl	
18.37 min	20%	m/z = 269 $[M^+]$, 254 $[M - CH_3]^+$	86%
		Estra-1,3,5(10)-trien-17-one, 2,3-bis[(trimethylsilyl)oxy	
20.73 min	20%	m/z = 430 $[M^+]$, 415 $[M - CH_3]^+$,400 $[M - 2CH_3]^+$	91%
		Hexadecanoic acid, trimethylsilyl ester	
23.36 min	10%	m/z = 328 $[M^+]$, 313 $[M - CH_3]^+$, 299 $[M - CH_2CH_3]^+$	99%
		Octadecanoic acid, trimethylsilyl ester	
25.14 min	10%	m/z = 356 $[M^+]$, 341 $[M - CH_3]^+$, 313 $[M - CH_2CH_2CH_3]^+$	99%
		Silylated di hydroxybenzohyroquinone	
27.75 min	20%	m/z = 484 $[M^+]$, 469 $[M - CH_3]^+$, 413 [M – trimethyl-silane]$^+$	9%

2,5-Dihydroxy-1,4-benzoquinone/^{14}N /org.ph/100C°/ violet organic layer in EE+BSTFA

Retention time	Relative percentage	Name of compound	probability
		1,2-Bis(trimethylsiloxy)ethane	
9.21 min	3%	m/z = 206 $[M^+]$, 194 $[M - CH_3]^+$, 179 $[M - 2CH_3]^+$	64%
		Silane, (1-cyclohexen-1-yloxy)trimethyl	
10.85 min	2%	m/z = 170 $[M^+]$, 155 $[M - CH_3]^+$, 125 $[M - 3CH_3]^+$	93%
		Urea, N,N'-bis(trimethylsilyl	
14.12 min	2%	m/z = 204 $[M^+]$, 189 $[M - CH_3]^+$, 171 [M - CH_3 and H_2O]$^+$	38%
		2,5-di (trimethylsilyl) benzoquinone	
21.15 min	15%	m/z = 284 $[M^+]$, 269 $[M - CH_3]^+$, 254 $[M - 2CH_3]^+$	94%
		2,5-Dihydroxybenzyl alcohol, tris(O-trimethylsilyl)-	
22.07 min	35%	m/z = 356 $[M^+]$, 341 $[M - CH_3]^+$, 313 $[M - CH_2CH_2CH_3]^+$	60%
		Benzoic acid, 2,4,5-tris[(trimethylsilyl)oxy]-, propyl ester	
22.72 min	35%	m/z = 428 $[M^+]$, 413 $[M - CH_3]^+$, 357 [M – trimethyl-silane]$^+$	60%
		Hexadecanoic acid, trimethylsilyl ester	
23.38 min	1%	m/z = 328 $[M^+]$, 313 $[M - CH_3]^+$, 299 $[M - CH_2CH_3]^+$	97%
		Octadecanoic acid, trimethylsilyl ester	
25.16 min	2%	m/z = 356 $[M^+]$, 341 $[M - CH_3]^+$, 313 $[M - CH_2CH_2CH_3]^+$	99%
		Silylated benzohyroquinone	
27.57 min	5%	m/z = 484 $[M^+]$, 469 $[M - CH_3]^+$, 413 [M – trimethyl-silane]$^+$	9%

2,5-Dihydroxy-1,4-benzoquinone/^{14}N /org.ph/100C°/ soluble organic layer in EE

Retention	Relative	Name of compound	probability

time	percentage		
		Phenol, 2-methoxy-	
11.54 min	90%	m/z = 124 $[M^+]$, 109 $[M - CH_3]^+$, 81 $[M - OCH_3]^+$	97%
		Phenol, 2-methoxy-4-methyl-	
13.33 min	5%	m/z = 138 $[M^+]$, 123 $[M - CH_3]^+$, 107 $[M – OCH_3]^+$	96%
		4H-1-Benzopyran-4-one, 3,5-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy	
25.70 min	2%	m/z = 330 $[M^+]$, 313 $[M - OH]^+$, 299 $[M – OCH_3]^+$	
		2,2',5,5'-Tetramethoxybiphenyl	
26.70 min	3%	m/z = 274 $[M^+]$, 259 $[M - CH_3]^+$, 231 $[M - CH_3CO]^+$	53%
		2,5-Dihydroxy-1,4-benzoquinone/^{14}N /aq.ph/100C°/ in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Trimethylsilyl ether of glycerol	
14.61 min	60%	m/z = 308 $[M^+]$, 219 $[M - \text{tetramethyl-silane}]^+$	91%
		Silanamine, N-[(17á)-3,17-bis[(trimethylsilyl)oxy]estra-1,3,5(10)-trien-4-yl]-1,1,1-trimethyl-	
20.86 min	40%	m/z = 431 $[M^+]$, 416 $[M - CH_3]^+$,401 $[M - 2CH_3]^+$	
		Methylation/2,5-Dihydroxy-1,4-benzoquinone/^{14}N / org.ph/violet layer/100C°/ in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
		2,4-Hexadienoic acid, methyl ester	
14.91 min	5%	m/z = 126 $[M^+]$, 109 $[M - OH]^+$, 95 $[M – OCH_3]^+$	53%
		Cyclohexane-1,3-dione, 2-dimethylaminomethylene	
16.61 min	20%	m/z = 167 $[M^+]$, 152 $[M - CH_3]^+$, 136 $[M – OCH_3]^+$	22%
		1,2,4,5-Methoxybenzen	
17.11 min	20%	m/z = 212 $[M^+]$, 197 $[M - CH_3]^+$, 181 $[M – OCH_3]^+$	25%
		4-Petenoic acid,2-methoxy-,methyl ester	
17.27 min	10%	m/z = 144 $[M^+]$, 103 $[M - CH_2CHCH_2]^+$	22%
		N-Ethyl-5-methyl-5-undecanamine	
20.36 min	10%	m/z = 213 $[M^+]$, 198 $[M - CH_3]^+$, 184 $[M – CH_3CH_2]^+$	40%
		1,1'-Biphenyl, 2,,4,3',4'-tetramethoxy-4,6'-dimethyl	
24.36 min	10%	m/z = 302 $[M^+]$, 287 $[M - CH_3]^+$,272 $[M - OCH_3]^+$	60%
		Hexanedioic acid, dioctyl ester	
26.48 min	5%	m/z = 370 $[M^+]$, 341 $[M - CH_3CH_2]^+$, 313 $[M – CH_3CH_2CH_2CH_3]^+$	81%
		1,2-Benzenedicarboxylic acid, diisooctyl ester	
27.68 min	20%	m/z = 370 $[M^+]$, 341 $[M - CH_3CH_2]^+$, 313 $[M – CH_3CH_2CH_2CH_3]^+$	50%

It is evident from the pyrogram that ammoxidized organic phase ^{15}N at 100°C was divided into two layers during rotation, soluble layer and insoluble layer (violet layer). The insoluble layer after silylation was obtained 80% Silylated Dihydroxybenzohyroquinone, 10% 2,5-di (trimethylsilyl) benzoquinone, different amounts less than 10% of Trimethylsilyl ether of glycerol, Hexadecanoic acid trimethylsilyl ester, Octadecanoic acid trimethylsilyl ester and Hexanedioic acid bis(2-ethylhexyl) ester.

The soluble layer consist of 35% 4H-1-Benzopyran-4-one-3,5-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy, 30% 2-Methoxy-4-methylphenol, 20% 2,2',5,5'-Tetramethoxybiphenyl, 10% 2-Methoxy phenol and 5% Benzaldehyde.

Silylated ammoxidized aqueos phase ^{15}N at 100°C contains 60% Benzoic acid-2,4,5-tris[(trimethylsilyl)oxy]-propyl ester, 20% Silylated dihydroxybenzohyroquinone Ethanimidic acid, N-(trimethylsilyl)-trimethylsilyl ester, 1,2-Bis(trimethylsiloxy)ethane, Butanedioic acid, bis(trimethylsilyl) ester, Urea-N,N'-bis(trimethylsilyl) and 2,5-Dihydroxybenzyl alcohol-tris(O-trimethylsilyl).

Ammoxidized organic phase N^{15} at 25°C was only Butanoic acid-3-oxo- ethyl ester.

Silylated ammoxidized aqueos phase ^{15}N at 25°C has, 25% Silylated dihydroxybenzohyroquinone, 20% Benzoic acid-2,4,5-tris[(trimethylsilyl)oxy]-propyl ester, Trisiloxane-octamethyl, 1,2-Bis(trimethylsiloxy)ethane, 2-Furancarboxylic acid trimethylsilyl ester, Benzoic acid trimethylsilyl ester, Trimethylsilyl ether of glycerol and 2,5-Dihydroxybenzyl alcohol tris(O-trimethylsilyl).

Ammoxidized organic phase ^{15}N at 25°C and ambient pressure was only Butanoic acid-3-oxo-ethyl ester.

Silylated ammoxidized aqueos phase N^{15} at 25°C and ambient pressure obtained different amounts of Trisiloxane octamethyl-1,2-Bis(trimethylsiloxy)ethane, 2-Furancarboxylic acid trimethylsilyl ester, Benzoic acid trimethylsilyl ester, Trimethylsilyl ether of glycerol, 2,5-Dihydroxybenzyl alcohol tris(O-trimethylsilyl), Benzoic acid-2,4,5-tris[(trimethylsilyl)oxy]-propyl ester and the main was Silylated di hydroxybenzohyroquinone.

Ammoxidized organic phase ^{14}N at 100°C like ^{15}N at 100°C was divided into two layers during rotation and contained the same compounds.

The insoluble layer after methylation was obtained 2,4-Hexadienoic acid methyl ester, 1,2,4,5-Methoxybenzen, 4-Petenoic acid-2-methoxy-methyl ester, 2,,4,3',4'-tetramethoxy-4,6'-dimethyl, Hexanedioic acid dioctyl ester and 1,2-Benzenedicarboxylic acid diisooctyl ester

Silylated ammoxidized aqueos phase N^{14} at 100°C has mainly like aqueos phase ^{15}N at 100°C.

From GC/MS it found that, the existence of Nitrogen that incorporated into compounds very little. May be due to N- compounds were not completely dissolved during silylation processes. It was necessary to perform the GC/MS for the aqueous phases of ammoxidized phenolic model compounds in solid state by using pyrloisis GC/MS analysis.

5.2.3. Studies on the aqueous phase of ammoxidized phenolic model compounds by means of Curie-point pyrolsis GC/MS

The results obtained completely supported the results which were obtained from GC/MS.

5.2.3.1. Hydroquinone

Table: 26. Pyrolsis GC/MS results of the aqeous phase of ammoxidized Hydroquinone.

Retention time	Relative percentage	Name of compound	Propability
4.18 min	30%	Acetamide m/z = 59 $[M^+]$, 44 $[M - CH_3]^+$, 28 $[M - OCH_3]^+$, 16 $[M - COCH_3]^+$	91%
8.65 min	15%	p-Benzoquinone m/z = 108 $[M^+]$, 80 $[M - CO]^+$, 54 $[M – OCHCHCO]^+$	95%
11.25 min	5%	Phenol m/z = 94 $[M^+]$, 93 $[M - H]^+$, 77 $[M - OH]^+$	93%
20.42 min	50%	Hydroquinone m/z = 110 $[M^+]$, 109 $[M - H]^+$, 77 $[M – H_2]^+$, 57 $[M – C_4H_7]^+$	91%

It is evident from the pyrogram that pyrolsis GC/MS of aqeous phase ammoxidized hydroquinone obtained many compounds; the main is hydroquinone with different percentage of acetamide, p-Benzoquinone and phenol.

5.2.3.2. 4-Methyl catechol.

Table: 27. Pyrolsis GC/MS results of aqeous phase ammoxidized 4-methyl catechol.

Retention time	Relative percentage	Name of compound	Propability
3.026 min	5%	Formamide m/z = 45 $[M^+]$, 29 $[M – NH_2]^+$, 17 $[M - CO]^+$	90%
4.521 min	5%	Acetamide m/z = 59 $[M^+]$, 44 $[M - CH_3]^+$, 28 $[M - OCH_3]^+$, 16 $[M - COCH_3]^+$	91%
6.096 min	2%	1H-Pyrrole, 4-methyl- m/z = 81 $[M^+]$, 53 $[M – CH^2CH_3]^+$	86%
14.279 min	10%	Phenol, 4-methyl m/z = 108 $[M^+]$, 107 $[M - H]^+$, 93 $[M – CH_3]^+$	96%
18.150 min	3%	Catechol m/z = 110 $[M^+]$, 109 $[M - H]^+$, 77 $[M – H_2]^+$, 57 $[M – C_4H_7]^+$	95%
19.278 min	5%	Phenol, o-amino m/z = 109 $[M^+]$, 93 $[M – NH_2]^+$, 92 $[M - OH]^+$	64%
20.934 min	60%	1,2-Benzenediol, 4-methyl m/z = 124 $[M^+]$, 109 $[M - CH_3]^+$, 81 $[M - OCH_3]^+$	95%
22.856 min	5%	3,4-(Methylenedioxy)toluene m/z = 136 $[M^+]$, 121 $[M - CH_3]^+$	42%
23.310 min	5%	Phenol, 2-amino-4-methyl m/z = 123 $[M^+]$, 107 $[M – NH_2]^+$, 105 $[M – H_2O]^+$	93%

Aqeous phase ammoxidized 4-methyl catechol obtained many compounds; Formamide, Acetamide, 4-methyl Phenol, Catechol, Phenol-o-amino, 4-methyl-1,2-benzenediol and 2-amino-4-methyl Phenol

5.2.3.3. 2-Methoxy-4-methylphenol.

Table: 28. Pyrolsis GC/MS results of aqeous phase ammoxidized 2-Methoxy-4-methylphenol.

Retention time	Relative percentage	Name of compound	Propability
3.253 min	5%	Formamide m/z = 45 $[M^+]$, 29 $[M - NH_2]^+$, 17 $[M - CO]^+$	90%
4.687 min	5%	Acetamide m/z = 59 $[M^+]$, 44 $[M - CH_3]^+$, 28 $[M - OCH_3]^+$, 16 $[M - COCH_3]^+$	91%
6.083 min	2%	1H-Pyrrole, 4-methyl m/z = 81 $[M^+]$, 53 $[M - CH_2CH_3]^+$	91%
14.313 min	3%	Phenol, 4-methyl m/z = 108 $[M^+]$, 107 $[M - H]^+$, 93 $[M - CH_3]^+$	96%
14.553 min	5%	Phenol, 2-methoxy m/z = 124 $[M^+]$, 109 $[M - CH_3]^+$, 81 $[M - OCH_3]^+$	95%
17.910 min	30%	Phenol, 2-methoxy-4-methyl m/z = 138 $[M^+]$, 123 $[M - CH_3]^+$, 107 $[M - CH_3O]^+$	95%
44.247 min	40%	1,1'-Biphenyl, 2',3',4'-trimethoxy-6-hydroxymethyl- m/z = 274 $[M^+]$, 259 $[M - CH_3]^+$, 231 $[M - CH_3O]^+$	52%

Aqeous phase ammoxidized 2-Methoxy-4-methylphenol obtained many compounds; Formamide, Acetamide, 1H-Pyrrole 4-methyl, Phenol 4-methyl, Phenol 2-methoxy and 2-methoxy-4-methyl

5.2.3.4. Catechol.

Table: 29. Pyrolsis GC/MS results of aqeous phase ammoxidized Catechol.

Retention time	Relative percentage	Name of compound	Propability
3.020 min	5%	Formamide m/z = 45 $[M^+]$, 29 $[M - NH_2]^+$, 17 $[M - CO]^+$	90%
4.321 min	3%	Acetamide m/z = 59 $[M^+]$, 44 $[M - CH_3]^+$, 28 $[M - OCH_3]^+$, 16 $[M - COCH_3]^+$	81%
11.049 min	5%	Propanamide, 2-methyl m/z = 87 $[M^+]$, 72 $[M - CH_3]^+$, 44 $[M - OCH_3]^+$	50%
15.461 min	7%	Benzoxazole, 2-methyl m/z = 133 $[M^+]$, 105 $[M - CO]^+$, 92 $[M - NCCH_3]^+$	97%
18.344 min	80%	Catechol m/z = 110 $[M^+]$, 109 $[M - H]^+$, 77 $[M - H_2]^+$, 57 $[M - C_4H_7]^+$	91%

There is some evidence from the pyrograms that aqeous phase ammoxidized catechol obtained many compounds; Formamide, Acetamide, 2-methyl Propanamide, 2-methyl Benzoxazole and the most was Catechol.

5.2.3.5. Methoxyhydroquinone.

Table: 30. Pyrolsis GC/MS results of aqeous phase ammoxidized Methoxy hydroquinone.

Retention time	Relative percentage	Name of compound	Propability
3.895 min	10%	Formamide m/z = 45 $[M^+]$, 29 $[M - NH_2]^+$, 17 $[M - CO]^+$	64%
19.96	20%	Hydroquinone m/z = 110 $[M^+]$, 109 $[M - H]^+$, 77 $[M - H_2]^+$, 57 $[M - C_4H_7]^+$	70%
36.132 min	20%	n-Hexadecanoic acid m/z = 256 $[M^+]$, 241 $[M - CH_3]^+$, 227 $[M - CH_2CH_3]^+$	27%
46.144 min	50%	1,2-Benzenedicarboxylic acid, diisooctyl ester m/z = 390 $[M^+]$, 375 $[M - CH_3]^+$, 361 $[M - CH_2CH_3]^+$, 317 $[M - COOCH_2CH_3]^+$	80%

Aqeous phase ammoxidized methoxyhydroquinone have many compounds; Formamide, n-Hexadecanoic acid and 1,2-Benzenedicarboxylic acid diisooctyl ester.

5.2.3.6. 2-Methoxyphenol.

Table: 31. Pyrolsis GC/MS results of aqeous phase ammoxidized 2-Methoxyphenol.

Retention time	Relative percentage	Name of compound	Propability
3.212 min	5%	Formamide m/z = 45 $[M^+]$, 29 $[M - NH_2]^+$, 17 $[M - CO]^+$	91%
4.493 min	5%	Acetamide m/z = 59 $[M^+]$, 44 $[M - CH_3]^+$, 28 $[M - OCH_3]^+$, 16 $[M - COCH_3]^+$	91%
14.671 min	60%	Phenol, 2-methoxy m/z = 124 $[M^+]$, 109 $[M - CH_3]^+$, 81 $[M - OCH_3]^+$	95%
17.835 min	5%	Phenol, 2-methoxy-4-methyl m/z = 138 $[M^+]$, 123 $[M - CH_3]^+$, 107 $[M - CH_3O]^+$	95%
21.359 min	5%	2-Methoxy-4-vinylphenol m/z = 150 $[M^+]$, 135 $[M - CH_3]^+$, 105 $[M - OCH_3]^+$	87%
24.643 min	3%	Benzonitrile, 4-hydroxy-3-methoxy- m/z = 149 $[M^+]$, 134 $[M - CH_3]^+$, 118 $[M - OCH_3]^+$	95%
25.858 min	2%	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- m/z = 166 $[M^+]$, 165 $[M - H]^+$, 149 $[M - OH]^+$	87%
27.313 min	5%	4-Hydroxy-3-methoxyphenylacetonitrile m/z = 163 $[M^+]$, 148 $[M - CH_3]^+$, 132 $[M - OCH_3]^+$	91%
28.040 min	5%	3-Hydroxy-4-methoxybenzoic acid m/z = 168 $[M^+]$, 153 $[M - CH_3]^+$, 137 $[M - OCH_3]^+$, 125 $[M - C_3H_7]^+$	97%
32.359 min	10%	3-Isopropoxy-4-methoxybenzamide m/z = 209 $[M^+]$, 194 $[M - CH_3]^+$, 195 $[M - NH_2]^+$	47%

Aqeous phase ammoxidized 2-Methoxylphenol obtained many compounds; Formamide, Acetamide, 2-methoxy Phenol, 2-methoxy-4-methyl Phenol, 2-Methoxy-4-vinylphenol, 4-Hydroxy-3-methoxy benzonitrile, 4-Hydroxy-3-methoxyphenylacetonitrile and 3-Hydroxy-4-methoxybenzoic acid.

