

# HETEROGENEOUS ESTERIFICATION OF EXTRACTED FIBERS FROM *Leptadenia pyrotechnica* AND *Phoenix dactylifera* L.

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Received 2023/12/11

Revised 2024/02/08

Accepted 2024/02/29

*The aim* of the study was to investigate the use of direct heterogeneous esterification method of extracted fibers from *Leptadenia pyrotechnica* khimp (*Leptadenia pyrotechnica*) and date palm tree (*Phoenix dactylifera* L.) using adipic and citric acids. Homogeneous esterification leads to the degradation of lignocellulosic material, making it impossible to obtain a pure ester of extracted crude fiber by this method.

*Methods.* The esterification reaction was carried out from three samples of the plant *Leptadenia pyrotechnica*, *Phoenix dactylifera* L. leaf, and fiber) were extracted as crude fibers and used in the heterogeneous esterification process. The total esterified fibers were six esters (each sample esterified with citric and adipic acid). The study employed ordinary laboratory equipment together with Fourier Transformation Infrared (FTIR) spectroscopy.

*The results* showed that the ester contents were in the range 21.6% to 28%. The degree of substitutions was in the range 0.38 to 0.57.

*Conclusion.* This process was simple and effective in producing esterified extracted plants fibers with a desirable degree of substitution.

**Key words:** crude fibers, heterogeneous, esterification, *Leptadenia pyrotechnica*, *Phoenix dactylifera* L., adipic acid, citric acid.

Esterification can be regarded as the transformation of carboxylic acids or their derivatives into an ester [1]. Owing to the presence of numerous hydroxyl groups, cellulose provides a unique platform for the preparation of new materials via versatile chemical modifications [2], this review aimed to present the advances in nanomaterials based on cellulose derivatives with a focus on cellulose esters. The review starts with the introduction of the first fundamental aspects of diverse esterification techniques used up to now to modify cellulose. According to the literature review, the esterification of cellulose and lignocelluloses can take place through two esterification processes; those are homogenous and heterogeneous methods. Biranchinarayan [3] stated that the esterification of cellulose by reacting with acid anhydrides in the presence of a mineral acid catalyst is the most widely known

process, particularly for the manufacture of cellulose acetate on a commercial scale. Acetylation by this process involves four steps: pre-treatment of cellulose, acetylation, hydrolysis, and purification. The most common one is the treatment with acetic acid either alone or in the presence of a part or all of the esterification catalyst. The esterification reaction is carried out by adding an excess of anhydride to the activated cellulose. A complete solution of cellulose indicates the end of the esterification reaction. The cellulose ester is then precipitated and washed to remove all the uncombined acids. This type of esterification utilizes a multistep process, which involves high costs. Moreover, the cellulose is degraded during the processing steps for which highly pure esterified products are difficult to obtain. Kongala [4] focuses on esterification of cellulose using lithium chloride-*N*, *N*-dimethylacetamide

(LiCl/DMAc) solvent system with acetic anhydride and maleic anhydride system using pyridine as a catalyst. The long-chain cellulose esters with different side-chain lengths were synthesized by Pia and Jarmo [5] using the homogenous esterification methods. Due to its complicated components, the esterification mechanism of bagasse esterified with glutaric anhydride in ionic liquids has not been studied by Huihui [6]. The homogenous esterification of bagasse with glutaric anhydride was comparatively investigated with the isolated cellulose, hemicelluloses, and lignin in 1-allyl-3-methylimidazolium chloride (AmimCl) to reveal the reaction mechanism. The commercial process of cellulose esterification with acid anhydrides in the presence of catalysts (mineral acids) is exclusively carried out under heterogeneous reaction conditions. The formation of ester linkages in cellulosic materials during drying and heating was studied [7, 8]. The heterogeneous esterification of cellulose nanocrystals (CNC) with succinic anhydride was investigated [9]. Carmen [10] investigated the controlled heterogeneous partial modification of cellulose fibers with fatty acids, partially preserving the fiber structure. Regarding the above statement, this study will focus on heterogeneous esterification of extracted crude fibers from *Leptadenia pyrotechnica* and *Phoenix dactylifera L.* by adipic and citric acids.

