



Producing petrochemicals from catalytic fast pyrolysis of corn fermentation residual by-products generated from citric acid production



Xiangyu Li ^{a, b}, Guangyu Li ^{b, c}, Jian Li ^b, Yanqing Yu ^b, Yu Feng ^b, Qun Chen ^d, Sridhar Komarneni ^e, Yujue Wang ^{b, *}

^a China National Tobacco Quality Supervision and Test Center, No. 2 Fengyang Street, Zhengzhou 450001, China

^b School of Environment, Tsinghua University, Beijing 100084, China

^c Ramu Nico Management (MCC) Limited, MCC Tower, No. 28, Shuguangxili, Beijing 100028, China

^d Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

^e Department of Ecosystem Science and Management and Material Research Institute, 205 MRL Building, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:

Received 14 August 2015

Received in revised form

27 November 2015

Accepted 28 November 2015

Available online xxx

Keywords:

Pyrolysis

Catalysis

Zeolite

Aromatic hydrocarbon

Olefin

ABSTRACT

Citric acid production from corn fermentation generates significant amounts of fermentation residual by-products that need to be disposed of. To valorize the corn fermentation residues (CFRs), this study investigated catalytic fast pyrolysis (CFP) of CFRs alone or with low-density polyethylene (LDPE) to produce petrochemicals (aromatic hydrocarbons and olefins) using ZSM-5 zeolites as the catalyst. Results indicate that ZSM-5 zeolites decreased the activation energy of CFRs thermal decomposition by ~15%. In addition, the introduction of ZSM-5 dramatically changed the compositions of condensable products from predominantly oxygenated compounds (e.g., furans, ketones, and acids) in non-CFP of CFRs to essentially aromatic hydrocarbons (e.g., benzene, toluene, and xylenes (BTX)) in CFP. Petrochemical yield of 30.4 C% was obtained in CFP of CFRs alone, and further improved to 40.3–52.1 C% when 10–33.3 wt.% LDPE was co-fed with CFRs in CFP. Important primary petrochemicals (BTX, ethylene and propylene) constituted the predominant fractions (66.8–71.1%) of the petrochemical products from CFP of CFRs alone and co-feed CFP with LDPE. These results indicate that CFRs are an attractive biomass feedstock for the production of high value-added petrochemicals by CFP process.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Citric acid is the second largest fermentation product in the world and has a global annual production of more than 1.7 million tons [1]. It is one of the most commonly used flavors and preservatives in the food industry. In addition, it is also widely used as additives in numerous useful products such as detergents, pharmaceuticals, cosmetics, and toiletries [2]. Due to its wide applications, the market demand for citric acid has been increasing stably in the world. For example, a recent survey estimated that the world's production of citric acid is increasing at a rate of 5% annually [1].

Citric acid is mainly produced from fermentation of inexpensive starch- and sucrose-based feedstocks, such as corn and cassava [3]. In particular, corn is the most commonly used feedstock for citric acid production in China, which is the largest producer of citric acid and produces about 70–80% of the total production in the world. The production process involves mainly three steps: (i) pretreatment of corn by grinding, liquefaction, and enzymatic saccharification to convert macromolecular polysaccharides into smaller carbohydrates that are easier for bio-utilization; (ii) conversion of the biodegradable content of corn (e.g., sucrose, glucose) to citric acid by microorganisms such as *Aspergillus niger* during fermentation; (iii) recovery of citric acid products from the fermented broth via a series of separation processes such as precipitation, extraction, or adsorption [2].

During citric acid production, significant amounts of fermentation residues are generated as by-products, which usually accounts

* Corresponding author.

E-mail address: wangyujue@tsinghua.edu.cn (Y. Wang).

for approximately 50 wt.% of the citric acid products when corn is used as the feedstock. Thus, it is estimated that more than 0.5 million tons of corn fermentation residues (CFRs) are generated from citric acid production each year in China. The major components of CFRs include cellulose, hemicellulose, sugars, and proteins. Currently, CFRs are mainly disposed of as solid wastes, or used occasionally to make low-price animal feed additives. This represents a considerable waste of potentially valuable biomass feedstock, and might cause environmental problems when CFRs were not properly disposed of. Therefore, there is a need to develop a more economically competitive and environmentally sustainable alternative for the valorization of CFRs.

To this end, this study tested the possibility of producing petrochemicals (aromatic and olefinic hydrocarbons) from CFRs by catalytic fast pyrolysis (CFP) with zeolite catalysts. Petrochemicals are conventionally produced from petroleum, and then used to manufacture a broad range of important products (e.g. plastics, fibers, solvents, and medicines). Due to the rapid depletion of petroleum reserves on the earth, producing petrochemicals from renewable biomass resources has gained increasing interests. In this regard, CFP of biomass with zeolite catalysts has emerged as a promising technology because it can rapidly convert solid biomass feedstock directly into high value-added petrochemicals [4,5]. During CFP, biomass is rapidly heated to ~450–650 °C in the presence of catalysts. The primary pyrolysis products, which are predominantly oxygenated compounds (e.g., acids, aldehydes, furans, and phenols), then undergo a series of zeolite-catalyzed reactions including cracking, deoxygenation, oligomerization, cyclization, and aromatization to yield the desired final hydrocarbon products. The whole conversion process can be completed in a single reactor with short reaction time [4,6,7]. We thus expected that CFP may provide an attractive way to valorize CFRs to highly valuable petrochemical products.