The pyrogram reveals increasing nitrogeneous compound percentage than analysis by GC/MS in liquid state as we predicted before. The most of nitrogeneous compounds were amides forms. For determination the definite percentage of incroperated nitrogen during ammoxidation processes, elemental analysis was performed.

As aqueous phases seemed to be very polar, several derivatization techniques have been applied in order to convert at least a certain part of this fraction into less polar compounds which could be then studied by GC/MS. Table 32 provides the yields of the silylated "aqueous phases" of ammoxidized phenolic model compounds.

Table: 32. Yields of silylated compounds after silylation of the dried aqueous phases of ammoxidized phenolic model compounds and Indulin AT^{TM}.

	Amount of compound		
Compound name	**before silylation**	**after silylation**	**Percentage of silylated compoundwt.-%**
Ammoxidized Hydroquinone aqueous phase by ^{14}N	50 mg	41 mg	18%
oxidation Hydroquinone aqueous phase by NaOH	50 mg	11 mg	78%
Ammoxidized 4-Methylcatechol aqueous phase ^{14}N	50 mg	36 mg	28%
Oxidation 4-Methylcatechol aqueous phase NaOH	34.5 mg	31 mg	11%
Ammoxidized 2-Methoxy-4-methylphenol aqueous phase ^{14}N	50 mg	15 mg	70%
Ammoxidized Catechol aqueous phase by ^{14}N	50 mg	37 mg	26%
Ammoxidized Methoxyhydroquinone aqueous phase ^{14}N	50 mg	44 mg	12%

Oxidation Methoxyhydroquinone aqueous phase NaOH	50 mg	27 mg	46%
Ammoxidized 2-Methoxyphenol aqueous phase ^{14}N	50 mg	32 mg	36%
Ammoxidized Methoxybenzoquinone aqueous phase ^{15}N	50 mg	37 mg	26%
Ammoxidized Indulin AT aqueous phase ^{14}N	50 mg	42 mg	16%
Ammoxidized 2,5-Dihydroxy-1,4-benzoquinone aqueous phase ^{14}N	50 mg	33 mg	34%
Oxidation 2,5-Dihydroxy-1,4-benzoquinone aqueous phase NaOH at 100°C	50 mg	39 mg	22%
Oxidation 2,5-Dihydroxy-1,4-benzoquinone aqueous phase NaOH at 25°C	50 mg	15 mg	35%

Table 33 reveld that yields were obtained after silylation processes was partially for ammoxidized phenolic model compounds and indulin. This result supported what we have mentioned above about GC/MS silylated aqueous phases results.

5.2.4. Elemental analysis

Table: 33. Elemental analysis of aqueous phases ammoxidized phenols.

Compound name	**wt.-% C**	**wt.-% H**	**wt.-% N**
Hydroquinone	47.59	4.31	13.18
4-Methylcatechol	51.31	4.99	11.38
2-Methoxy-4-methylphenol	46.80	5.85	12.16
Catechol	43.97	4.27	13.54
Methoxyhydroquinone	45.42	4.69	12.65
2-Methoxyphenol	38.62	5.19	18.40
Methoxybenzoquinone	51.54	4.38	11.13
Indulin AT	53.84	5.63	5.92
Indulin AT reduced by Zn/HCl	54.04	4.66	2.79

2,5-Dihydroxy-1,4-benzoquinone	43.54	4.37	21.90

From the elemental analysis and the GC/MS measurements it became evident that the organic phases consisted mainly of the educts and some by-products not of larger amounts of nitrogeneous compounds. Hence, most nitrogen is bound in that fraction which was referred to "aqueous phase". Aqueous phase of ammoxidized 2,5-Dihydroxy-1,4-benzoquinone obtained the highest nitroge percentage 21.90% (tab. 32). The lowest nitrogen percentage was in reduced ammoxidized Indulin At due to reduction amides into amines compounds. In general hydrogen ranged from 4 to 5% and carbon from 40 to 50%. Quinones were more incroperated nitrogeneous compounds. Ammoxidized indulin obtained 6% nitrogen; it was in actuality nice result as fertilizer compound.

5.2.5. Studies on the type of nitrogen binding forms by means of X-ray photoelectron spectroscopy

5.2.5.1. 2,5-dihydroxy-1,4-benzoquinone

Table 34 displays the elemental contents of ammoxidized 2,5-dihydroxy-1,4-benzoquinone which were determined by both combustion of the bulk sample in an oxygen atmosphere and X-ray photoelectron spectroscopy at the surface of the sample. In case of the XPS measurements the employed UNIFIT 2008 programme has a sensitivity of 0.1[AT] %).

Table 34 shows the results of the deconvoluted X-ray photo-electron spectrum of ammoxidized 2,5-dihydroxy-1,4-benzoquinone using the programme UNIFIT 2008.

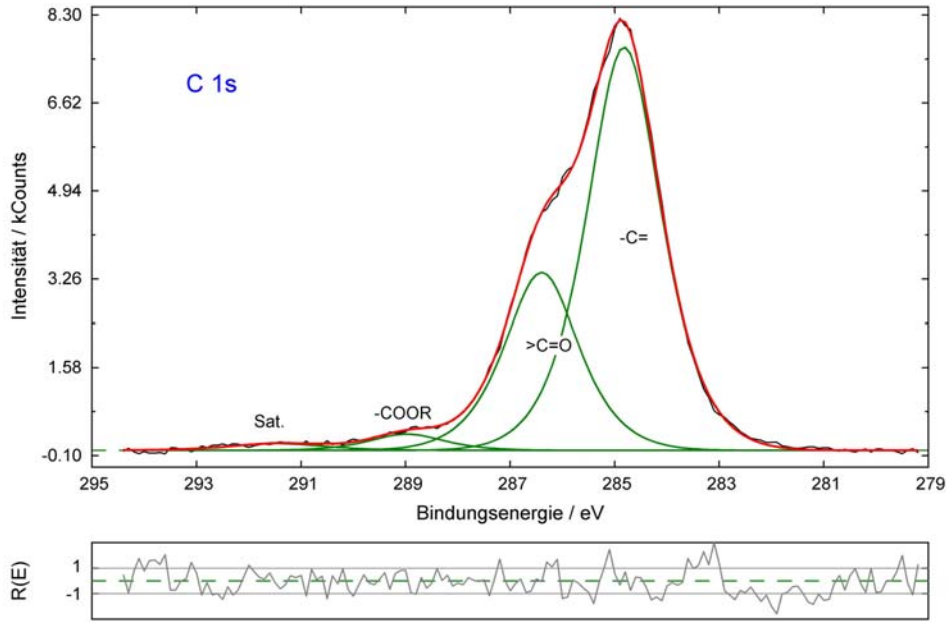
Table: 34. Elemental contents of ammoxidized 2,5-dihydroxy-1,4-benzoquinone.

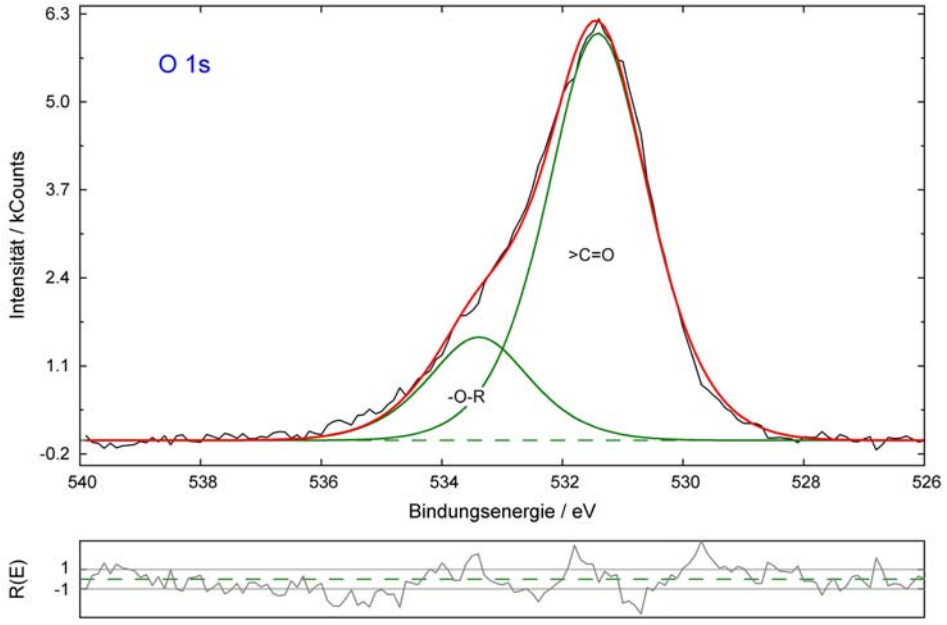
Method	C	O	N	C/N
XPS	65.4	18.6	16.0	4.1
Elemental analysis	43.54	34.56	21.90	2

The elemental contents of ammoxidized 2,5-dihydroxy-1,4-benzoquinone was measured by combustion of the balk sample in an oxygen atmosphere and XPS were different. The ratio of carbon in case of XPS was more than combustion method and Vis versa the oxygen and nitrogen ratio.

Table: 35. Results of the evaluation of the single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized 2,5-dihydroxy-1,4-benzoquinone.

Spectrum	HWB	Peak 1		Peak 2		Peak 3		Peak 4	
	[eV]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]
C 1s	1.94	284.8	57	286.8	29	288.6	11	290.6	3.5
O 1s	2.10	531.4	80	533.4	20				
N 1s	1.88	399.6	87	401.6	11	404.0	2		





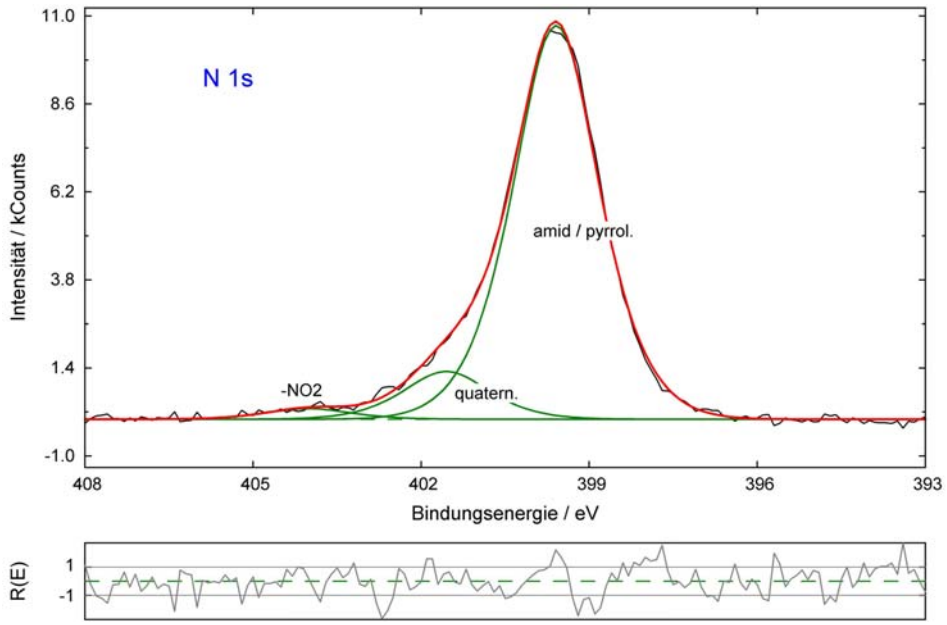


Figure 29. Single C 1s, O 1s, and N 1s X-ray photoelectron spectra of ammoxidized 2,5-dihydroxy-1,4-benzoquinone.

The deconvolution of the C 1s x-ray spectrum (figure 28) using the programme UNIFIT 2008 yields four peaks which can be assigned to aliphatic carbon (E_B 284.8 eV; most likely methylen groups), carbonyl carbon (E_B 286.6 eV), and esters of carboxylic acids (E_B 288.6 eV). The appearance of the fourth peak at E_B 290.6 eV is obviously due to satellite effects.
The binding energies E_B of the two peaks deconvoluted from the O 1s spectrum (figure 28) are indicative for the presence of carbonyl (E_B 531.4 eV) and ether groups (E_B 533.4 eV).
The binding energies E_B of the observed three peaks after deconvoluting the N 1s spectrum of ammoxidized 2,5-dihydroxy-1,4-benzoquinone reveal the presence of 1) amide or pyrrol-type nitrogen (E_B 399.6 eV), 2) quaternary ammonia salts (E_B 401.6 eV) and 3) a small percentage of nitro groups (E_B 404.0 eV). The amide or pyrrol-type nitrogen (E_B 399.6 eV) 87% was found to represent the largest nitrogen portion of ammoxidized 2,5-dihydroxy-1,4-benzoquinone, aliphatic carbon (E_B 284.8 eV; most likely methylen groups) 57% and carbonyl (E_B 531.4 eV) 80% were also the largest carbon and oxygen portion respectively **(**table 35**).**

5.2.5.2. Methoxyhydroquinone [90]

Table: 36. Elemental contents of ammoxidized methoxyhydroquinone.

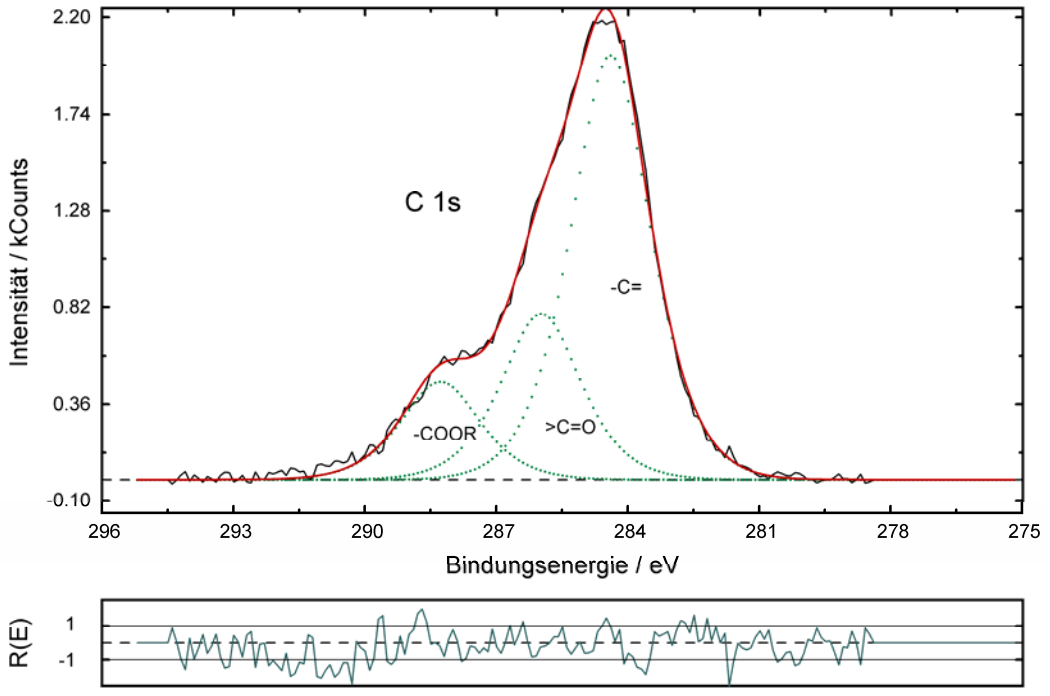
Method	C 1s	O 1s	N 1s	C/N
XPS	66.6	22.2	11.2	3.12
Elemental analysis	45.42	41.93	12.65	3.59

The elemental contents of ammoxidized methoxyhydroquinone which were determined by both combustion of the bulk sample in an oxygen atmosphere and X-ray photoelectron spectroscopy at the surface of the sample (table 36). The ratios of elements of ammoxidized methoxyhydroquinone in the two methods were different, in case of XPS carbon (66.6) was more than carbon obtained by combustion method (45.42) and Vis versa the oxygen and nitrogen ratio (table 36).

Table 37 shows the results of the deconvoluted X-ray photo-electron spectrum of ammoxidized methoxyhydroquinone using the programme UNIFIT 2008.

Table 37: Results of the evaluation of the single C 1s, O s, and N 1s x-ray photoelectron spectra of ammoxidized methoxyhydroquinone.

Spectrum	HWB	Peak 1		Peak 2		Peak 3	
	[eV]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]
C 1s	2.23	284.4	61.7	286.0	24.1	288.3	14.3
O 1s	2.40	530.9	48.8	532.5	51.2		
N 1s	1.94	398.5	31.5	399.5	52.8	401.0	15.7



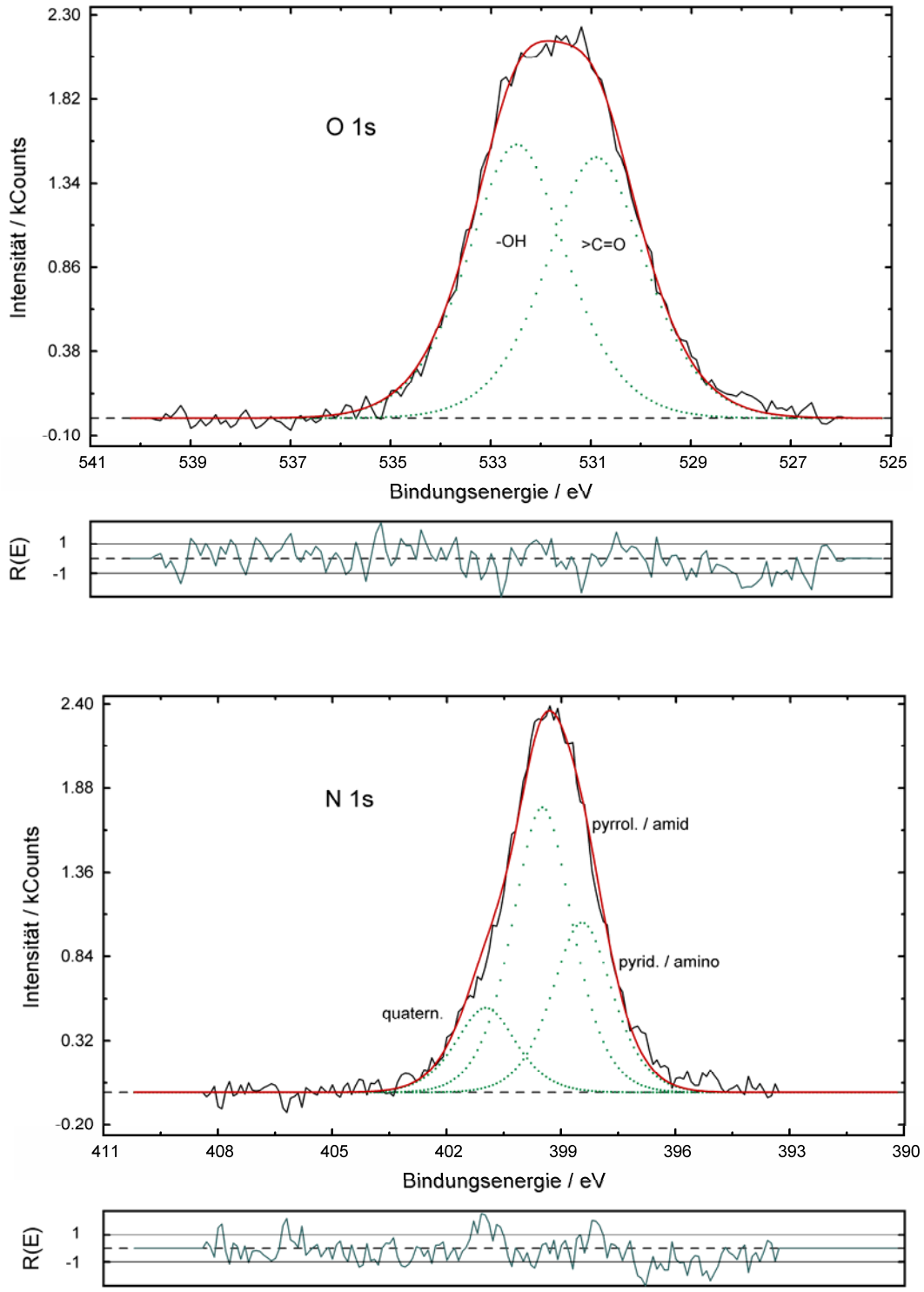


Figure 29. Single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized methoxyhydroquinone

The deconvolution of the C 1s x-ray spectrum (figure 29) using the programme UNIFIT 2008 yields three peaks which can be assigned to aliphatic carbon (E_B 284.8 eV; most likely methylen groups), carbonyl carbon (E_B 286. eV), and esters of carboxylic acids (E_B 288.6 eV).

