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# Hydrodeoxygenation of prairie cordgrass bio-oil over Ni based activated carbon synergistic catalysts combined with different metals

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**Bio-oil can be upgraded through hydrodeoxygenation (HDO). Low-cost and effective catalysts are crucial for the HDO process. In this study, four inexpensive combinations of Ni based activated carbon synergistic catalysts including Ni/AC, Ni-Fe/AC, Ni-Mo/AC and Ni-Cu/AC were evaluated for HDO of prairie cordgrass (PCG) bio-oil. The tests were carried out in the autoclave under mild operating conditions with 500 psig of $H_2$ pressure and 350°C temperature. The catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission electron microscope (TEM). The results show that all synergistic catalysts had significant improvements on the physicochemical properties (water content, pH, oxygen content, higher heating value and chemical compositions) of the upgraded PCG bio-oil. The higher heating value of the upgraded bio-oil (ranging from 29.65 MJ/kg to 31.61 MJ/kg) improved significantly in comparison with the raw bio-oil (11.33 MJ/kg), while the oxygen content reduced to only 21.70–25.88% from 68.81% of the raw bio-oil. Compared to raw bio-oil (8.78% hydrocarbons and no alkyl-phenols), the Ni/AC catalysts produced the highest content of gasoline range hydrocarbons (C6–C12) at 32.63% in the upgraded bio-oil, while Ni-Mo/AC generated the upgraded bio-oil with the highest content of gasoline blending alkyl-phenols at 38.41%.**

## Introduction

The world's energy consumption is increasing due to population growth and economic developments. More than 80% of the world primary energy consumption is derived from the utilization of depleting fossil fuels [1]. However, the massive application of fossil fuels causes many global problems such as global warming [2]. Renewable biomass, which is carbon neutral, is a reasonable and promising energy source which can reduce the world's dependence on fossil fuels [3]. Fast pyrolysis is an effective method to convert biomass to liquid bio-oil, and it is the thermochemical process in which biomass is heated to 400–600°C in the absence of air at a short vapor residence time [4,5]. However, the bio-oil produced has a high water and oxygen content. As a result, it exhibits acidic and corrosive properties and has a relatively low higher heating values compared with conventional petroleum-derived fuels, making it unusable as transport fuels [6]. Consequently, bio-oil upgrading is needed to reduce its water and oxygen content. Hydrodeoxygenation (HDO) is considered an effective method for bio-oil upgrading, and it involves the stabilization and selective removal of oxygen from untreated bio-oil through its catalytic reaction with hydrogen [6,7]. Catalysts play a critical role in bio-oil HDO, and many catalysts have been investigated. For instance, hydrodesulfurization (HDS) catalysts such as sulfided Co-Mo and Ni-Mo supported on alumina have been tested [8,9]. But the sulfided catalysts are less suitable for bio-oil HDO due to the economic factors of using sulfur, product contamination and the poor stability of alumina support (deactivation by water)

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[10]. Also, noble metal catalysts, such as Pd/C, Rh/$ZrO_2$, Pt/C, and Ru/C were used for in bio-oil upgrading studies [11–14]. However, the availability and high cost of noble metals are main challenges for their application. Recently, non-noble catalysts such as metallic Ni, Cu, Fe or their bimetallic combination supported on $Al_2O_3$ were tested, and they are very active in bio-oil HDO [15,16]. However, the problem of alumina's poor tolerance to water still existed in these tests, which can easily cause catalyst deactivation [17].

Cu can retard the catalyst deactivation caused by coking and prevent methanization of oxygen-containing compounds in bio-oil hydrodeoxygenation process [18]. Fe had a high selectivity for the formation of hydrocarbons without much aromatic ring hydrogenation in the HDO of guaiacol [19]. Mo served as an active element in the hydrodeoxygenation of bio-oil model compound (2-ethylphenol) [20], and Mo catalysts were more active supported on activated carbon (AC) than on alumina or silica due to the weak acidity [21,22].

Catalyst supports played a crucial role in dispersing and stabilizing active phases of catalysts, decreasing the cost of catalysts [23]. The alumina ($Al_2O_3$) support can partially transform into boehmite (AlO(OH)) in the presence of water [24,25]. The alumina can also oxidize active metals such as Ni to metal oxides [26], which caused catalyst deactivation [27]. In comparison, activated carbon (AC) can be utilized as a support for catalysts due to its low affinity for carbon deposition and economical features [28]. Besides, activated carbon (AC) support can provide an increasing selectivity for direct oxygen removal at low hydrogen consumption [29]. Moreover, the hydrophobic nature of activated carbon support can resist the deactivation of metal catalysts from water produced in the hydrodeoxygenation reaction [29]. Furthermore, AC could be produced from bio-char, one of the main products generated in biomass fast pyrolysis process [30]. To the best of our best knowledge, few studies have been reported to use bimetallic Ni based (Ni combined with Fe, Mo and Cu) catalysts supported on activated carbon (AC) for bio-oil hydrodeoxygenation.

