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# Microwave-assisted acetylation of *Eucalyptus Camaldulensis Dehn* cellulose

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**Abstract:** A comparative study on the acetylation of wood (cellulose) of *Eucalyptus Camaldulensis Dehn* (prepared of a species in the campus of Gonbad University) by reaction with acetic anhydride in the presence of pyridine has been undertaken. The reaction was done under microwave irradiation which is described and compared with conventional methods. In this study the reactivity of wood with regards to acetic anhydride was examined using two techniques; Bench-top reflux system, and microwave instrument as two separately methods. In MW method, the process was pretty clean and the acetylated product was pure to comparing the simple reflux system. Acetylated products which are afforded from MW method were characterized by FT-IR spectroscopy.

**Keywords:** Cellulose, *Eucalyptus camaldulensis dehn*, Acetylation, Microwave irradiation, Acetic anhydride

## Introduction

Chemical modification of wood for improved dimensional stability and decay protection has been the subject of research for many years. A wide variety of chemicals have been studied including anhydrides, acid chlorides, carboxylic acids, isocyanates, acetals, esters, alkyl chlorides, b-propiolactone, acrylonitrile, and epoxides. The most studied of all of the chemical modification chemistries is acetylation. Wood esterification has been shown to be very effective in improving the material performances [1, 2]. In particular, wood acetylation with aceticanhydride has received the most attention and the acetylated product is now commercialized in Europe since 2007. Many studies have shown that the dimensional stability, fungal resistance, photostability and weathering of wood could be greatly enhanced by this treatment [1, 3-9].

Other acetylation methods involving acetyl chlorides [10, 11], thioaceticacid [10, 12], ketene [6, 13] or more recently vinylacetate [14], have been also proposed.

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Acetylated materials are produced in all cases but different reactions can lead to different performances, the benefits of the treatment depending strongly on the process conditions. For instance, the by-products generated by the different acetylation methods may have a variable impact on the material properties. With acetyl chloride as reactant, a strong acid–hydrochloric acid is released, which catalyses the hydrolysis is of holocellulose and leads to important strength losses of the material [6]. A weaker acid–acetic acid is liberated when acetylation is performed with acetic anhydride, but this compound is generally hard to remove from wood after reaction, imparting an undesirable odour to the wood and causing strength losses or the corrosion of metal fasteners [8, 15, 16]. Recently, wood has been successfully acetylated by a new method based on the transesterification of vinyl acetate [14]. Fourier-transformed infrared spectroscopy (FT-IR) was evaluated as an analytical technique for the estimation of the chemical composition and functional properties of natural polymers such as cellulose [17].

In the last few years, microwave-induced organic reaction enhancement (MORE) chemistry has gained popularity as a non-conventional technique for rapid

synthesis [18] and many researchers have described accelerated organic reactions, with a large number of papers proving the synthetic utility of MORE chemistry in routine organic synthesis [19, 20] event it can be termed "e-chemistry" because it is easy, effective, economical and eco-friendly and is believed to be a step toward green chemistry and especially for pilot plan and industrial scales.

In the present paper, a comparative study on the acetylation of wood by reaction with aceticanhydride (AA) is proposed. Wood was acetylated by AA by two procedures: using of general reflux system on bench-top and employing of *MICROSYNTH* microwave source of energy as a driving force for acetylation reaction. The products were characterized by FT-IR.

## Results and discussion

Acetylation of wood using acetic anhydride has mainly been done in two procedures. a) Microwave Reflux system b) Reflux by oil bath (Figure **1**). The reaction has been done without catalyst and using organic solvent.

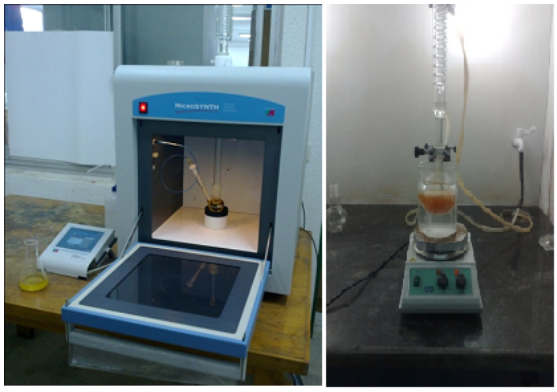
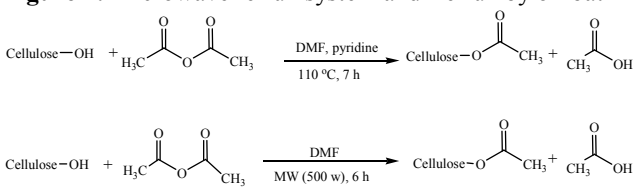


**Figure 1:** Microwave reflux system and Reflux by oil bath




**Scheme 1:** Comparing acylation reaction of cellulose in presence of pyridine and without pyridine.

In this reaction, accessible hydroxyl groups in the wood cell wall were acetylated by esterification mechanism. In this reaction, acetic acid is produced as a by-product and it is important to remove this as well as unreacted acetic anhydride at the end of the reaction (Scheme **1**). The color of the resulted product is apricot`s color or light yellow-orange that was showed in Figure **2** to comparing with the crude cellulose. For evaporation and removing the solvent from the mixture of reaction the low pressure system was employed.

