Upgrading of Pyrolysis Bio-oil using Nickel Phosphide Catalysts

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Abstract

Pyrolysis bio-oil is a promising source of liquid fuels, but requires upgrading to remove excess oxygen and produce a satisfactory fuel oil. Nickel phosphide has been shown to be an active composition for hydrodeoxygenation (HDO) of bio-oil model compounds. In this study, nickel phosphide catalysts were used for direct upgrading of an actual pyrolysis bio-oil derived from cedar chips. The activity of Ni_2P deposited on an amorphous SiO_2 support for HDO was first verified using the model compound, 2-methyltetrahydrofuran (2-MTHF), at the temperature of the pyrolysis oil treatment of 350 °C. The $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst showed high activity for 2-MTHF hydrodeoxygenation under atmospheric pressure hydrogen with low cracking activity.

Fast pyrolysis and catalytic upgrading were conducted sequentially using a laboratory-scale, two-stage system consisting of a fluidized bed pyrolyzer and a fluidized bed catalytic reactor both operating at 0.1 MPa, with a hydrogen partial pressure of 0.06 MPa. It was found that the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst was moderately effective in upgrading the biomass pyrolysis vapors and producing a refined bio-oil with decreased oxygen content. The deoxygenation of the bio-oil was confirmed by elemental analysis and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis. Gas chromatography-mass

spectrometry (GC-MS) analysis showed that the treated bio-oil mainly consisted of phenolic compounds, and the MS spectra before and after upgrading suggested that reactions including hydrodeoxygenation, hydrogenation, decarbonylation, and hydrolysis occurred during the upgrading. Furthermore, Ni₂P supported on ZSM-5 zeolite eliminated oxygen in the bio-oil with smaller reduction in the oil yield than Ni₂P supported on SiO₂. The deoxygenation of the nickel phosphide catalysts was higher than that of conventional catalysts such as Pd/C and an FCC-catalyst.

1. Introduction

Biomass-derived fuels have been attracting great interest because of their short CO₂ cycle, and the abundance of bioresources on earth [1], and because biofeedstocks are the only renewable energy source that can be readily converted into liquid fuels [2]. Liquid fuels are indispensable, especially in the transportation sector, because electrical energy is difficult to store and distribute. There have been many methods established to convert biomass into liquid fuels such as thermal, biological and physical processes. Fast pyrolysis is a thermal decomposition process which is conducted at moderate temperature (~ 500 °C) and short reaction time (~ 2 s) to give high yields of bio-oil [3]. Fast pyrolysis of biomass to bio-oil is one of the most efficient thermal processes to obtain liquid fuel from biomass and has already been demonstrated and semi-commercialized [4, 5].

Although fast pyrolysis is a promising method to obtain bio-oil, the high content of oxygenated molecules in pyrolysis bio-oil is a problem. The high oxygen content in bio-oil results in low heating value, immiscibility with hydrocarbon fuels, and chemical and thermal instability [6, 7]. Therefore, pyrolysis bio-oil must be upgraded to remove oxygen to obtain a satisfactory fuel oil. One promising upgrading method is hydrotreatment of bio-oil using hydrodeoxygenation (HDO) catalysts [8-10]. There have been many studies of HDO catalysts, for example, transition metal sulfides (e.g. NiMoS, CoMoS) [11], noble metals (e.g. Ru, Rh,

and Pt) [12, 13] and base metals (e.g. Fe, Ni and Cu) [14]. However, problems of deactivation or expense, in the case of the noble metals, have also been reported for these catalysts [9] [15, 16].

Transition metal phosphides of base metals have recently attracted attention as HDO catalysts [17, 18]. In particular, nickel phosphide has been shown to be a highly active catalysts for HDO of model compounds such as guaiacol [19], dibenzofuran [20], and 2-methyltetrahydrofuran (2-MTHF) [21]. Advanced methods such as EXAFS (extended X-ray absorption fine structure) have been used for structural characterization including in situ analysis during reactions [22, 23]. Many studies over nickel phosphide catalysts have been conducted to elucidate the reaction mechanism of HDO on these model compounds. Differing from these fundamental studies, in this research nickel phosphide catalysts were used for the hydrotreatment of an actual pyrolysis oil.