Existing bio-oil hydrodeoxygenation methods suffered from serious drawbacks such as the requirement of extreme reaction conditions (high pressure ranging from 1088 to 4351 psig), which resulted in high hydrogen consumption and severe design standard of HDO reactors [31]. However, the monometallic and bimetallic Ni catalysts were found to be highly selective for oxygen removal under mild HDO conditions [32,33], which can reduce the hydrogen consumption and equipment cost.

In this study, non-precious monometallic (Ni) and bimetallic (Ni combined with Fe, Mo and Cu) catalysts supported on activated carbon were utilized for PCG bio-oil HDO process to produce upgraded biofuels under low operating pressure (500 psig). The objective of the study is to investigate the catalyst selectivity of oxygen removal at lower catalysts cost (non-noble metals), lower operating cost (low hydrogen pressure) and lower coke formation (AC support).

The PCG bio-oil upgrading experiments were conducted in the autoclave in order to identify catalytic effects of different catalysts on product yields and quality. The catalysts are evaluated with focus on their ability to reduce the oxygen content of the bio-oil, while maintaining the organic fraction yield at acceptable levels. In order to evaluate the catalysts' selectivity toward desirable gasoline range products including alkyl phenols and hydrocarbons, the composition of the organic fraction was also studied.

## Materials and methods

### Feedstock

Prairie cordgrass bio-oil was used as the feedstock, and it was produced from prairie cordgrass (PCG) pyrolysis in a fixed bed reactor at 500°C. The properties of the bio-oil are listed in Table 1. In each test, 100 g of bio-oil was added to the autoclave.

### Catalyst

The activated carbon (AC) was provided by Norit Company. The nickel (II) nitrate hexahydrate (crystalline), ammonium molybdate tetrahydrate (81–83 wt%), iron (III) nitrate nonahydrate (98 wt%), copper (II) nitrate hemi (pentahydrate) (99 wt%) were purchased from Sigma–Aldrich and used as received. The Ni/AC, Ni-Fe/AC, Ni-Mo/AC and Ni-Cu/AC catalysts were prepared by the wet impregnation method. AC powers were impregnated with aqueous solutions of a given amount of nickel (II) nitrate hexahydrate, ammonium molybdate tetrahydrate, iron (III) nitrate nonahydrate and copper (II) nitrate hemi (pentahydrate). The catalysts were dried in oven at 120°C for 4 h, and then calcined in furnace in inert nitrogen at 550°C for 5 hours. All AC catalysts were based on 6% metal content. 5 g of catalysts was used in each test.

### Apparatus

The 500 mL Parr 4575 autoclave reactor was used to carry out batch PCG bio-oil hydrodeoxygenation experiments. The reactor's allowable maximum pressure and temperature were 5000 psi and 500°C respectively. The Parr controller was used to control the vessel temperature and impeller mixing speed, and it also monitored the vessel pressure. The impeller mixing speed was set at 1000 rpm through all tests. Hydrogen was supplied from a hydrogen cylinder via a pressure regulator.

## Experiment design

### Catalyst reduction

Water and catalyst slurry was used to reduce the catalysts [34]. 5 g catalysts (6%Ni/AC, 6%Ni–6%Fe/AC, 6%Ni–6%Mo/AC and 6%Ni–6%Cu/AC) and 150 g deionized water were firstly loaded into the autoclave vessel. The vessel was then shut completely and flushed with hydrogen at 40 psig for 3 times to remove the air inside. After charging the vessel with hydrogen at 500 psig, the catalyst and water slurry was stirred at 1000 rpm, and the vessel was heated to the temperature of 350°C by a furnace at a heating rate of 5°C/min. After 3.5 hours, the heater was removed and the

**TABLE 1**

**Properties of the PCG bio-oil at 20°C**

| Properties | Data |
|---|---|
| **Water content (wt%)** | 48.91 ±1 .41 |
| **pH** | 2.41 ± 0.01 |
| **Carbon content (wt%)** | 20.01 ± 1.87 |
| **Hydrogen content (wt%)** | 10.31 ± 0.57 |
| **Nitrogen content (wt%)** | 0.87 ± 0.05 |
| **Oxygen content[a] (wt%)** | 68.81 ± 2.49 |
| **Higher heating value (MJ/kg)** | 11.33 ± 0.08 |

[a] Calculated by difference.