*Asian J. of Adv. Basic Sci.: 2(3), 12-22*
*ISSN (Online): 2347 - 4114*
*www.ajabs.org*

# Harnessing economic potential of methylcellulose from Wheat Straw: A Review

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**ABSTRACT: Wheat Straw is the agricultural by-product obtained from different parts of wheat plant like stem, leaves etc. Wheat Straw is rich in cellulosic fibers, hemicelluloses, proteins, lignin and ash. All these elements together make wheat straw as most important and balanced substrate for microbial cultures for its diverse applications in fermentation, food, feed, medicine industries and in fields to increase soil fertility. It is the cheapest or low cost source of natural substrate.**
**Methylcelluloses is prepared and characterized from wheat straw. Alpha- Cellulose of wheat straw is used to prepare methylcellulose.Total chloride free(TCF)method is used to bleach the pulps with hydrogen peroxide. Iodomethane is used to synthesize methylcelluloses from TCF bleached pulps. Methylation is carried out in isopropanol with iodomethane at 60degree Celsius for 22 h and after that the TCF bleached pulps is mercerized in 40% NaOH solution for one hour.**
**Fourier transform infrared (FTIR) spectra of the synthesized methylcelluloses showed the existence of methoxyl groups on methylcellulose. The degrees of substitution of the synthesized methylcelluloses is measured by13C nuclear magnetic resonance (NMR) spectroscopy. The molecular weights of the water-soluble methylcelluloses is determined by size exclusion chromatography (SEC). Intrinsic viscosities of the synthesized methylcelluloses was measured in distilled water, 4% NaOH or dimethyl sulfoxide(DMSO). Methylcelluloses with better properties, such as greater degrees of substitution, molecular weights, viscosities, and intrinsic viscosities, were prepared from the pulps with higher accessibilities and reactivities.Water-soluble and alkali-soluble methylcellulose yields is determined by solvent extraction. Pulping severity is key factor influencing the properties of the methylcellulose prepared.**

**Keywords:** wheat straw, alpha cellulose, methylcellulose, mercerization, intrinsic viscosity, FTIR, NMR, SEC.

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## INTRODUCTION

This study contributes to find appropriate conditions for the production of methylcellulose from wheat straw.Methylcellulose is important cellulose ether[6,13,14,18,41,57,58,59].Cellulose is the most abundant biopolymer in the world.Methylcelluloses are important cellulose ether derivatives which become water soluble in an intermediate range of Degree of Substitution with an associative properties.Besides,this work is mainly concerned on expanding the use of it in other different fields.Methylcellulose has many applications such as construction,cosmetics,paints,food,pharmaceuticals,detergents,polymerization drugs[5,6,8,9,15,16,17], nutritional purposes,surfactant, glue,cell culture etc.[19,40.42,44,46].Methylcellulose is used as a surfactant because of the presence of both hydrophilic -OH and hydrophobic -$OCH_3$ groups on its chains[5]. The industry economically utilize wheat straw to produce methylcellulose for various commercial purposes without harming the plant diversity which can definitely prove to be economic as well as ecofriendly measures.
Wood is more expensive and more difficult to transport than non-woody materials, although non-woody materials have problems of collection, storage, and high ash contents[39,85].Wood is not available in sufficient quantities in many countries because of the increasing consumption of furniture, construction, paper, paperboard and cellulose derivatives [37,38,67].Because of the overproduction of agriculture crops and the shortage of wood, non woody materials received more attention in recent years for producing

cellulose derivatives[4,22,23,43].Rising energy dependency on fossil fuels, increasing emissions of greenhouse gases and risks associated with the price fluctuations on the international energy markets has led to a move towards the research and production of alternative, renewable, efficient and cost-effective energy sources with lesser emissions[93,94,95].In the recent past, much attention of the world agricultural research was focused on non -wood materials with perspective for environmental industrial utilization. Agricultural wastes constitute one of the main alternative raw materials for the pulp and paper industry [3,35].Most annual plants are attacked easily by microorganisms [77].For economic and environmental considerations,as well as the fact that it provides higher yields of cellulose,non-wood is gradually substituting wood as an alternative source of cellulose derivatives [4,7,21,48].The most common sources of cellulose for industrial uses are from wood pulp and cotton inters which nowadays are discouraged due to the cost of production and increasing environmental concerns[89].

