



Catalytic fast pyrolysis of furfural over H-ZSM-5 and Zn/H-ZSM-5 catalysts

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ABSTRACT

Furfural, a cellulose model compound, was converted into gasoline-range fuels through catalytic fast pyrolysis. H-ZSM-5-based catalysts were employed in a continuous fixed bed system. The reaction temperature, reactant contact time, and catalytic promoter are keys to manipulate the product distribution. The first step in furfural conversion is the decarbonylation of furfural to form furan, followed by furan conversion to intermediates (e.g., cyclohexene and 3,4-dimethylbenzaldehyde) in the ZSM-5 pores. These intermediates can then be transformed into aromatics, coke, light olefins, and carbon oxides. A reaction temperature of 500 °C generated the highest yield of aromatics and the lowest amount of coke. A long contact time (~1.5 s) also provided the highest aromatic selectivity. The promoter, zinc oxide, plays an important role in hydrogen atom transfer. This is attributed to the change of acid site concentration and Lewis acid sites created by anchored Zn ions.

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1. Introduction

The conversion of lignocellulosic biomass has the potential to be a renewable and carbon neutral method of producing fuels and chemicals [1–3]. Several groups have recently developed novel technologies, such as reactive flash volatilization [4,5] and catalytic fast pyrolysis [6,7], to overcome the difficulty of lignocellulosic biomass processing. The first step of these approaches is to disintegrate the solid lignocellulosic frameworks into reactive intermediates, which can then be transformed into desired products.

Furfural is a common intermediate in various biorefining processes. Woody biomass pyrolysis yields furfural in the form of dehydrated products from cellulose and hemicellulose [8–10]. Bio-oils derived from biomass liquefaction also contain significant amounts of furfural [2,11]. Thus, furfural is a popular model compound of lignocellulosic derivatives. For example, Elliott and Hart used furfural as a cellulosic model compound in the catalytic hydroprocessing of a bio-oil-like mixture [12]. An effective method of furfural conversion should facilitate lignocellulosic biorefining.

Hydrogenation and aqueous phase processing are currently the two most encountered approaches of converting furfural into fuel-grade chemicals [2]. The major products of furfural hydrogenation are furfuryl alcohol, methylfuran, tetrahydrofurfuryl alcohol, and methyltetrahydrofuran (MTHF) [2], which is a key component in P-Series fuels [13]. Aqueous phase processing allows furfural to

couple with acetone to form dimers through aldol-condensation. A series of hydrodeoxygenation steps can then transform these dimers into gasoline-range alkanes (C₇–C₁₅) [14–16].

Pyrolysis in the presence of zeolites is another method for biomass upgrading that involves oxygen removal through a series of dehydration, decarbonylation, and decarboxylation reactions. This process was introduced in Mobil's pioneering research on methanol-to-gasoline (MTG) production [17–19]. Chen et al. [20] showed that ZSM-5-based catalysts can convert glucose solutions into olefins and aromatics. Diebold et al. [21,22] invented an integrated process of fast pyrolysis with catalytic cracking to upgrade pyrolysis vapors. Their research stimulated follow-up studies on reactor design [23–26].

Zeolite design for biomass pyrolysis is another common research topic. A research group at the University of Saskatchewan investigated the performance of various zeolites in bio-oil upgrading [27–29]. Zeolites selection for lignocellulosics pyrolysis has recently been investigated in numerous institutes, such as Åbo Akademi University [30,31], Aston University [32,33], and National Renewable Energy Laboratory [34]. ZSM-5 plays an essential role in each case, and is almost omnivorous for different feedstocks.

Unlike the catalytic pyrolysis of biomass and its derivatives, relatively few studies investigate the catalytic pyrolysis of furfural, especially in a fast pyrolysis environment. The Dao group [35,36] studied glucose-related compounds, including furfural, over ZSM-5-based catalysts. They achieved poor yields of hydrocarbon products (less than 10%), with mostly furan and CO derived from furfural decarbonylation. Grandmaison et al. [37] employed ZSM-5 in both furfural and furan conversion, proving that the latter was more stable than the former. Nevertheless, converting furanic

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