

Microwave Assisted Degradation of Lignin to Monolignols

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Abstract

Objective: To carry out lignin degradation under very mild conditions using microwave technique.

Methods: Lignin salt purchased from HiMedia laboratories was dissolved in distilled water and the solution was introduced to Biotage Initiator microwave. The reaction temperature was varied between 100-150°C with average power 85-90 W. Mass spectra were recorded in ACN-H₂O (3:7) solution on Bruker microTOF QII mass spectrometer in +ve ESI mode. Acetonitrile and water were HPLC grade and were bought from Sigma Aldrich while Sodium fluoride was purchased from Spectrochem. SEM images were recorded on ZEISS EVO LS10 scanning electron microscope with prior coating of silver using Quorum Q150R ES coating machine.

Results: 1 g of lignin dissolved in 10 ml distilled water was irradiated under microwaves. Aliquots of samples were withdrawn and mass spectra were recorded after every 10 min. Maximum conversion of lignin to monolignols was observed after 90 min. Effect of NaF was also observed when catalytic amount of NaF (10 mg) was used in each reaction. Surprisingly, the results obtained in the previous conditions after 90 min were achieved only after 30 min in the presence of NaF.

Conclusion: Lignin was degraded to its monomeric units when its aqueous solution in presence of catalytic amount of NaF was irradiated under microwaves at 150°C for 30 min. Hence, this technique could be used to degrade lignin into various lower lignols along with monolignols. Using this technique, revolutionary change could be made in paper, pulp and leather industry. Above all, several pharmaceutical raw materials could be synthesized efficiently from important monolignols produced from lignin degradation.

Keywords: Lignin; Depolymerization; Degradation; Mass spectrometry; Microwaves; SEM; Sodium fluoride

Abbreviations: ACN: Acetonitrile; ESI: Electrospray ionization; MWI: Microwave irradiation; NaF: Sodium fluoride; SEM: Scanning electron microscope

Introduction

Succeeded by cellulose, lignin holds a major part of the biomass. It

is the key constituent of secondary cell wall of plants and is present in some algae too. The worldwide production of lignin comprises of 1.1 million metric tons per year [1]. The lignocellulosic material includes around 30% by weight of lignin; [2] out of which, it is primarily used in combustion processes and only <5% is utilized for other purposes [3].

Chemically, lignin is a copolymer of three different phenylpropane monomer units, viz., *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. They are linked through β -O-4 aryl ether bonds within the compact network system of lignin (Figure 1). Depolymerization of lignin could be a source of value based molecules that can be used as efficient fuels and for other basic applications [4]. It has a major application in food industry and perfumery along with the sources of various pharmaceutical products. For example, monolignols like vanillin have a broader scope in the synthesis of numerous pharmaceutical ingredients [5].

As per the available reports, [6] the depolymerisation of lignin has been achieved by (i) acid catalyzed, [7,8] (ii) base catalyzed, [9-11] (iii) metal catalyzed, [12-15] (iv) ionic liquid aided [16-18] and (v) supercritical fluid assisted chemical reactions [19-21]. Acid and base catalyzed depolymerisation involves the use of large amounts of acids/bases (2-10 weight %) keeping the reaction temperature >250°C. Also,

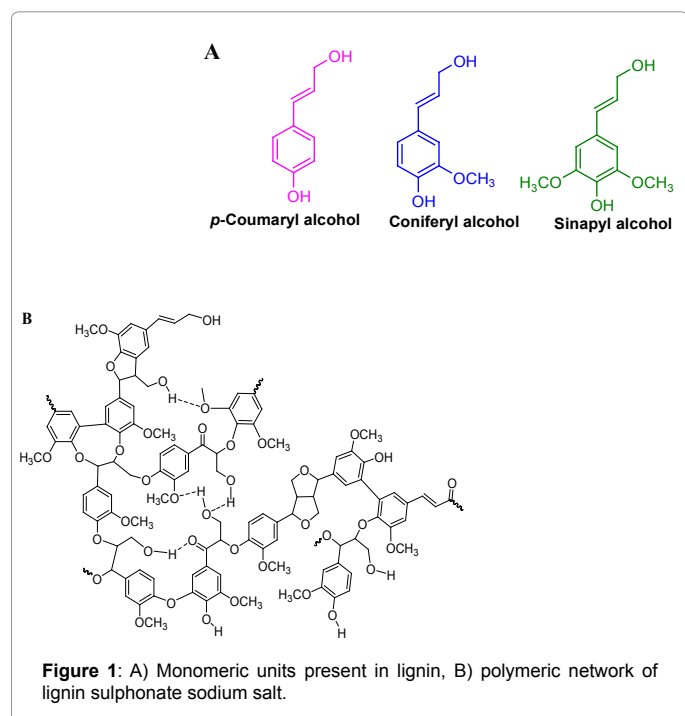


Figure 1: A) Monomeric units present in lignin, B) polymeric network of lignin sulphonate sodium salt.

