

Research article

Catalytic cracking of fast and tail gas reactive pyrolysis bio-oils over HZSM-5☆



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ABSTRACT

Hydrodeoxygenation (HDO) of pyrolysis oil is well understood as an upgrading method; however, the high processing pressures associated with it alone justify the exploration of alternative upgrading solutions, especially those that could adapt pyrolysis oils into the existing refinery infrastructure. Catalytic cracking is one such alternative industrial practice that can be carried out at near-atmospheric pressure using zeolite-based FCC catalysts. The present study focuses on the catalytic cracking of pyrolysis oil of different starting compositions over HZSM-5 to inform the extent of upgrading in the liquid phase. After establishing a catalyst bed temperature of 500 °C as the optimum operating condition with regard to deoxygenation and yield of mono-aromatics in the products obtained, the performances of conventional pyrolysis and tail gas reactive pyrolysis (TGRP) bio-oils as starting liquids for the cracking were compared. The results indicate that the formation of naphthalenes was favored, while the formation of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds was slightly depressed in the case of the TGRP oil. We attribute this finding to the formation of naphthalenes from BTEX molecules already found in the TGRP oil. Subsequent reuse of the catalysts showed that the cracking of TGRP bio-oil exhibited slightly greater deactivation after a third cycle, likely due to the increased formation of naphthalenes and coke which can block HZSM-5 pores. The results obtained from this study will help determine the issues that need to be addressed when developing a catalytic cracker with HZSM-5 for regular pyrolysis oil and TGRP oil.

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1. Introduction

Fast pyrolysis generates a crude liquid oil (pyrolysis oil, or bio-oil), solid biochar, and non-condensable gases [1,2]. The liquid pyrolysis oil can be catalytically upgraded to value-added chemicals and transportation fuels. Unfortunately, pyrolysis oil has a low energy density and chemical stability relative to petroleum fuels due to high oxygen content and acidity. In fact, pyrolysis oil is known to contain over 300 highly oxygenated compounds, the most prominent being acetic acid, glycolaldehyde, phenol, and levoglucosan [3,4]. Therefore, bio-oils must be deoxygenated before they can be blended with or replace crude petroleum oils. Currently, there are two main routes widely investigated for the upgrading of pyrolysis oil. One is catalytic hydrotreating, in which pyrolysis oil is treated with catalysts under high pressures of hydrogen (30–140 bar) and elevated temperatures (>300 °C). Catalytic hydrotreating in petroleum refineries removes

heteroatoms present in the crude oil, such as nitrogen (hydrodenitrogenation) and sulfur (hydrodesulphurization), while catalytic hydrotreating of pyrolysis oil removes mainly oxygen (hydrodeoxygenation) from the pyrolysis oils [5–7]. While these processes may be performed analogously with pyrolysis oil, HDO, in particular, may result in excessive and costly consumption of hydrogen. Alternatively, pyrolysis oil can be upgraded through catalytic cracking with solid acid catalysts, typically zeolites, at atmospheric pressure without hydrogen consumption [8–10], which may make catalytic cracking more economical than HDO if acceptable yields can be achieved. In fact, catalytic cracking technology has been widely used in petroleum refineries to convert high molecular weight hydrocarbons, such as vacuum gas oil, into more valuable lighter hydrocarbons including olefins, gasoline, and diesel. Due to the high content of heavy molecules, primarily pyrolytic lignin, in pyrolysis oil many efforts have been made to introduce pyrolysis oil or to co-process pyrolysis oil with heavy petroleum distillates in a catalytic cracker [8,11]. Co-processing of raw pyrolysis oils and vacuum gas oil (VGO) was performed in a demonstration-scale FCC reactor (150 kg/h), and the system generated similar product distributions as obtained from VGO cracking, such as LPG and gasoline. It was reported that about 30% of carbon in pyrolysis oils ended up in liquid products [12]. Additionally, Lindfors et al. conducted smaller scale co-processing of raw or upgraded pyrolysis oils with VGO

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in a micro activity test (MAT) unit [11]. The experiments demonstrated that coke increased with increasing pyrolysis oil concentration in the mixture, and the upgraded pyrolysis oils generated lower amounts of coke due to the lighter chemical compositions.

Zeolites have been the most active and widely used catalysts for cracking of biomass-derived feedstocks (vapors/liquids) as well as petroleum-based feedstocks. Many researchers have investigated the impacts of zeolite catalyst pore size on product yields and selectivities [8, 13] when cracking biomass-derived feedstocks. Shape selectivity of zeolites – i.e. the selective mass transfer limitations of specific compounds – is important in generating aromatic hydrocarbons from biomass-derived oxygenated compounds. For example, shape selectivity prevents large reactants from entering the pores, thus preventing the formation of high molecular weight compounds which are larger than the pore size. For this reason, the medium pore size of HZSM-5 (~6.3 Å) generates small BTEX-type compounds (benzene, toluene, ethylbenzene, xylenes; kinetic diameter of ~6.0 Å) rather than large polyaromatic compounds (kinetic diameter of 6.2 Å–6.8 Å), as compared to other zeolites [13,14]. Additionally, catalytic pyrolysis of glucose using zeolites with small pore sizes, such as ZK-5 and SAPO-34 (3.9 Å and 4.3 Å, respectively), produces high amounts of coke without any aromatic hydrocarbon formation [13]. Others have studied the catalytic cracking of pyrolysis oil model compounds over HZSM-5 to probe overall reaction pathways of pyrolysis oil cracking [10,15]. For example, carboxylic acids were proposed to undergo two reaction pathways during catalytic cracking: 1) decarboxylation to form carbon dioxide and ethane and 2) deoxygenation followed by condensation and aromatization to form water and aromatic hydrocarbons.

