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Master Thesis Defense

Entitled

SELECTIVE PRODUCTION OF LEVOGLUCOSAN (LG) FROM PYROLYSIS OF DATE PITS AND ITS CATALYTIC TRANSFORMATION INTO TRANSPORTATION FUELS

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Date & Venue

Monday, 11 Dec 2023

10:00 AM

F1-0046

Abstract

Levoglucosan (LG) or (1,6-anhydro-*β*-D-glucopyranose) signifies an important sugar derivative that is produced in appreciable quantities from thermochemical and biochemical degradation of biomass. It is often regarded as an important platform chemical for the synthesis of value-added products, most notably styrene and furans. The work in this thesis entails two broad aims; to produce LG from pyrolysis of date pits; and then convert the LG into transportation fuels through a hydrodeoxygenation (HDO) reaction. The particular choice of date pits stems from its local relative abundance as a waste biomass. Aiming to further improve the yield of levoglucosan yields from pyrolysis of date pits, pre-treatment methods were carried out via washing the biomass with different concentrations of selected acids (sulfuric acid: 1 M /3M, nitric acid:1M / 3M), also well as with hot water. Chemical and elemental compositions of the five considered samples were thoroughly analyzed and characterized by a wide array of techniques such as Neutral Detergent Fiber (NDF %), ASH content and organic Matter (%) and Mineral Nutrients Profile (ppm). By utilizing Py-GC/MS system, the products distribution from pyrolysis of raw and treated date pits were obtained at a range of temperatures between 300-500 °C . Compared to the raw date pits, pyrolysis of treated date pits by 1 M H_2SO_4 acid exhibited a dramatic increase in the concentration of levoglucosan due to the profound removal of the various categories of minerals in date pits and increasing the NDF % . Results show that the highest yield of (~ 72%) was attained after pre-treatment with 1 M H_2SO_4 solution at a temperature 300 °C. A positive correlation prevails between the removal efficiency of alkali/alkaline earth metals (AAEMs) and the yield of LG. The former catalyzes ring opening reaction that results in the destruction of sugar derivatives. On the Other hand, the water pretreatment increases the yield of LG compared to the raw date pits. Outcomes demonstrated herein convey a practical method to enhance the production of commodity chemicals from waste biomass. The second part of the thesis presents a viable gaseous hydrodeoxygenation (HDO) route for Levoglucosan (LG) that leads to the formation of non-oxygenated hydrocarbon cuts that make commercial transportation fuels, namely gasoline, diesel, and jet fuels. The outlined process encompasses HDO of an evaporated stream of dissolved LG over 5% Ni-CeO_2 catalysts between 100°C–500°C. It is found that the load of the aliphatic compounds attains values between 68.1% and 75.3% across the investigated temperature window. Similarly, fractions of aromatic compounds remain within 8.1%–13.9%. Major observed aliphatic compounds include tetradecane, dodecane, octane, and decane. Alkylated benzenes appear in appreciable quantities. Governing HDO's mechanisms were mapped out by density functional theory (DFT) calculations. Utilizing a 10% load of Ni has slightly reduced the relative area of aliphatic compounds. The combined area of the oxygenated compounds remains less than 10% at all temperatures. This finding entails a profound HDO's capacity of the deployed catalyst and opens a direct venue for the effective utilization of LG in fuel production. Overall, this research underscores the utilization of lignocellulosic biomass, specifically date pits, as a valuable carbon source in the biorefinery concept.