A two-stage reactor consisting of a pyrolyzer and a catalytic reformer is effective and practical for vapor phase upgrading [24, 25]. In this process, pyrolyzed vapor is introduced directly to the catalytic reactor and upgraded bio-oil is obtained continuously. This two-stage process is sometimes called ‘ex situ catalytic fast pyrolysis’, while catalytic fast pyrolysis conducted in one pyrolyzer that contains a catalyst is called ‘in situ catalytic fast pyrolysis’. Because the term “in situ” for catalysis studies refers to examination of catalysts in their working state, here the term “two-stage reactor” will be used for the ex situ system.

Two-stage catalytic fast pyrolysis using H-ZSM-5 zeolite has been conducted and a decrease of oxygenated compounds in the resulting bio-oil was reported, though the oil yield also decreased from 34 wt% to 27 wt% [27]. A Co doped ZSM-5 zeolite was also tested, and in this case, the oil yield decreased from 37 wt% to 17 wt%, while the oxygen content also decreased from 39 wt% to 28 wt% [28]. As described above, the catalyst studies for bio-oil synthesis via two-stage catalytic fast pyrolysis have mainly focused on zeolites or mesoporous materials, but the results obtained are not sufficient for bio-oil processing because of the limited deoxygenation activity or rapid catalyst deactivation [29-32]. Therefore, there is a need for more research on HDO catalysts.

In this study, the effectiveness of nickel phosphide catalysts for the upgrading of actual pyrolysis oil was investigated using a two-stage reactor. At first, the activity of a $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst for HDO was verified using the model compound 2-MTHF at the conditions of the pyrolysis oil treatment of 350 °C and atmospheric pressure. Then, a laboratory-scale, reactor at atmospheric pressure (hydrogen partial pressure 0.06 MPa) was used for fast pyrolysis and successive catalytic upgrading. The work here departs from conventional in that hydrogen was used in the pyrolysis reactor, rather than an inert gas, in order to make possible subsequent catalytic upgrading. The deoxygenation activity of a $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst toward pyrolysis bio-oil was investigated and compared to other metal catalysts and also acid catalysts.

2. Experimental

2.1 Materials

The presursors for $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts were provided by Japan Gas Chemical Catalysts and Chemicals Ltd. (JGCCC). The nickel content of both $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts was 1.16 mmol/g-support. The silica-alumina and FCC-catalyst were also provided by JGCCC. A ZSM-5 zeolite of Si/Al ratio 1500 (HSZ-890HOA) was obtained from the Tosoh Nikkemi Corporation and was also employed as support material for Ni_2P . The chemicals $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, 99.999%), $(\text{NH}_4)_2\text{HPO}_4$ (Sigma–Aldrich, > 99.0%), HNO_3 (TCI, 67%), and the catalyst 5 wt% Pd/C (Sigma-Aldrich) were used as received. The chemicals used as reactants were 2-methyltetrahydrofuran (Sigma–Aldrich, > 99.0%) and benzene (TCI, > 99.0%).

2.2 Catalyst preparation

The $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{ZSM-5}$, and Ni/SiO_2 catalysts were synthesized by temperature-programmed reduction (TPR) of supported precursors. The precursor of $\text{Ni}_2\text{P}/\text{ZSM-5}$ was prepared by incipient wetness impregnation and subsequent calcination. An aqueous solution for impregnation was prepared by dissolving $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. The amount of water was determined to be equal to the pore volume of the ZSM-5 ($0.18 \text{ cm}^3/\text{g}$). The nickel content was 1.16 mmol/g-support, and

the initial P/Ni molar ratio was 2, similar to those of the $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 precursors.