Highly deoxygenated, stable tail-gas reactive pyrolysis (TGRP) oil has been generated at USDA-ARS, a pyrolysis process that provides a reducing environment for pyrolysis by recycling the product gases [16, 17]. TGRP bio-oils overall possess lower average molecular weights and narrower chemical compound distributions. Therefore, based on the aforementioned HZSM-5 structural properties, we hypothesized that TGRP oils could more effectively undergo cracking for production of mono-aromatics. To compare the performance of TGRP oil with that of fast pyrolysis oil for catalytic cracking, two different pyrolysis oils having different chemical speciations were catalytically cracked using HZSM-5 (Si/Al = 30) and the elemental/chemical compositions, product yields and aromatic selectivities were compared. We also investigated the impact of catalyst bed conditions on the yield and selectivity of BTEX and naphthalenes.

2. Experimental

2.1. Pyrolysis oil production

Fast pyrolysis and TGRP of switchgrass was conducted at the Eastern Regional Research Center (ERRC) using a bubbling fluidized bed reactor

system to obtain pyrolysis oil (as described previously [18]). Briefly, 2 kg/h of ground and dried biomass feedstock was fed into the fluidized bed reactor set at 500 °C. Solid biochar particles generated during pyrolysis were collected using a cyclone. The hot vapors exiting the reactor and cyclone were condensed in a series of condensers and electrostatic precipitators (ESP). Non-condensable gases leaving the condenser system were analyzed using an online micro-GC/TCD. For the TGRP process, a fraction of the product gases was mixed with the N₂ stream and introduced into the reactor bed as the fluidizing gas [16].

2.2. Catalytic cracking

Ex-situ catalytic cracking of pyrolysis oil was performed in a catalyst bed externally coupled with a microwave heater (Milestone RotoSYNTH); Fig. 1 depicts the *ex situ* microwave arrangement. The system consists of a 300 ml quartz reaction vessel for pyrolysis oil vaporization, a quartz catalyst bed for catalytic cracking of the vapors, a series of condensers (cold water condenser and liquid nitrogen trap) for liquid collection, and a gas reservoir for non-condensable gas collection. Approximately 30 g of pyrolysis oil and 1.5 g of activated charcoal (Darco®, 20–40 mesh particle size, granular) were placed into the vessel. The charcoal acts as a microwave absorber and heat transfer medium. In the case of TGRP experiments, additional water was added to the pyrolysis oil to match the contents of the fast pyrolysis oil. To evaluate the longevity of the catalyst while cracking two pyrolysis oils, each catalyst bed was re-used without regeneration for catalytic cracking at 500 °C twice after the original experiment. Prior to catalytic cracking, the reaction system was purged with N₂ three times. The microwave power was set to 1200 W during a run (for 15 min). Experiments were performed in duplicate and the average yields are reported.

2.3. Product characterization

Liquid products were collected from the cold water condenser (CW) and liquid nitrogen traps (LN) after each run. Liquid products in the CW fraction were isolated using acetone, and then the organic phase was separated from the aqueous phase via extraction with ethyl acetate. The extraction solvent was removed by rotary evaporation (at 35 °C) to obtain the solvent-free liquid products. For the LN fraction, the liquid products were collected by decanting from the liquid nitrogen trap, due to negligible water content in the LN fraction. The CW fraction contained less volatile compounds, such as naphthalenes and phenolic compounds, while the LN fraction contained mainly volatile compounds like benzene, toluene, ethyl benzene, and xylenes (BTEX). To obtain overall liquid product yields and selectivities, concentrations in the two fractions were added while considering yields of each fraction. GC–MS analyses of the organic phases were performed on a Shimadzu GCMS QC-2010. The column used for chromatographic separation was

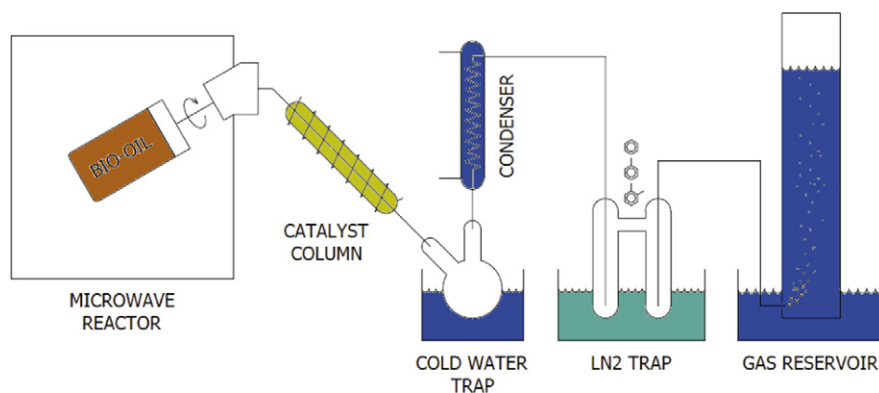


Fig. 1. Schematic diagram of microwave system with ex-situ catalytic cracking and product collection system.

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