Catalytic fast pyrolysis of lignocellulosic biomass in a process development unit with continual catalyst addition and removal

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HIGHLIGHTS

- Continuous aromatic production from wood is achieved in fluidized bed reactor by CFP.
- Low fluidization flow, low WHSV and high catalyst:feed ratio maximize aromatic yield.
- CO and CO_2 in simulated recycle do not inhibit aromatization.
- Simulated recycle of olefins allows for additional aromatization.
- ZSM-5 catalyst is stable throughout repeated reaction/regeneration cycles.

GRAPHICAL ABSTRACT
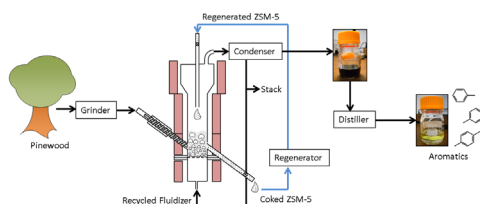
ABSTRACT

Catalytic fast pyrolysis (CFP) of wood was studied using a spray-dried ZSM-5 catalyst in a process development unit (PDU) consisting of a bubbling fluidized bed reactor with on-stream particle input and output. The PDU was capable of maintaining constant product yield of aromatics over an extended reaction period (6 h) with continuous catalyst addition and removal. The yields and selectivity for aromatics and olefins were dependent on temperature, biomass weight hourly space velocity (WHSV), catalyst to biomass ratio, fluidization gas velocity, and catalyst bed weight. The overall aromatic yield increased up to 15.5 carbon% with decreasing gas velocities due to the increased vapor residence time and the improved mass transfer from smaller bubble sizes. A simulated recycle stream of CFP product gases consisting of CO, CO_2 and olefins was used to test the viability of subsequent olefin aromatization in the presence of CO and CO_2. Olefins were converted into additional aromatics while CO and CO_2 remained inert during CFP. The spray-dried ZSM-5 catalyst was stable in a series of 30 reaction/regeneration cycles.

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1. Introduction

Lignocellulosic biomass is the only economically sustainable source of carbon for production of renewable liquid fuels or chemicals (Huber et al., 2006). Catalytic fast pyrolysis (CFP), which involves pyrolysis of biomass in the presence of a zeolite catalyst, is a promising technology to convert raw solid biomass directly into hydrocarbons (aromatics and olefins) (Carlson et al., 2011, 2009b, 2008; Compton et al., 2011; Fanchiang and Lin, 2012; French and Czernik, 2010; Jeon et al., 2013; Li et al., 2012; Ma et al., 2012; Mullen et al., 2011; Neumann and Hicks, 2012; Park et al., 2010; Pattiya et al., 2010; Wang and Brown, 2013; Zhang et al., 2012, 2009b). CFP has significant advantages over other biomass conversion processes due to its simplicity and low process cost. In this single step process, biomass is thermally decomposed into pyrolysis vapors which enter the zeolite catalyst and are converted into desired aromatics and olefins along with CO, CO_2, H_2O, and

coke (Cheng et al., 2012). The mechanisms for production of aromatics by CFP of biomass have been reported in the literature (Carlson et al., 2009a, 2010; Cheng and Huber, 2011; Lin et al., 2009). In brief, the cellulosic portion of biomass is initially pyrolyzed into levoglucosan and other anhydrosugars. These anhydrosugars are further dehydrated to furan derivatives in the presence of zeolite catalysts. Furans then diffuse into the zeolite micropores and are converted into aromatics through a hydrocarbon pool mechanism. Monocyclic aromatics may further react with oxygenates to form polycyclic aromatics. ZSM-5 has the highest aromatic production for CFP of lignocellulosic biomass of any zeolite catalyst due to its medium pore size and moderate internal pore space (Foster et al., 2012; Jae et al., 2011; Mihalcik et al., 2011; Perego and Bosetti, 2011).

CFP of solid biomass has been primarily studied in a variety of fluidized bed reactors, including bubbling-fluidized-bed (Agblevor et al., 2010; Aho et al., 2007, 2008, 2011; Carlson et al., 2011; Mullen et al., 2011; Zhang et al., 2009a), spouted-bed (Atutxa et al., 2005; Olazar et al., 2000), and circulating-fluidized-bed (Lappas et al., 2002) reactors. A major obstacle in CFP operation is catalyst deactivation due to the formation of carbon residues. The carbon residues are formed from either pyrolysis of biomass (char) or by heterogeneous chemistry (coke). For example, it has been reported that the ZSM-5 catalyst deactivates during the CFP of pinewood sawdust during 90 min time on stream (Carlson et al., 2011). Thus for CFP of biomass, it is desirable to use a regeneration furnace alongside the fluidized bed to allow for steady state operation. In such configurations, a regeneration furnace combusts char and coke deposited on (and amidst) the catalyst particles reactivating the catalyst before it is returned to the reactor.