### Materials and Methods

The plant samples were collected from their local areas. The crude fibers were extracted previously by the authors. All chemicals (citric acid, adipic acid, ethanol, sulfuric acid, acetic anhydride sodium hydroxide, and hydrochloric acid) used are of analytical grade (BDH, India).

Ordinary laboratory tools. Infrared spectra were recorded on A Shimadzu 8400S FTIR spectrophotometer calibrated with polystyrene film.

The esterification of extracted fiber with two different carboxylic acids has been studied, namely citric and adipic acid. Such factors as pH, reaction time, temperature, and constant heating have been examined. The esterification procedures described [8, 11] were modified to obtain optimum results. The actual conditions for the esterification of the extracted fibers were as follows: 2 g sample and 3 g acid were refluxed in 50 ml of ethanol for 2 hours. The pH of the mixture was adjusted to < 2. Five drops of a mixture of sulfuric acid (3 drops) and acetic anhydride (7 drops) were used as a catalyst.

*Characterization of the esterified fiber Fourier Transform Infrared Spectroscopy (FTIR).* Functional groups of esterified fibers were analyzed by FTIR spectra of powder samples by the KBr technique. The analysis was carried out in a Shimadzu 8400S FTIR instrument with frequency variation from 4000 cm to 400cm (with a resolution of 4 cm and a total of 10 scans).

*Characterization of the esterified fiber Titration method.* A purified sample (0.5 g) was stirred for 30 min in 40 ml of aqueous ethanol (70%). After the addition of 20 ml of a 0.5 N NaOH aqueous solution, the stirring was continued for 48h at 50 °C. The unreacted NaOH was back-titrated with 0.5 N aqueous HCl. Ester content was calculated [11].

### Results and Discussion

Esterification reaction may be either homogenous that needs to dissolve the lignocellulosic components or heterogeneous as in this study. The homogenous esterification leads to degradation of the lignocellulosic material so it is impossible to obtain a pure ester of extracted crude fiber in this way. Esterification reaction was carried out for the three samples under study by using adipic and citric acid as esterified agents. The esterification reaction of commercial cellulose, hemicelluloses, and lignin was conducted by many researchers but according to the published works no one esterified an extracted crude fiber as complex and Anna et al [8] stated that in their recommendation. However, modification of esterification reaction conditions is needed to match the objectives of the study. The results obtained showed that the optimum conditions for this type of reaction were 2 hours reaction time, the amount of crude fiber and organic acid was (2 : 3) respectively, and pH < 2. After this treatment, the esterified fibers were subjected to the characterization step without further purification. The FTIR spectra showed the absence of hydroxyl groups in most cases, which indicates the ester formation.

*Fourier transform infrared spectroscopy (FTIR).* As (FTIR) deals with functional groups; the disappearance of hydroxyl groups from the extracted crude fiber after modification with carboxylic acids gives strong evidence for the esterification reaction.

*Titration method.* The relationship between cellulose ester structure and biodegradability has only recently begun to be examined. The degradation behavior of several cellulose

Table 1

FTIR frequencies for sample one esterified fiber by adipic acid

The functional group	Esterified fiber	Crude fiber	Reference Band cm
-OH (stretching)	3564 (very weak)	3446	3650–3200
SP2 C-H (stretching)	3032		3100–3020
SP3 C-H (stretching)	2920	2902	2970–2860
-C = O (stretching)	1732, 1693, 1622	1734, 1683, 1653	1780–1650
Benzene ( from lignin)	1562, 1500	1558–1506	1600–1500
SP3 C-H (bending)	1462	1448	1450–1420
Crystallinity region of cellulose	1430	1425	1430–1420
C-H cellulose, hemicellulose	1371	1373	1380–1340
Phenolic hydroxyl	1246	-	1260–1234
-C-O-C (stretching)	1161, 1111	-	1250–1050
-C-O(H) stretching	1033	-	1040
Amorphous region of cellulose	896	896	897
-OH (out of plane bending)	669 (very weak)	663	669
SP2 C-H (bending)	607	617	1000–600