The binding energies E_B of the two peaks deconvoluted from the O 1s spectrum (figure 29) are indicative for the presence of carbonyl (E_B 530.9 eV) and hydroxyl groups (E_B 532.5 eV).

The binding energies E_B of the observed three peaks after deconvoluting the N 1s spectrum of ammoxidized methoxyhydroquinone reveal the presence of 1) (pyrid./amino)-type nitrogen (E_B 398.5 eV), 2) amide or pyrrol (E_B 399.5 eV) and 3) quaternary ammonia salts (E_B 401.0 eV). The amide or pyrrol-type nitrogen (E_B 399.5 eV) 52.8% was found to represent the largest nitrogen portion of ammoxidized methoxyhydroquinone, aliphatic carbon (E_B 284.4 eV; most likely methylen groups) 61.7% and hydroxyl groups (E_B 532.5 eV) 51.2% were also the largest carbon and oxygen portion respectively **(**table 37**).**

5.2.5.3. Indulin AT™

Table 38 has the elemental contents of ammoxidized indulin AT which were determined by both combustion of the bulk sample in an oxygen atmosphere and X-ray photoelectron spectroscopy at the surface of the sample. In case of the XPS measurements the employed UNIFIT 2008 programme has a sensitivity of 0.1 (AT-%).

Table: 38. Elemental contents of ammoxidized indulin AT.

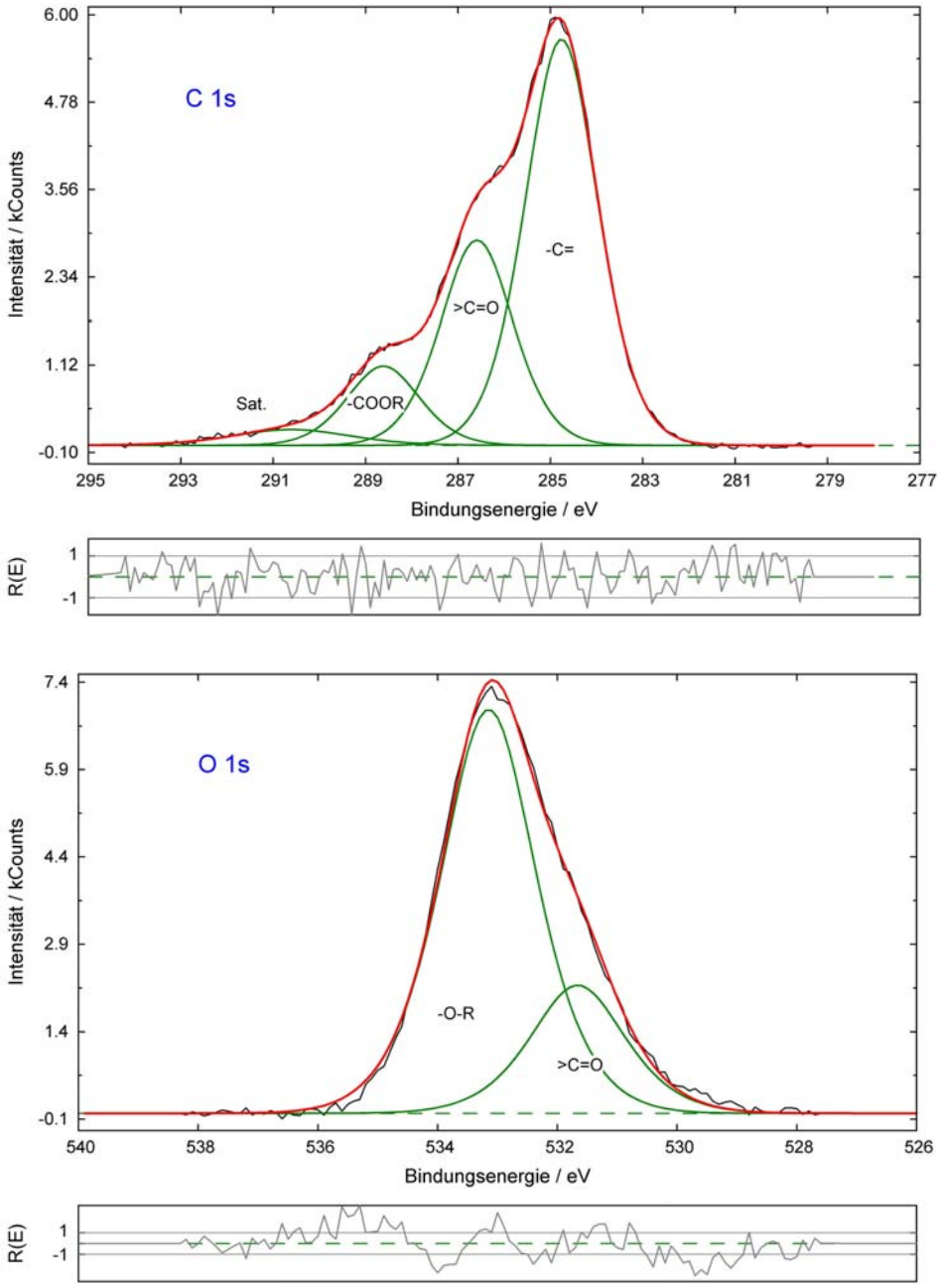
Method	C	O	N	C/N
XPS	74.7	21.8	3.5	21.3
Elemental analysis	53.84	40.24	5.92	9

The elemental contents of ammoxidized Indulin AT™ measured by combustion of the bulk sample in an oxygen atmosphere and XPS were different. The carbon contents were higher for the XPS measurements whereas higher oxygen and nitrogen contents were determined by elemental analysis.

Table 39 shows the results of the deconvoluted X-ray photo-electron spectrum of ammoxidized indulin AT using the programme UNIFIT 2008.

Table 39: Results of the evaluation of the single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized indulin AT.

Spectrum	HWB	Peak 1		Peak 2		Peak 3		Peak 4	
	[eV]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]
C 1s	1.74	284.8	67	286.4	29	289.0	3	291.5	1.5
O 1s	1.95	531.7	24	533.0	76				
N 1s	2.4	399.1	24	400.1	60	401.9	15		



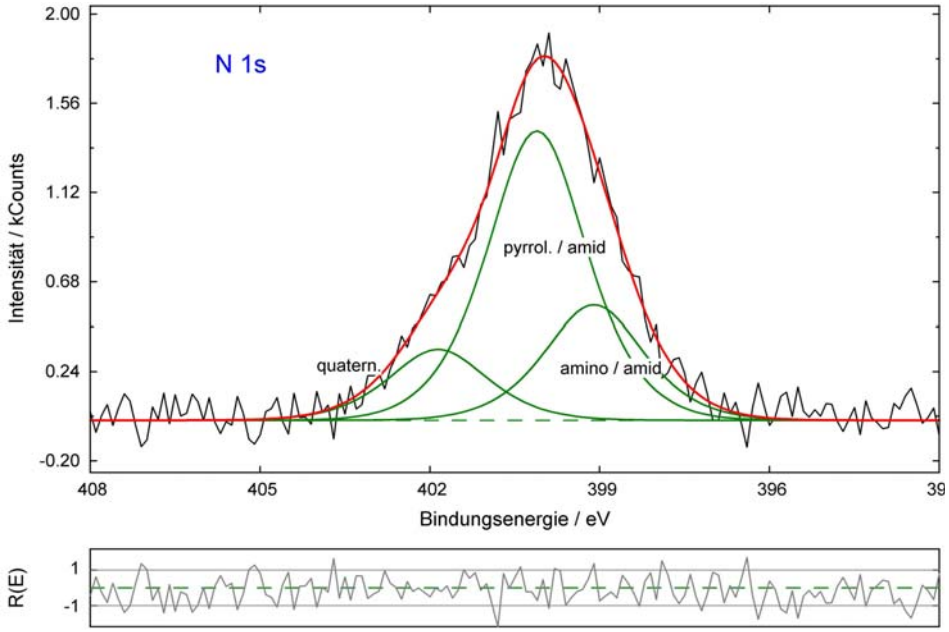


Figure 30. Single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized indulin AT

The deconvolution of the C 1s x-ray spectrum (figure 30) using the programme UNIFIT 2008 yields four peaks which can be assigned to aliphatic carbon (E_B 284.8 eV; most likely methylen groups), carbonyl carbon (E_B 286.4 eV), and esters of carboxylic acids (E_B 289.0 eV). The appearance of the fourth peak at E_B 291.5 eV is obviously due to satellite effects.
The binding energies E_B of the two peaks deconvoluted from the O 1s spectrum (figure 17) are indicative for the presence of carbonyl (E_B 531.7 eV) and ether groups (E_B 533.0 eV).
The binding energies E_B of the observed three peaks after deconvoluting the N 1s spectrum of ammoxidized indulin AT reveal the presence of 1) amino or amide-type nitrogen(E_B 399.1 eV), 2) amide or pyrrol (E_B 400.1 eV), 3) and quaternary ammonia salts (E_B 401.9 eV). The amide or pyrrol-type nitrogen (E_B 400.1 eV) 60% was found to represent the largest nitrogen portion of ammoxidized indulin AT, aliphatic carbon (E_B 284.8 eV; most likely methylen groups) 67% and ether (E_B 533.0 eV) 76% were also the largest carbon and oxygen portion respectively **(**table 39**).**

5.2.5.4. Sucrolin [90]

Table 40 has the elemental contents of ammoxidized Sucrolin which were determined by X-ray photoelectron spectroscopy at the surface of the sample. In case of the XPS measurements the employed UNIFIT 2008 programme has a sensitivity of 0.1 (AT-%).

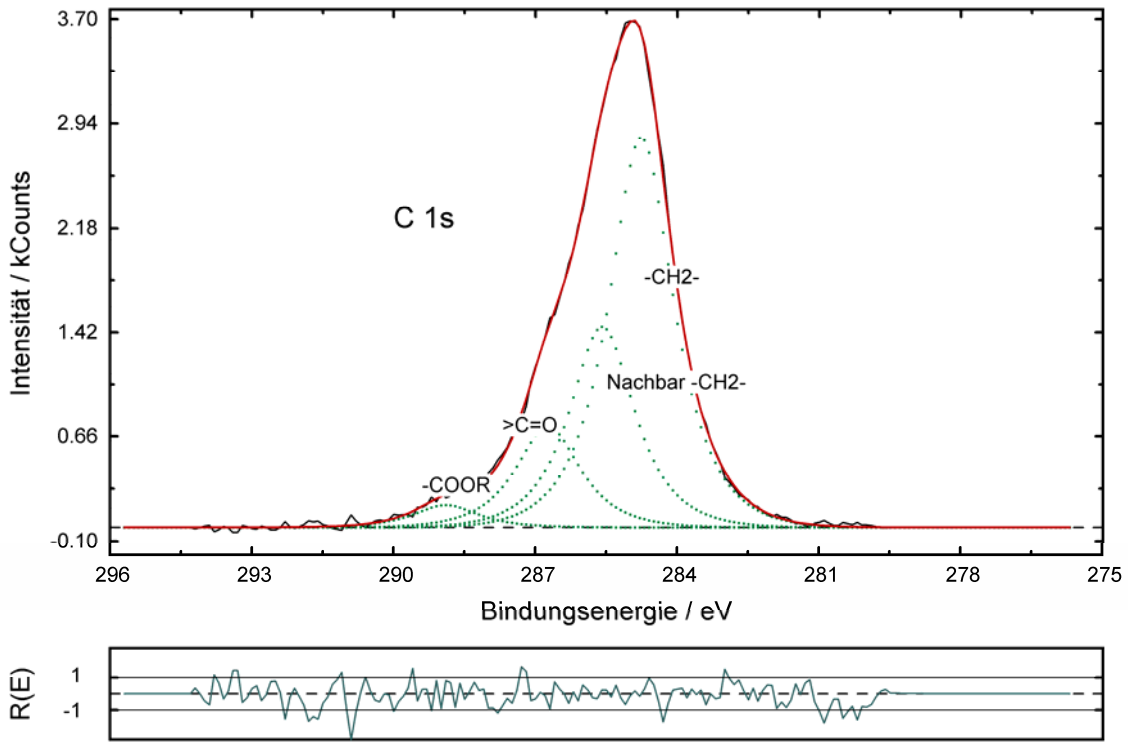
Table: 40. Elemental contents of ammoxidized ammoxidized Sucrolin

Method	C	O	N	C/N
XPS	78.3	18.2	3.5	22.37

Table 41 shows the results of the deconvoluted X-ray photo-electron spectrum of ammoxidized Sucrolin using the programme UNIFIT 2008.

Table 41: Results of the evaluation of the single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized Sucrolin.

Spectrum	HWB	Peak 1		Peak 2		Peak 3		Peak 4	
	[eV]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]	E_B [eV]	[%]
C 1s	1.64	284.8	54.7	285.6	28.2	286.7	14.1	288.9	3.1
O 1s	2.01	530.7	6.7	532.1	28.2	533.3	61.3		
N 1s	1.76	398.6	16.4	400.0	60.1	401.5	23.5		



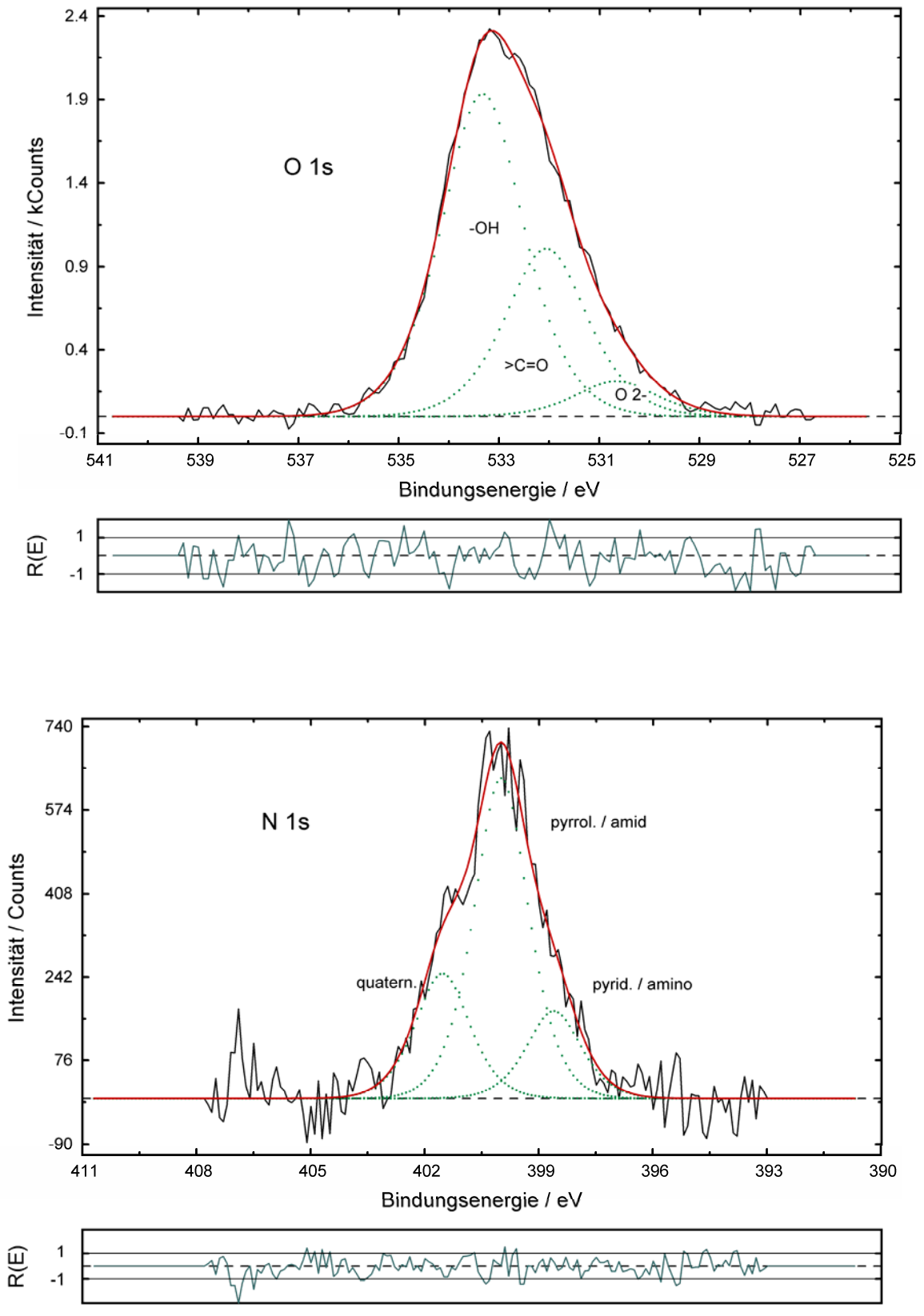


Figure: 31. Single C 1s, O 1s, and N 1s x-ray photoelectron spectra of ammoxidized Sucrolin

The deconvolution of the C 1s x-ray spectrum (figure 31) using the programme UNIFIT 2008 yields four peaks which can be assigned to aliphatic carbon (E_B 284.8 eV; most likely methylen groups), aliphatic carbon long chain (E_B 285.6 eV), carbonyl carbon (E_B 286.7 eV) and esters of carboxylic acids (E_B 288.9 eV).
The binding energies E_B of the three peaks deconvoluted from the O 1s spectrum (figure 18) are indicative for the presence of (O^{2-}) group (E_B 530.7 eV), carbonyl (E_B 532.1 eV) and hydroxyl groups (E_B 533.3 eV).
The binding energies E_B of the observed three peaks after deconvoluting the N 1s spectrum of ammoxidized Sucrolin reveal the presence of 1) pyridine or amino-type nitrogen (E_B 398.6 eV), 2) amide or pyrrol (E_B 400.0 eV), 3) and quaternary ammonia salts (E_B 401.5 eV). The amide or pyrrol-type nitrogen (E_B 400.0 eV) 60.1% was found to represent the largest nitrogen portion of ammoxidized Sucrolin, aliphatic carbon (E_B 284.8 eV; most likely methylen groups) 54.7% and hydroxyl groups (E_B 533.3 eV) 61.3% were also the largest carbon and oxygen portion respectively **(**table 41**).**

After these four XPS results we can briefly summarize that all N 1s XPS spectra of all four studied ammoxidized technical lignins (Sucrolin, Indulin) and phenolic model compounds (methoxyhydroquinone, 2,5-dihydroxybenzoquinone) look similar. There is some evidence from deconvoluting the spectra that the ammoxidized compounds contain nitrogen mainly in the form of ammonia, amides and pyrrol-type heterocycles. Amide-type nitrogen compounds are the most aboundent nitrogen-tybe compounds (60-80%).

