



Short Communication

Catalytic conversion of bio-oil to oxygen-containing fuels by simultaneous reactions with 1-butanol and 1-octene over solid acids: Model compound studies and reaction pathways


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HIGHLIGHTS

- ▶ SSA was an improved catalyst for model bio-oil upgrading with olefins/alcohols.
- ▶ A reaction pathway for bio-oil upgrading with olefins/alcohols was proposed.
- ▶ The complex reaction path involves simultaneous competing reactions and equilibria.
- ▶ Olefins reduce bio-oil water content during refining.
- ▶ Oxygenated fuels containing all of the starting bio-oils original caloric content are formed.

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ABSTRACT

Upgrading bio-oil by addition reactions across olefins represents a route to refine bio-oil to combustible and stable oxygen-containing fuels. Development and application of highly active strong solid acid catalysts with good hydrothermal stability has become a key determinant for success, because bio-oil's complexity includes large amounts of water. Temperatures of 120 °C or more are needed for satisfactory kinetics. Batch upgrading of a model bio-oil (phenol/water/acetic acid/acetaldehyde/hydroxyacetone/D-glucose/2-hydroxymethylfuran) over five water-tolerant solid acid catalysts (Dowex50WX2, Amberlyst15, Amberlyst36, silica sulfuric acid (SSA) and Cs_{2.5}H_{0.5}PW₁₂O₄₀ supported on K-10 clay (Cs_{2.5}/K-10, 30 wt.%)) with 1-octene/1-butanol were studied at 120 °C/3 h. SSA, (SiO₂)₂-OSO₃H, exhibited the highest water tolerance and activity. Upgrading using olefin/1-butanol is complex, involving many simultaneous competing esterification, etherification, olefin hydration, phenol alkylation, aldol condensation, sugar dehydration etc. reactions.

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1. Introduction

Bio-oils, obtained from fast pyrolysis or liquefaction of biomass, are potential precursors of valued chemicals and renewable liquid fuels (Mohan et al., 2006; Ragauskas et al., 2006). However, serious bio-oil drawbacks include poor volatility, immiscibility with conventional fuels, low heating values, catalyst coking, significant water contents, lower storage stability, high viscosity, acidic pH values, strong odor, refusal of refineries to cofeed it with crude oil and corrosiveness (Mohan et al., 2006). These severely limit its usage as replacements or supplements for typical diesel or gas-

oline transportation fuels. Upgrading is necessary to transform bio-oil's oxygen molecules into more suitable fuels.

Numerous studies to refine bio-oil have been carried out, including zeolite cracking, hydrodeoxygenation, steam reforming, esterification and catalytic pyrolyses (Elliott, 2007; Marcelo et al., 2008; Venderbosch and Prins, 2010; Mortensen et al., 2011; Bulushev and Ross, 2011; Bridgwater, 2012; Zhang et al., 2011a; Zabeti et al., 2012). Catalytic cracking offers significant processing and economic advantages over hydrotreating, but bio-oil cracking produces extensive tars and catalyst coking. Hydrodeoxygenation can increase bio-oil's energy content and stability; however, substantial hydrogen consumption and high pressures are needed. Steam reforming of bio-oils produces syn-gas, which can be converted further into a range of fuels. However, high temperatures are needed and extensive coke deposits formed in the reactor must be gasified. Esterification can convert bio-oil's carboxylic acids,

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