Table 2

FTIR frequencies for sample two esterified fiber by adipic acid

The functional group	Esterified fiber	Crude fiber	Reference band cm
-OH (stretching)	3354	-	3650–3200
SP3 C-H (stretching)	2953	2931	2970–2860
-C = O (stretching)	1651	1734	1780–1650
Benzene ( from lignin)	1558	1610, 1521	1600–1500
Crystallinity region of cellulose	1419	-	1430–1420
C-H cellulose, hemicellulose	1356	1375, 1363	1380–1340
Phenolic hydroxyl	1230	-	1260–1234
-C-O-C (stretching)	1138	1109	1250–1050
-OH (out of plane bending)	661	-	669

butyrates with different DS values (range 0.2–2.4) reveals that degradability is significantly related to DS. The higher the values of DS, the smaller the number of unsubstituted anhydroglucose sequences available for scission. In addition, esters with larger substituents, e.g., laurate (C12) and myristate (C14) do not degrade, even at DS levels of < 1.0 [12]. To calculate the degree of substitution it is essential to determine the ester content (EC) (Table 7). The ester content was calculated according to the following equation:

$$EC(\%) = \frac{[(A-B) \times N_B - (D-C) \times N_A] \times M}{10 \times w}$$

*Note.* A and B represent the volumes (ml) of NaOH solution added to the sample and blank, respectively.  $N_B$  and  $N_A$  are respective normalities of NaOH and HCl. D and C represent the volumes (ml) of HCl solution added to the sample and blank, respectively. M is the molecular weight of the grafted acyl residue (112.14 for adipic residue and 141 for citric residue), and w is the weight of the sample (dry basis, in g).

Table 3

FTIR frequencies for sample three esterified fiber by adipic acid

The functional group	Esterified fiber	Crude fiber	Reference band cm
-OH (stretching)	3336, 3275	-	3650-3200
SP2 C-H (stretching)	3024	-	3100-3020
SP3 C-H (stretching)	2918	2901	2970-2860
-C = O (stretching)	1728, 1678	1734-1683	1780-1650
Benzene ( from lignin)	1593	1558-1506	1600-1500
SP3 C-H (bending)	1464	1448	1450-1420
C-H cellulose, hemicellulose	1375	1375, 1338	1384-1346
Phenolic hydroxyl	1244	-	1260-1234
-C-O-C (stretching)	1163	1161, 1107	1250-1050
-C-O(H) stretching	1040	-	1040
Amorphous region of cellulose	854	896	897
-OH (out of plane bending)	665	-	669
SP2 C-H (bending)	769, 721	771, 696,600	1000-600

Table 4

FTIR frequencies for sample one esterified fiber by citric acid

The functional group	Esterified fiber	Crude fiber	Reference band cm
-OH (stretching)	3446	-	3650-3200
SP2 C-H (stretching)	3032	-	3100-3020
SP3 C-H (stretching)	2943	2902	2970-2860
-C = O (stretching)	1747, 1732	1734, 1683, 1653	1780-1650
Benzene ( from lignin)	1506	1558-1506	1600-1500
SP3 C-H (bending)	1456	1448	1450-1420
Crystallinity region of cellulose	1425	-	1430-1420
C-H cellulose, hemicellulose	1338	1373	1380-1340
Phenolic hydroxyl	1244	1246	1260-1234
-C-O-C (stretching)	1143	1161, 1111	1250-1050
-C-O(H) stretching	1033	-	1040
Amorphous region of cellulose	898	896	897
-OH (out of plane bending)	667	663	669
SP2 C-H (bending)	617	-	1000-600

The degree of substitution was then calculated as:

$$DS = \frac{162 \times EC}{M \times 100 - EC \times (M - 1)}$$

Note. 162 is the molecular weight of anhydro-glucose monomer.