In this light, the main objective of this study was to investigate the production of petrochemicals from CFRs using the CFP technology. ZSM-5 zeolites were used as the catalyst in CFP because it usually produces the highest petrochemical yields from CFP of biomass among the various catalysts (e.g., beta, Y, and mordenite zeolites) that had been previously tested [7,8]. The effects of ZSM-5 on the kinetics of CFRs thermal decomposition were evaluated using thermogravimetric analysis (TGA). Note that although the heating rates that can be obtained in TGA pyrolysis (e.g., several to tens centigrade per minute) are considerably lower than those involved in CFP of biomass (e.g., hundreds centigrade per second), TGA can still provide important information regarding the reaction kinetics of biomass pyrolysis, for example, the activation energy of biomass thermal decomposition is usually considered nearly constant for specific feedstocks and not affected significantly by the heating rates [9–11]. The product distributions from non-CFP (i.e., fast catalysis in the absence of zeolites) and CFP of CFRs with ZSM-5 zeolites were analyzed using gas chromatography-mass spectrometry and other techniques. In addition, several previous studies have demonstrated that when certain types of biomass and (waste) plastics (e.g., cellulose and polyethylene) are co-fed in CFP with ZSM-5, they can have significant synergistic effects for petrochemical production [12–15]. Co-feed CFP of CFRs and LDPE was therefore also investigated in this study.

2. Materials and methods

2.1. Materials

CFRs samples were collected from a citric acid production plant in Jiangsu Province, China where corn was used as the raw material to produce citric acid. In our lab, the CFRs sample was dried at 60 °C

overnight, then crushed with a high-speed rotary cutting mill to pass 140 mesh sieves (0.105 mm). Low-density polyethylene (LDPE) powder (<0.105 mm) was purchased from Li Yang Technology Corporation (Shanghai, China). ZSM-5 zeolites (SiO₂/Al₂O₃ ratio of 38, H type, d₅₀ of 2 μm) were acquired from the Catalyst Plant of Nankai University (Tianjin, China).

For CFP tests, ZSM-5 zeolite was mixed with a particular reactant (CFRs, LDPE, and their co-feed mixture) in a catalyst-to-reactant ratio of 15:1. It is noted that high catalyst-to-reactant ratios (e.g., 10–20) are usually required in bench-scale CFP tests to ensure that the primary pyrolysis products of biomass/plastics can be effectively converted to the desired hydrocarbon products within the framework of catalysts [16,17].

2.2. Elemental and component analysis

The elemental compositions of CFRs and LDPE were analyzed with an elemental analyzer (CE-440, Exeter Analytical, Inc., North Chelmsford, MA). The components of CFRs (e.g., cellulose, hemicellulose, and lignin) were analyzed using the protocol of Goering and Van Soest [18].

2.3. Thermogravimetric analyzer (TGA) pyrolysis

Approximately 1 ± 0.01 mg of CFRs were used in the TGA analysis. For catalytic TGA pyrolysis, CFRs were mixed with ZSM-5 zeolite in a catalyst-to-reactant ratio of 15:1. Samples were placed as a thin layer at the bottom of an alumina pan in a thermogravimetric analyzer (TGA/DSC 1, Mettler-Toledo Inc., and Switzerland). The samples were then heated from ambient temperature to 800 °C at a heating rate of 20 °C/min under 20 mL/min high-purity argon. It is noted that the heating rates in TGA tests can have a large influence on the kinetics of the process, and a previous study of Van de Velden et al. [10] has suggested that a heating rate of at least 80 °C/min is required to simulate the reactions of biomass fast pyrolysis. However, to minimize the temperature gradients that may develop within samples at high heating rates and thus better evaluate the activation energy of biomass decomposition [19–21], a lower heating rate (20 °C/min) was used in this present study. To preclude the influence of possible mass loss of alumina pans and catalysts on the analysis of biomass pyrolysis kinetics, two separate TGA runs were conducted using an empty pan and a pan plus 15 mg ZSM-5 under the same conditions. These two TGA curves were used for baseline corrections when evaluating the TGA profiles of non-catalytic and catalytic TGA pyrolysis, respectively. Duplicate TGA tests were performed for each sample; the reproducibility was found to be excellent within a relative experimental error of ±2%.

2.4. Fast pyrolysis analysis

Fast pyrolysis tests were conducted with Pyroprobe 5200 analytical pyrolyzer (CDS Analytical, Inc.) using a protocol described elsewhere [12]. About 1 mg (for non-CFP) or 4 mg (for CFP) of sample was rapidly heated to 600 °C at a heating rate of 20 °C/ms, and then held for 60 s under high-purity helium flux during fast pyrolysis. The volatiles emitted via this fast heating were carried by helium through a heated transporting tube (300 °C) to a gas chromatograph (Agilent 7890A) that was equipped with a mass spectrometer (5975C MSD), a flame ionization detector (FID), and a thermal conductivity detector (TCD). The GC injector was kept at 300 °C, and the inject split ratio were 50:1. The condensable pyrolysis products were separated with an HP-INNOWax column (60 m × 0.25 mm i.d. × 0.25 μm film thickness, Agilent Technologies, Inc.). The temperature ramp started with an isothermal step of 5 min at 40 °C, followed by a gradient of 5 °C/min to 240 °C, and

Download English Version:

<https://daneshyari.com/en/article/6766261>

Download Persian Version:

<https://daneshyari.com/article/6766261>

[Daneshyari.com](https://daneshyari.com)