



## LIGNIN EXTRACTION AND USE AS FLAME RETARDANT EXTERIOR

S.K.Bidwai<sup>1</sup>, Prof.S.K.Nanwatkar<sup>2</sup>, Prof.J.K.Shinde<sup>3</sup><sup>1</sup>UG Student, Department of Chemical Engineering, Anuradha Engineering College, (MS), India, [skbidwai13@gmail.com](mailto:skbidwai13@gmail.com)<sup>2</sup>Assistant Professor, Department of Chemical Engineering, Anuradha Engineering College, (MS), India, [shrikant611988@gmail.com](mailto:shrikant611988@gmail.com)<sup>3</sup>Assistant Professor, Department of Chemical Engineering, Anuradha Engineering College, (MS), India, [jkshinde28@gmail.com](mailto:jkshinde28@gmail.com)

## Abstract

The spent liquid after the pulping process in paper mill known as black liquor, containing lignin and carbohydrate during the pulping process black liquor viscosity mainly depend on dissolved lignin ,after the lignin extraction from black liquor by soxhlet extractor analysis done by FTIR, gas chromatography and UV-Spectrometer. In this work lignin extracted by different types of solvent and lignin used as flame retardant exterior, it is prepared from Urea, Formaldehyde and sodium lignosulphonate with different concentration by the method of padding and drying then retardency of treated fabric was compared to temperature generation curve. This test done by thermogravimetry and FTIR done by treated and washed fabrics also mechanical properties check like Impact strength and bending test finally result % of bonding of flame retardant is increases.

**Keywords:** Black liquor, Lignin, FTIR, Carbohydrate, Gas chromatography, Flame retardant, Urea, Thermogravimetry

\*\*\*

## 1. INTRODUCTION

Lignin has a much more complex structure than the carbohydrate polymers. The term lignin is derived from the Latin word for wood lignum. Lignin is a major constituent in structural cell walls of all higher vascular land plants. Its polyphenolic structure is well known for its role in woody biomass to give resistance to biological and chemical degradation. This is due to its hydrophobic nature and insolubility in aqueous systems preventing access of degrading chemicals and organisms [1]. The monomeric units of phenylpropane in lignin polymers are linked in a complex network through different types of ether and ester bonds as well as carbon-carbon bonds. The lignin occurring in plant cell walls is commonly closely associated with polysaccharide structures of cellulose and hemicellulose. On account of the high content of Si in straw and the small scale, many papermaking enterprises have not found a proper method to treat wastewater in pulping process. With the more tension of environment protection, those enterprises have confirmed with the crisis of existence and improvement and they are looking for an appropriate treatment method, which ought to be not only suitable for their scales and straw material, but also feasible in economics [4].

In above paper black liquor with pine chips and coffee been as a row material were treated by isolation kraft process and reuse. The treatment, the solid material in black liquor were transferred into two by products (i. e. lignin and water reducing agent), which have extensive uses The lignin component being more thermally stable contributes more to char formation than does cellulose and hemicelluloses [2]. Increased char formation reduces flammable gas formation and help insulate wood from further thermal .As wood is used

in furniture, home decoration and building materials, it will be essential to make wood products flame resistant/retardant. It is well known that material made of wood can be treated with compounds containing urea formaldehyde resin; lignin, HMTA and resorcinol to increased their flame resistance and accelerate the formation of a carbonized layer on the material. Wood is an extensively used material and is present in many places in our everyday lives [6]. Not only is wood an integral part of most structures, especially in India, but is also the main source of furnishings found in homes, schools, and offices around the world [5].