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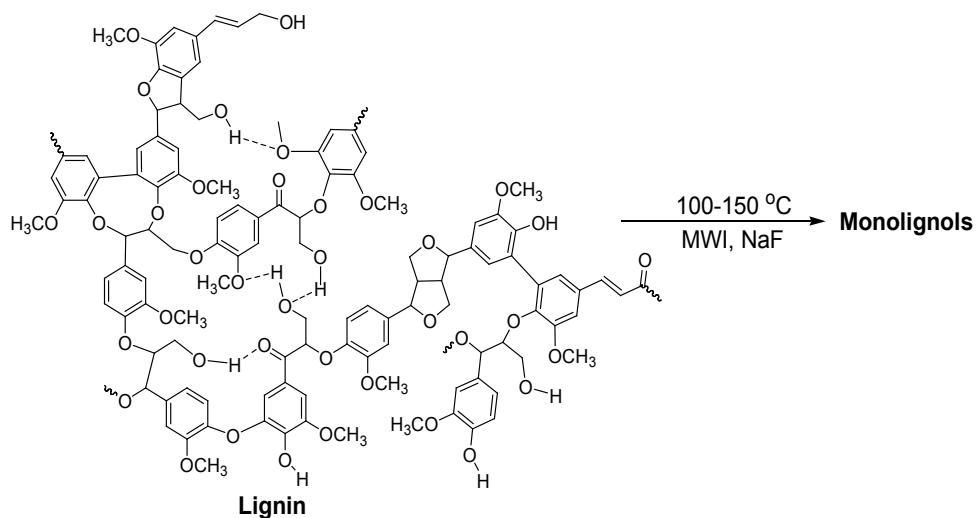


Figure 2: Chemical reaction and conditions involved in lignin degradation under present investigation.

