

玉米秸秆纤维素在亚/超临界乙醇中液化生成酮类化合物的机理探讨

陶红秀, 解新安, 汤成正, 田文广

华南农业大学 食品学院, 广东 广州 510642

Mechanism of ketones formation from cellulose liquefaction in sub- and supercritical ethanol

TAO Hong-xiu, XIE Xin-an, TANG Cheng-zheng, TIAN Wen-guang

College of Food Science, South China Agricultural University, Guangzhou 510642, China

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摘要 利用间歇式高压反应釜,在反应温度320℃、反应时间60 min条件下,研究乙醇用量对玉米秸秆纤维素液化生成酮类化合物的作用。当乙醇添加量为0时,酮类化合物的产率仅为1.25%。随着乙醇用量由0增加到160 mL,生物油产率不断的升高,酮类化合物产率增加至18.38%,乙醇促进了纤维素液化生成酮类化合物。利用GC/MS和FT-IR对生物油进行了定性分析,结果表明,在亚/超临界乙醇中,酮类化合物主要通过三条路径形成,纤维素脱水形成了含-C=O的活性纤维素,活性纤维素按逆Diels-Alder机理进行开环、脱水、异构化形成了4-羟基-4-甲基-2-戊酮等脂肪族酮类化合物;在乙醇自由基作用下,活性纤维素中C-O-C、C-C等键断裂、开环,形成环戊烯酮等脂环族酮类化合物,环戊烯酮与多种中间产物发生缩合、酯化形成2-甲酰基-1-苯基乙酮等芳香族酮类化合物;在高浓度乙醇自由基作用下,芳香族酮类化合物进一步发生裂解形成酸类、酮类等化合物。根据对酮类化合物生成机理的分析,建立了纤维素在亚/超临界乙醇中液化生成酮类化合物的反应网络。

关键词: 玉米秸秆纤维素 亚/超临界乙醇 酮类化合物 生成机理 反应网络

Abstract: Cornstalk cellulose was liquefied in sub- and supercritical ethanol using an autoclave at 320℃ for 60 min. Effects of ethanol dosages on ketones formation from cellulose liquefaction were investigated. The yield of ketones was 1.25% in the absence of ethanol and then increased to 18.38% while adding 160 mL ethanol. Ethanol favored the formation of ketones from cellulose liquefaction. The liquid products at different ethanol dosages were analyzed by FT-IR and GC/MS. The results were shown as follows: (1) Cellulose was converted to active cellulose which was transformed into aliphatic ketones such as 4-hydroxy-4-methyl-2-pentanone by dehydration, decomposition, ring-opening reactions, isomerization and aldol condensation. (2) The alicyclic ketones (cyclopentenone) was formed by the cleavage of C-O-C and C-C bonds of the active cellulose under the effects of ethanol free radicals. Aromatic ketones (2-(formyloxy)-1-phenyl ethanone) were generated by cyclopentenone reaction with intermediates. (3) Aromatic ketones were decomposed to carboxylic acids and small molecule ketones under ethanol free radicals. According to the above results, the reaction network of ketones formed from cellulose in sub- and supercritical ethanol was proposed.

Key words: cornstalk cellulose sub- and supercritical ethanol ketones mechanism reaction network

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通讯作者: 解新安(1964-),副教授,博士,主要从事生物质能利用与开发,食品加工过程模拟,能量系统优化等研究。Tel:020-85280266,E-mail: xinanxie@scau.edu.cn。 E-mail: xinanxie@scau.edu.cn

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