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### **Microwave Assisted Synthesis and Characterization of Carboxymethyl Lignin Biopolymer from Kraft Lignin Obtained from Biomass of Bagasse Pulping**

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#### **ABSTRACT**

A simple and efficient method is described for the synthesis of biodegradable soluble Carboxymethyl lignin (CML) using bagasse based insoluble Kraft lignin. The present study reveals that isolation of kraft lignin from Black liquor of sugar cane bagasse pulping (bio mass) and rapid synthesis of CML biopolymer in IPA medium with the assistance of microwave irradiation. The biopolymer CML's degree of substitution (D.S.) with respect to reaction time, microwave power and concentration of reactants were investigated. The characterization like FTIR, SEM and Particle size distribution (PSD) study was carried out to evidence the changes observed in the synthesized biopolymer CML.

**KEYWORDS:** Carboxymethyl lignin, Sugarcane bagasse, Microwave irradiation, Bio-polymer, Kraft lignin.

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## **INTRODUCTION**

Lignin is a naturally occurring biopolymer that is synthesized by most plants to act as a binder for cellulose and hemicelluloses. Hence it is one of the most abundantly available renewable biomaterial. Lignin can be sourced from by-product of the paper industry and the second generation biofuel industry<sup>1</sup>. Lignin is a polyphenol comprises by three monomers namely para-Coumaryl alcohol, Coniferyl alcohol, and Sinapyl alcohol. The chemical structures of lignin differs from plant to plant, even differs in parts of the plant.

About 70-90 million tons of lignin produced annually from the paper industry alone. Virtually all the lignin generated in paper industry is used as an inefficient fuel source for boiler, producing fewer energy per unit mass compared to coal<sup>2</sup>. Due to natural abundance, availability and naturally occurring form, lignin has a great prospective to be utilized as low cost filler for polymer. Extraction, derivatization and fictionalization of lignin biopolymer give a brief insight in the development of Lignosulfonate, Kraft Lignin, lignocellulose, lignophenol and organosolv lignin based polymers and knocked new doors for the development of well-designed biopolymers biomaterials, biodegradable films, and composites and for potential industrial applications.

The crystallinity and poor water solubility are limiting its extended application<sup>3</sup>. The usage of the lignin is limiting as a fuel only in-situ recovery boilers of paper mills in India as well as in globe. Lignin derivatives offers an alternative way of reutilization of wastes biomass resources. Lignin and lignin derivatives such as, butylated lignin<sup>4</sup>, depolymerized lignin<sup>5</sup> and nano lignin<sup>6</sup> can be used in diverse polymer applications directly or in combination with other synthetic polymers.

Among the derivatives of lignin only limited number of works has been reported on Carboxymethylated lignin (CML) which is a lignin derivative with hydrophilic carboxyl groups engrafted by carboxymethylation modification. The water-soluble carboxymethylated lignin synthesized by using conventional heating method from wheat straw alkali lignin (WAL) as the raw material<sup>7</sup>. CML synthesized from acid hydrolysis of sugarcane bagasse in the process of bio-ethanol production and reported a color removal application by complexing with the  $Fe^{3+}$  ion (CML-Fe) for the removal of Brilliant Red 2BE textile dye<sup>8</sup>. Sugarcane Bagasse lignin extracted from bioethanol production modified as CML, which was applied as stabilizing agent in aqueous ceramic suspension<sup>9</sup>. The modified lignin (CML) with Cobalt(III) and some metal ions find an application as remarkable filler in polystyrene polymer composites which can be used in packaging applications<sup>10</sup>.

Based on the relayed review of literature, the present work is undertaken with the aim of extraction of lignin and preparing microwave assisted inexpensive, effective, crystalline rapid synthesis of porous Carboxymethyl lignin (CML) using lignin extracted from black liquor a Bagasse

based kraft lignin biomass. With the reference of the work described by<sup>11</sup> for preparing Carboxymethyl starch (CMS) with microwave assistance, Carboxymethyl lignin (CML) was prepared by ‘Williamson Etherification’ by reacting Kraft lignin with mono chloroacetic acid in presence of sodium hydroxide under microwave irradiation.<sup>7</sup> see Fig.1.