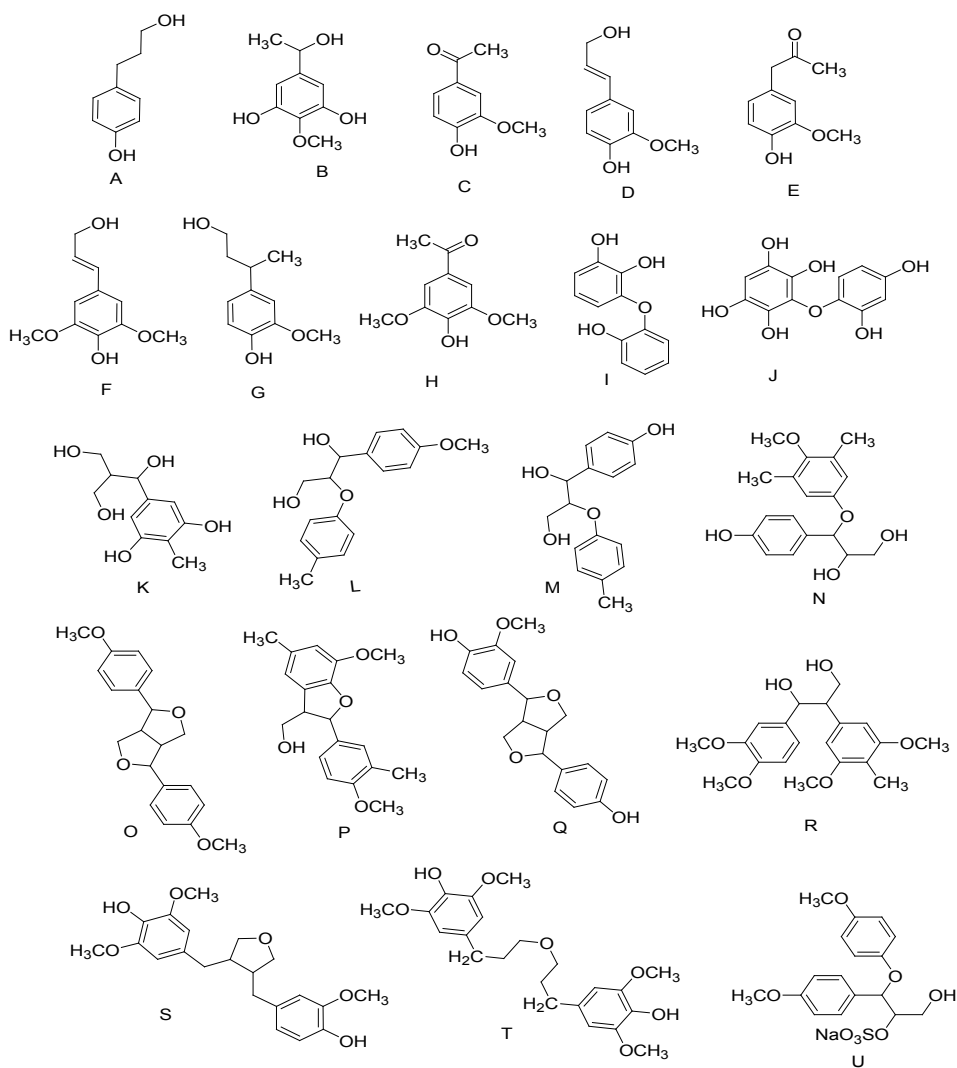


Chart 1: Various species detected in the mass spectra of depolymerized lignin sulphonate sodium salt.

very strong acids/bases viz., HCl, H₂SO₄, formic acid/ NaOH, KOH, LiOH, etc. are being employed in this type of lignin degradation. The metal catalyzed degradation involves the use of different heavy metal catalysts like, Pt, Pd, Ni, Ru, etc. along with quite high temperature of the reaction vessel. The use of ionic liquids and supercritical fluids is also practiced at high temperature and pressure. In continuation to our previous work on the degradation of biomass resources for preparing ample value added products where cellulose was successfully converted to glucose; [22] here, lignin is made to undergo degradation under the similar reaction conditions.

Materials and Methods

Reaction Procedure

Lignin sulphonic acid sodium salt (1 g) was dissolved in 10 ml distilled water and the solution was introduced to Biotage Initiator microwave. The reaction temperature was varied between 100-150°C with average power 85-90 W. The reaction was monitored by taking out the aliquots after every 10 min and recording the mass spectrum. NaF catalyzed reaction was also performed under similar conditions. Lignin sulphonic acid sodium salt (1 g) and 10 mg NaF were dissolved in 10 ml distilled water and the reaction mixture was subjected to microwave irradiations (Figure 2). The reaction was monitored by recording mass spectra after regular intervals of 10 min. When no further change in the mass spectra was visible, the reaction was stopped and the reaction mixture was distilled off *in vacuo* on rotary evaporator and a dark brown solid residue was obtained. Solid product was further dried *in vacuo* and SEM images were recorded.

Recording of mass spectra

Mass spectra were recorded in ACN-H₂O (3:7) solution on Bruker Micro TOFQII mass spectrometer in +ve ESI mode and the species formed were identified from their respective *m/z* values.

S.No.	Species detected	Mol. Formula	Calcd <i>m/z</i> [M + Na] ⁺	Exptl <i>m/z</i> [M + Na] ⁺
1	A	C ₉ H ₁₂ O ₂	175.0730	175.1133
2	B	C ₉ H ₁₂ O ₄	185.0808*	185.1238*
3	C	C ₉ H ₁₀ O ₃	189.0312	189.0323
4	D	C ₁₀ H ₁₂ O ₃	203.0679	203.0505
5	E	C ₁₀ H ₁₂ O ₃	203.0679	203.0505
6	F	C ₁₁ H ₁₄ O ₄	211.0965*	211.0320*
7	G	C ₁₁ H ₁₆ O ₃	219.0992	219.0439
8	H	C ₁₀ H ₁₂ O ₄	219.0992	219.0439
9	I	C ₁₂ H ₁₀ O ₄	241.0471	241.0245
10	J	C ₁₂ H ₁₀ O ₇	267.0499*	267.0909*
11	K	C ₁₁ H ₁₆ O ₆	267.0839	267.0909
12	L	C ₁₇ H ₂₀ O ₄	289.1434*	289.1739*
13	M	C ₁₆ H ₁₆ O ₄	297.1097	297.1039
14	N	C ₁₈ H ₂₂ O ₅	319.1540*	319.2211*
15	O	C ₂₀ H ₂₂ O ₄	327.1591*	327.1185*
16	P	C ₁₉ H ₂₂ O ₄	337.1410	337.1771
17	Q	C ₁₉ H ₂₀ O ₅	351.1567	351.1912
18	R	C ₂₀ H ₂₆ O ₆	385.1622	385.1602
19	S	C ₂₁ H ₂₆ O ₆	397.1622	397.2298
20	T	C ₂₂ H ₃₀ O ₇	429.1884	429.0588
21	U	C ₁₇ H ₁₉ O ₅ SO ₃ Na	487.1009	487.0940