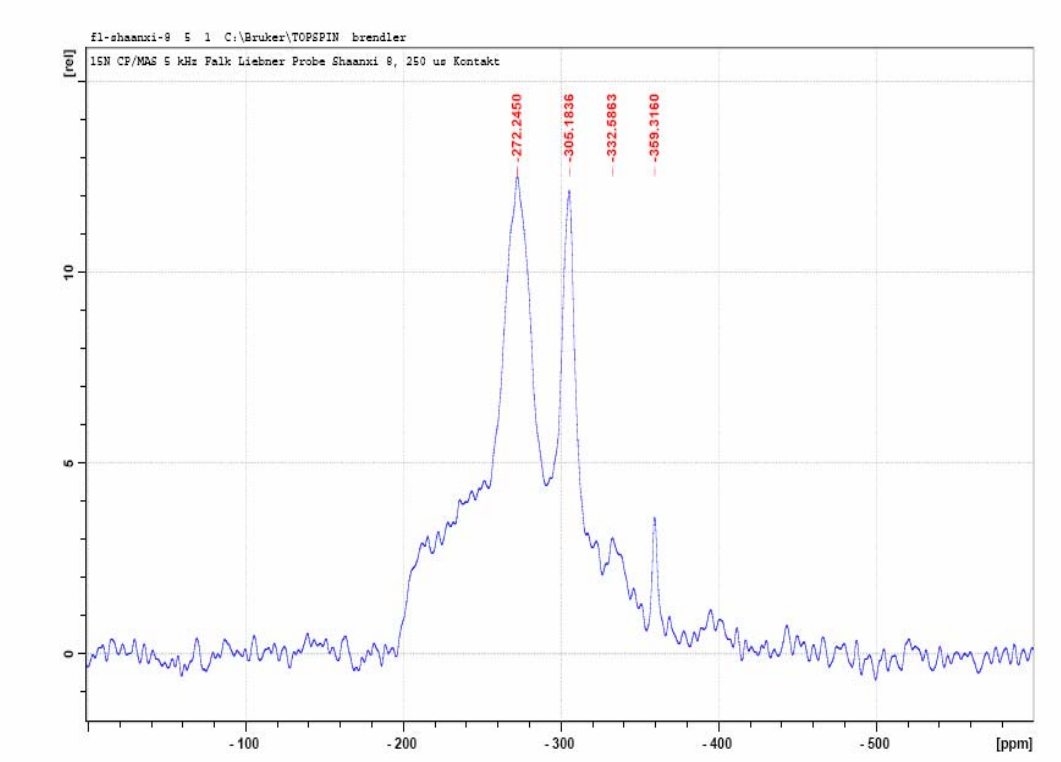
5.2.6. Studies on the type of nitrogen binding forms by ^{15}N CPMAS NMR

As surface analytical techniques such as XPS may yield unreliable results in some cases mainly caused by surface contamination, additional use of a complimentary technique such as NMR is recommended. However, the binding energy peak pattern of certain chemical groups observed by X-ray photoelectron spectroscopy and the resonance signal pattern in solid-state NMR are very similar in many cases (Lambert et al. 1999).
The non-favorite gyromagnetic ratio (low sensitivity) and the low natural occurrence of the ^{15}N nucleos do not favour NMR measurements of nitrogen containing compounds. Hence, the ^{15}N content of the samples studied in the scope of this project was increased prior to the CPMAS NMR spectroscopic studies by adding a certain amount of ^{15}N labelled ammonium hydroxide to the reaction mixture (cf. chapter materials and methods)..

^{15}N CPMAS NMR spectroscopic studies of Sucrolin^{TM} which was ammoxidized by using a 5 % NH_4OH solution containing 4 atom-% of ^{15}N strongly support the results of XPS spectroscopy as the most intense signals were found in the amide range (-260 to -290 ppm; reference: CH_3NO_2). Deconvolution of the spectrum furthermore reveals the presence of larger amounts of urea (-305 ppm), amines (-340 ppm), and smaller amounts of compounds resonating in the range of -200 to -225 ppm which can be obviously assigned to pyrrol-type nitrogeneous compounds (figure 32, right). Another broad signal was found in the chemical shift range between -210 and -275 ppm. The occurrence of this signal is indicative for the presence of a larger amount of rigid -NH- groups as they are found in benzoxazin(on)es, benzoxazolones or polyamides, for example. Ammonia groups peaking at -355 ppm were also detected but the signal intensity shown in figure 32 can not be compared with the other signals due to the completely different relaxation behaviour of ammonia nitrogen (Liebner et al. 2008).

In general, all resonance signals in the ^{15}N NMR spectra were very broad which is indicative for the presence of either paramagnetic species or stable radicals, the latter being known to occur in ligneous structures. The ^{15}N CPMAS NMR spectrum of the mixed softwood Kraft lignin Indulin AT^{TM} was quite similar to the spectrum obtained for the South-African bagasse lignin Sucrolin [figure 32, reference liebner 11].

Interestingly, it was found that the isolated aqueous phases of the ammoxidized phenolic model compounds gave NMR spectra which were very similar to those spectra obtained from both studied technical lignins.



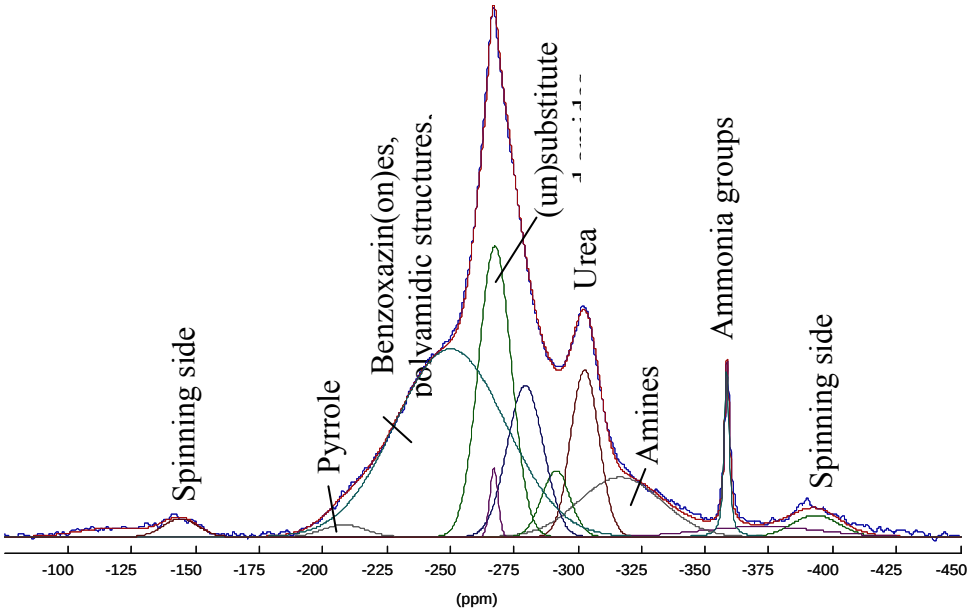


Figure: 32. Indulin and Sucrolin ^{15}N CPMAS NMR respectively.

Hydroquinone

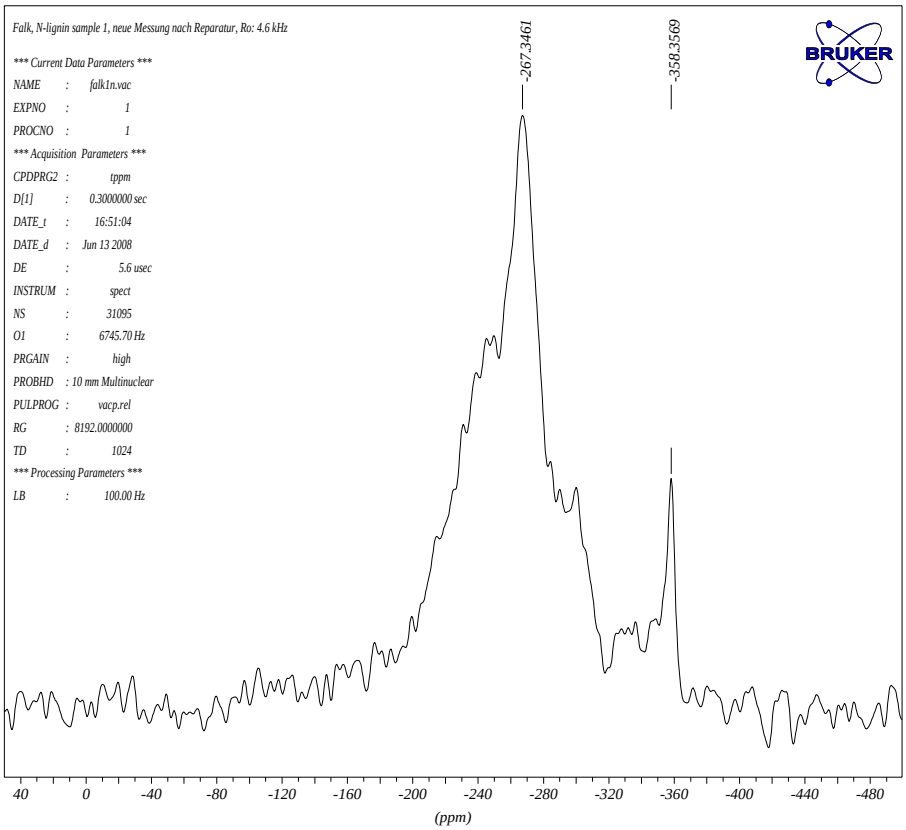
Tabel: 42. ammoxidized hydroquinone ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-260 to -290	amides	broad, high
-358	ammonia	sharp, high

4-methyl catechol

Tabel: 43.ammoxidized 4-methyl catechol ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-149	pyrrols derivatives	sharp, low
-267	amides	broad, high
-302	urea	broad, high
-358	ammonia	sharp, high



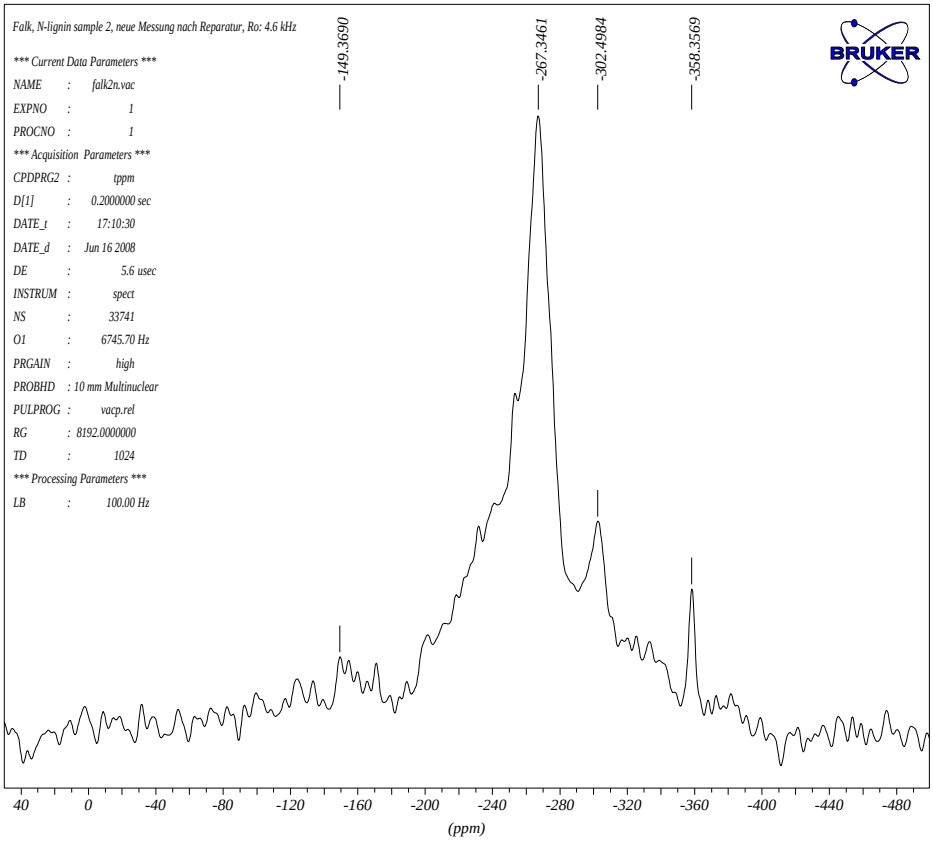


Figure 33.. Hydroquinone and 4-Methyl catechol ^{15}N CPMAS NMR spectra

2-Methoxy-4-methylphenol

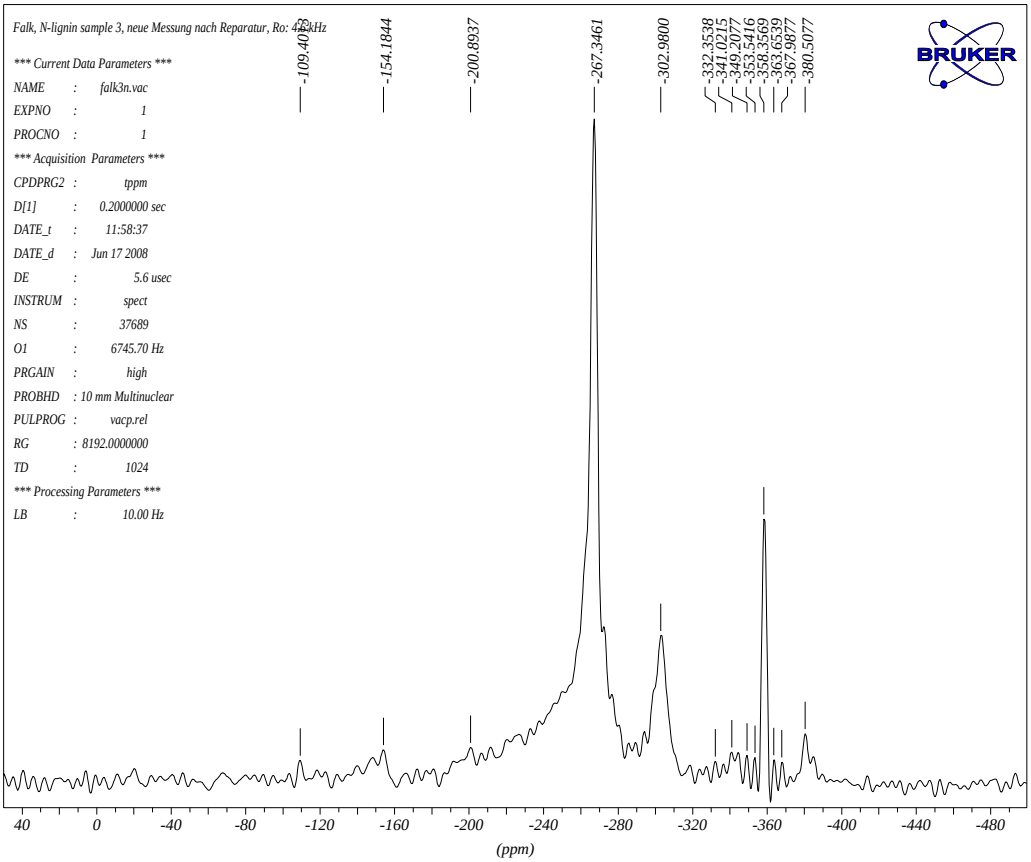
Tabel: 44. Ammoxidized 2-methoxy-4-methylphenol ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-267	amides	sharp, high
-302	urea	broad, low
-358	ammonia	sharp, high

Catechol

Tabel: 45. Ammoxidized catechol ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-152	pyridine	broad, low
-266	amides	broad, high
-302	urea	broad, low
-358	ammonia	sharp, high



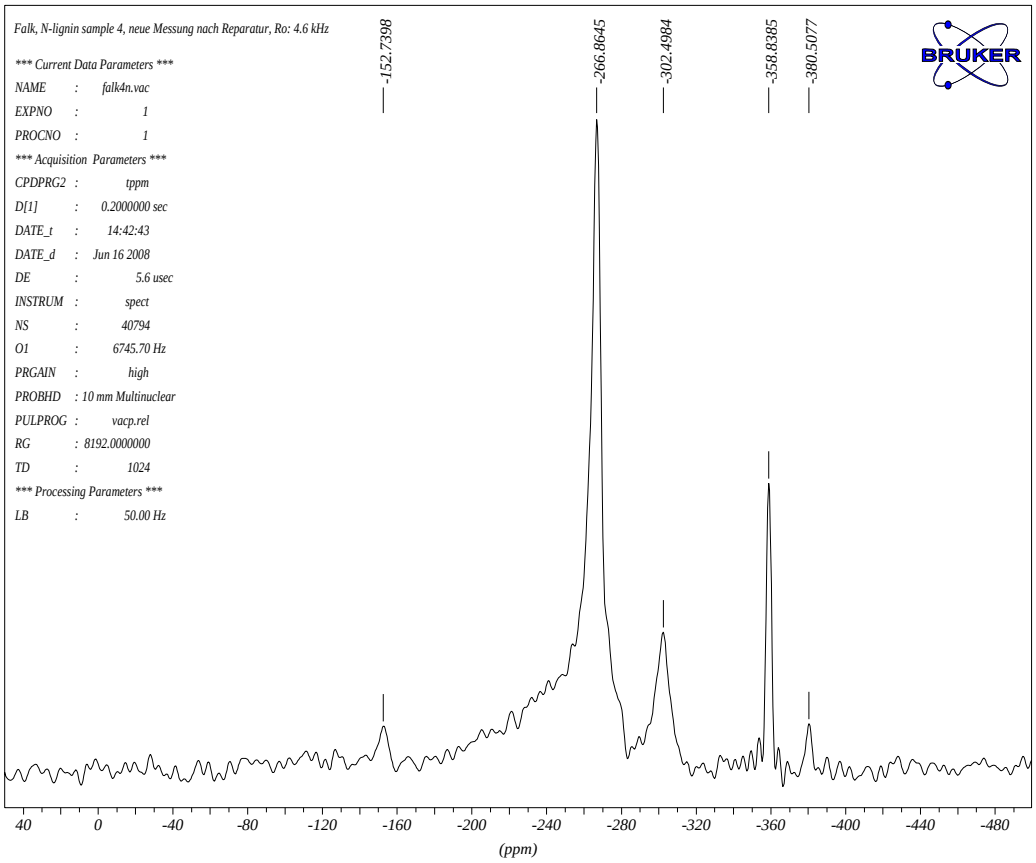


Figure: 34. 2-Methoxy-4-methylphenol and Catechol ^{15}N CPMAS NMR spectra

Methoxyhydroquinone

Tabel: 46. Ammoxidized Methoxyhydroquinone ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-152	pyridine	broad, low
-266	amides	broad, high
-348	amino	broad, low
-358	ammonia	sharp, high

2-Methoxy phenol:

Tabel: 47. Ammoxidized 2-Methoxy phenol ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-150 to -220	heteroaromatic	broad, low
-267	amides	broad, high
-303 to -325	urea	broad, low
-358	ammonia	sharp, high

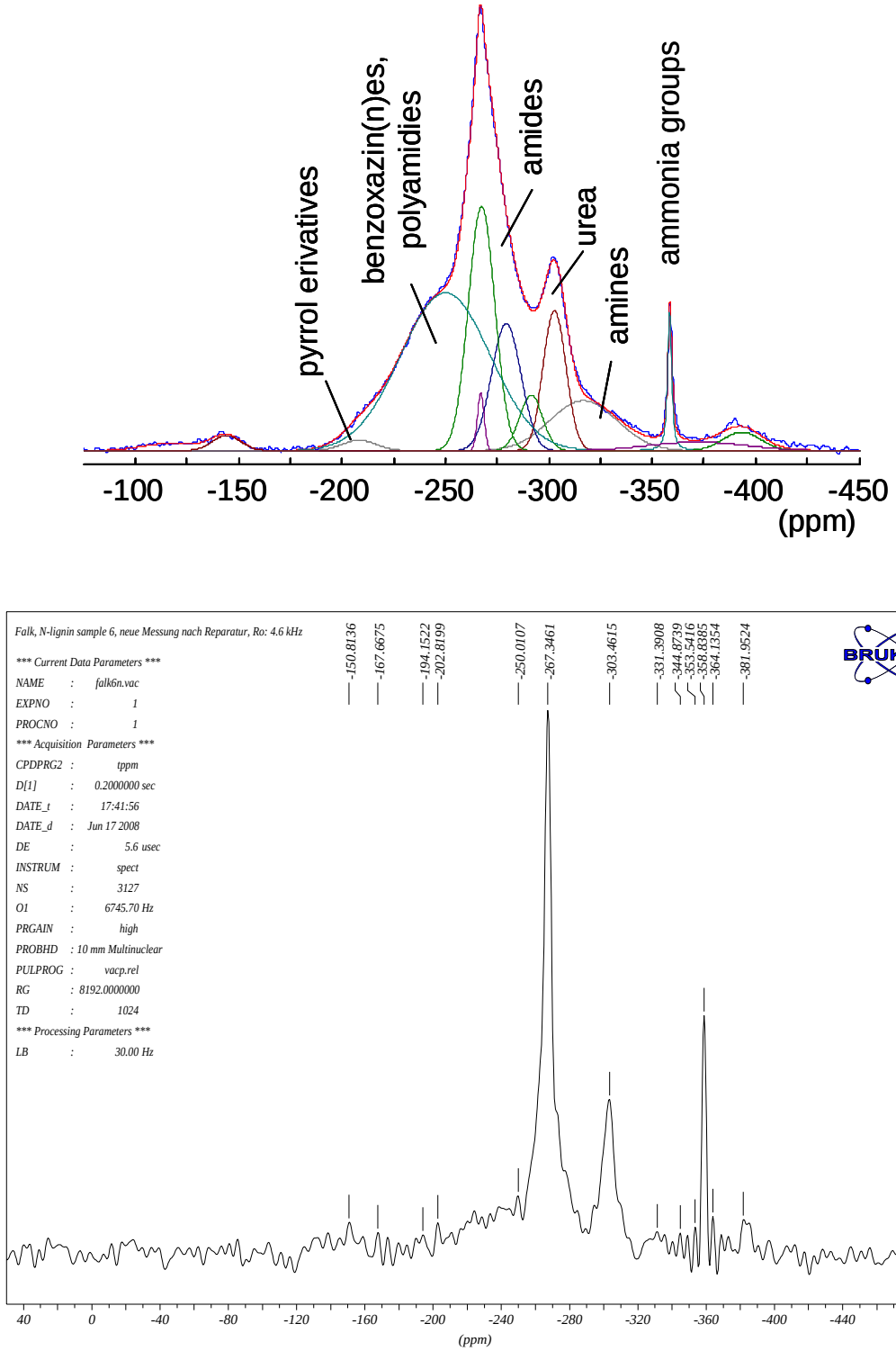


Figure 35. Ammoxidized Methoxyhydroquinone and 2-Methoxy phenol ^{15}N CPMAS NMR specra