Because of increasing deforestation and the increasing consumption of cellulose products,the cellulose industry is investigating such new resources as overproduced crops,agricultural waste and unconventional plants to investigate whether it is feasible to use them to produce cellulose derivatives methylcellulose as an additive for cement, food and drugs[21].

The chemical industry is estimated to meet about 10% of its raw material needs from the renewable raw materials.Wheat straw is primarily composed of cellulose, hemicellulose and lignin which contain various functional groups suitable for chemical functionalization [99,100]. The main fractions of Wheat Straw are nodes, internodes and leaves[1,91]. Chemical analysis of Wheat Straw shows that it is rich in carbohydrates (cellulose, hemicellulose, lignin), proteins, minerals (calcium and phosphorous), silica, acid detergent fibres and ash.Wheat straw is a good raw material for bioethanol production[51].The cell walls of wheat straw consist mostly of cellulose fibres.Cellulose is a linear crystalline polymer of (1-4)-β-D-glucose[24,51]. Cellulose is the most abundant renewable and biodegradable or natural polymer.Cellulose based derivatives have a number of advantages including recyclability, reproducibility, biocompatibility, biodegradability, cost effectiveness and availability in a wide variety of forms[117]. It is the promising feedstock for the production of chemicals for their applications in various industries[101,102].It consists of long chain which is made up of linking of smaller molecules. For industrial purposes, Cellulose is mostly obtained from wood pulp and cotton[79]. Celluloses from annual plants have different chemical composition and structures [7,71].Biodegradable polymers are materials that undergo bond scission in the backbone of a polymer through chemical, biological and physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics [54,95,96].Wheat straw has a content of cellulose, aproxmately34 %[50,56]which make it suitable for the preparation of methylcellulose[2,4,21,52,55,65,66]. During 1920-1930s,the first cellulose ether which gains economic significant was carboxymethylcellulose (CMC) followed by methyl cellulose and hydroxyethyl cellulose[90].Cellulose cannot dissolve in water. Introducing hydrophilic groups along the chain of cellulose cleaves hydrogen bonds and renders its derivatives soluble in conventional solvents, widening its applications to functional cellulose ethers and esters [19,16,61,78].Introducing ester and ether groups separates the cellulose chains so completely that the fiber structure is either altered or destroyed. The solubility of a cellulose derivative in a solvent or in water depends on the type of substituent's, the degree of substitution and the molecular weight [19,57,72,73,74].Cellulose from annual plants can be used to produce methylcellulose [20,21,22,23], though the quality depends strongly on the source [83,20,21].Methylcellulose is a chemical compound derived from cellulose. It is a hydrophilic white powder in pure form and dissolves in cold but not in hot water, when dissolved it forms a clear viscous solution. It is used as a thickener and emulsifier in various food, cosmetic products and also as a treatment of constipation. It is non-digestible, non toxic and non allergenic[80].In this investigation ,first step is the pulping which separates stalks component to obtain cellulose and the second step is the methylcellulose preparation in which dimethyl sulphate and iodomethane is used because of their straightforward operation and apparatus[10,11,36]. Degree of substitution (DS) increased as the concentration of NaOH was increased up to 50%. Increasing the amount of methylating agent DMSO decreased the DS values when all the other reaction conditions were kept constant[120].

Suida first synthesized methylcellulose with dimethyl sulfate in 1905[6,25]. Since then, many researchers [11, 12, 36,86,87,88] have successfully prepared it in either heterogeneous or homogeneous media. In industry, methylcellulose is produced by methylation with methyl chloride in heterogeneous reaction media at high pressure [5, 8]. Commercially produced methylcelluloses have two types: water-soluble methylcelluloses with degrees of DS ranging from 1.4 to 2.0,and alkali-soluble methylcelluloses with DS ranging from 0.25 to 1.0 [5].Commercial methylcelluloses are usually produced with a DS ranging from 1.4 to 1.9 and a viscosity ranging from 10 to 15000mPas of 2% aqueous solutions at 20ºC and 20 rpm. Methylcelluloses of different DS and their diverse applications [60.]