The extra phosphorus is needed for complete phosphidation [33, 34] and improved dispersion [35] of the catalyst. Part of the excess P is volatilized as PH_3 during reduction [36] and part remains as hydrogen phosphates on the support [37]. For example, for 10 g of ZSM-5, 3.06 g $(\text{NH}_4)_2\text{HPO}_4$ and 3.37 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 1.8 g of distilled water. A small amount of HNO_3 aqueous solution (67%) was added to the mixture until the precipitate formed in the solution was dissolved. The amount was 2.5 mL for the case of 10 g of ZSM-5. The obtained transparent green solution was used to impregnate the ZSM-5 support, which was dried at 120 °C for more than 10 h. Then, the impregnated support was dried at 120 °C for 12 h and calcined at 500 °C for 4 h. After the calcination, the precursor was pelletized and sieved to a size of 650–1180 μm .

The TPR was conducted at the same conditions for $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{ZSM-5}$ and Ni/SiO_2 catalysts. A quantity of 10 g of precursor was reduced at one time. A flow of 33 vol% H_2/N_2 at a flow rate of 0.15 L/min $\text{g}_{\text{-precursor}}$ was used, and the temperature was raised to 600 °C for $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{ZSM-5}$ and 500 °C for Ni/SiO_2 at a heating rate of 3 °C/min. The final temperature was maintained for 2 h, after which the samples were cooled to room temperature in N_2 flow. The gas was then changed to 0.5 vol% O_2/N_2 at a flow rate of 1L/min and the catalysts were passivated for 4 h.

2.3 Catalyst characterization

X-ray diffraction (XRD) analysis was conducted to determine the crystal structure of the catalysts. The diffractometer (Rigaku, RINT-2400) was operated with Cu K α monochromatized radiation generated at 40 kV and 100 mA. Scans were obtained at a speed of 2°/min with step width of 0.02° for 2θ values from 10° to 80° .

Transmission electron microscopy (TEM) images of Ni₂P/SiO₂ and Ni/SiO₂ were taken to observe the morphology of supported nanoparticles using a JEOL JEM 2000EXII microscopy at 200 kV. A carbon-coated copper grid was used as a substrate and the catalyst was dispersed in ethanol and put on the grid.

The Brunauer–Emmett–Teller (BET) specific surface area and pore volumes were calculated from isotherms of nitrogen adsorption at liquid nitrogen temperature obtained using a BELL Japan Bellsorp-mini II. Before the measurement, samples were pretreated at 200 °C in vacuum for 2 h.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-9000 instrument with a Mg K α X-ray source and a spherical section analyzer. For the measurement, the catalyst samples were ground and pelletized (diameter: 10 mm, thickness: c.a. 1 mm).

2.4 Study of catalytic activity with a model compound

Activity measurements using the model compound 2-methyltetrahydrofuran (2-MTHF) were conducted in a tubular fixed-bed reactor (quartz, inner diameter of 0.8 cm) at atmospheric pressure. For the measurements, 0.1 g of the Ni₂P/SiO₂ or Ni/SiO₂ catalyst were mixed with 0.1 g of quartz sand to make the catalyst loading section about 2 cm long in the middle of the reactor. Results are presented in Fig. S1 in the supplementary information, and will be discussed later.

Before the activity testing, the catalysts were pretreated in H₂ flow (150 cm³(NTP)min⁻¹) at 480 °C (Ni₂P/SiO₂) and at 350 °C (Ni/SiO₂) for 2 h. After the pretreatment, the temperature was fixed to 350 °C for both catalysts. A reactant solution containing 95 vol% 2-MTHF and 5 vol% benzene as an internal standard was sent to a vaporizer with a liquid pump at a flow rate of 3.0 μmol/s, vaporized there and mixed with H₂ to give a reactant stream of 3 mol% 2-MTHF in H₂. Then the mixed gas at a flow rate of 237 cm³(NTP)/min was sent to the reactor with catalyst. Products were detected by on-line gas chromatography (Shimadzu, GC-14A) with a flame ionization detector (FID) and a thermal conductivity detector (TCD) using Molecular Sieve 5A and a commercial HP-1 capillary column (100 m × 0.250 mm × 0.50 mm), respectively. The HDO activity was expressed as 2-MTHF conversion and product selectivity as described below.