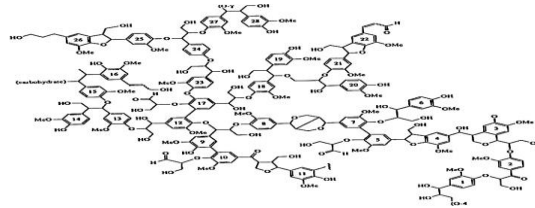


Fig.1. Monomer structure of Lignin

## 1.1 Types of lignin:

Gymnosperm lignin, Dicotyledonous lignin, Angiosperm lignin etc

Table 1. Cellulose, Hemicellulose, and Lignin Contents in Common Agricultural Residues and Waste

lignocellulosic material	Cellulose (%)	hemicellulose (%)	lignin (%)
Hardwood steam	40-55	24-40	18-25
Softwood steam	45-50	25-35	25-35

Nut shell	25-30	25-30	30-40
Grasses	25-40	35-50	10-30
Wheat straw	30	50	15
Sorted refuse	60	20	20

## 1.2 Lignin separation method

### Lignin Separation Methods

Numerous techniques are available for the partition and cleansing of lignin from black liquor. These techniques are based on the changes of lignin solubility, the differences between the molecular weight/size of lignin or a combination of both. The criteria used for the separation methods are, firstly, that lignin should be isolated with a high yield, secondly, the isolated lignin should be free from contaminants and, thirdly, the procedure should be simple and easy to perform<sup>[9]</sup>.

### Fire retardant method

#### Chemical action:

This method is in general targeted at interfering with radical reaction which take place during gas phase and aims to protect internal material from heating during char creation solid phase.

#### Physical action:

This method is based on decreasing temperature by endothermic reaction, reducing the fire distribution by fluxing oxygen with non combustible gases and promoting the formation of protective impenetrable surface layer.

**Table 2. Fire Retardant Theories**

S.N.	Theories	Mechanism
1	Barrier theories	These theory posit the formation of glassy layer which impedes the liberation of volatile gases, preventing oxygen from reaching the substrate and protecting the material surface from the influence of elevated temperature.
2	Thermal theories	Retardant additives enhance the thermal conductivity of the organic material and adsorb energy, since an endothermic reaction is triggered during their decomposition.
3	Theory of non combustible gas	In this case mechanism works in the vapor phase and retardant surface additives decompose and emit non-flammable gases available for reaction.

## 2. EXPERIMENTAL SECTION

### 2.1 Chemical And Materials

In above experiment following analytical grade chemical is used. The detail of the chemicals used is as follows What man #4 filter paper, 0.5 gm of EDTA-2Na<sup>+</sup>, 2 M H<sub>2</sub>So<sub>4</sub>, 100 ml Black liquor, 9:1 dioxine : water solution, Water, Buckner Funnel, Conical Flask, Sintered Glass Funnel, Soxhlet Extractor, Rotary evaporator, Centrifuged machine, Urea commercial (NH<sub>2</sub>CONH<sub>2</sub>), melting at 35°C locally available.

Formaldehyde commercially type (37%) (CH<sub>2</sub>O) of density 1-0.85 at 20°C. Resorcinol (C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>), 99% melting at 111°C, and density 1.272 g/cm<sup>3</sup>. Solid waste lignin brown color, and different arrangement of wood

### 2.2 Synthesis of black liquor

Firstly black liquor is collected form Ballarsha pulp and paper industry of chandrapur district in Maharashtra state of India after collecting of black liquor black liquor is filtered with what man #4 filter paper over than 7 days approx. Then purified black liquor is used for lignin extraction and other filtered contain organic contain is used for other purposed.