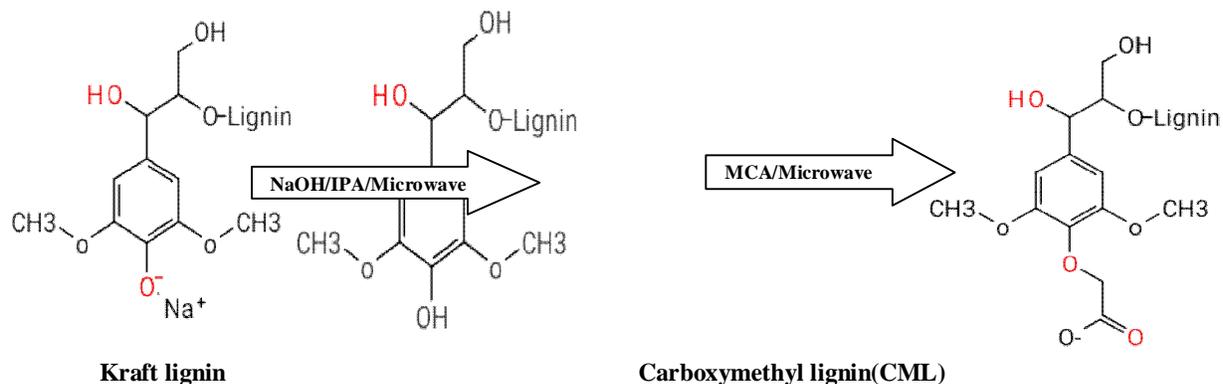


Figure.1 Reaction scheme of synthesis of Carboxymethyl Lignin

## MATERIALS AND METHODS

Black Liquor was obtained from a Grade-A paper mill in India. This black liquor was spent liquor from the Kraft pulping of sugarcane waste bagasse. The other chemicals are purchased and used without further purification. All the chemicals were analytical grade and prepared as a solution with double distilled water.

### *Extraction of Kraft lignin from Black liquor of bagasse pulping*

The lignin was precipitated using acid hydrolysis method described in the procedure with some minor modifications<sup>10</sup>. Black liquor (65% in solid content), obtained from the alkaline pulping of bagasse was heated to 75°C under stirring and control of pH. Acidified with con. sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) up to pH of 1.5. Acidified mixture was heated up to 100°C in water bath with continuous stirring. Precipitated lignin (Kraft Lignin-KL) was cooled to room temperature, filter in Buchner funnel, and then washed with hot water till the pH becomes neutral. The final product was air dried at ambient conditions. Thus extracted lignin (KL) was re-dissolved in 20% NaOH and precipitated with H<sub>2</sub>SO<sub>4</sub>. The precipitated lignin was filtered and then washed with hot water until the filtrate was clean and then air dried at ambient laboratory conditions.

### *Preparation of Carboxyl methyl lignin by microwave irradiation*

10 g of the Kraftlignin (KL) was introduced in a 250 mL beaker containing Isopropyl alcohol (IPA): water (80: 20 v/v) mixture. Then required amount of sodiumhydroxide pellets based on the amount of monochloro acetic acid was added to the mixture. The reaction mixture was mixed well

and stirred in heating magnetic stirrer at 35°C for 30 minutes. 12 g of monochloro acetic acid (MCA) in IPA was then added gradually with agitation. Subsequently, the reaction was allowed to proceed with temperature of 70°C/180W and duration of reaction 20 min in the microwave oven. At the end, the excess of sodium hydroxide was neutralized with glacial acetic acid and filtered. Purification of CML was carried out by washing with methanol (80-90%) to washout sodium lignate, sodium chloride and sodium acetate, and dried under vacuum at 70°C for constant weight.

