



The effect of hydrothermal treatment of FCC catalysts and ZSM-5 additives in catalytic conversion of biomass

Ofei D. Mante^{a,*}, F.A. Agblevor^b, S.T. Oyama^{c,d}, R. McClung^e

^a Biological Systems Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, United States

^b Biological Engineering, Utah State University, Logan, UT, United States

^c Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, United States

^d Chemical Systems Engineering, The University of Tokyo, Tokyo, Japan

^e BASF Inc., Florham, NJ, United States

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ABSTRACT

Fresh fluid catalytic cracking (FCC) catalysts and ZSM-5 additives were hydrothermally treated with 100% steam at 732 °C (1350 °F) and 788 °C (1450 °F) for 4 h in a fluidized bed reactor. The catalytic pyrolysis of hybrid poplar wood with fresh and steam treated catalysts was conducted in a 50 mm bench scale bubbling fluidized bed reactor at 475 °C and a weight hourly space velocity (WHSV) of 2 h⁻¹. BET surface area measurements showed a reduction of 24% and 34% in the surface area of the FCC catalyst after steam treatment at 732 °C and 788 °C respectively. The non-phosphorus based ZSM-5 additive lost about 15% of its surface area after mild steaming at 732 °C. However, the phosphorus impregnated ZSM-5 additive was not affected at both steaming conditions. The hydrothermal treatment of the catalysts influenced the catalytic product distribution and the quality of the bio-oil. The steamed FCC catalyst produced higher organic liquid and gas yields and lower formation of coke and water. The viscosity and the density of the bio-oils produced from the steamed FCC catalyst were lower than those produced with the fresh FCC catalyst. In the case of the ZSM-5 additives, the steam treatment affected only the organic liquid and gas yields. The organic liquid yield increased and the gas yield decreased. Steaming of the ZSM-5 additive did not show any effect on the char/coke yield as was seen with the FCC catalyst due to the lower tendency of ZSM-5 to form coke. The GC analysis of the product gases suggested that steam treatment influenced the catalyst selectivity in the formation of CO, CO₂, H₂, CH₄ and C₂–C₅ hydrocarbons. The ¹³C NMR analysis of the bio-oil showed generally that steaming of the FCC catalyst increased the selectivity for the production of aromatic hydrocarbons.

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1. Introduction

Petroleum refineries in the future will be under economic pressure to consider processing readily available alternative feedstocks due to limited oil sources, soaring petroleum prices, potential instabilities in Middle-East politics and climbing demand due to the rise in industrialization and population. Catalytic pyrolysis is one of the emerging promising technologies that converts biomass into bio-oil for further processing to bio-based gasoline, diesel and jet fuel using existing infrastructure [1–11]. Catalytic pyrolysis of biomass, in contrast to conventional pyrolysis, seeks to increase the usability and compatibility of bio-oils with petroleum feedstocks by deoxygenating functionalities such as, carbohydrates, guaiacyl and syringyl groups, aldehydes, ketones and carboxylic acids into hydrocarbon fractions. In essence, catalytic pyrolysis of biomass

is analogous to fluid catalytic cracking (FCC); an important downstream process used in the petroleum refinery to convert heavy feedstocks (atmospheric gas oil (AGO) and vacuum gas oil (VGO)) into more valuable products such as naphtha, liquefied petroleum gases (LPG) and FCC gas oil.

The cracking catalyst used in the FCC process consists of crystalline Y-zeolite, matrix, and filler [12–15]. The acidic Y-zeolite with a framework of 7.4 Å pore openings is the primary active component [12,16–18]. Other types of catalyst are however used to supplement the Y-zeolite to fulfill specific product requirements and environmental regulations. Mobil's patented ZSM-5, a 10-membered sieve containing channel openings of 5.1–5.6 Å is the most widely used additive in the FCC process to increase olefins production for alkylation and boost gasoline research/motor octane number [19–25].

Extensive studies have shown that ZSM-5 and Y-zeolite based FCC catalyst are as well effective at cracking biomass derived molecules into hydrocarbon rich bio-oils and chemicals. Progress in this area of research has been reviewed in literature by

* Corresponding author. Tel.: +1 5404491980.
E-mail address: omante@vt.edu (O.D. Mante).