Methoxy benzoquinoine:

Tabel: 48. Ammoxidized Methoxy benzoquinone ^{15}N CPMAS NMR results

Chemical shift (CH_3NO_2) [ppm]	Assignment	Peak form
-117	nitriles	broad, low
-267	amides	broad, high
-303	urea	broad, low
-357	ammonia	sharp, high

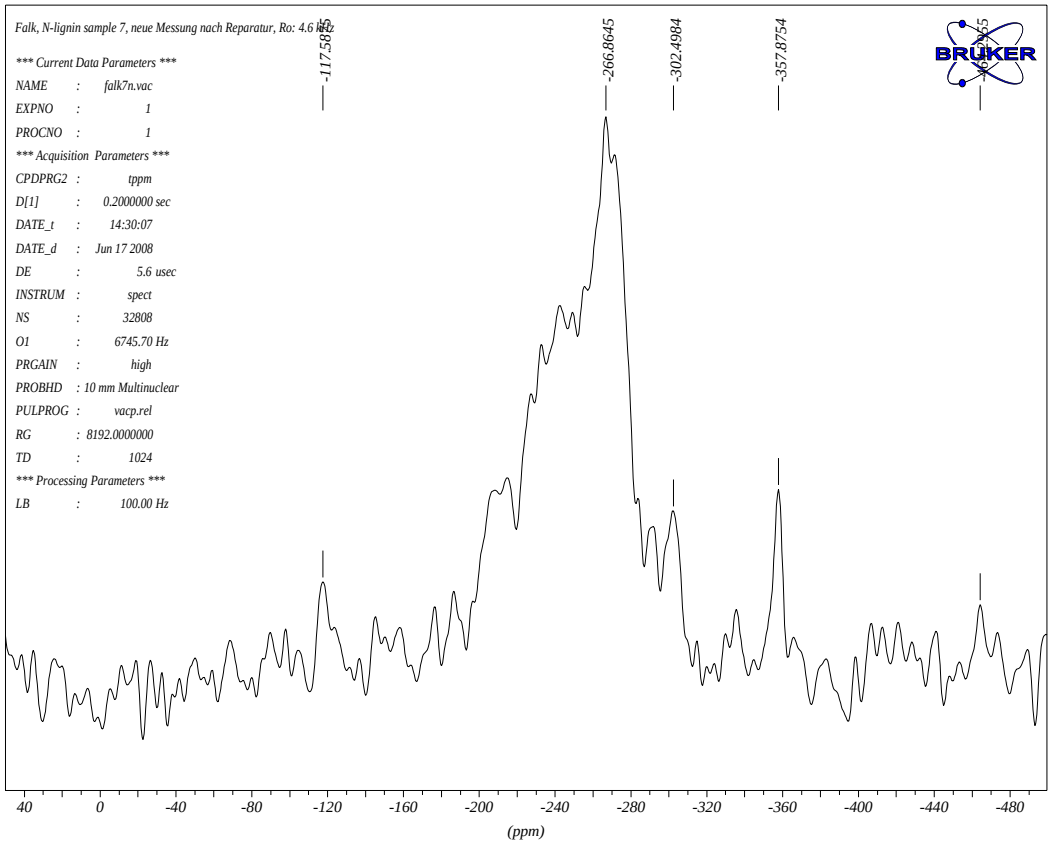


Figure 36. Ammoxidized Methoxy benzoquinone ^{15}N CPMAS NMR specra

From all spectra we can conclude that, the most intense and very broad signal was found in amid form (-267 ppm; reference: CH_3NO_2); a second large peak at -358 ppm is indicating the presence of ammonia groups. There were found a couple of small signals which indicate that some nitrogeneous by-products were also formed. In case of 4-methyl catecol beside amides and ammonia compounds a low peak at -149 ppm reveals the presence of pyrrols derivatives;

occurance of signal at -302 ppm is indicative for the presence of urea in comparison with catechol the spectrum contains a smaller peak in the urea range (-302 ppm) and at -152 ppm could be caused by pyridine-type nitrogen moieties.

2-methoxy-4-methylphenol occurance of signal at -302 ppm is indicative the presence of urea; some low signals in the range of -325 to -350 ppm indicate the presence of amino groups ($-NH_2$); Ammonia (-358 ppm) groups were found to be present in rather larger amounts. There were found a couple of small signals which indicate that some nitrogeneous by-prodzucts were also formed. 2-methoxy-phenol has a couple of peaks can be found in the range of -150 to -220 ppm indicate the presence of heteroaromatic nitrogeneous compounds and (-303 to -325 ppm) indicate the presence of urea.

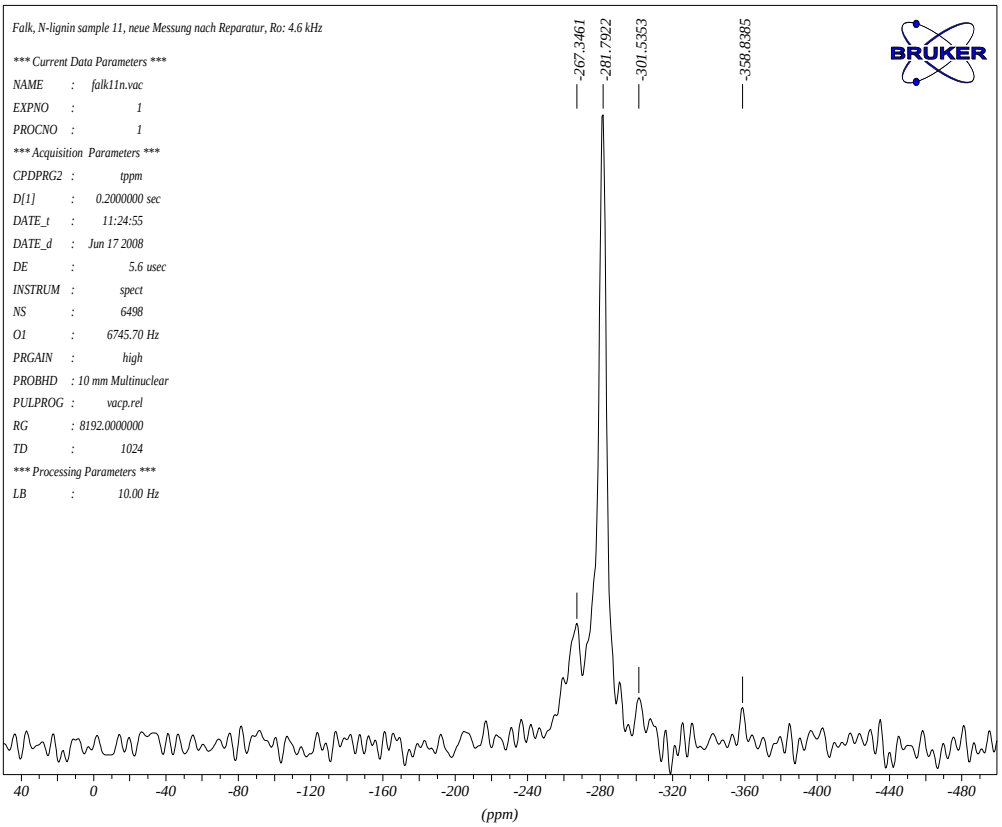
Methoxyhydroquinone have Pyridine-type nitrogeneous compounds at -152 ppm and small peak at - 348 ppm indicate the presence of free amino groups ($-NH_2$). Methoxy benzoquinone at -117 ppm low concentration of nitriles group compounds and -303 ppm peak indicate the presence of urea.

In order to study the influence of oxygen pressure and temperature on the type of nitrogen binding forms, 2,5-dihydroxybenzoquinone was ammoxidized under different reaction conditions (cf. table 49).

Table: 49. Ammoxidized 2,5-dihydroxybenzoquinone under different reaction conditions

p O_2 [bar]	T [°C]	Chemical shift [ppm] and peak assignment
2	100	-250 to -285 (amide), -301 (urea), -358 (ammonia)
2	25	-358 (ammonia)
1	25	-358 (ammonia)

Ammoxidized aqeouse phase of 2,5-dihydroxy-1,4-benzoquinone at 100°C have the most intense signal was foune in the amide ; urea and ammonia . Otherwise ammoxidation at 25°C and 25°C in ambient pressure have only ammonia.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EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
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DATE_d : Jun 17 2008
DE : 5.6 usec
INSTRUM : spect
NS : 6498
O1 : 6745.70 Hz
PRGAIN : high
PROBHD : 10 mm Multinuclear
PULPROG : vacp.rel
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TD : 1024
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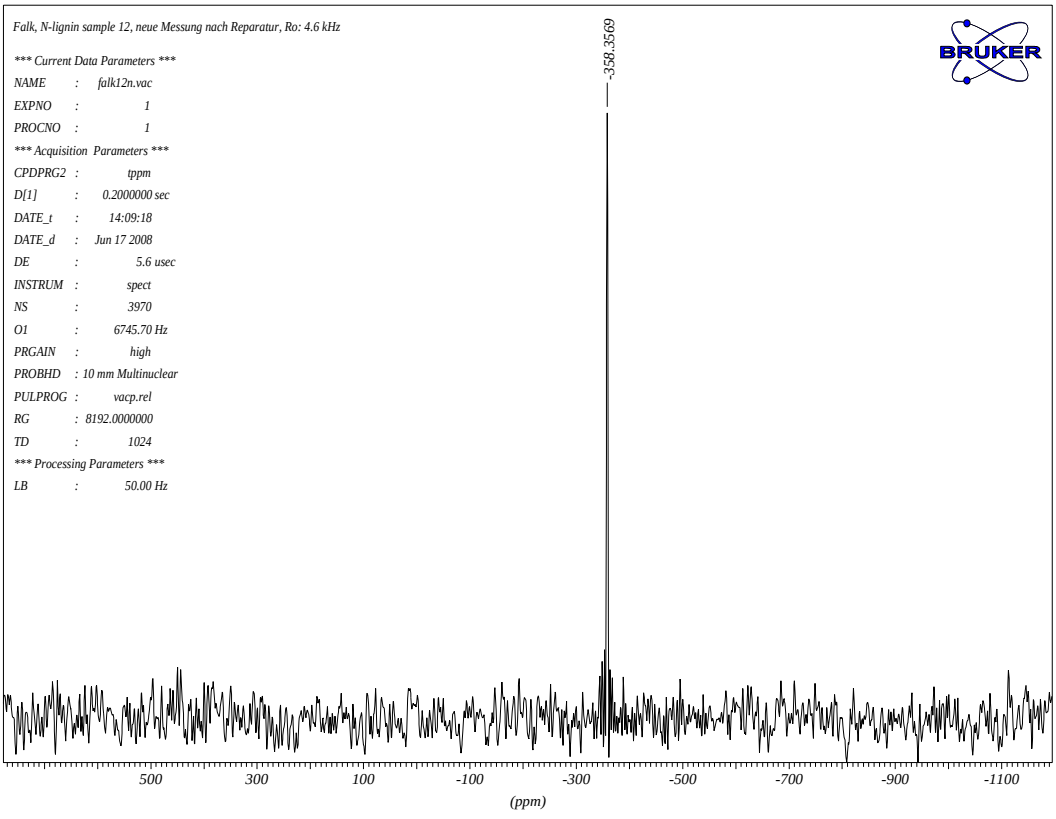
BRUKER
40 0 -40 -80 -120 -160 -200 -240 -280 -320 -360 -400 -440 -480
(ppm)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DE : 5.6 usec
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PRGAIN : high
PROBHD : 10 mm Multinuclear
PULPROG : vacp.rel
RG : 8192.0000000
TD : 1024
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(ppm)

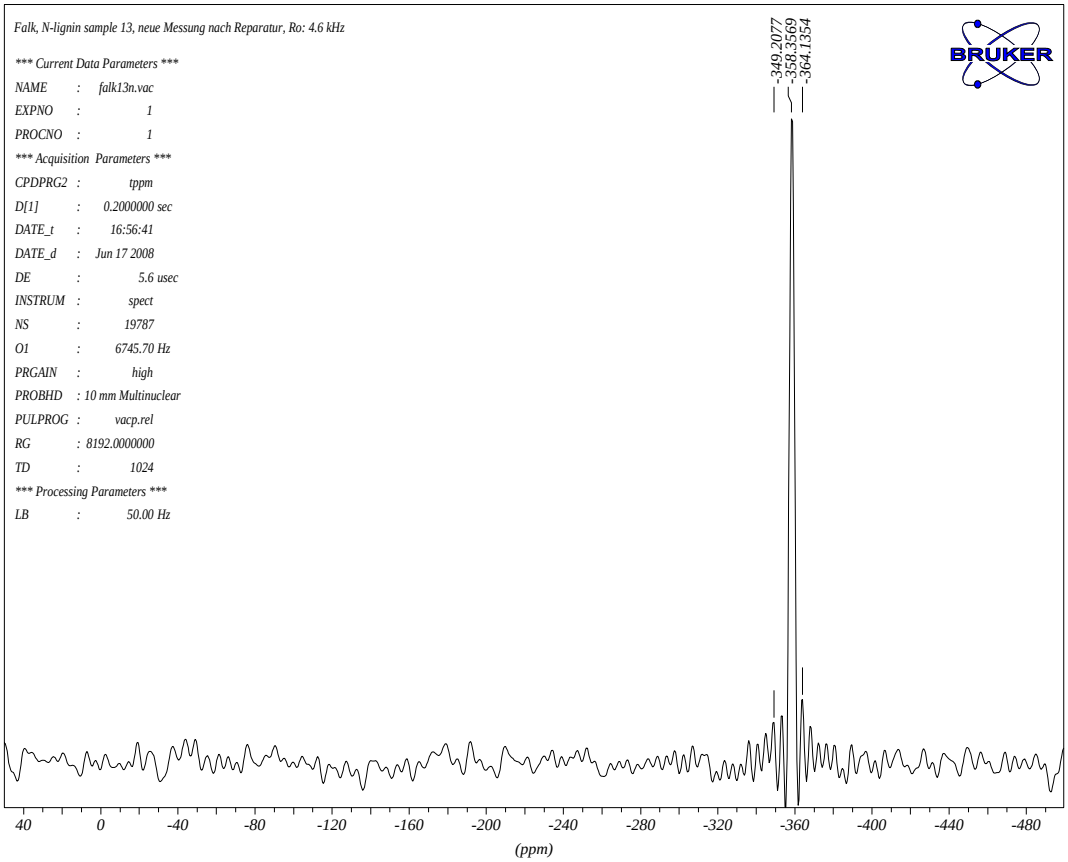
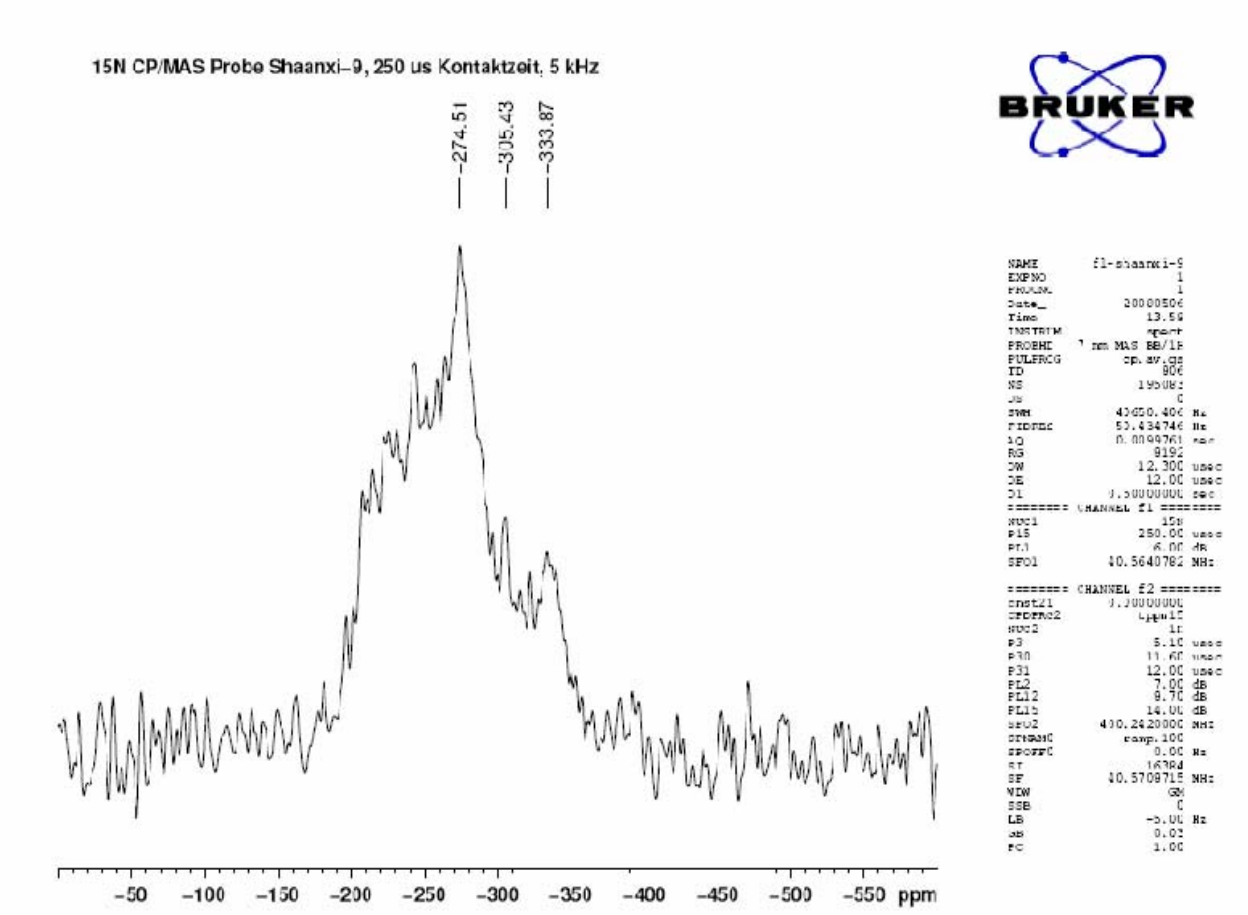


Figure 37. Ammoxidized_2,5-dihydroxy-1,4-benzoquinone at 100°C, 25°C and 25°C in ambient pressure ^{15}N CPMAS NMR spectra

Conclusion: Main nitrogen binding forms in all aqueous phases of ammoxidized phenolic model compounds were amides, ammonia and some pyrrol-type nitrogen. There were found a couple of small signals which indicate that some nitrogeneous by-products were also formed like amine, urea and heteroaromatic nitrogeneous compounds.