On a laboratory scale, dimethyl sulphate and iodomethane are used because of their straightforward operation and apparatus[5, 6, 10]. Methylcellulose is a water soluble cellulose derivative that exhibits thermal gelation [97].Due to strong intermolecular hydrogen bonding between the hydroxyl groups on the cellulosic chains; unmodified cellulose is insoluble in water. However, methylation of cellulose introduces hydrophobic groups on the cellulosic chains producing methyl cellulose which can be easily dissolved in cold water [118].Methyl cellulose contains methoxide groups which induce hydrophobic interaction between the methyl cellulose chains causing them to aggregate at the lower critical solution temperature [119].It has excellent film forming properties and provides an effective barrier to lipid but non-effective barrier to oxygen and water vapour. To improve the barrier properties to water vapour, oxygen and carbon dioxide mixtures of methylcellulose with polysaccharides have been made[98].The reactivity and toxicity of dimethyl sulphate are higher than those of iodomethane [5,6,10].

In heterogeneous methylation,Caustic alkaline solutions is used to mercerize cellulose and form methylcellulose is synthesized in organic slurry with toluene or isopropanol[81,82]. Taipa C. synthesized methylcelluloses from commercial pulps with dimethyl sulfate and iodomethane in 2-propanol slurry at 30degree Celsius [27].A total chloride free (TCF) bleaching method is used to obtain pulps with low lignin contents. It is easier to compare and analyze the experimental results of methylcellulose synthesized from iodomethane,which had amplified different properties.The properties of methylcellulose are DS, molecular weight, molecular weight distribution, degree of polymerization (DP), and distribution of methoxyl groups along the glucose unit and the polymer chain[53]. These properties strongly depend on the methylation conditions and properties of cellulose, which depend on bleaching conditions, pulping parameters, plant species, the time that the plant was harvested and even parts of the plant. Methylation is strongly influenced by the accessibilities and reactivities of the celluloses of TCF bleached pulps [20]. When the bleached pulp is used to synthesize methylcellulose rather than the pure cellulose, the William etherification mechanism,combined with the macro heterogeneous methylation of pulp[62,63],causes the methylation to become more in homogeneous and incomplete because of the difficulty of reagent diffusion,competitive reactions of lignin and hemicellulose,the inaccessible fibril interiors, and the crystalline cellulose interiors [58,62]. The pulp species and pretreatments are compared for the synthesis of methylcelluloses [20,32,47].Most commonly used alkali in the alkali pretreatment processes are NaOH, KOH, $NH_4OH$ and $Ca(OH)_2$.This process results in (i) the removal of all lignin and part of hemicelluloses, and (ii) increased the reactivity of cellulose in further hydrolysis steps especially, enzymatic hydrolysis. Effective removal of lignin minimizes adsorption of enzyme onto lignin and thus allows for effective interactions with cellulose. NaOH causes swelling of the fibers and with increase in internal surface area, allowing the penetration of water molecule into the inner layers and break the bonds between hemicellulose and lignin. This also decreases the degree of polymerization and crystallinity of cellulose. Pretreatment with NaOH increases the digestibility cellulose from 14% to 55% while decreasing the lignin content from 25 to 20 % . Further, pretreated switch grass revealed a great deal of pore formation in the NaOH pretreatment increasing the accessible surface area to the enzymes as well as decreasing lignin content [114].Alkali pretreatment processes shows decreased sugar degradation and are more effective on agriculture residues as compared to wood materials. Between NaOH and $Ca(OH)_2$, pretreatment with $Ca(OH)_2$ is preferable because it is less expensive, more safer as compared to NaOH and it can be easily recovered from the hydrolysate by reaction with $CO_2$ [115]. Combination of dilute NaOH treatment with other treatment seems more efficient1[16]. The high cellulose content and low lignin content make these

annual plants valuable for producing cellulosic products [7].The good yields and stable productions of these annual plants in recent years make it feasible to try to exploit them as alternative new resources of methylcelluloses [84]. Therefore, the present research may be used to control and optimize the quality of methylcelluloses prepared from wheat straw.

## OBJECTIVE OF THE STUDY

As there had been no literature available for the extraction of cellulose and preparation of methylcellulose from wheat straw, therefore an attempt has been made for the first time to study harnessing economically potential of methylcellulose from wheat straw.