Conversion

$$X_{MTHF} = \left(\frac{n_{MTHF,0} - n_{MTHF}}{n_{MTHF,0}} \right) \times 100\%$$

Product selectivity for species i

$$S_i = \left(\frac{\text{Carbon number} \times n_i}{\sum \text{Carbon number} \times n_i} \right) \times 100\%$$

$n_{MTHF,0}$ = Moles of 2- MTHF in the feed n_{MTHF} = Moles of 2- MTHF in the product

n_i = Moles of product i

2.5 Fast pyrolysis and catalytic upgrading using two-stage reactor

Cedar chips were used as biomass reactant and their characteristics are shown in Table 1.

The water content of cedar chips was determined by calculating the weight loss after drying at 110 °C for two weeks.

Table 1 Characteristics of cedar chips used in fast pyrolysis experiments

Particle diameter / mm	Elemental analysis / wt%				Water content / wt%
	C	H	N	O (diff.)	
ca. 2	46.8	6.4	0.0	46.8	9

The equipment used in these studies consisted of a laboratory-scale continuous fluidized-bed reactor (quartz, inner diameter of 26 mm) used as a pyrolyzer and a catalytic

reactor (quartz, inner diameter of 45 mm) (Fig. 1). The diameter of the catalytic reactor was chosen to be larger than that of the pyrolyzer in order to decrease the linear velocity of the gas to prevent entrainment of the catalyst in the flow. This is because pyrolysis requires short contact times compared to catalysis. The contact times will be presented below. The activity of Ni₂P/SiO₂ for the upgrading of bio-oil was studied and compared with Ni/SiO₂, Ni₂P/ZSM-5, a commercial Pd/C catalyst, a commercial FCC-catalyst, amorphous silica alumina, and commercial ZSM-5 zeolite.

The nominal contact times in the reactor system are summarized in Tables 2 and 3 below at the different conditions and with the different catalysts used in this study. The densities are apparent densities obtained from the volume and weight of material.

Table 2 Residence Time in the Pyrolysis Reactor

Sample	Density / g cm ⁻³	Contact time / s		
		450 °C	550 °C	650 °C
Sand	1.6	1.8	1.6	1.4

Table 3 Residence Time in the Catalytic Reactor

Sample	Density / g cm ⁻³	Contact time / s	
		300 °C	350 °C
SiO ₂	1.8	1.0	0.96
Ni/SiO ₂	1.4	0.79	0.73
Ni ₂ P/SiO ₂	1.3	0.74	0.68
ZSM-5	1.4	0.76	0.70
Ni ₂ P/ZSM-5	1.2	0.71	0.65
FCC	1.2	0.70	0.64
SiO ₂ -Al ₂ O ₃	1.8	1.0	0.96

Fig. 1 Diagram of the two-stage reactor for the bio-oil upgrading

The total length of the pyrolyzer was 550 mm, and a glass mesh filter located 350 mm from the top of the pyrolyzer was used to support the fluidizing sand. Silica sand (Japanese Industrial Standards (JIS) class 8, particle diameter of 50-200 μm) was used for the experiments and the amount in the pyrolyzer was approximately 50 g.

The total length of the catalytic reactor was 560 mm, and another glass mesh filter located 340 mm from the top of the reactor was used to support the catalysts. A quantity of 20 g of catalysts was normally used for the upgrading experiments, unless specified otherwise. Before the experiment, the catalysts were pretreated at 480 °C ($\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{ZSM-5}$), 350 °C (Ni/SiO_2), 150 °C (Pd/C) in hydrogen flow ($700 \text{ cm}^3(\text{NTP})\text{min}^{-1}$) for 2 h. After the pretreatment, the catalytic reactor and pyrolyzer were adjusted to the reaction temperature (300 °C or 350 °C for the catalytic reactor, and 550 °C for the pyrolyzer). The pyrolysis temperature was fixed at 550 °C in every experiment. The pyrolysis temperature was determined in separate experiments conducted in the pyrolyzer without the catalytic reformer which showed that the yield of oil was highest at that temperature (see Supporting Information, Fig. S2-S6).