In order to prove if the broad signal appearing in the chemical shift range between -265 and -290 ppm is indeed caused by amides, the aqueous phase of the ammoxidized Indulin AT^{TM} was reduced with Zn/HCl as it is known that reduction of carboxylic amides results in the formation of amines. As expected, the broad intensive signal was reduced significantly by Zn/HCl reduction. Since no increase in the amine range (-320 to -350 ppm) was observed one can conclude that low molecular alkyl amines were formed from amides of lower molecular carboxylic acids such as formamide, acetamide or even amids of muconic acid derivatives which can be formed in the course of ammoxidation. The low molecular reaction products were removed during the work-up procedure and hence, were not part of the sample which was studied by NMR.

A similar clear picture was obtained from the reduction of ammoxidized Indulin with NaOBr. The Hoffmann degradation of primary amides proceeds via the formation of isocyanates and results in the formation of primary amines which have one carbon atom less than the original amide. Interestingly, only a weak, broad resonance signal between -200 and -270 ppm remained in the ^{15}N CPMAS NMR spectrum after treating the aqueous phase of ammoxidized Indulin with sodium hypobromide. This suggests that the majority of the total organic nitrogen seems to be bound in amide moieties.



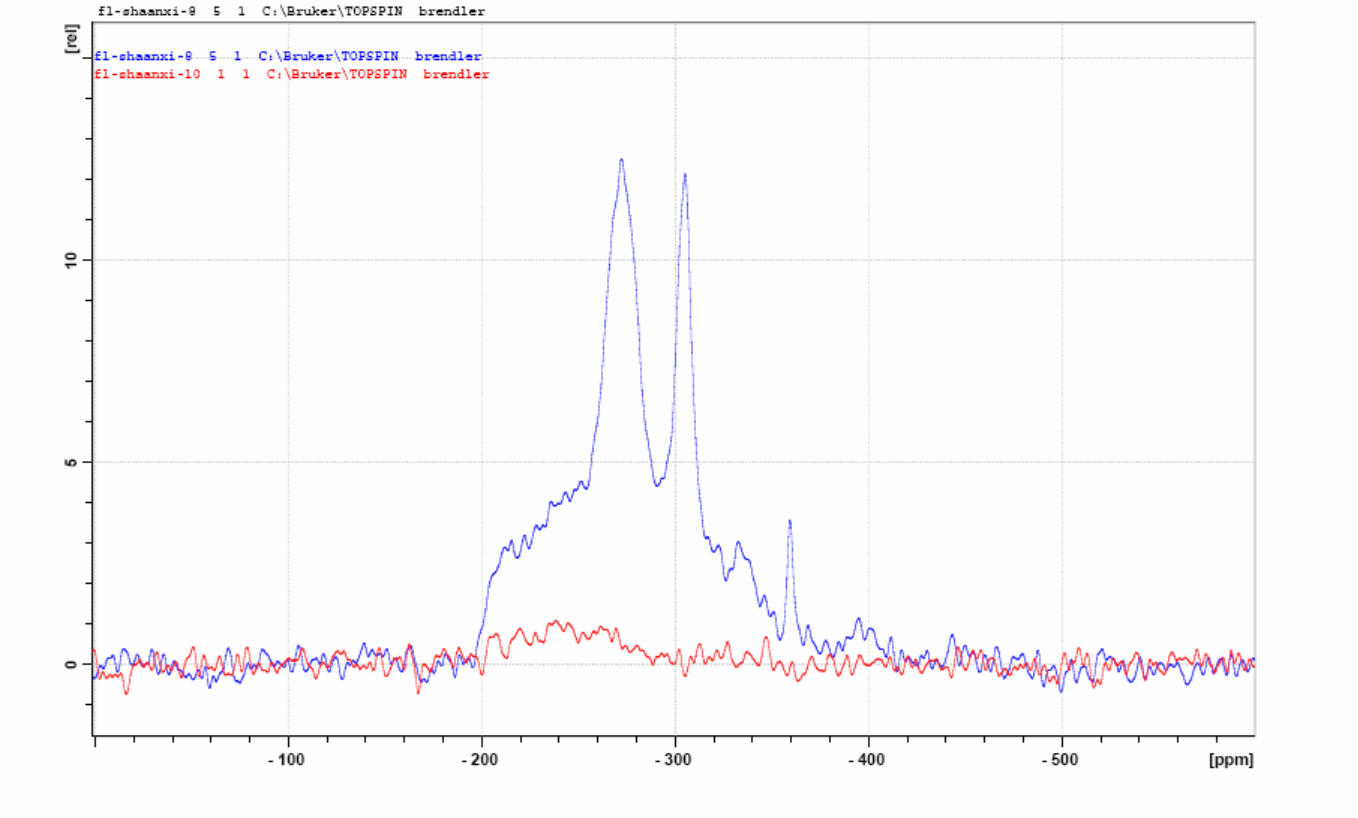


Fig. 38.Ammoxidized indulin AT after reduction by Zn/HCl and NaOBr ^{15}N-spectra

5.2. GC/MS of reduced Urea and Acetamide by NaOBr

Urea and acetamide are quantitatively reduced by NaOBr in alkaline medium. Therefore, treating an ammoxidized lignin with NaOBr in alkaline medium should result in complete removal of primary amide and urea moieties, and the corresponding peaks in the 15N CPMAS NMR spectra should dissapear.

Table: 50. GC/MS results of urea, acetamide, reduced urea and reduced acetamide.

		10 mg of Urea in Ethanol	
Retention time	**Moleculer weight**	**Name of compound**	**propability**
		Urea	
12.62 min	100%	m/z = 60 [M^+], 59 [M - H]$^+$, 58 [M – H_2]$^+$, 44 [M – NH_2]$^+$	90%
		10 mg of reduced Urea by NaOCl in Ethanol	
Retention time	**Moleculer weight**	**Name of compound**	**propability**
		Silane, diethoxydimethyl	
4.26 min	20%	m/z = 148 [M^+], 133 [M - CH_3]$^+$, 119 [M – C_2H_5]$^+$	95%
9.00 min	70%	Disiloxane, 1,3-diethoxy-1,1,3,3-tetramethyl	91%

		m/z = 222 [M^+], 207 [M - CH_3]$^+$, 193 [M – C_2H_5]$^+$, 177 [M – OC_2H_5]$^+$ Tetraethyl silicate	
9.61 min	10%	m/z = 208 [M^+], 193 [M - CH_3]$^+$, 179 [M – C_2H_5]$^+$, 163 [M – OC_2H_5]$^+$	99%

10 mg of Acetamide in Ethanol

Retention time	Moleculer weight	Name of compound	propability
		Acetamide	
6.84 min	100%	m/z = 59 [M^+], 58 [M - H]$^+$, 44 [M - CH_3]$^+$, 43 [M – NH_2]$^+$	90%

10 mg of reduced Acetamide by NaOCl in Ethanol

Retention time	Moleculer weight	Name of compound	propability
		Urethane	
5.74 min	4%	m/z = 89 [M^+], 74 [M - CH_3]$^+$, 60 [M – C_2H_5]$^+$	90%
		Carbamic acid, methyl-, ethyl ester	
6.76 min	6%	m/z = 103 [M^+], 88 [M - CH_3]$^+$, 74 [M – C_2H_5]$^+$	90%
		Carbamic acid, acetyl-, ethyl ester	
10.03 min	20%	m/z = 131 [M^+], 116 [M - CH_3]$^+$, 102 [M – C_2H_5]$^+$	91%
		Ethanol,2-(ethylamino)	
12.90 min	70%	m/z = 89 [M^+], 88 [M - H]$^+$, 74 [M - CH_3]$^+$, 60 [M – C_2H_5]$^+$	9%

GC/MS results of reduced urea and acetamide by NaOCl supported results of NMR- soild state that, urea and acetamide dissapered from ammoxidized indulin AT after reduction. Reduced urea have Silane diethoxydimethyl and Disiloxane 1,3-diethoxy-1,1,3,3-tetramethyl. Reduced acetamide gave different compounds at different retention time, Urethane, Carbamic acid methyl-ethyl ester and Ethanol,2-(ethylamino).

5.4. GC/MS of Silylated ammonium oxalate

The ammonia salt of organic acids (if formed during ammoxidation processes) should be detectable by means of GC/MS after silylation with BSTFA.

Table: 51. GC/MS results of silylated ammonium oxalate.

Ammonium oxalate in EE+BSTFA

Retention time	Moleculer weight	Name of compound	propability
		Oxalic acid, bis(trimethylsilyl) ester	
12.38 min	100%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	90%

GC/MS results of silylated ammonium oxalate supported that, the ammonium salts of organic acids which formed during ammoxidation processes disapper after silylation and convetrted into two, oxalic acid -bis (trimethylsilyl) ester. This result indicates that the deficiency of

nitrogenous compound in aqueous phases of ammoxidized phenolic models is duto conversation of ammonium salts of organic acids by silylation into silylated organic acids.

5.5. Oxidation of phenols and lignins.

In order to figure out the influence of ammonia, comparatitive oxidation reactions using sodium hydroxide where carried out with the same phenolic model compounds.
Interestingly, oxidation of the phenolic model compounds dissolved in aqeous NaOH instead of aqueous NH_4OH gave quite different results. Yields of organic phases (educts) by oxidation were more than after ammoxidation and Vis versa aqoues phases (products). The yields indicated that demethylation is an important step in the overall oxidation process. The initial reaction of phenols and lignins with sodium hydroxide may consist almost exclusively of demethylation. The phenolic models were completely dissolved in 20 ml NaOH and pH changes were measured by pH-meter. The pH values of the phenolic models were reduced with time, after 15 min pH became constant. Aqeouse phases have different compounds than produced by ammoxidation processes according to GC/MS results.

5.5.1. GC/MS results

The products identified from the reaction of phenols and lignins with alkaline sodium hydroxide are listed in tables (52-59). All of the major peaks on the gas chromatography were identified. A number of minor peaks representing carboxyl-containing degradation products also were present of which only a few were characterized.

5.5.1.1. Hydroquinone

The reaction sequences in tabel 52 account for all of the major products and several of the minor ones. Although the scheme consists basically of two competing processes, oxidative fragmentation (A) and dimerization (B), the former occurs far more extensively and probably is responsible for most of the sodium hydroxide consumed.
Table: 52. GC/MS results of oxidized hydroquinone and its drevatives.

		Hydroquinone /NaOH/org.ph/in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
14.53 min	100%	Hydroquinone m/z = 110 $[M^+]$, 109 $[M-H]^+$, 108 $[M-2H]^+$, 81 $[M-C_2H_5]^+$, 53 $[M-C_4H_5]^+$	95%
		Hydroquinone /NaOH/aqu.ph/silylated	

Retention time	Relative percentage	Name of compound	probability
		Trimethylsilyl ether of glycerol	
14.62 min	5%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	91%
		2-Butenedioic acid (Z)-, bis(trimethylsilyl) ester	
15.01 min	5%	m/z = 260 [M^+], 245 [M - CH_3]$^+$, 217 [M - CH_3CO]$^+$	83%
		Silane, [1,4-phenylenebis(oxy)]bis[trimethyl	
16.34 min	90%	m/z = 254 [M^+], 239 [M - CH_3]$^+$, 112 [M – 2(trimethyl-silane]$^+$	96%

Methylation/ Hydroquinone /NaOH/aqu.ph

Retention time	Relative percentage	Name of compound	probability
		Benzene, 1,4-dimethoxy	
12.83 min	80%	m/z = 138 [M^+], 137 [M-H]$^+$, 123 [M - CH_3]$^+$, 95 [M - CH_3CO]$^+$	96%
		Benzene, 1,4-dimethoxy-2-methyl	
14.16 min	5%	m/z = 152 [M^+], 137 [M - CH_3]$^+$, 109 [M - CH_3CO]$^+$	74%
		Benzoic acid, 2,5-dimethoxy-, methyl ester	
18.25 min	5%	m/z = 196 [M^+], 195 [M-H]$^+$, 181 [M-CH_3]$^+$, 153 [M - CH_3CO]$^+$	62%
		2,2',5,5'-Tetramethoxybiphenyl	
24.32 min	3%	m/z = 247 [M^+], 232 [M - CH_3]$^+$, 204 [M - CH_3CO]$^+$	99%
		Benzoic acid, 5-methoxy-2-(2,3,4-trimethoxyphenyl)-, methyl	
25.92 min	2%	m/z = 332 [M^+], 317 [M - CH_3]$^+$, 289 [M - CH_3CO]$^+$	93%
		1,1'-Biphenyl, 2,3,4,4'-tetramethoxy-5-methyl-6'-hydroxymethyl-	
26.19 min	5%	m/z = 318 [M^+], 317 [M-H]$^+$, 303 [M - CH_3]$^+$, 275 [M - CH_3CO]$^+$	53%

From the table 52 it is clear that the organic phase after oxidation is only hydroquinone. Aqueous phase after silylation have many peaks at different retention times. The main is Silane [1, 4-phenylenebis (oxy)]bis[trimethyl with little amount of Trimethylsilyl ether of glycerol. Methylation aqueous phase after oxidation also contains different peaks and the main is 1,4-dimethoxy benzene with different amounts of organic acids.

5.5.1.2. 4-Methyl catechol

Table: 53. GC/MS results of oxidized 4-methyl catechol and its drevatives.

4-Methyl catechol /NaOH/org.ph/in EE

Retention time	Relative percentage	Name of compound	probability
		Catechol	
13.51 min	100%	m/z = 110 [M^+], 109 [M - H]$^+$, 108 [M – H_2]$^+$, 81 [M – C_2H_5]$^+$	94%

4-Methyl catechol /NaOH/aqu.ph/silylated

Retention time	Relative percentage	Name of compound	probability
		Ethanol, 2-(trimethylsilyl)-, acetate	
8.41 min	3%	m/z = 160 [M^+], 145 [M - CH_3]$^+$, 117 [M - CH_3CO]$^+$	64%
		Propanedioic acid, methyl-, bis(trimethylsilyl) ester	
8.52 min	5%	m/z = 262 [M^+], 247 [M - CH_3]$^+$, 120 [M – 2(trimethyl-silane]$^+$	52%

8.58 min	10%	Trifluoromethyl-bis-(trimethylsilyl)methyl ketone m/z = 256 [M^+], 241 [M - CH_3]$^+$, 114 [M – 2(trimethyl-silane]$^+$	91%
10.62 min	2%	Propanedioic acid, ethyl-, bis(trimethylsilyl) ester m/z = 316 [M^+], 301 [M - CH_3]$^+$, 273 [M - CH_3CO]$^+$	38%
10.85 min	3%	Silane, (1-cyclohexen-1-yloxy)trimethyl m/z = 170 [M^+], 155 [M - CH_3]$^+$, 125 [M - 3CH_3]$^+$	74%
11.08 min	2%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 200 [M - CH_3CO]$^+$	86%
15.68 min	10%	Methylmaleic acid, bis(trimethylsilyl) ester m/z = 274 [M^+], 259 [M - CH_3]$^+$, 229 [M - 3CH_3]$^+$	83%
16.22 min	60%	silylated 4-methyl catechol m/z = 268 [M^+], 253 [M - CH_3]$^+$, 233 [M - 3CH_3]$^+$	91%
17.34 min	5%	2,3-Dimethyl-3-hydroxyglutaric acid, tris(trimethylsilyl) m/z = 392 [M^+], 377 [M - CH_3]$^+$, 252 [M - 3CH_3]$^+$	40%

Methylation/4-Methyl catechol /NaOH/aqu.ph			
Retention time	**Relative percentage**	**Name of compound**	**probability**
11.16 min	2%	Butanedioic acid, methyl-, dimethyl ester m/z = 160 [M^+], 145 [M - CH_3]$^+$, 117 [M - CH_3CO]$^+$	72%
11.68 min	3%	cis-2-Methyl-2-butenedioic acid, dimethyl ester m/z = 158 [M^+], 115 [M - CH_3]$^+$, 87 [M - CH_3COCO]$^+$	91%
14.02 min	5%	3,4-Dimethoxytoluene (methylated 4-methyl catechol) m/z = 152 [M^+], 137 [M - CH_3]$^+$, 109 [M - CH_3CO]$^+$	95%
22.42 min	35%	2,6-Bis(1,1-dimethylethyl)-4-(1-oxopropyl)phenol m/z = 248 [M^+], 233 [M - CH_3]$^+$, 203 [M - 3CH_3]$^+$	59%
23.13 min	45%	1,2-Dimethoxy-4-(2-methoxyethenyl)benzene m/z = 194 [M^+], 179 [M - CH_3]$^+$, 151 [M - CH_3CO]$^+$, 108 [M - 2CH_3CO]$^+$	35%

Organic phase after oxidation is catechol. Aqueous phase after silylation have many peaks at different retention times. Silylated 4-methyl catechol is mainly part with another amounts of Propanedioic acid-methyl- bis(trimethylsilyl) ester, Silane, (1-cyclohexen-1-yloxy)trimethyl, and Propanoic acid-2-[(trimethylsilyl)oxy]- trimethylsilyl ester,.

Methylation aqueous phase after oxidation obtains different compound also, Butanedioic acid- methyl-dimethyl ester, cis-2-Methyl-2-butenedioic acid dimethyl ester, 3,4-Dimethoxytoluene (methylated 4-methyl catechol) and 1,2-Dimethoxy-4-(2-methoxyethenyl)benzene.

5.5.1.3. 2-Methoxy-4-methylphenol

Table: 54. GC/MS results of oxidized methoxy phenol and its drevatives.

2-Methoxy-4-methylphenol /NaOH/org.ph in EE			
Retention time	**Relative percentage**	**Name of compound**	**probability**
13.35 min	100%138	2-Methoxy-4-methylphenol m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M - CH_3CO]$^+$	95%

2-Methoxy-4-methylphenol /NaOH/aq.ph in EE+BSTFA

Retention time	Relative percentage	Name of compound	probability
11.09 min	3%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 101 [M – 2(trimethyl-silane]$^+$	27%
11.36 min	2%	Acetic acid, [(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 220 [M^+], 205 [M - CH_3]$^+$, 78 [M – 2(trimethyl-silane]$^+$	64%
13.85 min	2%	2-Methoxyphenol trimethylsilyl ether m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	94%
17.34 min	3%	Butanedioic acid, bis(trimethylsilyl) ester m/z = 262 [M^+], 247 [M - CH_3]$^+$, 120 [M – 2(trimethyl-silane]$^+$	60%
19.32 min	5%	Vanillyl alcohol, bis(trimethylsilyl)- deriv. m/z = 298 [M^+], 283 [M - CH_3]$^+$, 255 [M - CH_3CO]$^+$	81%
20.77 min	10%	Trimethylsilyl O-(trimethylsilyl)isohomovanillate m/z = 326 [M^+], 311 [M - CH_3]$^+$, 283 [M - CH_3CO]$^+$	20%
24.44 min	15%	Butanedioic acid, 2-[(tert-butyldimethylsilyl)oxy]-, bis(tert-butyldimethylsilyl) ester m/z = 476 [M^+], 461 [M - CH_3]$^+$, 431 [M - $3CH_3$]$^+$	
24.53 min	60%	Acetopyruvic acid, tris(trimethylsilyl)- m/z = 346 [M^+], 331 [M - CH_3]$^+$, 204 [M – 2(trimethyl-silane]$^+$	10%

Methylation/2-Methoxy-4-methylphenol /NaOH/aq.ph

Retention time	Relative percentage	Name of compound	probability
11.15 min	2%	Butanedioic acid, methyl-, dimethyl ester m/z = 160 [M^+], 145 [M - CH_3]$^+$, 117 [M - CH_3CO]$^+$	78%
11.67 min	2%	cis-2-Methyl-2-butenedioic acid, dimethyl ester m/z = 158 [M^+], 115 [M - CH_3]$^+$, 87 [M - CH_3COCO]$^+$	90%
12.53 min	3%	Benzene, 1,2-dimethoxy- m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M - CH_3CO]$^+$	96%
14.04 min	3%	3,4-Dimethoxytoluene m/z = 152 [M^+], 137 [M - CH_3]$^+$, 109 [M - CH_3CO]$^+$	64%
24.31 min	70%	1,1'-Biphenyl, 4,2',3',4'-tetramethoxy-6-methyl- m/z = 288 [M^+], 273 [M - CH_3]$^+$, 245 [M - CH_3CO]$^+$, 202 [M - $2CH_3CO$]$^+$	41%
25.76 min	20%	1,1'-Biphenyl, 2-methoxycarbonyl-4',5',6'-trimethoxy m/z = 302 [M^+], 287 [M - CH_3]$^+$, 259 [M - CH_3CO]$^+$, 216 [M - $2CH_3CO$]$^+$	50%

Organic phase after oxidation contained only 2-Methoxy-4-methylphenol. Aqueous phase after silylation contains many peaks at different retention times. Butanedioic acid-methyl-bis(trimethylsilyl)ester, propanoic acid-2-[(trimethylsilyl)oxy]- trimethylsilyl ester and acetic acid [(trimethylsilyl)oxy]- trimethylsilyl ester.