#### ***Determination of Yield of CML***

Carboxymethyl lignin (CML) yield was measured based on a dry weight basis, CML yield was calculated as follows

$$\text{CML Yield (\%)} = \frac{\text{Weight of the prepared CML in g}}{\text{Weight of the dry Kraft lignin used in g}} \times 100$$

#### ***Determination of Degree of Substitution (D.S)***

The DS of carboxymethylated lignin (CML) was determined by the method ASTM D1439-03 reported elsewhere for determining the degree of substitution of CMC<sup>12</sup>. The carboxymethyl groups in the CML were first converted into an acid form with acid (HCl). The acidified lignin was then recovered by precipitation with methanol, then, 0.2 M NaOH (20 ml) was added to a suspension of accurately weighed CML in 30 ml of purified water. The mixture was transferred into a 100-ml volumetric flask and adjusted to the mark with purified water. The solution (25 ml) was transferred into a beaker and titrated with 0.04 M HCl using pH meter up to pH 7.0. The degree of substitution (D.S) was calculated using following equations.

$$\text{DS} = \frac{0.151A}{1 - 0.058A}$$

Where D.S is degree of substitution

A is milli equivalent of acid consumed per gram of sample

162= is Molecular mass of lignin part (Cumaryl alcohol) unit<sup>12</sup>

58 is molecular mass of substituted carboxylmethyl unit.

The carboxymethylation, degree of substitution (D.S) was studied with respect to concentration of reactants, microwave power and reaction time.

#### ***FTIR Spectral study of CML***

Unmodified Lignin bio-polymer (extracted lignin -KL), and modified lignin derivative (CML) samples were separately mixed with KBr at a concentration of 1/100 mg KBr (w/w) for FT-

IR analysis. The spectra was taken in absorption mode in the range of 400–4000  $\text{cm}^{-1}$  in an FT-IR Shimadzu spectrophotometer with resolution of  $4\text{cm}^{-1}$  as described recently.

### ***Scanning electron microscopy***

The surface morphology of Kraft lignin and Carboxymethyl lignin (CML) biopolymer was observed with scanning electron microscopy. To analyze the prepared biopolymer was grinded and the topography was analyzed with Vega3, TESCAN (Czech Republic), Scanning Electron Microscope, GRI-SEM, Gandhigram, Tamilnadu.

### ***Particle size analysis (PSD)***

The particle size distribution of the CML was determined by a laser diffraction apparatus (Horiba Laser diffraction analyser LA950, Japan). The synthesized CML was first grinded and dispersed in ethanol and ultrasonicated at 40 W with 60 % pulse rate for 2 min<sup>13</sup>. To improve the sample dispersion, 25 % Sodium meta bisulphate is used as a dispersant.

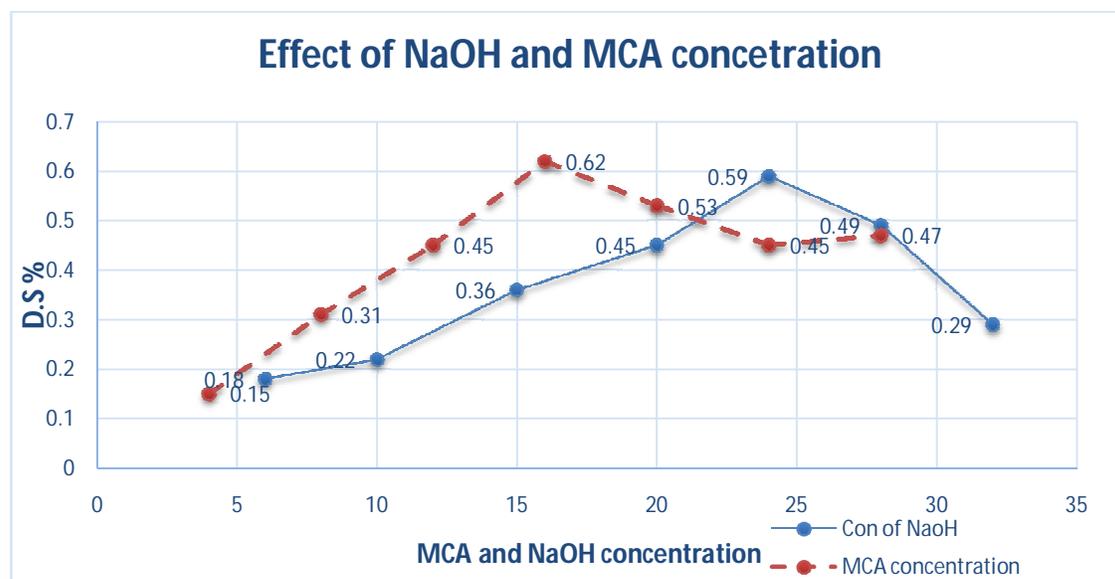
## **RESULTS AND DISCUSSION**

Carboxymethyl lignin (CML) was prepared by reacting lignin with MCA in presence of NaOH under microwave irradiation (Fig.1). The carboxymethylation reaction of bagasse kraft lignin (KL) is studied with respect to the variables like concentration of the reactants, reaction time and power of microwave irradiation.