Table 5

FTIR frequencies for sample two esterified fiber by citric acid

The functional group	Esterified fiber	Crude fiber	Reference band cm
-OH (stretching)	3412	3354	3650-3200
SP2 C-H (stretching)	3026	-	3100-3020
SP3 C-H (stretching)	2935	2931	2970-2860
-C = O (stretching)	1737, 1716	1734	1780-1650
Benzene ( from lignin)	1558, 1506	1610, 1521	1600-1500
Crystallinity region of cellulose	1419	-	1430-1420
C-H cellulose, hemicellulose	1380	1375, 1363	1380-1340
Phenolic hydroxyl	1238	1230	1260-1234
-C-O-C (stretching)	1112	1109	1250-1050
-OH (out of plane bending)	667	661	669
SP2 C- H (bending)	896	900	1000-600

Table 6

FTIR frequencies for sample three esterified fiber by citric acid

The functional group	Esterified fiber	Crude fiber	Reference band cm
-OH (stretching)	3336, 3275	-	3650-3200
SP2 C-H (stretching)	3024	-	3100-3020
SP3 C-H (stretching)	2920	2901	2970-2860
-C = O (stretching)	1732, 1716	1734-1683	1780-1650
Benzene ( from lignin)	1558, 1506	1558-1506	1600-1500
SP3 C-H (bending)	1464	1448	1450-1420
Crystallinity region of cellulose	1425	-	1430-1420
C-H cellulose, hemicellulose	1375, 1338	1375, 1338	1384-1346
Phenolic hydroxyl	1244 (weak)	1244	1260-1234
-C-O-C (stretching)	1163, 1114	1161, 1107	1250-1050
-C-O(H) stretching	1033	1040	1040
Amorphous region of cellulose	898	896	897
-OH (out of plane bending)	661(weak)	665	669
SP2 C-H (bending)	719, 615	771, 696,600	1000-600

Table 7

The degree of substitutions for 6 esterified fibers under study

Esterified fiber	Ester content (%)		Degree of substitution	
	With citric acid	With adipic acid	With citric acid	With adipic acid
Sample one	26.6	27.9	0.42	0.56
Sample two	27%	21.6	0.42	0.40
Sample three	25	28	0.38	0.57

Ester substituents in this study were considered to be suitable in their size (citric and adipic acid). As the degree of substitutions was  $< 1$ ; so all esterified fibers can be used to prepare the biodegradable composites.

### Conclusion

Ester formed in the cellulosic chain was considered to be one of the adhesion

mechanisms in the production of environmentally friendly composites without glue. The esterification of crude fibers was carried out in a simple and reliable method, and the ester contents were above 25%.

### Funding

The authors gratefully thank the University of Khartoum for their financial support.

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**ГЕТЕРОГЕННА ЕТЕРИФІКАЦІЯ  
ВИТЯЖЕНИХ ВОЛОКОН З *Leptadenia pyrotechnica* ТА *Phoenix dactylifera* L.**

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*Метою* роботи було дослідити використання прямого гетерогенного методу етерифікації волокон рослин *Leptadenia pyrotechnica* та *Phoenix dactylifera* L. за допомогою адипінової та лимонної кислот. Однорідна етерифікація призводить до деградації лігноцелюлозного матеріалу, що унеможливорює отримати чистий етер екстрагованої сировини волокон цим способом.

*Методи.* Реакцію етерифікації проводили на трьох зразках рослин (*Leptadenia pyrotechnica*, *Phoenix dactylifera* L. листя та волокно), які виділяли як сировинне волокно і використовували в гетерогенному процесі етерифікації. Загальна кількість етерифікованих волокон становила шість етерів (кожен зразок етерифікували лимонною та адипіновою кислотою). У дослідженні використовували звичайне лабораторне обладнання для проведення інфрачервої спектроскопії з перетворенням Фур'є (FTIR).

Отримані результати показали, що вміст етерів становив від 21,6% до 28%. Ступінь заміщення знаходився в діапазоні від 0,38 до 0,57.

*Висновок.* У роботі описано простий і ефективний процес аналізу етерифікованих рослинних волокон з бажаним ступенем заміщення.

***Ключові слова:*** сировинні волокна, гетерогенність, етерифікація, *Leptadenia pyrotechnica*, *Phoenix dactylifera* L., адипінова кислота, лимонна кислоти.