*[M+H]⁺

Table 1: The species detected in mass spectra of depolymerized lignin.

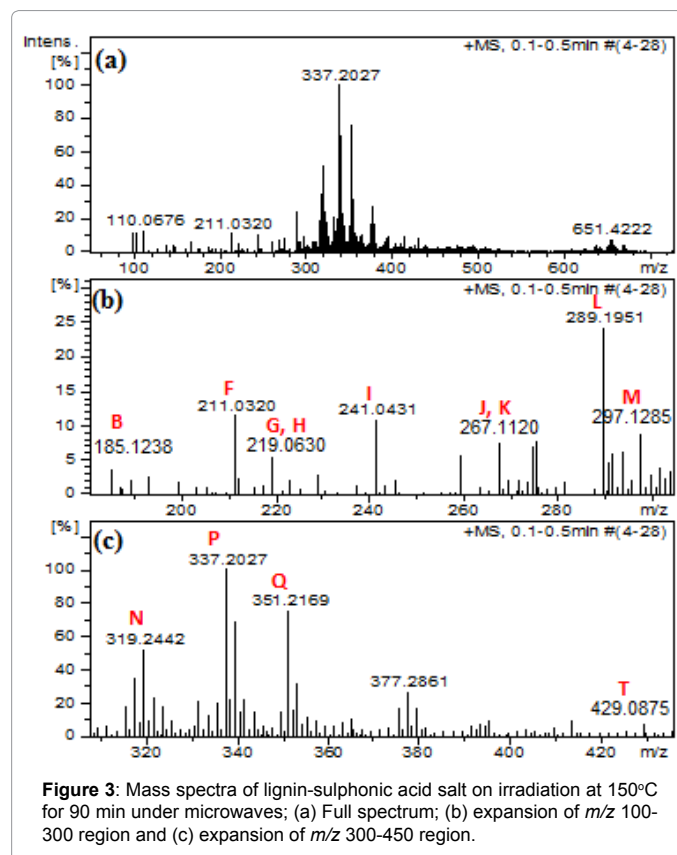


Figure 3: Mass spectra of lignin-sulphonic acid salt on irradiation at 150°C for 90 min under microwaves; (a) Full spectrum; (b) expansion of *m/z* 100-300 region and (c) expansion of *m/z* 300-450 region.