The biomass sample was fed at a feed rate of 0.5 g min^{-1} with entrained nitrogen gas ($200 \text{ cm}^3(\text{NTP})\text{min}^{-1}$) from a biomass feeder which was located at the top of the pyrolyzer. Fluidizing sand was also fed from a sand feeder at the top of the pyrolyzer at a feed rate of 5 g/min with entrained nitrogen gas ($100 \text{ cm}^3(\text{NTP})\text{min}^{-1}$). Hydrogen gas ($600 \text{ cm}^3(\text{NTP})\text{min}^{-1}$) was introduced from the bottom of the pyrolyzer and was used for the fluidization of the bed.

In the pyrolyzer, the biomass was contacted with the hot fluidized sand and converted into volatile compounds and char (carbonized wood). The produced char overflowed through a

diagonal outlet at the middle of the pyrolysis reactor along with some of the fluidizing sand. Nitrogen gas ($200 \text{ cm}^3(\text{NTP})\text{min}^{-1}$) was introduced in countercurrent flow at this outlet to prevent volatile compounds from exiting. At these conditions the motion of the catalyst bed was observed from outside through the transparent wall of the reactor. The gas velocity in the catalyst bed at 350°C was 2 cm/s , which was 40 times higher than the minimum fluidization velocity which can be calculated as 0.05 cm/s at 350°C . The volatile species from the pyrolysis reactor were passed through a glass extraction thimble filter (Whatman[®], product number 2814-259, with a $0.8 \mu\text{m}$ nominal particle size retention) which was maintained at 480°C by a tape heater together with the rest of the transfer line, and introduced to the catalytic reactor. The volatile products after the upgrading were cooled in several stages first through another glass extraction thimble (110°C), then a condenser (-5°C), and finally a cold trap (-70°C). The reaction was normally continued for 60 min. These conditions are summarized in Table 4.

Table 4 Pyrolysis conditions

Biomass supply rate / g min ⁻¹	0.5
Sand supply rate / g min ⁻¹	5
Amount of sand in fluidized bed / g	50
H ₂ flow / cm ³ (NTP)min ⁻¹	600
Total N ₂ flow / cm ³ (NTP)min ⁻¹	500
Temperature in pyrolyzer / °C	550
Supply time / min	60

During reaction for 60 min (or other times), the products in each exit stage were collected separately. The organic compounds which condensed in the glass extraction thimble filter (110 °C) are hereafter denoted as refined bio-oil or simply bio-oil. They were washed out by tetrahydrofuran from the filter and purified by vacuum distillation. The organic compounds condensed in the condenser (-5 °C) and cold trap (-70 °C) are hereafter denoted as light oxygenates. The light oxygenates contained substantial water, therefore, Karl Fisher (KF) analysis was conducted for the mixture to determine the amount of water using a KF moisture titrator (Kyoto Electronics Manufacturing CO., LTD, EBU-610-KF). The effluent gases (CO, CO₂, CH₄, C₂H₂, C₂H₄ and C₂H₆) after liquid separation were analyzed with a micro GC (Agilent Technologies, 3000A). The char was collected with the fluidized sand which blew down from the pyrolyzer and its amount was calculated from the weight loss in a

thermogravimetric analysis. The coke on the catalyst was defined as the increase of catalyst weight after reaction. The yields of these products were calculated on a dry base yield considering that the water content of the cedar chips was 9.0 wt%. Note that the amount of biomass used and the amount of water produced are thus corrected by 9% in the formula.