Methylation aqueous phase after oxidation consists of different peaks, butanedioic acid-diethylester, butanedioic acid-methyl-dimethylester and cis-2-methyl-2-butenedioic acid-dimethylester.

5.5.1.4. Catechol

Table: 55. GC/MS results of oxidized catechol and its drevatives.

Catechol /NaOH/org.ph in EE			
Retention time	**Relative percentage**	**Name of compound**	**probability**
13.32 min	100%	1,2-Benzenediol (Catechol) Catechol m/z = 110 $[M^+]$, 109 $[M - H]^+$, 108 $[M - H_2]^+$, 81 $[M - C_2H_5]^+$	95%
Catechol /NaOH/aq.ph in EE+BSTFA			
Retention time	**Relative percentage**	**Name of compound**	**probability**
10.86 min	1%	Silane, (1-cyclohexen-1-yloxy)trimethyl m/z = 170 $[M^+]$, 155 $[M - CH_3]^+$, 125 $[M - 3CH_3]^+$	97%
11.11 min	1%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 $[M^+]$, 219 $[M - CH_3]^+$, 101 [M – 2(trimethyl-silane]$^+$	68%
13.27 min	2%	Propanedioic acid, methyl-, bis(trimethylsilyl) ester m/z = 262 $[M^+]$, 247 $[M - CH_3]^+$, 120 [M – 2(trimethyl-silane]$^+$	27%
14.13 min	2%	Benzoic acid trimethylsilyl ester m/z = 194$[M^+]$, 193 $[M-H]^+$, 179 $[M-CH_3]^+$, 151 $[M - CH_3CO]^+$	96%
14.61 min	3%	Trimethylsilyl ether of glycerol m/z = 308 $[M^+]$, 219 [M - tetramethyl-silane]$^+$	93%
15.18 min	5%	Silane, [1,2-phenylenebis(oxy)]bis[trimethyl- (silylated Catechol) m/z = 254 $[M^+]$, 239 $[M - CH_3]^+$, 112 [M – 2(trimethyl-silane]$^+$	96%
15.55 min	2%	2-Butenedioic acid (E)-, bis(trimethylsilyl) ester m/z = 260 $[M^+]$, 245 $[M - CH_3]^+$, 118 [M – 2(trimethyl-silane]$^+$	91%
23.37 min	5%	Hexadecanoic acid, trimethylsilyl ester m/z = 328 $[M^+]$, 313 $[M - CH_3]^+$, 299 $[M - CH_3CH_2]^+$	98%
27.59 min	80%	Cholest-2-eno[2,3-a]naphthalene, 3'-methyl- m/z = 484 $[M^+]$, 469 $[M - CH_3]^+$, 455 $[M - CH_3CH_2]^+$	30%
Methylation / Catechol /NaOH/aq.ph			
Retention time	**Relative percentage**	**Name of compound**	**probability**
10.48 min	1%	Butanedioic acid, dimethyl ester m/z = 146 $[M^+]$, 131 $[M - CH_3]^+$, 103 $[M - CH_3CO]^+$	72%
12.53 min	4%	Benzene, 1,2-dimethoxy- m/z = 138 $[M^+]$, 123 $[M - CH_3]^+$, 121 $[M - OH]^+$, 95 $[M - CH_3CO]^+$	97%
14.02 min	2%	3,4-Dimethoxytoluene m/z = 152 $[M^+]$, 137 $[M - CH_3]^+$, 109 $[M - CH_3CO]^+$	91%
19.74 min	50%	1,2-Dimethoxy-4-(1-methoxyethenyl)benzene m/z = 194$[M^+]$, 193 $[M-H]^+$, 179 $[M-CH_3]^+$, 151 $[M - CH_3CO]^+$	40%
20.50 min	10%	Benzo[d]-1,3-dioxolane-2-spiro-3'-(oxolane-2,5-dione) m/z = 206 $[M^+]$, 178 $[M - CO]^+$, 150 $[M - 2CO]^+$	38%
26.47 min	30%	Hexanedioic acid, bis(2-ethylhexyl) ester m/z = 370 $[M^+]$, 355 $[M - CH_3]^+$, 341 $[M - CH_3CH_2]^+$	98%
27.68 min	3%	1,2-Benzenedicarboxylic acid, diisooctyl ester m/z = 390 $[M^+]$, 375 $[M - CH_3]^+$, 361 $[M - CH_3CH_2]^+$	68%

From the table 55 it is clear that the organic phase after oxidation is only Catechol. Aqueous phase after silylation have many peaks at different retention times. Silane (1-cyclohexen-1-yloxy) trimethyl, Propanoic acid-2-[(trimethylsilyl)oxy]- trimethylsilyl ester, Trimethylsilyl ether of glycerol, Silane [1,2-phenylenebis(oxy)]bis[trimethyl (silylated Catechol), 2-Butenedioic acid (E)-bis(trimethylsilyl) ester and Hexadecanoic acid trimethylsilyl ester.
After methylation there are many compounds were found, Benzene-1,2-dimethoxy, 1,2-Dimethoxy-4-(1-methoxyethenyl)benzene and Hexanedioic acid bis(2-ethylhexyl) ester.

5.5.1.5. Methoxhydroquinone

Table: 56. GC/MS results of oxidized methoxy hydroquinone and its drevatives.

		Methoxyhydroquinone/NaOH/org.ph in EE	
Retention time	**Relative percentage**	**Name of compound**	**probability**
16.28 min	100%	1,4-Benzenediol, 2-methoxy (Methoxyhydroquinone) m/z = 140 $[M^+]$, 125 $[M - CH_3]^+$, 109 $[M - CH_3O]^+$	97%
		Methoxyhydroquinone/NaOH/aq.ph in EE+BSTFA	
Retention time	**Relative percentage**	**Name of compound**	**probability**
14.63 min	5%	Trimethylsilyl ether of glycerol m/z = 308 $[M^+]$, 219 $[M - \text{tetramethyl-silane}]^+$	91%
17.53 min	2%	Butanedioic acid, [(trimethylsilyl)oxy]-, bis(trimethylsilyl) ester m/z = 350 $[M^+]$, 335 $[M - CH_3]^+$, 305 $[M - 3CH_3]^+$	91%
18.12 min	20%	Silane, [1,4-phenylenebis(oxy)]bis[trimethyl (silylated hydroquinone) m/z = 254 $[M^+]$, 239 $[M - CH_3]^+$, 112 $[M - 2(\text{trimethyl-silane}]^+$	50%
22.35 min	3%	Benzeneacetic acid, 2,5-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 384 $[M^+]$, 369 $[M - CH_3]^+$, 242 $[M - 2(\text{trimethyl-silane}]^+$	50%
26.47 min	10%	Hexanedioic acid, bis(2-ethylhexyl) ester m/z = 370 $[M^+]$, 355 $[M - CH_3]^+$, 341 $[M - CH_3CH_2]^+$	95%
27.06 min	30%	1,4-Bis(trimethylsilyl)-3-methylbenzene m/z = 536 $[M^+]$, 521 $[M - CH_3]^+$, 394 $[M - 2(\text{trimethyl-silane}]^+$	50%
27.58 min	30%	Trimethylsilyl catecholpyruvate tris(trimethylsilyl) ether m/z = 484 $[M^+]$, 469 $[M - CH_3]^+$, 455 $[M - CH_3CH_2]^+$	45%
		Methylation / Methoxyhydroquinone/NaOH/aq.ph	
Retention time	**Relative percentage**	**Name of compound**	**probability**
12.57 min	5%	Butanedioic acid, methoxy-, dimethyl ester m/z = 176 $[M^+]$, 161 $[M - CH_3]^+$, 117 $[M - CH_3OCO]^+$	80%
14.24 min	5%	2-Butenedioic acid, 2-methoxy-, dimethyl ester m/z = 174 $[M^+]$, 159 $[M - CH_3]^+$, 131 $[M - CH_3O]^+$	98%
15.88 min	40%	1,2,4-Trimethoxybenzene m/z = 168 $[M^+]$, 153 $[M - CH_3]^+$, 125 $[M - CH_3O]^+$, 82 $[M - 2CH_3O]^+$	98%
19.79 min	5%	Ethanone, 1-(2,5-dimethoxyphenyl) m/z = 180 $[M^+]$, 165 $[M - CH_3]^+$, 137 $[M - CH_3O]^+$, 94 $[M - 2CH_3O]^+$	50%
20.75 min	5%	Benzoic acid, 3,4,5-trimethoxy-, methyl ester m/z = 226 $[M^+]$, 211 $[M - CH_3]^+$, 183 $[M - CH_3O]^+$	90%

		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.46 min	5%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	81%
		Di-n-octyl phthalate	
27.68 min	35%	m/z = 390 [M^+], 375 [M - CH_3]$^+$, 333 [M – C_4H_9]$^+$	95%

Organic phase after oxidation was Methoxyhydroquinone. Oxidised aqueous phase after silylation has different compounds at different retention times as follow: Trimethylsilyl ether of glycerol, Butanedioic acid [(trimethylsilyl)oxy]-bis(trimethylsilyl) ester, silylated hydroquinone, Benzeneacetic acid-2,5-bis[(trimethylsilyl)oxy]- trimethylsilyl ester, Hexanedioic acid bis(2-ethylhexyl) ester and Trimethylsilyl catecholpyruvate tris(trimethylsilyl) ether.

Methylated oxidised aqueous phase after contains different compounds at different retention times as follow: Butanedioic acid methoxy- dimethyl ester, 1,2,4-Trimethoxybenzene (methylated methoxy hydroquinone), Hexanedioic acid bis(2-ethylhexyl) ester and Di-n-octyl phthalate.

5.5.1.6. 2-Methoxy phenol

Table: 57. GC/MS results of oxidized 2-methoxy phenol and its drevatives.

2-Methoxyphenol /NaOH/org.ph in EE			
Retention time	**Relative percentage**	**Name of compound**	**probability**
		2-Methoxy phenol	
11.61 min	100%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	95%
2-Methoxyphenol /NaOH/aq.ph in EE+BSTFA			
Retention time	**Relative percentage**	**Name of compound**	**probability**
		Silane, (1-cyclohexen-1-yloxy)trimethyl-	
10.86 min	1%	m/z = 170 [M^+], 155 [M - CH_3]$^+$, 140 [M – 2 CH_3]$^+$	98%
		Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.11 min	2%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	91%
		Acetic acid, [(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.37 min	1%	m/z = 220 [M^+], 205 [M - CH_3]$^+$, 78 [M – 2(trimethyl-silane]$^+$	90%
		2-Methoxyphenol trimethylsilyl ether	
13.83 min	2%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	96%
		Benzoic acid trimethylsilyl ester	
14.14 min	4%	m/z = 194[M^+], 193 [M-H]$^+$, 179 [M-CH_3]$^+$, 151 [M - CH_3CO]$^+$	94%
		Trimethylsilyl ether of glycerol	
14.62 min	4%	m/z = 308 [M^+], 219 [M - tetramethyl-silane]$^+$	91%
		Butanedioic acid, bis(trimethylsilyl) ester	
15.12 min	1%	m/z = 262 [M^+], 247 [M - CH_3]$^+$, 120 [M – 2(trimethyl-silane]$^+$	95%
		Silane, [1,2-phenylenebis(oxy)]bis[trimethyl-	
15.19 min	1%	m/z = 254 [M^+], 239 [M - CH_3]$^+$, 112 [M – 2(trimethyl-silane]$^+$	60%
		Benzoic acid, 3-methoxy-4-[(trimethylsilyl)oxy]-, trimethylsilyl	
20.64 min	4%	m/z = 312 [M^+], 297 [M - CH_3]$^+$, 269 [M - CH_3CO]$^+$	96%
		Hexadecanoic acid, trimethylsilyl ester	
23.36 min	10%	m/z = 328 [M^+], 313 [M - CH_3]$^+$, 299 [M - CH_3CH_2]$^+$	94%

		Diisooctyl adipate	
26.46 min	10%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	95%
		Cholest-2-eno[2,3-a]naphthalene, 3'-methyl-	
27.59 min	60%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 455 [M - CH_3CH_2]$^+$	22%

Methylation /F/NaOH/aq.ph in EE

Retention time	Relative percentage	Name of compound	probability
		But-2-enedioic acid, dimethyl ester	
10.27 min	2%	m/z = 144 [M^+], 129 [M - CH_3]$^+$, 101 [M - CH_3O]$^+$, 58 [M - $2CH_3O$]$^+$	80%
		Butanedioic acid, dimethyl ester	
10.48 min	2%	m/z = 146 [M^+], 131 [M - CH_3]$^+$, 103 [M - CH_3O]$^+$, 60 [M - $2CH_3O$]$^+$	90%
		Phenol, 2-methoxy	
11.53 min	3%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	97%
		Butanedioic acid, methoxy-, dimethyl ester	
12.54 min	5%	m/z = 176 [M^+], 161 [M - CH_3]$^+$, 133 [M - CH_3O]$^+$, 90 [M - $2CH_3O$]$^+$	91%
		Fumaric acid, dimethyl ester, 2-methoxy	
13.61 min	4%	m/z = 174 [M^+], 159 [M - CH_3]$^+$, 131 [M - CH_3O]$^+$, 88 [M - $2CH_3O$]$^+$	95%
		3,4-Dimethoxytoluene	
13.98 min	2%	m/z = 152 [M^+], 137 [M - CH_3]$^+$, 105 [M - CH_3O]$^+$, 66 [M - $2CH_3O$]$^+$	93%
		1-Propene-1,2,3-tricarboxylic acid, trimethyl ester	
16.70 min	2%	m/z = 216 [M^+], 201 [M - CH_3]$^+$, 173 [M - CH_3O]$^+$, 130 [M - $2CH_3O$]$^+$	95%
		Benzoic acid, 3,4-dimethoxy-, methyl ester	
17.65 min	70%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	98%
		1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	
21.69 min	2%	m/z = 334 [M^+], 319 [M - CH_3]$^+$, 278 [M – C_4H_9]$^+$	90%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.46 min	3%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	99%
		Di-n-octyl phthalate	
27.68 min	5%	m/z = 390 [M^+], 375 [M - CH_3]$^+$, 333 [M – C_4H_9]$^+$	91%

Oxidized organic phase was 2-Methoxy phenol at 11.61 min. Oxidized aqueous phase after silylation has different compounds, Silane (1-cyclohexen-1-yloxy) trimethyl, Propanoic acid 2-[(trimethylsilyl)oxy]- trimethylsilyl ester, Acetic acid [(trimethylsilyl)oxy]- trimethylsilyl ester, 2-Methoxyphenol trimethylsilyl ether, Benzoic acid trimethylsilyl ester, Trimethylsilyl ether of glycerol, Butanedioic acid bis(trimethylsilyl) ester, Silane [1,2-phenylenebis(oxy)]bis[trimethyl, Benzoic acid- 3-methoxy-4-[(trimethylsilyl)oxy]- ,trimethylsilyl ester, Hexadecanoic acid trimethylsilyl ester and Diisooctyl adipate.

Oxidized aqueous phase after methylation has different compounds, But-2-enedioic acid dimethyl ester, Butanedioic acid dimethyl ester, 2-methoxy Phenol, Butanedioic acid methoxy-dimethyl ester, Fumaric acid dimethyl ester-2-methoxy, 3,4-Dimethoxytoluene, 1-Propene-1,2,3-tricarboxylic acid trimethyl ester, (2-Methoxyphenoxy) acetic acid methyl ester, 1,2-Benzenedicarboxylic acid bis(2-methylpropyl) ester, Hexanedioic acid bis(2-ethylhexyl) ester and Di-n-octyl phthalate.

5.5.1.7. Apocynol

The products identified from the reaction of apocynol with sodium hydroxide are listed in table: 53. As in the case of hydroquinone, all major peaks on the gas chromatograms were identified.The sequences in fig. 33 define the relationships existing between the various identified products. Owing to the presence of benzyl alcohol grouping, apocynol undergoes several reactions which were not observed with hydroquinone. These reactions are discussed in detail in the following sections. For the sake of convenience, the overall reaction has been divided into four parts: (1) oxidation to acetoguaiacone followed by a Dakin reaction; (2) "Dakin-like" reaction; (3) oxdative demethylation; and (4) oxidative ring rupture and fragmentation of intermediates.

Table: 58. GC/MS results of oxidized apocynol and its drevatives.

Apocynol/NaOH/org.ph/100C° in EE			
Retention time	**Relative percentage**	**Name of compound**	**probability**
8.90 min	1%	Benzaldehyde m/z = 106 [M^+], 105 [M - H]$^+$, 76 [M – CH_2O]$^+$	94%
10.49 min	1%	Benzyl Alcohol m/z = 108 [M^+], 91 [M - OH]$^+$, 77 [M – CH_2OH]$^+$	98%
11.58 min	5%	Phenol, 2-methoxy m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	97%
13.30 min	5%	Phenol, 2-methoxy-4-methyl m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M - CH_3CO]$^+$	97%
14.59 min	3%	Phenol, 4-ethyl-2-methoxy m/z = 152 [M^+], 137 [M - CH_3]$^+$, 105 [M - CH_3O]$^+$, 66 [M - $2CH_3O$]$^+$	91%
15.22 min	30%	2-Methoxy-4-vinylphenol m/z = 150 [M^+], 135 [M - CH_3]$^+$, 119 [M - OCH_3]$^+$	91%
16.32 min	1%	Vanillin m/z = 152 [M^+], 151 [M - H]$^+$, 121 [M - OCH_3]$^+$	95%
17.35 min	15%	Apocynol m/z = 168 [M^+], 153 [M - CH_3]$^+$, 125 [M - OCH_3]$^+$	60%
17.52 min	4%	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- m/z = 166 [M^+], 151 [M - CH_3]$^+$, 123 [M - OCH_3]$^+$	95%
18.61 min	2%	2,3-Dimethyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione m/z = 240 [M^+], 225 [M - CH_3]$^+$, 210 [M - $2CH_3$]$^+$	60%
23.36 min	3%	3-Benzyloxy-4-methoxybenzoic acid m/z = 258 [M^+], 257 [M - H]$^+$, 240 [M – OH]$^+$	22%
26.07 min	25%	Benzaldehyde, 4-(acetyloxy)-3-methoxy m/z = 194 [M^+], 151 [M - OCH_3]$^+$	60%
28.47 min	5%	3,3',4,4'-Tetramethoxystilbene m/z = 300 [M^+], 285 [M - CH_3]$^+$, 257 [M - OCH_3]$^+$	43%
Apocynol/NaOH/aq.ph/100C° in EE+BSTFA			
Retention time	**Relative percentage**	**Name of compound**	**probability**
9.97 min	2%	Ethanedioic acid, bis(trimethylsilyl) ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	60%

