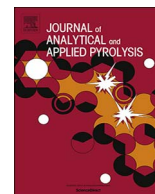




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Catalytic co-pyrolysis of switchgrass and polyethylene over HZSM-5: Catalyst deactivation and coke formation[☆]

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ABSTRACT

Conducted in the presence of a zeolite catalyst such as HZSM-5, fast pyrolysis of biomass can promote the rejection of oxygen and the formation of aromatic hydrocarbons in the organic liquid products. Unfortunately, this pathway removes hydrogen from the already hydrogen deficient biomass starting material, limiting the yield of hydrocarbons and leading to coke formation which results in catalyst deactivation. Co-pyrolysis of biomass and a low cost hydrogen rich material such as waste plastic has been considered as one strategy for mitigating hydrogen-deficiency with an added benefit of disposing of waste plastics effectively. Previous work has shown an enhancement of aromatic yields when polyolefins were coprolyzed with biomass over fresh HZSM-5, but studies on the effect of catalyst deactivation with repeated use of the catalyst are lacking. In this study, pyrolysis coupled with gas chromatography and mass spectrometry (py-GC/MS) with an external catalytic reactor was used to perform *ex situ* catalytic co-pyrolysis of switchgrass and polyethylene (1:1 w:w) in the presence of HZSM-5. The catalyst (~15 mg) was exposed to ~1 mg biomass and/or plastic in a series of 30 or 60 pulsed experiments for a cumulative feedstock to catalyst ratio of 2:1 and 4:1, respectively. Results showed that the initial rate of catalyst deactivation (up to feed:catalyst 2:1), as measured by the decrease in production of aromatic hydrocarbons, was significantly decreased, estimated at only ~28% of the rate of deactivation that processing of switchgrass alone caused. However, over the continued use of the catalyst, up to a feed to catalyst ratio of 4:1, the rates of deactivation from the blended feedstock increased to near expected rates based on the rate of deactivation for the switchgrass and HDPE individually.

1. Introduction

Over the last several years, there has been a continuous increase in interest in converting lignocellulosic biomass resources, the largest reserve of renewable carbon available [1], into fuels and chemicals that can decrease society's dependence on non-renewable petroleum based products. Biomass conversion via pyrolysis technologies has emerged among the most promising pathways for sustainable production of renewable fuels and chemicals, but conventional pyrolysis methods produce a thermally unstable oxygenated bio-oil that makes further refining to finished fuels or chemicals difficult and expensive [2].

One variation on the conventional fast pyrolysis process, is catalytic fast pyrolysis (CFP) over ZSM-5 type zeolites which produces mostly deoxygenated aromatic hydrocarbons, although only in modest yields at best [3–9]. Because biomass is hydrogen deficient, with effective H/C ratios of only 0–0.3 [10], and more hydrogen is removed during dehydration and dehydrogenation reactions that happen during CFP,

theoretical hydrocarbon yields are low and coke is an inevitable by-product [11,12]. Coke formation, in addition to reducing the potential carbon conversion to fungible liquid products, causes rapid catalyst deactivation. Although, coke can be removed by combustion, rapid coking-regeneration inevitably leads to a reduction in catalyst activity and therefore increases catalyst demand [13].

Recently, some efforts, including our own, to address conversion of biomass to more desirable compounds as well as reduce the rate of HZSM-5 deactivation have centered on pyrolysis of biomass with carbon and hydrogen rich feedstocks. Particularly, the addition of polyolefins to the pyrolysis of biomass in the presence of HZSM-5 has been shown to improve production of aromatic hydrocarbons and reduce coke formation when using fresh catalysts [14–19]. Although the utilization of waste plastics is adding fossil carbon to the final products, it is recycled fossil carbon and therefore could decrease use of newly extracted petroleum. Furthermore, an added benefit of using plastics as a co-feedstock is that it offers a method for the disposal of this waste

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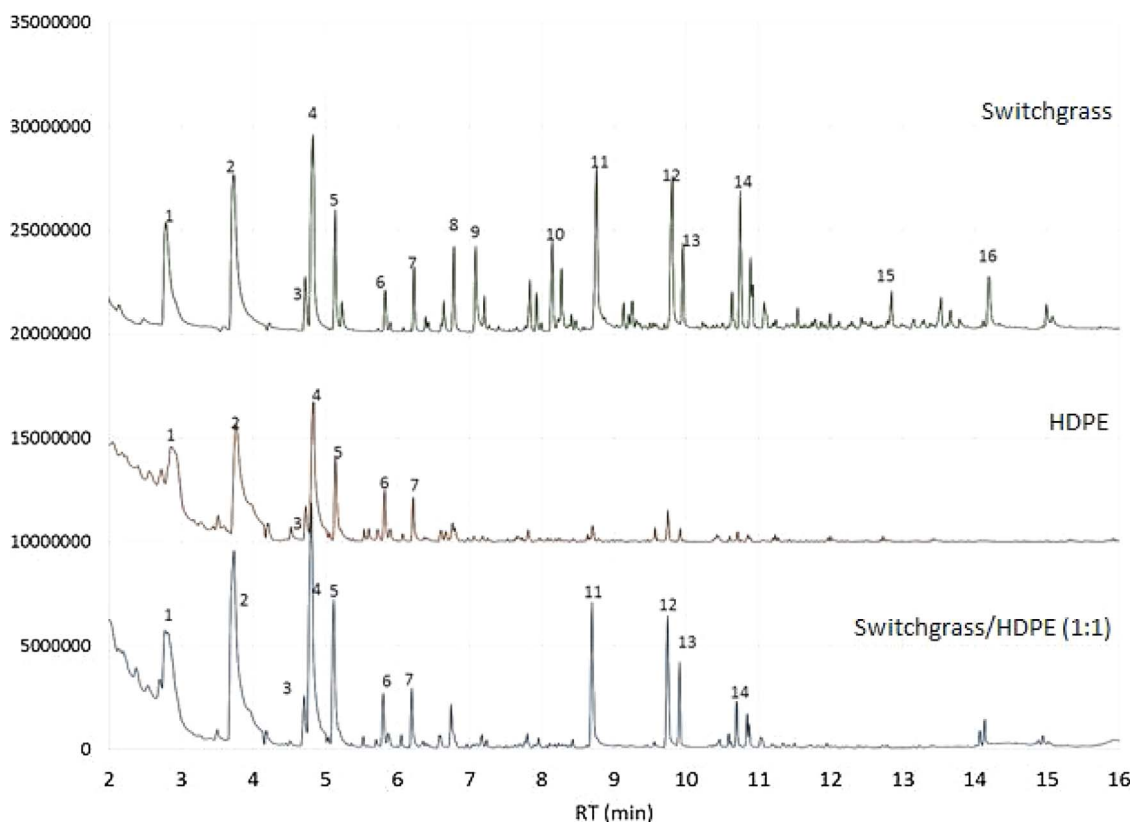


