



Improving carbon retention in biomass conversion by alkylation of phenolics with small oxygenates

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ABSTRACT

Alkylation of phenolics with alcohols is an efficient way to retain carbon from small oxygenates in the liquid products of pyrolysis bio-oil. In this contribution, we have investigated the alkylation of m-cresol with several alkylating agents over H-Beta zeolite. The alkylation activity follows the sequence 2-propanol > propylene > 1-propanol. In all cases, propylene is the actual alkylation agent since the alcohols dehydrate at a faster rate than the rate of alkylation. A two-stage process is proposed to convert fractions of bio-oil rich in small aldehydes and ketones together with phenolics. In the first stage, aldehydes and ketones are selectively hydrogenated to alcohols. In the second stage, the resulting alcohols alkylate the phenolic compounds and get incorporated into the upgraded liquid. To illustrate this concept, two consecutive catalyst beds have been used. The first bed contains a metal catalyst for the selective hydrogenation. Among several catalysts investigated, Cu/SiO₂ and Pt-Fe/SiO₂ were found to exhibit good selectivity to hydrogenate the aldehyde and ketone, respectively, while preserving the aromatic ring of the phenolic compound. The second bed contains an H-Beta zeolite for the alkylation stage.

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1. Introduction

Bio-oil produced by fast pyrolysis of lignocellulosic biomass has attracted considerable attention as an intermediate liquid product towards the production of fuels. However its chemical instability, high viscosity, and corrosiveness limit their processability and storage [1–4]. Among several bio-oil upgrading approaches [5–7], hydroprocessing at high pressures over metal catalysts has been the most extensively investigated [8,9]. Severe hydrotreating may result in fungible fuel components, which are desirable. However, this process fails to retain small oxygenates such as acetic acid, acetol and small aldehydes. Direct hydrodeoxygenation of these small oxygenates, which constitute a large carbon fraction of the whole bio-oil, results in production of light gases with significant losses in liquid yield. Therefore, to retain the carbon of the small oxygenates in the liquid is necessary to carry out C–C bond formation reactions to bring them to the fuel range before carrying out the hydrodeoxygenation. An attractive approach is to take advantage of the high reactivity of the oxygen functionalities before eliminating them. Based on this concept, we have investigated different catalytic strategies to enlarge the molecular weight of oxygenates, including ketonization/aldol condensation [10], transalkylation [11], and aromatization [7,12]. Therefore, when investigating this strategy

the subsequent hydrogenation step should not be considered on raw bio-oil but on the product of an initial ketonization step. One would expect that out of this step the product would be mostly ketones and some aldehydes. Accordingly, in this contribution, we will explore alkylation as an alternative path to incorporate C2 and C3 oxygenates in phenolic compounds and form C8–C13 phenolics, which subsequently can be deoxygenated to obtain drop-in fuel components, or stabilized feedstocks that can be further upgraded in a refinery.

Scheme 1 shows a simplified depiction of the process concept. Small aldehydes and ketones cannot be used directly to alkylate phenolic compounds. Therefore, as a first step, we plan to hydrogenate the aldehydes or ketones to alcohols, which are effective alkylating agents, while avoiding hydrogenating the aromatic ring of the phenolic compounds. Metal catalysts such as Ni, Ru, Pd, and Cu can be used to catalyze the hydrogenation of the short oxygenates [13,14], while acidic zeolites are highly effective for the alkylation step. Acidic catalysts such as H-Beta, HY, H-mordenite, HZSM-5, and MCM-41 have been previously used for alkylating phenol and cresol with small alcohols [15–17] and with olefins [18]. In general, large-pore zeolites, such as H-Beta and HY zeolites are more effective in alkylation of cresol and other substituted phenolics than small-pore zeolites, such as HZSM-5 [15,18]. In this study, meta-cresol together with 1-propanol, 2-propanol, propanal, and acetone have been selected as model compounds to represent phenolics and small oxygenates, respectively.

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