### ***Effect of Concentration of reactants***

Degree of substitution (D.S) increases with increasing both MCA and NaOH concentration. It was found that IPA: water [80: 20] constitutes the most favorable medium for the carboxymethylation reaction.

Fig.1 shows the effects of NaOH and MCA concentration on the carboxyl group substitution. It is observed that there is increase in the degree of substitution (D.S) of CML with NaOH concentration up to 24.0% and thereafter the trend shows decreased order. The maximum DS of 0.59% is obtained, for said NaOH concentration. The pH increases to provide alkaline environment for reaction and also aids to dissolving KL in solution for homogeneous reaction. At particular pH range of 10.5–11.0, the yield and DS of CML reach the maximum values, which are due to the greater ability of nucleophilic substitution of the hydroxyl group under this particular alkali strength<sup>4</sup>.



**Figure.2 Effect of reactant concentration**

As shown in Fig. 2, the effects of MCA concentration on degree of substitution (D.S) of CML, which is found that the carboxyl group content of CML increase with increasing of MCA concentration until they reach the maximum values of 0.62% with dosage of 16.0% MCA. The initial increase in MCA concentration accelerates the formation of CML. However, at higher MCA concentration (>16.0%), the excessive MCA can lead to usage of NaOH due to undesired side reactions to form sodium glycol ate. Moreover, pH changes from alkaline to acidic, which results in precipitation of WAL for heterogeneous reaction. Finally, the efficiency of reaction decreases with the excessive of monochloroacetic acid.

### ***Effect of microwave power and time***

Carboxymethylation reaction is carried out at five different reaction temperatures (120 to 400KW), as shown in Fig. 3. The maximum degree of substitution (D.S) of 0.63 % obtained at the reaction temperature related 180KW microwave power. The pH declines constantly with the rise of reaction temperature. The increase in reaction temperature facilitates the diffusion and collision of reactant reagents and WAL, which results in creation of better reaction environment for carboxymethylation.

Degree of substitution (D.S) was greatly enhanced by increasing the reaction time. The time dependency for the reaction measured under microwave irradiation environment. The same variation trend is observed as in the temperature parameter. The initial increase in time may be sufficient to