### 2.3 Methodology

Black liquor is first filtered through whatman #4 filter paper after that 0.5 gm EDTA-2Na was added for every 100 ml black liquor. The liquor were neutralized with 2M H<sub>2</sub>SO<sub>4</sub> until a PH of approx 6was reached. Then the solution acidified to a PH of 3 and frozen at -20<sup>0</sup>C. After that solution collected in medium sintered glass funnel and washed with vigorously at 0<sup>0</sup>C. After air dried solution soxhlet extractor is used for removing the sulfur and other impurity and solution is purified with 9:1 dioxine water solution and stirred and dioxine is removed by rotary evaporation and the purified kraft lignin freezed dried and purified kraft lignin used for the mankind and industrial used<sup>[7]</sup>. 30 gm of formaldehyde and 20 gm of urea are charged with agitation in 1 lit water solution, three naked flask equipped with stirrer, reflux condenser and thermometer. After the Lignin Preparation urea was dissolved at the temperature range between 20-25<sup>0</sup>c and P<sub>H</sub> was adjusted with the range 7.5-8 using 5 N formic acid and sodium hydroxide. The mixture was heated at the temperature between 90-100<sup>0</sup>c with vigorous agitation until the reaction was completed for 2 hrs. The sample was left to cool at room temperature before measuring P<sub>H</sub> and viscosity. The PH was controlled to be 7.5-8 and viscosity was checked every 10 min. and to obtained a resin is known as urea formaldehyde resin<sup>[9]</sup>.

### 2.4 Preparation of composite structures

The final product resin was treated with a hexamethylenetetramine (7gm) and various mass ratio adhesion-promoter resorcinol 12-30 gm/urea formaldehyde to obtained solid cured product mixed with different types of lignin with a same proportion and apply as a coating on wood surface and dried in sun light after drying the wood surface deeps in 9:1 H<sub>2</sub>SO<sub>4</sub> water solution for 3 days to better strength<sup>[11]</sup>.

### 3. Characterization of lignin and Flame Retardent Exterior

FTIR, GCMS and UV-Spectrometer analyses were carried out for characterization of lignin extraction, Thermogravimetry

#### 3.1 FTIR analysis of Lignin

The FTIR spectra of lignin are shown in fig 1. The peaks of wave number of 3100 and 3000 cm<sup>-1</sup> are the C=C-H Asymmetric stretching vibration and C-C=C Symmetric stretch vibration at 1600 and 1580cm<sup>-1</sup> are due to phenol and alcohols. A broad pick in the range of 1730-1650cm<sup>-1</sup> is due to carboxylic acid formation with lignin extraction. Peaks at

wave number  $3400-2400\text{cm}^{-1}$  are due to Hydrogen – bonded O-H stretching. This overall stretching done on FTIR analysis, It was confirmed that a lignin synthesized contain a Aromatic rings, Phenol & Alcohol carboxylic acid and cellulosic functional group.

**3.2 GCMS ANALYSIS of Lignin**

For GCMS analysis, approximately 25 gm of lignin powder are tested in Anacon laboratory Nagpur Maharashtra state India. And by qualitative analysis following organic compounds are obtained in GCMS report that is as fallows.

a-Dodecanol, n-Dodecane ,1-Hexadecanol, n-Tetradecane, 10-Heneicosane, Octatriacontyl pentafluoropropionate, Propanoic acid, 2-(3-acetoxy-4,4,14-trimethyl androst-8-en-17-yl), Acetophenone, 4-hydroxy 3,5-dimethoxy, Erucic acid, Palmitic acid methyl ester, Ethyl iso-allocate, Linoleic acid methyl ester, Oleic acid methyl ester.

**3.3 Characterization of Flame Retardant Exterior**

**Impact test:**

The capacity of material to absorb energy and hence to predict failure load under dynamic condition. Izod and Charpy impact instrument was used for this test.

**Three point bending test:**

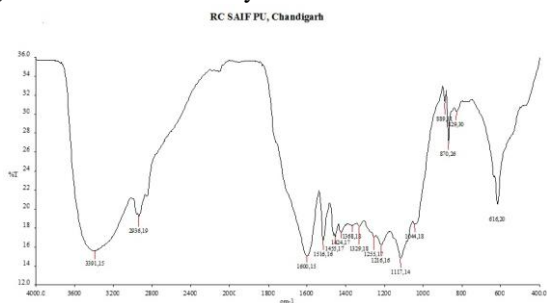
Three point bending tester was used to determine the resistance to distortion. This test was carried out according to (ASTM-D-790) test.