The extracted crude cellulose is showed the OH group around 3500 $cm^{-1}$ and also around the 1600 to 1800 $cm^{-1}$ is not showed any sharp signals (see Figure **3**). It means the acetyl groups with carbonyl are not presented in the crude primary cellulose. But the acetylated extracted cellulose is confirmed by FT-IR spectrum (see Figure **4**). The signals of acetyl groups in the FT-IR spectrum are observed at 1749$cm^{-1}$ ($\upsilon_{(C=O)}$), 1400$cm^{-1}$ ($\upsilon_{(CH3)}$) and 1100–1250 $cm^{-1}$ ($\upsilon_{(C-O)}$).

**Figure 2.** The extracted crude extracted cellulose.

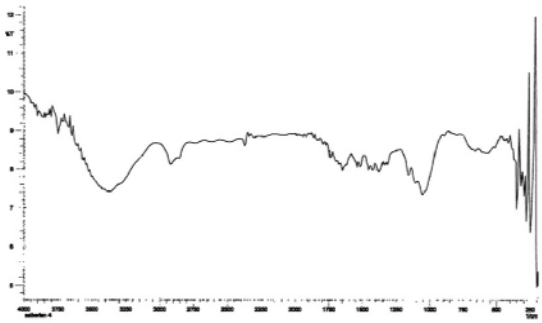


**Figure 3.** FT-IR spectroscopy of unmodified wood.

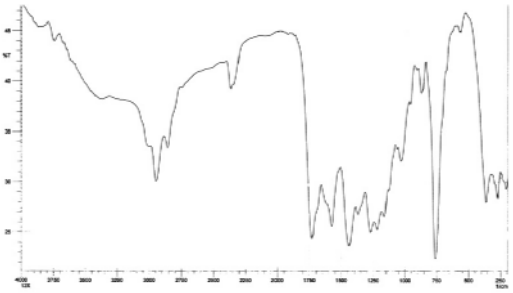


**Figure 4.** FT-IR spectroscopy of the residue dissolved in DMF after acetylation with AA.

## Conclusion

A facile microwave-assisted method for the acetylation of wood has been developed which is faster and less costly than all previous methods. The resulted spectra by using of MW reflux system is similar to using of general and conventional heating, but the main advantages of microwave heating are a strong

reduction in reaction time and a high potential to contribute to green and sustainable chemistry.

## Experimental

*Materials and Methods:*

All the experimental was done in chemical lab and the material was purchased from Merck, Fluka and TCI companies. The crude and primary samples of wood were prepared from *Eucalyptus Camaldulensis Dehn* wood. Organic solvent and acids were used without more purification. IR instrument in this work was used Nicollet Magna 550-FT spectrometer.

*Plant Material:*

The plant samples *Eucalyptus Camaldulensis Dehn* were provided from the campus of Gonbad Kavous University.

*Instruments:*

IR spectra were acquired on a Nicollet Magna 550-FT spectrometer, and TLC was employed under a UV light with 254 nm Wavelength and the reaction was done in a type of *MICROSYNTH* from Mylestone Company.

*Reagents and Solutions:*

Analytical substances: acetone, nitric acid, ethanol, *N,N*-dimethyl formamide, acetic Anhydride provided by Fluka and Merck companies.

*Preparation of extractive free wood:*

The plant samples *Eucalyptus Camaldulensis Dehn* were provided from the campus of Gonbad Kavous University and 20 g of crud wood was used in the process. The extraction was used by three different extracting solvents: E1-extracted with methanol, E2-extracted with water and E3-extracted with 50% of Diethyl ether ($Et_2O$): aceton. The yiled of extract was best by using of diethyl ether and aceton. The powdered plant material was extracted with each of the above solvents using reflux apparatus and soxhilet at 78 $^oC$ for 1 h, and then filtrates were completed to 25 ml by the same extracting solvent. Then the collected dried cellulose was used for acetylation reaction.

All chemical reactions were performed under a standard set of conditions, in a round bottomed flask equipped with a condenser and a calcium chloride drying tube. For 1g of dry starting material (Extracted cellulose of *Eucalyptus Camaldulensis Dehn* wood), solutions containing 14 mol of AA and 20 ml of DMF were used. The reaction was performed on two methodology one was run in the reflux system by using of heater-stirrer on bench top and the other one was employing of the Microwave (With the type of *MICROSYNTH* from Mylestone Company) reflux system. Hence, in this research, we have used Microwave-irradiation as green source energy for acylation reaction. The conditions for AA-acetylation in bench top was performed at 110 °C and 7 h in the presence of pyridine as a catalyst (7 mmol/g dry wood), but in MW was done on 500 W power and 110 $^oC$ of temperature for 6h without pyridine. Eventually, the work-up process was continued by filtration and then the product over the filtration paper washed by organic solvents such as acetone and ethanol.

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