		Silane, (1-cyclohexen-1-yloxy)trimethyl-	
10.86 min	2%	m/z = 170 [M^+], 155 [M - CH_3]$^+$, 140 [M – 2 CH_3]$^+$	98%
		Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.11 min	3%	m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	91%
		2-Methoxyphenol trimethylsilyl ether	
13.82 min	5%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	96%
		Benzoic acid trimethylsilyl ester	
14.12 min	1%	m/z = 194 [M^+], 193 [M-H]$^+$, 179 [M-CH_3]$^+$, 151 [M - CH_3CO]$^+$	93%
		Trimethylsilyl ether of glycerol	
14.62 min	4%	m/z = 308 [M^+], 219 [M - trimethyl-silane]$^+$	91%
		Hexadecanoic acid, trimethylsilyl ester	
23.37 min	3%	m/z = 328 [M^+], 313 [M - CH_3]$^+$, 299 [M - CH_3CH_2]$^+$	98%
		9,12-Octadecadienoic acid (Z,Z)-, trimethylsilyl ester	
24.90 min	2%	m/z = 352 [M^+], 337 [M - CH_3]$^+$, 307 [M - $3CH_3$]$^+$	99%
		Octadecanoic acid, trimethylsilyl ester	
25.15 min	5%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 327 [M - CH_3CH_2]$^+$	98%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.47 min	3%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	95%
		Oleamide, N-trimethylsilyl	
26.63 min	23%	m/z = 353 [M^+], 338 [M - CH_3]$^+$, 308 [M - $3CH_3$]$^+$	90%
		Trimethylsilyl catecholpyruvate tris(trimethylsilyl) ether	
27.59 min	47%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 455 [M - CH_3CH_2]$^+$	40%

Methylation/Apocynol/NaOH/aq.ph/100C° in EE

Retention time	Relative percentage	Name of compound	probability
		Benzene, 1,2-dimethoxy-	
12.51 min	5%	m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M - CH_3CO]$^+$	96%
		3,4-Dimethoxytoluene	
13.97 min	10%	m/z = 152 [M^+], 151 [M - H]$^+$, 121 [M - OCH_3]$^+$	94%
		4-Ethoxy-3-methoxyphenol	
14.30 min	30%	m/z = 168 [M^+], 153 [M - CH_3]$^+$, 135 [M – OC_2H_5]$^+$	40%
		Benzoic acid, 3,4-dimethoxy-, methyl ester	
18.692 min	30%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	98%
		Pentadecanoic acid, methyl ester	
21.19 min	5%	m/z = 256 [M^+], 241 [M - CH_3]$^+$, 197 [M – $COOCH_3$]$^+$	95%
		11-Hexadecenoic acid, methyl ester	
22.00 min	1%	m/z = 268 [M^+], 253 [M - CH_3]$^+$, 209 [M – $COOCH_3$]$^+$	95%
		Hexadecanoic acid, methyl ester	
22.20 min	3%	m/z = 270 [M^+], 255 [M - CH_3]$^+$, 211 [M – $COOCH_3$]$^+$	98%
		Dibutyl phthalate	
22.65 min	1%	m/z = 278 [M^+], 263 [M - CH_3]$^+$, 221 [M – C_4H_9]$^+$	95%
		11-Octadecenoic acid, methyl ester, (Z)	
23.90 min	2%	m/z = 296 [M^+], 281 [M - CH_3]$^+$, 237 [M – $COOCH_3$]$^+$	99%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.48 min	3%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	93%
		Di-n-octyl phthalate	
27.70 min	5%	m/z = 390 [M^+], 375 [M - CH_3]$^+$, 333 [M – C_4H_9]$^+$	96%
		Cholest-8(14)-en-3à-ol	
27.94 min	5%	m/z = 386 [M^+], 371 [M - CH_3]$^+$, 329 [M – C_4H_9]$^+$	96%

Apocynol/NaOH/org.ph/25C° in EE

Retention time	Relative percentage	Name of compound	probability
		Phenol, 2-methoxy	
11.65 min	2%	m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	80%
		Phenol, 2-methoxy-4-methyl	
13.38 min	2%	m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M -	91%

		$CH_3CO]^+$	
		Phenol, 4-ethyl-2-methoxy	
14.65 min	1%	m/z = 152 $[M^+]$, 151 $[M - H]^+$, 121 $[M - OCH_3]^+$	91%
		2-Methoxy-4-vinylphenol	
15.16 min	60%	m/z = 150 $[M^+]$, 135 $[M - CH_3]^+$, 119 $[M - OCH_3]^+$	90%
		Apocynol	
17.23 min	35%	m/z = 168 $[M^+]$, 153 $[M - CH_3]^+$, 125 $[M - OCH_3]^+$	41%

Apocynol/NaOH/aq.ph/25C° in EE+BSTFA

Retention time	Relative percentage	Name of compound	probability
		Ethanedioic acid, bis(trimethylsilyl) ester	
9.97 min	20%	m/z = 234 $[M^+]$, 219 $[M - CH_3]^+$, 191 $[M - CH_3CO]^+$	60%
		Silane, (1-cyclohexen-1-yloxy)trimethyl-	
10.85 min	2%	m/z = 170 $[M^+]$, 155 $[M - CH_3]^+$, 140 $[M – 2\ CH_3]^+$	97%
		Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	
11.13 min	3%	m/z = 234 $[M^+]$, 219 $[M - CH_3]^+$, 191 $[M - CH_3CO]^+$	91%
		2-Methoxyphenol trimethylsilyl ether	
13.85 min	1%	m/z = 196 $[M^+]$, 181 $[M - CH_3]^+$, 153 $[M - CH_3CO]^+$	96%
		Trimethylsilyl ether of glycerol	
14.62 min	4%	m/z = 308 $[M^+]$, 219 $[M$ - trimethyl-silane$]^+$	91%
		Hexadecanoic acid, trimethylsilyl ester	
23.36 min	5%	m/z = 328 $[M^+]$, 313 $[M - CH_3]^+$, 299 $[M - CH_3CH_2]^+$	98%
		Octadecanoic acid, trimethylsilyl ester	
25.14 min	5%	m/z = 356 $[M^+]$, 341 $[M - CH_3]^+$, 327 $[M - CH_3CH_2]^+$	98%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.42 min	5%	m/z = 370 $[M^+]$, 355 $[M - CH_3]^+$, 341 $[M - CH_3CH_2]^+$	95%
		Trimethylsilyl catecholpyruvate tris(trimethylsilyl) ether	
27.59 min	55%	m/z = 484 $[M^+]$, 469 $[M - CH_3]^+$, 439 $[M - 3CH_3]^+$	40%

Methylation/Apocynol/NaOH/aq.ph/25C° in EE

Retention time	Relative percentage	Name of compound	probability
		1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	
21.71 min	5%	m/z = 278 $[M^+]$, 263 $[M - CH_3]^+$, 221 $[M – C_4H_9]^+$	78%
		Pentadecanoic acid, 14-methyl-, methyl ester	
22.23 min	2%	m/z = 270 $[M^+]$, 255 $[M - CH_3]^+$, 211 $[M – COOCH_3]^+$	97%
		1,1'-Biphenyl, 4,2',3',4'-tetramethoxy-6-methyl-	
23.71 min	3%	m/z = 288 $[M^+]$, 273 $[M - CH_3]^+$, 245 $[M - CH_3CO]^+$	93%
		Octadecanoic acid, methyl ester	
24.14 min	40%	m/z = 298 $[M^+]$, 283 $[M - CH_3]^+$, 239 $[M – COOCH_3]^+$	93%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.47 min	10%	m/z = 370 $[M^+]$, 355 $[M - CH_3]^+$, 341 $[M - CH_3CH_2]^+$	90%
		Di-n-octyl phthalate	
27.69 min	40%	m/z = 390 $[M^+]$, 375 $[M - CH_3]^+$, 333 $[M – C_4H_9]^+$	96%

Oxidized organic phase of apocynol at 100°C contains different compounds at different retention times. The mainly compounds are 2-Methoxy-4-vinylphenol 30% and apocynol 15% with minor amounts of different phenolic compounds and organic acids.

Silylated oxidized aqueous phase at 100°C contained, Silane, (1-cyclohexen-1-yloxy) trimethyl, Propanoic acid 2-[(trimethylsilyl)oxy]- trimethylsilyl ester, 2-Methoxyphenol trimethylsilyl ether, Trimethylsilyl ether of glycerol, Hexadecanoic acid trimethylsilyl ester, 9,12-Octadecadienoic acid (Z,Z)- trimethylsilyl ester, Octadecanoic acid trimethylsilyl ester,

Hexanedioic acid bis(2-ethylhexyl) ester, Oleamide N-trimethylsilyl and mainly of Trimethylsilyl catecholpyruvate tris(trimethylsilyl) ether.

Methylated oxidized aqueous phase at 100°C contained mainly of Benzoic acid 3,4-dimethoxy-, methyl ester 30%, 4-Ethoxy-3-methoxyphenol 30% and minor amounts from different organic acids like Benzoic acid 4-(acetyloxy)-3-methoxy-methyl ester and Tridecanoic acid-12-methyl- methyl ester

Oxidized organic phase at 25°C contained different compounds at different retention times,

The mainly compounds are 2-Methoxy-4-vinylphenol 60% and apocynol 35% with minor amounts of different phenolic compounds and organic acids less than oxidation in 100°C.

Silylated oxidized aqueous phase at 25°C is similar oxidation in100°C, have the same compounds but different amounts.

Methylated oxidized aqueous phase at 25°C contained mainly of Hexanedioic acid bis(2-ethylhexyl) ester 40%, Di-n-octyl phthalate 40% and minor amounts from different organic acids like Hexanedioic acid bis(2-ethylhexyl) ester.

5.5.1.8. 2,5-Dihydroxy-1,4-benzoquinone

Table: 59. GC/MS results of oxidized 2,5-Dihydroxy-1,4-benzoquinone and its drevatives.

		2, 5-Dihydroxy-1, 4-benzoquinone /NaOH/org.ph/100C°/ in EE	
Retention time	**Molecular weight**	**Name of compound**	**probability**
11.56 min	20%	Phenol, 2-methoxy- m/z = 124 [M^+], 109 [M - CH_3]$^+$, 81 [M - CH_3O]$^+$	97%
13.31 min	5%	Phenol, 2-methoxy-4-methyl- m/z = 138 [M^+], 123 [M - CH_3]$^+$, 121 [M - OH]$^+$, 95 [M - CH_3CO]$^+$	97%
25.70 min	60%	4H-1-Benzopyran-4-one, 3,5-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy m/z = 330 [M^+], 315 [M - CH_3]$^+$, 313 [M - OH]$^+$, 287 [M - CH_3CO]$^+$	40%
26.47 min	15%	Hexanedioic acid, bis(2-ethylhexyl) ester m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	98%
		2, 5-Dihydroxy-1, 4-benzoquinone /NaOH/aq.ph/100C°/ in EE+BSTFA	
Retention time	**Molecular weight**	**Name of compound**	**probability**
7.09 min	4%	Trisiloxane, octamethyl m/z = 236 [M^+], 221 [M - CH_3]$^+$, 191 [M – $3CH_3$]$^+$	91%
7.91 min	3%	Acetic acid, trimethylsilyl ester m/z = 132 [M^+], 117[M - CH_3]$^+$, 101 [M – OCH_3]$^+$	53%
9.58 min	6%	1,2-Bis(trimethylsiloxy)ethane m/z = 206 [M^+], 191 [M - CH_3]$^+$, 161 [M – $3CH_3$]$^+$	90%
10.86 min	2%	Silane, (1-cyclohexen-1-yloxy)trimethyl m/z = 170 [M^+], 155 [M - CH_3]$^+$, 140 [M – 2 CH_3]$^+$	98%
11.12 min	1%	Propanoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester m/z = 234 [M^+], 219 [M - CH_3]$^+$, 191 [M - CH_3CO]$^+$	90%

		2-Methoxyphenol trimethylsilyl ether	
13.83 min	2%	m/z = 196 [M^+], 181 [M - CH_3]$^+$, 153 [M - CH_3CO]$^+$	94%
		Trimethylsilyl ether of glycerol	
14.62 min	4%	m/z = 308 [M^+], 219 [M - trimethyl-silane]$^+$	91%
		Hexadecanoic acid, trimethylsilyl ester	
23.36 min	4%	m/z = 328 [M^+], 313 [M - CH_3]$^+$, 299 [M - CH_3CH_2]$^+$	98%
		9,12-Octadecadienoic acid (Z,Z)-, trimethylsilyl ester	
24.89 min	4%	m/z = 352 [M^+], 337 [M - CH_3]$^+$, 307 [M - $3CH_3$]$^+$	99%
		Octadecanoic acid, trimethylsilyl ester	
25.15 min	5%	m/z = 356 [M^+], 341 [M - CH_3]$^+$, 327 [M - CH_3CH_2]$^+$	99%
		Hexanedioic acid, bis(2-ethylhexyl) ester	
26.46 min	5%	m/z = 370 [M^+], 355 [M - CH_3]$^+$, 341 [M - CH_3CH_2]$^+$	94%
		silylated 2,5-Dihydroxy-1,4-benzoquinone	
27.58 min	60%	m/z = 484 [M^+], 469 [M - CH_3]$^+$, 439 [M - $3CH_3$]$^+$	70%

2, 5-Dihydroxy-1, 4-benzoquinone /NaOH/org.ph/25C°/ in EE

Retention time	Molecular weight	Name of compound	probability
		2,5-Dihydroxy-1,4-benzoquinone	
11.97 min	100%	m/z = 140 [M^+], 123 [M - OH]$^+$, 106 [M - 2OH]$^+$,	95%

2, 5-Dihydroxy-1, 4-benzoquinone /NaOH/aq.ph/25C°/ in EE+BSTFA

Retention time	Molecular weight	Name of compound	probability
		1,2-Bis(trimethylsiloxy)ethane	
9.21 min	10%	m/z = 206 [M^+], 191 [M - CH_3]$^+$, 161 [M – $3CH_3$]$^+$	74%
		Propanedioic acid, dimethyl-, bis(trimethylsilyl) ester	
10.62 min	10%	m/z = 276 [M^+], 261 [M - CH_3]$^+$, 205 [M – SiC_3H_9]$^+$	38%
		Silane, [1,2-phenylenebis(oxy)]bis[trimethyl-	
18.38 min	80%	m/z = 254 [M^+], 239 [M - CH_3]$^+$, 209 [M – $3CH_3$]$^+$	9%

Oxidized organic phase at 100°C contained different compounds at different retention times, 2-Methoxy phenol, 2-Methoxy-4-methylphenol, 4H-1-Benzopyran-4-one 3,5-dihydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy and Hexanedioic acid bis(2-ethylhexyl) ester.

Silylated oxidized aqueos phase at 100°C obtained mainly (60%) Silylated dihydroxybenzohyroquinone and minor amounts of Trisiloxane octamethyl, 1,2-Bis(trimethylsiloxy)ethane, Silane (1-cyclohexen-1-yloxy)trimethyl, Propanoic acid 2-[(trimethylsilyl)oxy]- trimethylsilyl ester, 2-Furancarboxylic acid trimethylsilyl ester, 2-Methoxyphenol trimethylsilyl ether, Trimethylsilyl ether of glycerol, Hexadecanoic acid trimethylsilyl ester, 9,12-Octadecadienoic acid (Z,Z)- trimethylsilyl ester, Octadecanoic acid trimethylsilyl ester and Hexanedioic acid bis(2-ethylhexyl) ester.

Oxidized organic phase at 25°C has only 2,5-Dihydroxy-1,4-benzoquinone. Silylated oxidized aqueos phase at 25°C has 1,2-Bis(trimethylsiloxy)ethane, Propanedioic acid-dimethylbis(trimethylsilyl) ester and Silane [1,2-phenylenebis(oxy)]bis trimethyl.

6. Summary

Soil erosion is one of the main causes of soil degradation, land loss and desertification. The erosion process alters the physical, chemical and microbiological properties of soil. Deprived of most of its mineralized nutrient and accumulated humus substance, it can no longer provide favorable conditions for plant growth. In order to restore vegetation in such highly degraded areas requires the application of organic (waste) materials to first help form humus fractions so that plants can eventually grow. Many countries suffer from desertification and the amount of available organic matter that could be used for soil improvement is not sufficient, therefore it became necessary to find out alternative humus pre-cursors. It has been found that technical lignins can be converted into artificial humic substances (organo-mineralic fertilizers) by ammoxidation process.

The objective of the present work was to study the structural changes in lignins and phenolic model compounds caused by ammoxidation under comparatively mild reaction conditions. The reactivity of the different phenolic and quinoide model compounds was studied at different pH values. For that purpose, the adsorption maxima of all model compounds were determined at pH 7, 8, 9, 10, and 11. Ammoxidation reaction were carried out at 100°C and 2bar oxygen, using a solution of 1g of the particular lignin or phenolic model compound in 20ml of 5% aqueous NH_4OH. The reaction time was 3 hours for all experiments. Selected phenolic model compounds and technical lignins were ammoxidized using ^{15}N labelled ammonium hydroxide in order to perform ^{15}N CPMAS NMR spectroscopic studies aiming at the elucidation of the type of nitrogen binding in the obtained products. All crude reaction products from the ammoxidation of the phenolic model compounds were extracted with ethyl acetate yielding the "organic phase". The residues are referred to as "aqueous phase". All of the aqueous phases were subjected to different derivatization procedures such as silylation, acetylation, and methylation in order to convert them into more lipophilic compounds which were then analysed by means of GC/MS. The acetylated aqueous phases were separated and characterized by column chromatography. The dried "aqueous phases" were studied with different instrumental-analytical methods such as Curiepoint Pyrolsis GC/MS, X-ray photoelectron spectroscopy, and ^{15}N CPMAS NMR spectroscopy. Furthermore, elemental analysis of the aqeous phases of the ammoxidized phenolic model compounds and lignins were performed. From the elemental analysis and the GC/MS measurements it became evident that the organic phases consisted mainly of the educts. Hence, most nitrogen is bound in that fraction which was referred to "aqueous phase". From the deconvoluted XPS spectra

there is some evidence that the ammoxidized compounds contain nitrogen mainly in the form of ammonia, amides and pyrrol-type heterocycles. Amide-type nitrogeneous compounds are found to contribute the major part of the organically bound nitrogen (60-80%).

As surface analytical techniques such as XPS may yield unreliable results in some cases mainly caused by surface contamination, additional use of a complimentary technique such as NMR is recommended. ^{15}N CPMAS NMR spectroscopic studies of Sucrolin^{TM}, Indulin AT^{TM} and different phenolic model compounds such as methoxyhydroquinone or 2,5-dihydroxybenzoquinone which were ammoxidized by using a 5 % NH_4OH solution containing 4 atom-% of ^{15}N strongly support the XPS results as the most intense signals were found in the amide fraction. Deconvolution of the spectra furthermore reveals the presence of larger amounts of ammonia, urea, amines and smaller amounts of pyrrol-type nitrogeneous compounds. In order to prove if the broad signal appearing in the chemical shift range between -265 and -290 ppm is indeed caused by amides, the aqueous phase of the ammoxidized Indulin AT^{TM} was reduced with Zn/HCl as it is known that reduction of carboxylic amides results in the formation of amines. As expected, the broad intensive signal was reduced significantly by a Zn/HCl treatment. Since no increase in the amine range (-320 to -350 ppm) was observed one can conclude that low molecular alkyl amines were formed from amides of lower molecular carboxylic acids such as formamide, acetamide or even amids of muconic acid derivatives which can be formed in the course of ammoxidation. A similar clear picture was obtained from the reduction of ammoxidized Indulin with NaOBr.

Urea and acetamide are quantitatively reduced by NaOBr in alkaline medium. Therefore, treating an ammoxidized lignin with NaOBr in alkaline medium should result in complete removal of primary amide and urea moieties, which could be approved by ^{15}N CPMAS NMR spectroscopy as the particular peaks disappeared in the spectra.

Furthermore, some ammonia salts of organic acids which were formed during the ammoxidation process were detected by means of GC/MS after silylation with BSTFA. Silylation and subsequent GC/MS measurement of ammonia oxalate gave proof that ammonia salts of carboxylic acids can be silylated by BSTFA as well and hence that the latter are also detectable by means of GC/MS.

In order to figure out the influence of ammonia, comparatitive oxidation reactions using sodium hydroxide where carried out with the same phenolic model compounds.

Interestingly, oxidation of the phenolic model compounds dissolved in aqeous NaOH instead of aqueous NH_4OH gave quite different results. Thus, the yields of the organic phases, i.e. the

recovery rate of the educts, were higher in the case of oxidation and a higher yield of the aqueous phase was obtained in almost all cases after ammoxidation.

From the whole results there is some evidence that amides play an important role as the main nitrogen binding form in ammonoxidized phenolic model compounds and lignins. It was established that nitrogen is present partly as ammonia salts, amines and urea, but it is mainly incorporated in the form of amides.

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