**Chemical resistance (Sweling degree):**

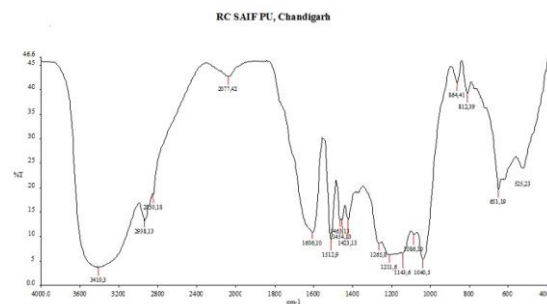
This type of test was achieved by soaking all composite samples in both moisture (100% H<sub>2</sub>O) and acidic solutions (10% H<sub>2</sub>SO<sub>4</sub>) for 7 days at 50 °C to estimate the change in weight.

**4. RESULT AND DISCUSSION**

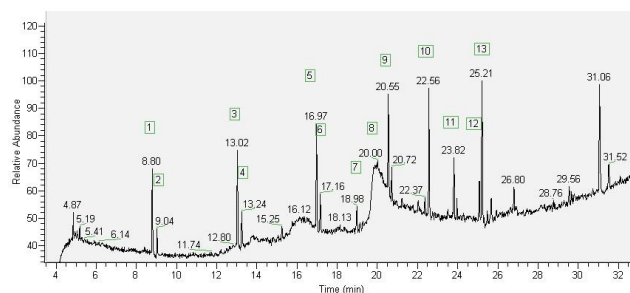
We make a different product by using lignin. We are using a different types solvent like Pentane, Di ethyl ether, for making of lignin. One of the key for the lignin market is its application in a wide range of low volume responsibility applications. Solubility in water is an important requirement of lignin in this research work. After the extraction of Lignin creation which is obtained from the different types of lignin with mixed with different chemicals. We have also plan to prepare different types of flame retardant Exterior from different lignin which also give better effect in daily mankind use and industrial use



**Fig 2. FTIR Report of Lignin Extract with Hexane**



**Fig 3. FTIR Report of Lignin Extract with Ethanol**

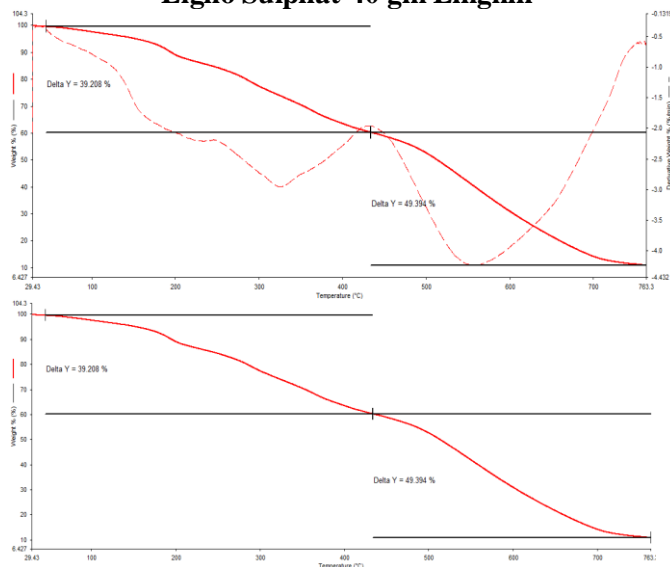


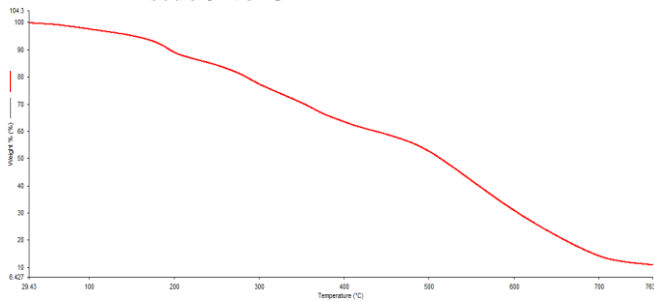
**Fig 4. GCMS Report of lignins**

**Table 3: Quantitative FTIR analysis of lignin sample extracted with different solvent**

Peak No.	Compound Name
1	a-Dodecanol
2	n-Dodecane
3	1-Hexadecanol
4	n-Tetradecane
5	10-Heneicosane
6	Ethyl Iso-Allocate
7	Oleic Acid methyl Ester
8	Linoleic Acid methyl Ester