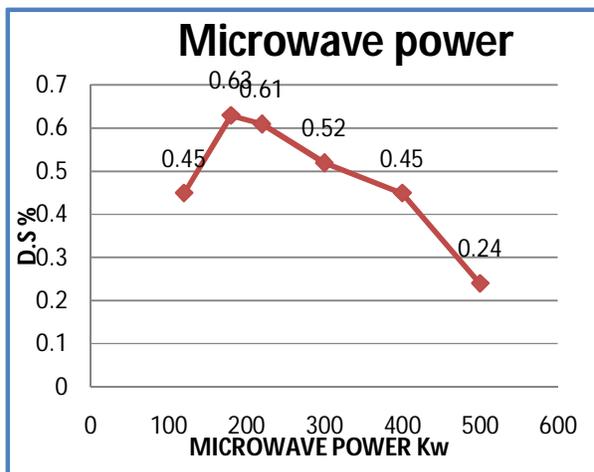


Fig.3 Effect of Microwave power D.S. of CML

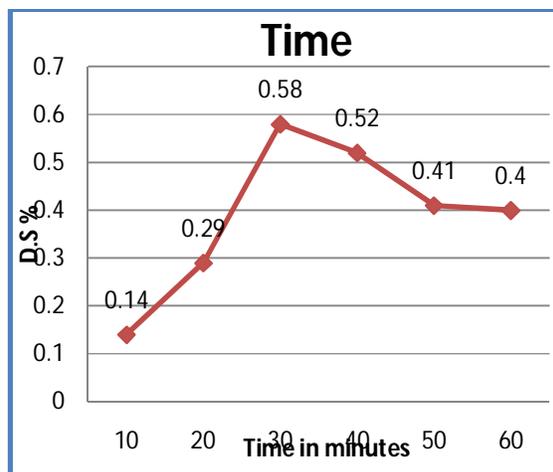


Fig.4 Effect of reaction time on D.S. of CML

Favor the carboxymethylation reaction. Increasing the time up to 30 minutes the degree of substitution (D.S) getting increased the product deterioration starting and yield of the CML gets lowered. Obviously the time required for complete reaction is very low (30minutes) that to compare with conventional method of heating 4-5 hours<sup>8</sup>.

Table.1 shows that the comparison of microwave synthesis of CML against the conventional method of heating. It reveals that the time *required* to achieve desired degree of substitution 0.6 is very less in microwave assisted synthesis. In the case conventional method of heating, the time required to complete reaction and yield the desired degree of substitution in 3-4 hours which is tedious.

Table.1 comparative study of CML synthesis by conventional heating and microwave environment

S.No	Lignin (g)	MCA (g)	NaOH (g)	Solvent selection	Reaction Environment	Time in Minutes	D.S.
1	20	18.9	16.0	IPA	MW (180Kw)	30	0.34
2	20	18.9	16.0	IPA	Thermal heating 55 <sup>o</sup> C	270	0.35
