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Esterification of bio-oil from mallee (Eucalyptus loxophleba ssp. gratiae) leaves with a solid acid catalyst: Conversion of the cyclic ether and terpenoids into hydrocarbons

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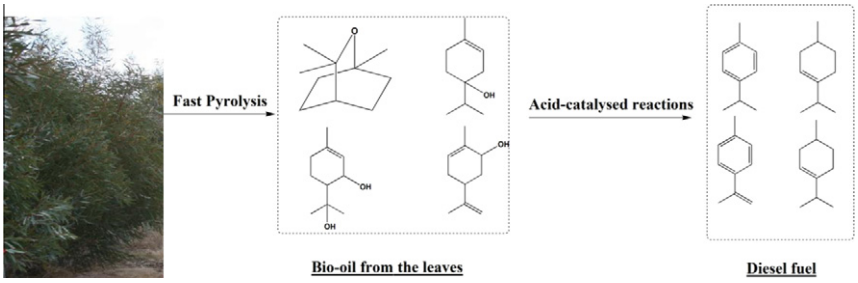
HIGHLIGHTS

- Esterification of bio-oil from eucalyptus leaves was investigated.
- N-containing organics in the bio-oil poisoned the solid acid catalyst.
- Cyclic ethers in bio-oil were converted into hydrocarbons during esterification.
- Terpenoids were converted into aromatics via dehydration, isomerisation, and aromatization.

GRAPHICAL ABSTRACT

The cyclic ethers and terpenoids, the main components in the bio-oil from the eucalyptus leaves, could be converted into the aromatics and hydrocarbons via a series of acid-catalysed steps including ring-opening, dehydration, isomerisation, and/or aromatization.



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ABSTRACT

Bio-oil from pyrolysis of mallee (Eucalyptus loxophleba ssp. gratiae) leaves differs from that obtained with wood by its content of cyclic ethers, terpenoids and N-containing organic compounds. Upgrading of the leaf bio-oil in methanol with a solid acid catalyst was investigated and it was found that the N-containing organics in the bio-oil lead to deactivation of the catalyst in the initial stage of exposure and have to be removed via employing high catalyst loading to allow the occurrence of other acid-catalysed reactions. Eucalyptol, the main cyclic ether in the bio-oil, could be converted into the aromatic hydrocarbon, *p*-cymene, through a series of intermediates including α-terpineol, terpinolene, and α-terpinene. Various steps such as ring-opening, dehydration, isomerisation, and aromatization were involved in the conversion of eucalyptol. The terpenoids in bio-oil could also be converted into aromatic hydrocarbons that can serve as starting materials for the synthesis of fine chemicals, via the similar processes.

1. Introduction

Fast pyrolysis is a promising technology to convert the solid biomass into the liquid bio-oil (Garcia-Perez et al., 2008), however, due to the corrosive effects of carboxylic acids in bio-oil (Mahfud et al., 2007; Zhang et al., 2006; Yu et al., 2011; Xiong et al., 2009; Yang et al., 2010), it has to be upgraded before its application as fuel for vehicles.

Esterification is a method to neutralize the carboxylic acids in bio-oil (Li et al., 2011a,b,c; Miao and Shanks, 2009; Lohitharn and Shanks, 2009; Tang et al., 2009; Nie et al., 2010; Zhang et al., 2010, 2011; Xu et al., 2011). The esterification of bio-oil from wood has been intensively investigated (Hilten et al., 2010; Moens et al.,

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2009; Wang et al., 2010; Li et al., 2011a,b,c). In addition to wood, leaves sometimes are an important part of woody biomass. Leaves contain less cellulose and hemicelluloses but more extractives and waxy materials (Richmond and Martin, 1959), and the presence of chlorophyll results in the formation of N-containing organics and some organics that are specially in leaf bio-oil. For example, bio-oil from mallee wood is rich in sugar derivatives while that from mallee leaves is rich in cyclic ethers (e.g. eucalyptol), terpenoids, and many extractives (King et al., 2006). Esterification of bio-oil from the fast pyrolysis of eucalyptol leaves has not previously been performed. Thus, in the present study, the effect of N-containing organics on the catalyst and the fate of the cyclic ethers and terpenoids during the esterification were studied in methanol with Amberlyst 70, a solid resin, as the catalyst.

2. Experimental section

2.1. Materials

The bio-oil used in this study was produced by fast pyrolysis of the leaves of mallee eucalypts (*Eucalyptus loxophleba* ssp. *gratiae*) in a fluidised-bed reactor at 500 °C (Garcia-Perez et al., 2008). The bio-oil separated into an upper, paste-like phase and a lower, water-like phase. The two phases were separated via centrifugation at 300 rpm for 10 min and the weight ratio between the paste-like phase and the water-like phase was 5.2:1. A detailed composition of the bio-oil is presented in Table S1 In Supporting information. The commercially available solid acid catalyst Amberlyst 70 (Rohm & Haas) was used as catalyst for esterification.

