University Code: 10384

Student ID No.: 20420131154525

厦门大学

MASTER DEGREE THESIS

Lignin and lignin-acetoderivative oxidative degradation into valuable aromatic aldehydes

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Date of Graduation: July, 2015

A THESIS SUBMITTED

FOR THE DEGREE OF MASTER OF ENGINEERING

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING

COLLEGE OF CHEMISTRY AND CHEMICAL ENGINEERING

XIAMEN UNIVERSITY

CERTIFICATION

I, Professor……, hereby certify that I have read this manuscript and recommend for acceptance by the Xiamen University a dissertation entitled "*Lignin and lignin-acetoderivative oxidative degradation into valuable aromatic aldehydes*" in fulfillment of degree of Master of Engineering at Xiamen University, People's Republic of China.

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ORIGINAL STATEMENT

The research described in this thesis for Master of Chemical Engineering was conducted under the supervision of Professor Yunquan Liu and Dr. Yue-Yuan Ye at the Institute for BioEnergy, School of Energy Research, Xiamen University. I hereby declare that the work submitted is my own and that appropriate credit has been given where reference has been made to the work of others. I also confirm that it has not been previously or concurrently submitted for any other degree, diploma or any other qualifications at Xiamen University, P.R China or other institutions.

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NAME OF STUDENT:

Date:

ACKNOWLEDGEMENT

In all humility, I would like to acknowledge the Almighty God for giving me the opportunity to advance my academic and professional carrier in China. I am enormously indebted to my research supervisor, Professor Yunquan Liu, for all of his advice, support and guidance and also for providing me with the opportunity to join his research group in his laboratory. I am also very grateful to Dr. Yue-Yuan Ye, Dr. Shui-Rong Li, Dr. Duo Wang for their limitless help, orientation, advice and guidance throughout my study period, I am as well thankful to my fellow lab mates for their great help especially for teaching me the methodology of various experiments, their patience and friendly attitude towards me. I humbly thank all the lecturers in the college of Energy, most especially the college principal, special thanks also goes to my Lecturers in the college of Chemistry and Chemical Engineering; I believe they are the driving force behind my achievement now and in the future. My special thanks go to the Government of the People's Republic of China under the communist party who through the Chinese Scholarship Council provided me the scholarship to study at Xiamen University, China.

Finally, I would like to express my gratitude to my family members back home in Uganda for their encouragement, moral and other support in various ways, then my friends; Faisal Soyekwo, Musa Mubiru Kisiriko and William Brown, you have been always there for me when I needed you most. May the almighty God, in His infinite mercy spread His blessings on all those who in diverse ways contributed to my success.

Abstract

The main objective of this work was to study the transformation of lignin and its by-products (acetoderivatives) into valuable aromatic aldehydes as well as the kinetics of acetoderivative degradation during the alkaline catalytic oxidation. Bamboo lignin was transformed into valuable aromatic aldehydes and acetoderivatives. Vanillin was recovered from acetovanillone with the application of copper catalyst. Syringaldehyde recovery from acetosyringone was reported for the first time, thus adding value to the lignin oxidation process through transformations of its by-products. A reliable and consistent relative response factor (RRF) method for the quantification of lignin and acetoderivatives products was successfully developed which was latter used in the GC-MS analysis. A total product yield of approximately 9.5% from bamboo lignin and a vanillin yield of 55% with greater than 90% selectivity from acetovanillone were achieved. The proposed reaction pathways suggest a two-step route towards the formation of value-added aromatic aldehydes from lignin via degradation of acetoderivatives. The kinetics study for the degradation of acetovanillone and the formation of vanillin were reported for the first time over the temperature range of 120-150 °C, with the activation energies of 85.29 kJ/mol and 120.7 kJ/mol respectively. Further kinetics studies on the oxygen concentration impacts indicated that the acetovanillone disappearance and the vanillin formation were of 0.5 and 1.6 reaction orders with respect to the oxygen concentration respectively. To date, catalytic wet air oxidation (CWAO) breaks down the lignin polymer and toxic phenolic compounds reasonably and effectively, producing value-added aldehydes, which could become a potential new route for the recovery of value-added products.

Key words: Lignin; Acetoderivatives; Catalytic oxidation; Vanillin; Syringaldehyde

摘要

本项工作研究了木质素的转化以及其副产品(乙酸基衍生物)转变为高附加值的芳香醛，乙酸基衍生物在碱性条件下催化氧化降解的动力学方程等问题。竹材木质素被转化为高附加值的芳香醛和乙酸基衍生物。在铜作为催化剂的条件下，香草乙酮被转化为香草醛。另外，乙酰丁香酮首次转化为丁香醛，从而通过降解木质素氧化过程中的副产物来提高整个过程的价值。本文用 GC-MS 分析得到了一种可靠的一致的相对影响因子法来定量木质素和乙酸衍生物。竹材木质素的总产率接近 9.5%，且香草醛的产率为 55%，其中 90%以上来自于香草乙酮。来源于木质素，通过降解乙酸衍生物而得到高附加值的芳香醛分为两步反应。文章首次研究了 120-150℃条件下香草乙酮的降解动力学和香草醛的形成，其活化能分别为 85.29 kJ/mol 和 120.7 kJ/mol。此外，对氧浓度的影响的研究表明香草乙酮的消失和香草醛的形成分别为 0.5 和 1.6 级反应。迄今为止，催化湿式氧化有效地降解了木质素聚合物和有毒酚类化合物，产生了高附加值的醛类，这将成为一种新的有潜力的回收高附加值物质的手段。

关键词：木质素，乙酸基衍生物，催化氧化，香草醛，丁香醛

Scope of the study

The extent and structural format of the thesis has been organized into the following five sections. A general introduction and a comprehensive review of the associated literature including the motivation resulting into this study is systematically presented in chapter one. In chapter two, the materials and experimental methods used in the study are introduced. Chapter three presents the detailed results and discussion on the depolymerization of lignin by catalytic oxidation in alkali aqueous solvent. More results are presented in chapter four where the catalytic acetoderivative degradation under alkali oxidation was investigated with the sole purpose of determining the fate of acetoderivatives during lignin oxidation as well as determining the possibility of recovery of value added products from them.

Finally in chapter five, the conclusions resulting from the study are noted and the prospects for future work are suggested.

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List of Symbols and Abbreviations

RRF- Relative Response Factor

ES-External Standardisation

V- Vanillin

AV- Acetovanillone

Av.-Average

STDEV-Standard Deviation

RSD-Relative Standard Deviation

Wt- Weight

LOPs- Lignin oxidized products

AS- Acetosyringone

SY- Syringaldehyde

C_{AV}- Concentration of acetovanillone

C_{V}- Concentration of vanillin

Ea- Activation energy, kJ/mol

k*i*- Empirical kinetic constant

Form.-Formation

Degrad.-Degradation

A- Constant in the Arrhenius equation

M-Concentration of NaOH, mol L^{-1}

m -Reaction order

P^0 -Water vapor pressure

P_{NaOH} -Water vapour pressure above NaOH solution, bar

P_{O2} -Oxygen partial pressure, bar

P_t -Total pressure in the reactor, bar

r_{AV} -Rate of AV hydrolysis to vanillin, g min^{-1} L^{-1}

r_V -Rate of V formation, g min^{-1} L^{-1}

T-Temperature, °C or K as appropriate

t -Time, min or s as appropriate

y_{O_2} -Oxygen mole fraction in the gas

CWAO-Catalytic Wet Air Oxidation

Eq.-equation

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