3	20	18.9	16	IPA/H <sub>2</sub> O	MW (180Kw)	30	0.63
4	20	18.9	16	IPA/H <sub>2</sub> O	Thermal heating 55 <sup>o</sup> C	240	0.60

### FTIR spectra (CML)

Kraft lignin and Carboxymethylated lignin are shown in Fig 5 and Fig. 6 respectively. In figure 5 it is evident that the broad absorption band at 3417.63 cm<sup>-1</sup> is assigned to the -OH stretching vibration. The band at 2935.46 cm<sup>-1</sup> is due to C-H stretching frequency of the methoxyl group and methylene group. C-C stretching vibration can be visible at 833.19cm<sup>-1</sup>, 667.32cm<sup>-1</sup>. There are three

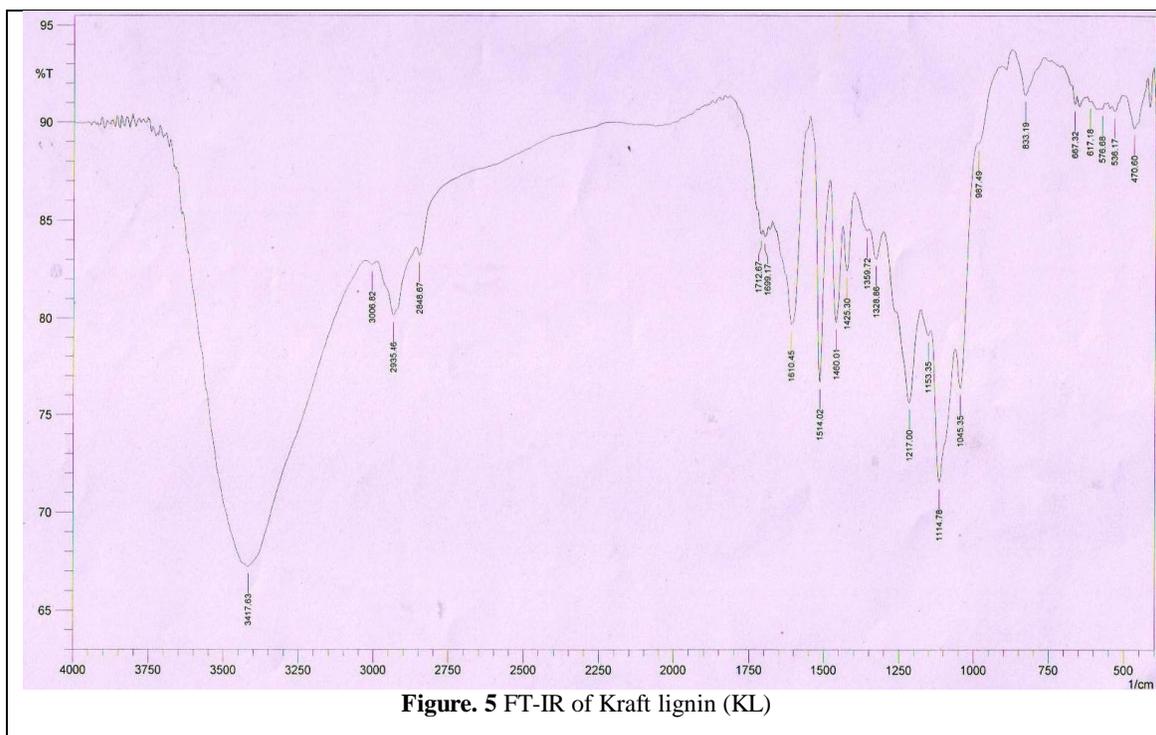
strong peaks at 1610.30 and 1425.30  $\text{cm}^{-1}$  assigned to aromatic skeletal vibrations as shown in Fig. 6, compared to KL, besides the typical absorptions of lignin, the main changes of the FTIR spectrum of CML against KL Fig.5. The appearances of three new and strong absorption bands at carbonyl (C=O) peak at 1645.17  $\text{cm}^{-1}$ , a  $-\text{CH}_2$  peak at 1417.58  $\text{cm}^{-1}$  and an ether peak at 1043.42  $\text{cm}^{-1}$  which confirms the presence of  $\text{COO}^-$  group in CML and the introduction of a  $-\text{O}-\text{CH}_2\text{COO}$  group into Kraft lignin molecule <sup>14</sup>.