1. Extraction of alpha cellulose from wheat straw
2. Isolation of pulp
3. Preparation of methylcellulose
4. Characterization of methylcellulose

## MATERIAL AND METHODS

Wheat straw is collected from local agriculture activities and stored in laboratory under atmospheric pressure and room temperature. Four sample of wheat straw is collected from Himachal Pradesh. First sample is take from District Hamirpur, second sample from District Bilaspur, third sample from District Mandi and fourth sample from District Kangra of Himachal Pradesh. Sun-dried, fine and sand free wheat straw was used as raw materials.Sample of known mass is kept for sufficient time to expel all free moisture content[45].

Pulping is the most common way to obtain cellulose from annual plants. Pulping is a process of de-lignification, whereby lignin is partially eliminated. Pulp is a collection of the cellulosic fibers which are liberated from the plant material and contains less lignin and hemicellulose [26].The most common commercial method for annual plant pulping is the soda method [76].Grinding wheat straw is immersed in 1.5% of sodium hydroxide for 22 hours at 10- 15 degree Celsius. At the end of the time, the straw is removed from the liquor and after draining for 30 min. Is throughly washed with water to remove excess sodium hydroxide. The straw is lost 20% of its weight in this treatment. The resulting material is called straw pulp. Straw pulp is dried in oven at 60 degree Celsius.The pulping of annual plants uses a lower temperature, a shorter cooking time, less chemical charge and less energy as well as newer pulping technologies. For the dissolving pulping process, pre-hydrolysis is often used to eliminate hemicellulose. For the production of cellulose derivatives, the pulping conditions should be modified to suit the specifications of the final cellulose required molecular weight, purity, ash content, lignin content, residual hemicellulose content, etc.[103,75,28,72].The pulping processes concentrate not only on optimizing pulp quality but also on improving pulp yields, reducing energy consumption, reducing chemical consumption, improving the recovery processes of the chemicals, reducing pollution and developing sulfur-free pulping processes and chlorine-free bleaching sequences[61].

Pulp bleaching is carried out in a sequence of several stages to eliminate as much residual lignin as possible. Usually lignins are physically dissolved in alkaline solution or chemically modified to form soluble chemicals in aqueous/alkaline solutions [31,75,106,107].During bleaching, the lignins are oxidized, degraded, dissolved and therefore decolored. The pulp is bleached with hydrogen peroxide by total chlorine free method.The hydrogen peroxide bleaching is performed with a sodium hydroxide and hydrogen peroxide solution for 1hour at 60 degree Celsius. At the end of the bleaching pulps is washed with distilled water[33,34].

The accessibility of the cellulose pulp mainly depends on the amorphous cellulose because the inaccessible crystalline region has little influence [63,58].After soda/AQ pulping,TCF bleaching and drying pulps usually have different chemical compositions,chemical distributions of components in their pulps [68] and morphological fibrous structures,such as cellulose fibril aggregation and cellulose structure [69,70], which strongly influence their accessibilities and reactivities [58]. During the pulping and bleaching of

annual plants, capillaries increase due to the dissolution of solid and to swelling [68,104]. Commercial cellulose derivatives are either ethers or esters that are soluble in water or organic solvents. The three free hydroxyl groups in the Anhydrous Glucose Units react with various functional substitution groups. The resultant substituent's therefore disturb the inter- and Intra-molecular hydrogen bonds in cellulose, reduce the hydrophilic character of the numerous hydroxyl groups, and increase the hydrophobicity[66].

