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硕士 学位 论文

能源植物芒草制备醋酸纤维素及催化剂筛选的研究

Cellulose acetate prepared with energy plant of miscanthus
and screening catalysts

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摘要

随着化石资源日益匮乏，利用生物质来代替化石资源受到全世界关注。本研究以能源植物芒草为原料，利用 NaOH/H₂O₂ 水溶液体系进行预处理，制备出较高纯度纤维素。芒草纤维素经活化、酯化反应后制备出高取代度的芒草醋酸纤维素，并筛选出氯化铁为催化剂制备醋酸纤维素，同时对制得样品进行表征。

(1) 以 NaOH/H₂O₂ 水溶液体系对芒草生物质预处理，制得芒草纤维素。以芒草纤维素组分含量、固相得率和组分脱除率为指标对预处理温度、时间和次数进行了优化，得到的芒草纤维素的最佳制备条件：预处理温度 70℃，预处理时间 3 h，预处理次数 3 次，制得芒草纤维素的纤维素、半纤维素和木质素含量分别为 75.3%、17.3%、5.1%。对芒草纤维素进行了扫描电镜 (SEM)、X 射线衍射 (XRD)、红外光谱分析 (FT-IR) 和热分析 (TG、DSC) 表征分析，结果表明 NaOH/H₂O₂ 水溶液体在有效脱除木质素的同时可以不破坏纤维素结构，保持原有的晶体结构。此方法操作简单，不会产生大量黑液，对环境友好。

(2) 以芒草纤维素为原料，采用冰醋酸/醋酸酐/浓硫酸体系制备高取代度的芒草醋酸纤维素。以芒草醋酸纤维素的取代度和特性黏度为指标对催化剂量、反应温度、反应时间、醋酸酐添加量进行了优化，得到芒草醋酸纤维素的最优制备条件：催化剂量 20 μL/g，反应温度 50℃，反应时间 60 min，醋酸酐添加量 6 mL/g，制备的芒草醋酸纤维素取代度 DS=2.8，特性黏度 [η]=1.24 dL/g。对制备的芒草醋酸纤维素样品进行了扫描电镜 (SEM)、X 射线衍射 (XRD)、红外光谱分析 (FT-IR) 和热分析 (TG、DSC) 表征分析。扫描电镜 (SEM) 图谱看出经过反应得到的样品，其原有的纤维素束状结构被完全破坏，变为颗粒状结构；X 射线衍射 (XRD) 图谱可以看出经过反应得到的样品其晶型发生改变，纤维素 I 型尖锐结晶峰消失；红外光谱 (FT-IR) 图谱得出 1755 cm⁻¹ 处和 1236 cm⁻¹ 处出现了酯基特征峰，1371 cm⁻¹ 处出现 CH₃—C=O—O 中 C—H 振动峰；以上表征结果，表明芒草纤维素发生了酯化反应，合成了芒草醋酸纤维素。热分析 (TG、DSC) 表明合成的芒草醋酸纤维素有较好的热稳定性。但是，

传统硫酸催化剂有一些缺点：反应时间长，副反应多，产品干燥易变灰色。因此，有必要筛选新型廉价的催化剂，克服上述缺陷。

(3) 对新型催化剂的催化效果进行考察，以氯化铁、氯化铝、氯化锌、氯化钠、盐酸、硫酸亚铁、硫酸铁、硫酸钠等作为催化剂，制备出醋酸纤维素的取代度分别为 2.95、0.21、0.31、0.11、0.3、2.12、0.29、0.10，在所选取的催化剂中氯化铁的催化效果最好，硫酸亚铁次之，可能主要与在醋酸/醋酸酐体系的溶解性和阳离子的吸电子效应有关，结果表明氯化铁适用于制备醋酸纤维素。新型氯化铁催化剂克服了传统硫酸催化剂的缺陷，纤维素不需要前期冰醋酸活化过程，无磺化等副反应，干燥过程中不会变色，而且氯化铁毒性小、成本低、操作简便。因此，有必要对新型氯化铁催化剂反应体系进行优化，并对产品进行表征。

(4) 以芒草纤维素为原料，采用冰醋酸/醋酸酐/氯化铁体系制备醋酸纤维素，以醋酸纤维素的取代度为指标对催化剂量、反应温度、反应时间进行了优化，得到的醋酸纤维素的最优制备条件：催化剂量 0.200 g/g，反应温度 50℃，反应时间 45 min，制备的醋酸纤维素取代度 DS=2.93。对制备的醋酸纤维素样品进行了扫描电镜 (SEM)、X 射线衍射 (XRD)、红外光谱分析 (FT-IR) 和液态核磁 (Solution-state NMR) 表征分析。扫描电镜 (SEM) 图谱看出经过反应得到的样品，其原有的纤维素束状结构被完全破坏，变为颗粒状结构；X 射线衍射 (XRD) 图谱可以看出经过反应得到的样品其晶型发生改变，纤维素 I 型尖锐结晶峰消失；红外光谱 (FT-IR) 图谱得出 1748 cm^{-1} 处和 1236 cm^{-1} 处出现了酯基特征峰， 1371 cm^{-1} 处出现 $\text{CH}_3-\text{C=O}-\text{O}$ 中 C—H 振动峰。液态核磁 (Solution-state NMR) 得出了碳氢原子各自的化学位移和碳氢连接关系，从分子结构证明了样品为醋酸纤维素。以上表征结果，表明纤维素发生了酯化反应，合成了醋酸纤维素。新型氯化铁催化剂克服了传统硫酸催化剂的缺陷，纤维素不需要前期冰醋酸活化过程，无磺化等副反应，干燥过程中不会变色，而且氯化铁毒性小、成本低、操作简便，制备出的醋酸纤维素取代度高达 2.93，符合美国联邦贸易委员会指南认定的三醋酸纤维素要求，因此，氯化铁可以作为催化剂制备醋酸纤维素。