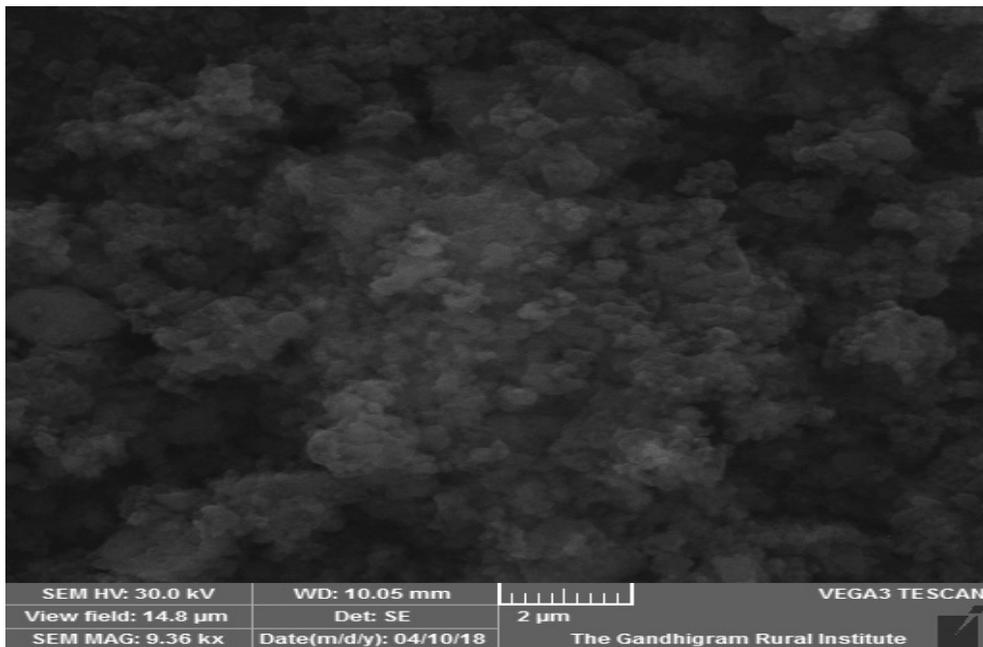
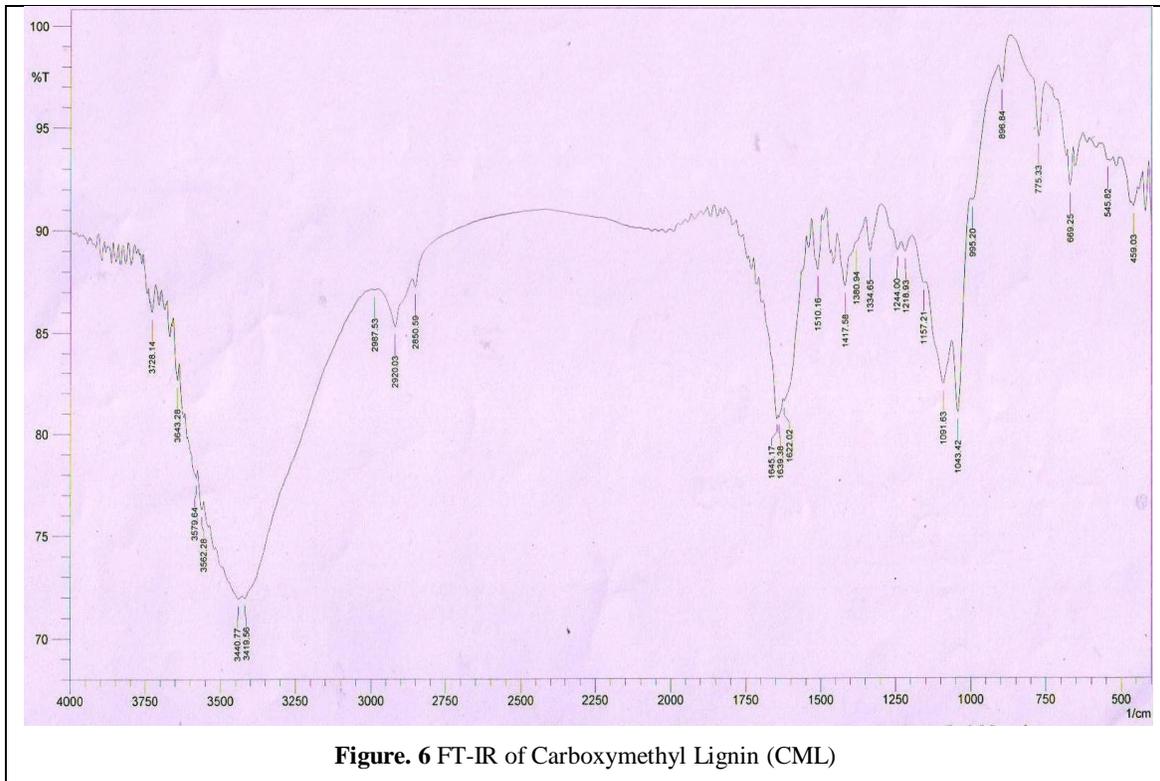
### ***Surface morphology***