**A. Urea-15ml, Resercinol-19 gm, HMTA-79 gm, Sodium Ligno Sulphat-40 gm Lignin**





**Fig 5. TGA of Flame Retardant Exterior**

#### 4. CONCLUSION

We successfully developed a facile route to extract lignin from black liquor for the use of flame Retardant Exterior. The developed method was proved to be efficient and simple, which are believed to be attractive for the lignin extraction processes from black liquor in pulping industry. The flame retardant treatment significantly improves the flame safety of wood products by reducing its heat contribution to a fire. For application where higher level of fire safety is desirable or necessary, fire-retardant-treated wood products provide a viable alternative to traditional non-combustible materials. Fire retardant surface are also used for to avoid the higher flame.

#### 5. ACKNOWLEDGEMENT

This research work partially supported by Anuradha Engineering College, Chikhli. We thank our colleagues from [Anuradha Engineering College, Chikhli] who provided insight and expertise that greatly assisted the research, although they agree with all of the conclusions of this paper. We also thank Prof. V. D. Gurudasani [Head, Department of Chemical Engineering] for his assistance in using sophisticated analysis equipments.

#### REFERENCES

[1]. Máté Nagy, Georgia institute of technology, “Biofuels from lignin and novel biodiesel analysis” December, 2009.

- [2]. Peter Axegård, STFI-Packforsk AB, Research Director, Division Fiber, Pulp Energy and Chemicals, Stfi-Packforsk, “The Kraft Pulp Mill As A Biorefinery”, 1999.
- [3]. Annie ngsunie, “Characterization of recovered black liquor and isolated lignin from oil palm empty fruit bunch soda pulping for semichemical and chemical pulps”, june 2008
- [4]. Nguyen Dang Luong ,Nguyen Thi Thanh Binh ,Le Dai Duong • Dong Ouk Kim • Dae-Sik Kim ,Seong Hoon Lee , Baek Jin Kim ,Yong Sang Lee, Jae-Do Nam , “An eco-friendly and efficient route of lignin extraction from black liquor and a lignin-based copolyester synthesis”, 879–890, 17 December 2011
- [5]. Henrik wallmo, Martin wimby, Anders Larsson, Mesto Power AB, Gothenburg, “Increase production in your recovery boiler with lignin”, Sweden, 2009
- [6]. Cecilia Johansson, “Advent of Biorefinery has developed several new sources of lignin”, Russia, 2005
- [7]. Sajeev John, Jeju M. Issac, Roselin Alex, International journal of emerging technology and advanced engineering, “Mechanical properties of natural rubber composites reinforced with lignin from caryota fibre”, volume 4, April 2014
- [8]. Olugbenga Oludayo Oluwasina, Labunmi Lajide, Bodunde Joseph Owolabi, Department of Chemistry, Federal University of Technology, “Performance of bonded boards using lignin-based resins”, Wood Material Science and Engineering, 18 June 2014
- [9]. Weizhen Zhu, “Equilibrium of Lignin Precipitation The Effects of pH, Temperature, Ion Strength and Wood Origins”, Forest Products and Chemical Engineering Department of Chemical and Biological Engineering, Chalmers University of Technology, ISSN 1652-943X, 28 march 2013
- [10]. Karolos Markesinis, Ilias katsampas, “Innovative and competitive chemical technology for production of fire retardant wood based panels”, 55131, 2005.
- [11]. Marina Nikolaeva, timo karki, “A review of fire retardant processes and chemistry, with discussion of the case of wood-plastic composites”, Baltic forestry, 17(2), 314-326, 2011