Fig. 1. Pyrograms from CFP of switchgrass (top), HDPE (middle) and a 1:1 mixture (bottom) over fresh HZSM-5. 1. Benzene, 2. Toluene, 3. Ethylbenzene, 4. *p*-xylene, 5. *o*-xylene, 6. Styrene, 7. 1,2,3-trimethylbenzene, 8. Indene, 9. Indane, 10. Methyindane, 11. Naphthalene, 12. 2-methylnaphthalene, 13. Dimethylindene, 14. 1-methylnaphthalene, 15. fluorene, 16. anthracene.

especially for plastic utilized in the production of biomass, or more specifically, agricultural plastics where traditional recycling of these materials is very limited [20].

Although work on catalytic co-pyrolysis of biomass and polyethylene have suggested reduced coke formation, the actual effects on catalyst deactivation have not been reported. Studies on the deactivation of HZSM-5 from biomass pyrolysis and its components [12,21–23] and from pyrolysis of polyethylene [24,25] have been conducted. In one study, Mukarakate et al. found HZSM-5 can be completely deactivated by exposure to vapors from biomass at biomass to catalyst ratios of only 3–4 [12]. On the other hand, a study on the catalytic pyrolysis of high density polyethylene (HDPE) found that the pores of HZSM-5 promote the flow of coke precursors outward which preserves its activity when compared to H-Beta and HY catalysts, allowing for a relatively long catalyst lifetime [25]. Previous work on the catalytic co-pyrolysis of biomass and polyethylene in the presence of HZSM-5 have mostly been limited to studies using fresh catalyst [14–19]. In this contribution, the longer term effects of biomass and polyethylene co-catalytic pyrolysis over HZSM-5 are explored, to our knowledge for the first time.

2. Material and methods

High density polyethylene (HDPE) (melt index 2.2 g/10 min (190 °C/2.16 kg) was purchased from Sigma-Aldrich and was milled using a Wiley Mill No. 1 (Arthur H. Thomas Co., Philadelphia, PA, U.S.A.) with a mesh size of 0.5 mm. Switchgrass was obtained from the McDonnell farm in East Greenville, Pennsylvania. Zeolite ammonium ZSM-5 powder (CBV 2314) was purchased from Zeolyst International and was converted to H-ZSM5 by heating the powder to 650 °C overnight.

Pyrolysis experiments were carried out in a Pyroprobe (PY) 5200

system (CDS Analytical, Oxford, PA) composed of a 5250-T Autosampler and 5250-TR 4 Zone Temperature Control External Reactor. Samples of approximately 1 mg of Switchgrass, HDPE and their mixture in a mass ratio of 1:1 (HDPE: Switchgrass) were loaded into quartz tubes 3.8 cm in length with a fire-polished tapered end. Approximately 0.3 cm of quartz wool was placed in the quartz tube followed by the sample material which was then covered with another 0.3 cm of quartz wool. The sample material was placed between the top and bottom quartz wool so that the sample material would be approximately 2.7 cm from the fire polished bottom end of the tube. A total of either 30 or 60 samples were prepared for each run. Triplicate runs were done for each total loading. The prepared quartz tubes were weighed and placed vertically in the Autosampler carousel, fire polished end down, in separate numbered slots. The quartz tubes are dropped sequentially into the pyrolysis zone, which is heated by a platinum filament coil, and pyrolyzed at 650 °C for 20 s. The 5250-TR contains a temperature controlled catalytic reactor down-stream from the pyrolysis zone. Prior to the beginning of each experiment the *ex situ* catalytic reactor is prepared by inserting a stainless steel reactor tube packed with quartz wool and HZSM-5 (1:15 switchgrass and/or HDPE: catalyst). The reactor temperature (500 °C), reactor oven temperature (300 °C) and the transfer line temperatures (300 °C) are set using a digital display on the 5250-TR. The pyrolyzer is interfaced to a HP 6890N gas chromatograph (GC) and HP 5973 mass spectrometer (Agilent Technologies). The GC analysis was performed using an RTX-1701 30 m × 0.25 mm fused silica capillary column with a 0.25 μm film thickness with the following oven program: 1 min at 40 °C then ramped at 15 °C/min up to 280 °C and held for 20 min for a total time of 37 min.

Coking on the catalyst was determined gravimetrically by taking the spent catalyst and collecting it separate from the quartz wool and placing the spent catalyst in a stainless steel cup. The spent catalyst was

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