The process of preparation of methylcelluloses from the annual plant stalks consisted of chipping, impregnation, steam pulping,screening, TCF bleaching,mercerization, methylation, and characterization of synthesized methylcelluloses.The process of preparation of methylcelluloses from the ECF bleached pulps consisted of pretreatments, mercerization, methylation and characterization of synthesized methylcelluloses[66].Wheat straw is mainly composed of alpha cellulose, hemicellulose and lignin. Alpha cellulose is used in experiments for methylating bleached pulps of wheat straw methylcellulose is carried out in isopropanol and iodomethane at 60 degree Celsius for 22hours.The iodine adsorption method was used to determine the accessibilities of celluloses[64,105]. Alpha cellulose is mercerized in 40% sodium hydroxide solution[64,105]. The mercerized pulp was filtered and pressed until the weight ratio of the pulp and the sodium hydroxide solution to be 0.2. Upon the filtration, the mercerized pulp, 150 ml 2-propanol, and 50 ml iodomethane is added into a flask.The methylation reaction lasted for 22 hours at 60 degree Celsius. The mercerization and methylation is repeated. At the end of methylation, the methylcellulose is collected by the vacuum filtration, neutralized with acetic acid, and washed three times by acetone and ethanol respectively. Finally,methylcellulose samples were stored in a cooler at 4degree Celsius. The mercerized pulp was dried in the air. The mercerization of the methylcellulose of low degree of substitution and its methylation is repeated to synthesize a methylcellulose with a high degree of substitution. The preparation of methylcellulose is focused on product with high degree of substitution. The methylation is repeated three or four times[66].Isolation of pulp would be done through TAPPI standard procedure[39,49].

## CHRACTERIZATION OF METHYLCELLULOSE

Fourier transformation infrared spectra (FTIR): FTIR spectra synthesized methylcellulose is dried in on oven at 105 degree Celsius until the weight is constant. FTIR shows that hydroxide groups of cellulose are partially substituted by methoxyl groups.

Nuclear magnetic resonance (NMR) spectroscopy: supramolecular substitution of methylcellulose is determined by $^{13}C$ NMR spectroscopy. Sample is dried in on oven at 105 degree Celsius until the weight is constant. After that sample is dissolved in dimethylsulfoxide (DMSO) at 80 degree Celsius. Degree of substitution is determined by $^{13}C$NMR spectroscopy.

Size exclusion chromatography (SEC): The molecular weight of methylcellulose is measured in DMSO by SEC. Methylcellulose solution for SEC is purified with distilled water. Amount of methylcellulose is weighed on an balance. The weighed methylcellulose and 10ml distilled water added in the vial. The solution is stirred for 2hours at room temperature and stored in a refrigerator at 4 degree Celsius for 24 hours. The vial is taken out of the refrigerator and the solution is stirred for 2hours at room temperature. The upper clear liquid is collected using syringe and filtered. The filtered solution is injected into HPLC vial for the SEC analysis.

Intrinsic viscosity of methylcellulose are measured in distilled water, 4% sodium hydroxide solution and DMSO. Rheological properties of methylcellulose is measured in DMSO, 4% sodium hydroxide or distilled water in which the synthesized methylcellulose has similar properties as commercial methylcellulose.

## RESULTS

The pulping parameters, methylation conditions, species pretreatments and morphological structures of pulps may influence the degrees of substitution of methylcelluloses prepared from the wheat straw. A higher impregnation severity, a higher pulping temperature and a longer pulping time may or may not

cause a higher degree of substitution. An increase in methylation reagent led to an increase of degree of substitution. Methylcelluloses of different degrees of substitution is synthesized from the pulps of different samples of wheat straw in same methylation condition. The pretreatments increase the degrees of substitution of methylcelluloses. Therefore the present research is used to control and optimize the quality of methylcelluloses prepared from wheat straw.

## SCOPE OF FUTURE RESEARCH

Methylcelluloses are important for many applications.Methylcelluloses are widely used in medicine and pharmaceuticals, electronics, porous materials, paper and food because of their availability, biocompatibility, biological degradability, and sustainability. Availability and continuous and inexpensive sources of crude material is essential for the stability and development of this new industry. Agricultural wastes are additional materials from harvested crops that have different usages. The cellulose industry is investigating such new resources as overproduced crops, agricultural waste, unconventional plants and common wild plants to decide whether it is feasible to use them to produce paper, paperboard and cellulose derivatives, such as tailor-designed methylcellulose as an additive for cement, food and drug.

## ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my supervisor, Dr.Yogesh Kumar Walia for his constant guidance, support and encouragement throughout my studies. I wish to thank the University (Career Point University) for providing me the opportunity to conduct meaningful research during my studies. Last but not the least, I wish to express my immense gratitude to my loving family and friends for their patience and moral support.

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