Yield of water

$$Y_{water} = \left(\frac{W_{water} - F_{biomass} \times 0.09}{F_{biomass} \times (1 - 0.09)} \right) \times 100\%$$

Yield of products i

$$Y_i = \left(\frac{W_i}{F_{biomass} \times (1 - 0.09)} \right) \times 100\%$$

$$W_i = \text{Weight of product i} \quad F_{biomass} = \text{Weight of biomass feed}$$

The results obtained using the empty catalytic reactor (350 °C) will be described as ‘without catalyst’ or ‘without upgrading’ for both 300 °C and 350 °C. Elemental analysis (Thermo Fisher Scientific K.K, Flash2000), viscosity measurements (Cambridge viscosity, Viscolab 4000), gas chromatography-mass spectrometry (Shimadzu, QP-5000) analysis, and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS, Bruker Daltonics Inc., Solarix) analysis were conducted to evaluate the characteristics of the bio-oil. Elemental analysis was conducted to determine the proportions of carbon, hydrogen, nitrogen, and

sulfur in the bio-oil. Oxygen content was determined by difference. The viscosity of the bio-oil was measured using 2 mL of samples at room temperature.

For the GC-MS analysis, the bio-oil sample was diluted with methanol (50 $\mu\text{L/mL}$), and a 0.1 μL of the diluted sample was injected into a commercial NEUTRA ND-5 capillary column (GL Science, 0.25 mm ID $\times$ 30 m) under He gas flow (99.9999% purity, 20 mL/min). The oven temperature program for the GC consisted of an initial 50 $^{\circ}\text{C}$ for 5 min, a ramp to 250 $^{\circ}\text{C}$ at a rate of 5.0 $^{\circ}\text{C/min}$ and a constant 250 $^{\circ}\text{C}$ for 15 min. The electron ionization (EI) method was used for ionization of the compound, and a full mass spectrometry scan was acquired in the range of $m/z = 35\text{-}700$ at a rate of 0.5 sec per scan. The GC chromatographic peaks were identified by the CLASS-5000 library (Shimadzu).

For the FT-ICR MS analysis using a 9.4 T superconducting magnet, the diluted samples were prepared by mixing the bio-oil samples and ethanol (1 $\mu\text{L/mL}$). Oleic acid ($\text{C}_{18}\text{H}_{33}\text{O}_2^-$; 281.24860 Da (Monoisotopic)) was used as internal standard for adjustment of the m/z axis. Negative-ion formation of the sample was performed by the electrospray ionization (ESI) method at 4.5 kV. A 2 Megabyte data set (3.84 M points) was acquired in the range of $m/z = 100\text{-}1200$. A number of 5 scans of FT-ICR data sets were added to enhance the S/N ratio. From the obtained negative-ion FT-ICR MS spectra, the estimated composition formulas determined by the actual m/z value below ± 1.0 ppm error were listed as the expected compounds ($\text{C}_{\alpha}\text{H}_{\beta}\text{O}_{\gamma}\text{N}_{\delta}$) in the sample.

3. Results and discussion

3.1 Characterization of catalyst

Fig. 2 TEM images and particle diameter distribution of (a) $\text{Ni}_2\text{P}/\text{SiO}_2$ and (b) Ni/SiO_2

The formation of supported nanoparticles was confirmed by TEM observations for both $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts. As shown in Fig. 2, nanoparticles with average diameter 10.0 nm, and 13.3 nm were observed in $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts, respectively. The Ni/SiO_2 catalyst had a wider particle size distribution than $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst and its standard deviation was 5.9 nm, while that of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst was 3.1 nm. The particle diameter distributions shown in the bottom of Fig. 2 were obtained by counting 28 particles for both the Ni_2P and Ni catalysts.

XRD analysis after passivation was conducted to confirm the crystal structure of the catalysts (Fig. 3). In the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst, the characteristic peaks of Ni_2P at $2\theta = 40.8^\circ$, 44.6° , 47.3° , 54.2° were observed. In the Ni/SiO_2 sample, sharp peaks at 44.5° , 51.9° , 76.4° due to the diffraction by metallic Ni were observed. No other peaks were seen, which indicated that pure Ni_2P and Ni had formed in the $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts. The crystallite sizes calculated according to the Scherrer equation were 12 nm for $\text{Ni}_2\text{P}/\text{SiO}_2$, and 44 nm for Ni/SiO_2 . Furthermore, the patterns for the spent catalysts which were used in the upgrading of bio-oil at 300°C retained the same peaks as those of the fresh samples. These results indicated that the $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 maintained their crystal structures during the upgrading experiments.