While the coupling of reaction–regeneration reactors is well-suited concept for biomass pyrolysis, only a few papers have been reported using this configuration for catalytic pyrolysis of biomass (Lappas et al., 2009, 2002; Zhang et al., 2013a, 2013b). Lappas et al. (2002) reported the use of a circulating fluid bed (CFB) reactor with continuous solid regeneration for catalytic pyrolysis of biomass. Their unit consists of a riser reactor, fluid bed regenerator, and a stripper. They presented 3-h steady state operation data using either a ZSM-5 additive or a fluid catalytic cracking (FCC) catalyst with continuous catalyst recirculation. They employed 400–500 °C for the reactor temperature and 700 °C for the regenerator temperature. They obtained organic liquid product yields of up to 21 wt% over the ZSM-5 additive. However, the liquid product was a mixture of acids, aldehydes, ketones, furans, and phenols with a very low hydrocarbon yield (0.58 wt%). Zhang et al. (2013b) also reported continuous catalytic pyrolysis of rice stalk in an internally interconnected fluidized bed (IIFB) reactor using a spray-dried ZSM-5 catalyst. In their reactor system, a catalytic pyrolysis bed is internally connected with a combustion bed so that the coke and char on the catalyst is combusted in the combustion bed and the regenerated catalyst is sent back to the catalytic pyrolysis bed for continuous operation. They reported total 20% carbon yield of aromatics and olefins with 3 h time on stream.

Our previous studies of CFP in fluidized beds were conducted for only between 30 min and 90 min before the catalyst deactivated due to coking on the catalyst surface. The objective of this paper is to demonstrate CFP technology at steady-state conditions by using a specially designed reactor that allows continual removal and addition of catalyst from a bubbling fluidized bed reactor. The aromatic and olefin yields are a function of temperature, biomass weight hourly space velocity (WHSV), and catalyst-to-biomass ratio. The effects of catalyst-bed mass and fluidization-gas velocity were also investigated to understand how the hydrodynamics (e.g. bubble growth and vapor residence time) affect CFP chemistry and reactor performance. In addition to inert fluidizers, a simulated

recycle stream of CFP product gases consisting of CO, CO_2 and olefins was used to test the viability of subsequent olefin aromatization in the presence of CO and CO_2. We also studied the stability of the spray-dried ZSM-5 catalyst by subjecting it to repeated reaction/regeneration cycles.

2. Experimental

2.1. Materials

The feedstock used in this study was eastern pine sawdust obtained from Cowls Building Supply (Cowls Building Supply, Amherst, MA). Prior to experiments, the wood was ground with a rotary cutter mill to pass a 1-mm screen. The ground wood was air-dried to reduce its moisture content to less than 5 wt%. The elemental analysis of the wood feed is shown in Table 1. The ash content was determined using TGA by combustion of wood at 700 °C for 1 h. The catalyst used was a commercial spray-dried 40% ZSM-5 catalyst with an average particle size of 98 μm (Intercat. Inc.). Since the company did not disclose the composition of the catalyst except the content of ZSM-5, more detailed information on the catalyst is not possible. Typically spray-dried catalysts contain above 40 wt% zeolite, 3–15 wt% phosphorus (P_2O_5), 15–45% kaolin ($Al_2Si_2O_5(OH)_4$) and above 10 wt% alumina (Carlson et al., 2011). We expect that the spray-dried 40% ZSM-5 catalyst used in this study has similar composition to the typical spray-dried catalyst. Zeolite crystals are typically ~1 μm in diameter, so it is necessary to bind them together to make particles suitable for fluidization; one such binding technique is spray-drying. All commercial fluidized bed processes use spray-dried catalysts that contain both the zeolite and binders.

Prior to reactions, the catalyst was calcined in a muffle furnace at 580 °C for 12 h. For a typical run, 550 g of the catalyst was loaded in the reactor. Simulated recycle stream experiments were conducted with a Ga-promoted spray-dried ZSM-5 prepared by incipient-wetness impregnation. A $Ga(NO_3)_3$ solution (with an amount of 2.5 wt% Gallium with respect to the whole spray-dried ZSM-5) was slowly added via dropper to calcined ZSM-5 until it became slurry. The impregnated Ga-ZSM-5 was then dried at 110 °C overnight and calcined at 600 °C for 12 h in a muffle furnace.

2.2. CFP of pine wood in a process development unit (PDU)

A schematic of the PDU is shown in Fig. 1. The PDU consists of a fluidized bed reactor, a catalyst hopper, a catalyst inlet line, a catalyst outlet line, a biomass hopper, and a biomass inlet line. The reactor is a 4-in. outer diameter 316 stainless-steel tube with a free board height of 30 in. The top of the freeboard expands to a 6-in. outer diameter to suppress entrainment of catalyst particles in the exit gas stream. The catalyst bed was supported by a distributor made from a 316 stainless-steel wire mesh (50×250 mesh). The portion of reactor below the distributor plate served as a gas preheater. This bottom section of the reactor was loosely packed

Table 1
Elemental analysis of eastern pine wood.

Elemental analysis (wt%)[b]			
C	H	O[a]	Ash
47.2	6.4	45.9	0.5

[a] By balance.
[b] Sample contains moisture up to 5 wt%.