2.2. Procedures

Experiments were performed in a Hastalloy batch autoclave reactor (Autoclave Engineers, Division of Snap-Tite Inc.). Typically, the reaction mixture (methanol and bio-oil with a total mass of 96 g and a mass ratio of 1.4:1) and 5–15 wt.% Amberlyst 70 were mixed and loaded into the reactor at room temperature. The autoclave was sealed and purged with nitrogen three times and heated to the desired reaction temperatures within 24 min with a temperature-programmed controller. The stirring rate was 700 rpm for all the experiments, as no mass transfer limitations were found with stirring rates above 300 rpm in preliminary experiments. The initial pressure in the autoclave was 1 bar before heating and the final pressure depended on the reaction temperatures (around 20 bar at 170 °C). A sample was taken immediately via the sampling tube fixed inside the autoclave after the desired reaction temperature was reached and then at 15 min intervals for 120 min.

2.3. Analytical methods

The products were analysed using an Agilent GC–MS (6890 series GC plus a 5973 MS detector) with a capillary column (HP-INNO-Wax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm of crosslinked polyethylene glycol). Acetone was used to dilute the samples. One microliter of acetone solution containing ca. 15 wt.% of sample was injected into the injection port set at 250 °C with a split ratio of 50:1. The column was operated at 35 °C for 1.8 min in a constant flow mode using 2.0 mL min^{-1} of helium as carrier gas. The MS acquisition occurred without delay

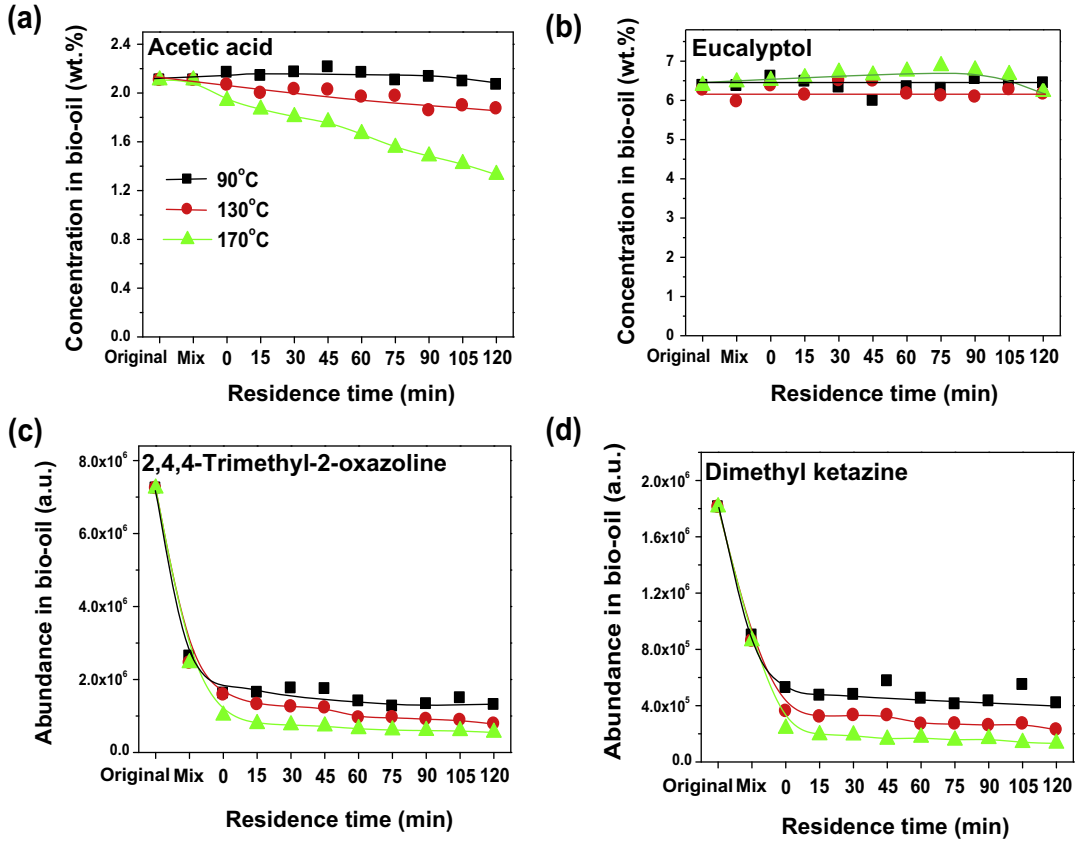

Fig. 1. Concentration of acetic acid, eucalyptol, and the N-containing organics versus the residence time and reaction temperatures. "Original" in the *x*-axis means the mixture of bio-oil with methanol at room temperature. "Mix" means the mixture of bio-oil, methanol, and Amberlyst 70 at room temperature. "0 min" means that the temperature just reached the required reaction temperatures. Experimental conditions: catalyst loading: 5 wt.%; methanol/bio-oil mass ratio: 1.4.