SEM imaging

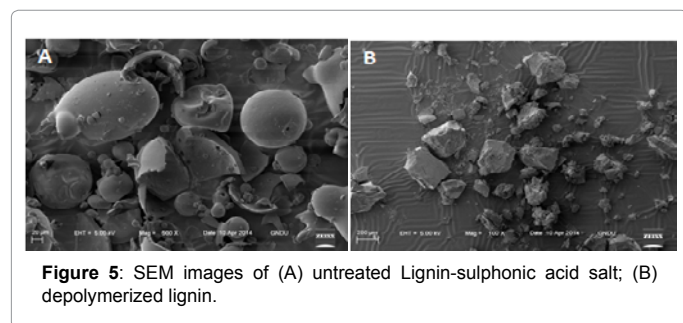
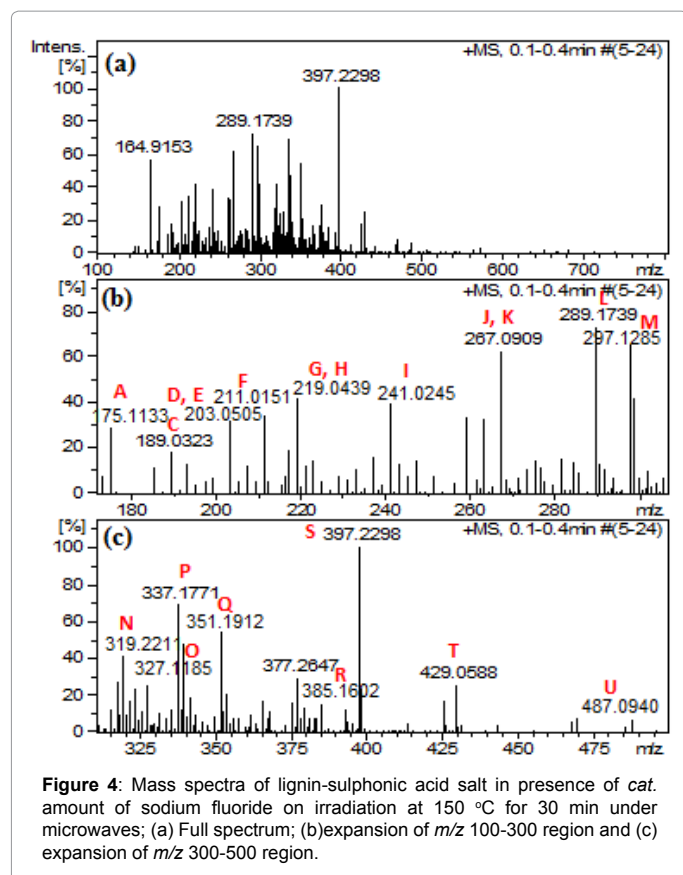
All the samples were vacuum dried and were precoated with silver using Quorum Q150R ES coating machine. SEM images were recorded on ZEISS EVO LS10 scanning electron microscope.

Results and Discussion

After the successful conversion of cellulose (major part of biomass) into glucose [22] under very mild reaction conditions (pH-6, NaF/NaCl) utilizing microwave technique by our group; we planned to degrade lignin (another major part of biomass) also under the microwave assisted mild reaction conditions. For the present investigation, sodium salt of lignin sulphonic acid was used (purchased from HiMedia laboratories) as the starting material. 1 g of the lignin salt was dissolved in 10 ml distilled water. The reaction mixture was subjected to microwave irradiation at 100-150°C at an average power of 85W. Aliquots of the samples were withdrawn from the reaction vials after regular intervals of 10 min for recording mass spectra. Formation of degraded species was detected after 90 min of irradiation at 150°C (Chart 1, Table 1, Figure 3).

Intriguingly, to see the effect of NaF on the degradation process, catalytic amount (10 mg) of NaF was added to the reaction mixture and it was irradiated under microwaves at 150°C. The sample aliquots were withdrawn after regular intervals and mass spectra were recorded. The chemical species detected after 30 min of reaction (Figure 4) were similar as observed after 90 min during the absence of sodium fluoride. Complete transformation of polymeric structure of lignin was accomplished in 30 min of microwave irradiation.

In general, it was observed that the intensity of chemical species with *m/z* <300 was low in the reaction mixture without NaF while these



species have quite intense peaks when the reaction was performed in presence of NaF (Figure 4). Moreover, the peaks with $m/z > 600$, though present in low intensities in the reaction mixture without NaF, were completely vanished in presence of NaF. Evidently, the microwave assisted degradation of lignin seems to be more effective in presence of NaF. Advantageously, the milder method used here involves only a small amount of an economical catalyst (NaF) as compared to the conventional methods used so far for lignin degradation where much higher temperatures and drastic conditions (acidic/basic) were used along with much expensive catalysts.

In order to spot out the morphological changes during the depolymerisation of lignin, SEM micrographs were recorded and a drastic change was observed between the polymerized and depolymerized states of lignin. From the much fine globular structures in case of polymerized lignin, morphology transformation to irregular and finer particles was taken place in case of depolymerized state (Figure 5).

Conclusions

A moderate technique for degradation of lignin has been demonstrated. The hydrogen bonding network of lignin was broken up and hydrolyzed so as to obtain mono and higher lignols. Microwave degradation technique was employed along with small amount of NaF. Since the presence of NaBr, NaI and NaCl did not affect the depolymerization process, F may be playing a strong H-acceptor role in breaking the H-bond network of the polymer. Since, this method involves the use of much lower temperature and milder catalyst (in small amount) as compared to the previously reported conventional methods; the method could be of considerable significance from the environmental as well as industrial point of view. Consequently, a number of chemical entities of pharmaceutical importance could be obtained from lignin.

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