The surface morphology of Kraft lignin and CML prepared was characterized by SEM. The SEM micrograph of Kraft lignin (KL) (Fig.7) and CML (Fig.8) clearly shows the amorphous nature of the CML biopolymer. Porous nature of the CML bio polymer explores that the possibility of usage as an adsorbent.

### ***Particle size distribution (PSD)***

The particle size distribution (PSD) curves of the CML showed the average particle size (D50) is 0.650 $\mu\text{m}$  and 78.5 % of the size falls on the size of 1.0  $\mu\text{m}$  (Fig. 9). Moreover 58.9% of the particle size falls on 0.4microns (<400 nm). This PSD finding of CML reveals that the nano scale particles (200-600nm) are easily obtained from CML and can combine with other synthetic polymers to form nanocomposites.





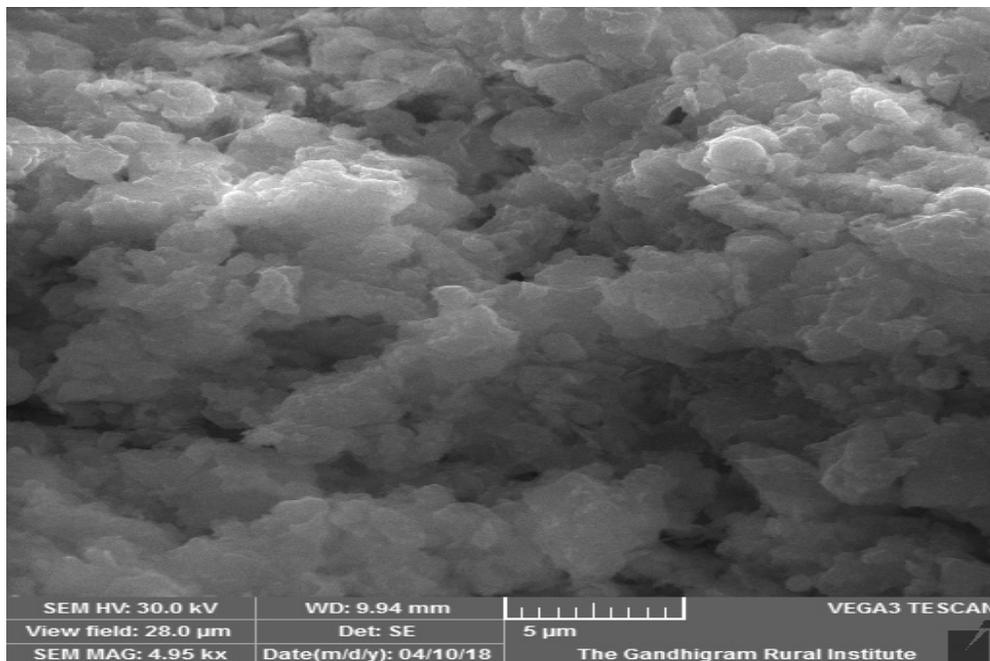


Figure. 8 SEM image of CML

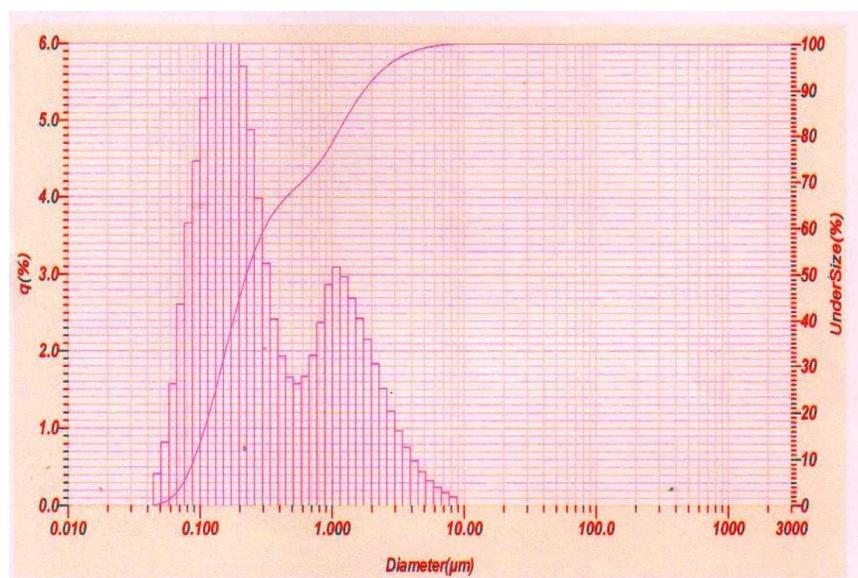


Figure. 9 PSD of CML

## CONCLUSION

Kraft lignin may be isolated from Black liquor generated from bagasse pulp mill and synthesis the Carboxymethyl lignin biopolymer a soluble derivative of kraft lignin. Moreover microwave irradiation technique is found to be efficient and rapid method for the preparation of carboxymethyl lignin (CML) bio polymer in IPA: Water (80:20) mixture. CML is prepared from kraft lignin biopolymer under microwave environment (18KW). Yield and DS of CML have large influences with changing the concentrations of NaOH and monochloroacetic acid, Microwave power

and time. The formation of carboxymethyl group was confirmed by FTIR spectroscopy. The surface morphology of the CML biopolymer indicates that porous and amorphous nature of the biopolymer may use adsorption applications. Time required to prepare CML is very low rather than the conventional method of heating (3-4 hours). The particle size distribution of the CML indicates a nanoscale particles presence and can be reinforced with other polymer and find suitable applications in polymer blends and composites.

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