关键词： 芒草 醋酸纤维素 取代度 优化 氯化铁

Abstract

With the shortage of fossil resources, using biomass as a substitute for fossil resources became a hotspot of study. A procedure for synthesizing cellulose acetate with high degree of substitution from miscanthus biomass was developed and we also choose ferric chloride as a new catalyst to prepare cellulose acetate. The miscanthus biomass, miscanthus cellulose and cellulose acetate were characterized by SEM, XRD, FT-IR, TG and DSC.

(1) The optimum conditions for pretreating miscanthus biomass with NaOH/H₂O₂ were determined. The pretreatment factors (pretreatment temperature, time and number of times) were optimized. The content of cellulose, hemicellulose and lignin for prepared miscanthus fiber under optimum condition (70°C, 3 h, 3 times) were 75.3%, 17.3%, 5.1%. The results of SEM, XRD, FT-IR, TG and DSC indicated that the method of NaOH/H₂O₂ could effectively remove lignin of miscanthus biomass without breaking crystal structure of cellulose. This method was simple and friendly to environment.

(2) The optimum conditions for preparing cellulose acetate with miscanthus fiber by reacting with acetic anhydride catalyzed with concentrated sulfuric acid in an acetic acid solvent were determined. The esterification factors (catalyst volume, reaction temperature, reaction time and acetic anhydride volume) were optimized. After optimization (20 μL/g, 50°C, 60 min, 6 mL/g) the degree of substitution (DS) of 2.8 and the intrinsic viscosity ([η]) of 1.24 dL/g for miscanthus cellulose acetate were achieved. The degree of substitution met the criteria of cellulose triacetate of the federal trade commission guidelines. The SEM images showed the structure of miscanthus cellulose was changed from sarciniform to granulate after esterification reaction. The XRD analysis indicated the crystalline region was broken by esterification reaction. The FT-IR analysis illustrated the hydrogen atoms were replaced by acetyl on the cellulose molecules. The thermal analysis confirmed

misanthus cellulose acetate had good thermal stability. However, the traditional sulfuric acid catalyst has some disadvantages: long reaction time, many side reactions and poor color. Therefore, it was necessary to screen new cheap catalyst to overcome the above defects.

(3) The catalytic effects of new catalysts were determined by titration method. The DS of prepared cellulose acetate catalyzed respectively by ferric chloride, aluminum chloride, zinc chloride, sodium chloride, hydrochloric acid, ferrous sulfate, ferric sulfate, sodium sulfate were 2.95, 0.21, 0.31, 0.11, 0.3, 2.12, 0.29, 0.10. The catalytic effects of ferric chloride was best, it might be related with the solubility in the acetic acid/acetic anhydride system and electronic absorption effect of the cation. The results show that ferric chloride was suitable for the preparation of cellulose acetate. The ferric chloride catalyst overcame the defects of tradarional catalyst and it was small toxicity, low cost and easy operation. Therefore, it is imperative to optimize the new ferric chloride catalyst reaction system and characterize the products.

(4) The optimum conditions for preparing cellulose acetate with miscanthus cellulose by reacting with acetic anhydride catalyzed with ferric chloride in an acetic acid solvent were determined. The esterification factors (catalyst volume, reaction temperature and reaction time) were optimized. The degree of substitution for prepared cellulose acetate under optimum condition (0.200 g/g, 50°C, 45 min) were 2.93, which was met the criteria of cellulose triacetate of the federal trade commission guidelines. The SEM images showed the structure of cellulose was changed from sarginiform to granulate after esterification reaction. The XRD analysis indicated the crystal structure was changed, the peak of cellulose I was disappeared. The FT-IR analysis illustrated the hydrogen atoms were replaced by acetyl on the cellulose molecules. The solution-state NMR showed the connection relation between carbon atom and hydrogen atom as well as chemical shift of groups, which confirmed the sample was cellulose acetate from the molecular structure. The ferric chloride catalyst overcame the defects of tradarional catalyst and it was small

toxicity, low cost and easy operation. And, The DS of cellulose acetate catalyzed by ferric chloride was 2.93. In conclusion, ferric chloride could be catalyst for preparing cellulose acetate.

Keywords: Miscanthus; Cellulose acetate; Degree of substitution; Optimization; Ferric chloride

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