Fig. 3 XRD patterns for (a) $\text{Ni}_2\text{P}/\text{SiO}_2$ and (b) Ni/SiO_2 . The blue patterns are for the fresh samples after passivation, the red patterns are for the spent catalysts which were used in bio-oil upgrading (300°C)

The results of nitrogen adsorption-desorption analysis for Ni₂P/SiO₂ and Ni/SiO₂ are shown in Table 5. After the formation of Ni₂P or Ni, the surface area and pore volume decreased because the pores of SiO₂ support were filled by the catalyst crystallites or because of some agglomeration of the SiO₂ support. The surface area and pore volume of both Ni₂P/SiO₂ and Ni/SiO₂ decreased slightly after reaction. This is likely due to coke deposition in the pores, as will be discussed later.

Table 5 Surface areas and pore volumes of Ni₂P/SiO₂ and Ni/SiO₂ catalysts before and after reaction

Sample	S _{BET} / m ² g ⁻¹		V _{tot} / cm ³ g ⁻¹	
	Before reaction	After reaction ^a	Before reaction	After reaction ^a
Ni ₂ P/SiO ₂	116	111	0.44	0.39
Ni/SiO ₂	219	178	0.68	0.55
SiO ₂	300		0.75	

^aUpgrading temperature: 300 °C

3.2 Study of catalytic activity with a model compound

The activity of Ni₂P for hydrodeoxygenation was verified using the model compound 2-MTHF. Previous work on this compound concentrated on low temperatures or higher pressures [38], so tests were conducted here at the conditions of the pyrolysis oil treatment of 350 °C at atmospheric pressure. Fig. 4 shows the product distributions for Ni₂P/SiO₂ and

Ni/SiO₂ at conversions around 50%, though the conversions gradually decreased during the reaction as shown in supporting information S1. The carbon balance was 94.2%-101% for Ni₂P catalyst, 98.4%-104% for Ni catalyst. The main product for Ni₂P/SiO₂ was *n*-pentane, (70%) followed by 2-pentanone (13%) and *n*-butane (10%) indicating that hydrodeoxygenation occurred without cracking (no lower hydrocarbons formed). In contrast to Ni₂P, methane, ethane and propane were major products for the Ni/SiO₂ catalyst, which is due to its high activity for cracking. From these results, it was confirmed that addition of phosphorous suppressed the cracking activity of Ni metal and enhanced deoxygenation activity.

Fig. 4 Product distributions on Ni₂P/SiO₂ and Ni/SiO₂ for 2-MTHF HDO (350 °C, atmospheric pressure of H₂, conversion ~ 50%)

3.3 Two-stage reactor studies: Comparison of Ni₂P/SiO₂, Ni/SiO₂ and Pd/C catalysts

Fig. 5(a) shows the product yields on a dry basis for Ni₂P/SiO₂, Ni/SiO₂ and Pd/C at 300 °C. For the Ni₂P/SiO₂ catalyst, the yield of refined bio-oil was 9.6 wt% and the yield of light oxygenates was 17.2 wt%. Water in the light oxygenate fraction was 21.0 wt%. The gases comprised 21.9 wt% CO, 9.7 wt% CO₂ and 3.9 wt% hydrocarbons. The leftover char amounted to 14.2 wt% and coke was 1.8 wt%. For the Ni/SiO₂ catalyst, the yield of refined bio-oil was 7.5 wt% and of light oxygenates was 18.9 wt%. The remaining components were 22.2 wt% water, 15.9 wt% CO, 9.6 wt% CO₂, 4.4 wt% hydrocarbons, 14.8 wt% char, and 7.6 wt% coke. When the Pd/C catalyst was used, the yield of refined bio-oil and light oxygenate was significantly decreased to 0.4 wt% and 6.3 wt%, respectively. The other components were 19.7 wt% water, 28.3 wt% CO, 9.7 wt% CO₂, 5.4 wt% hydrocarbons, 15.1 wt% char, and 13.1 wt% coke. Without catalyst, the yield of bio-oil and light oxygenate was 27.0 wt% and 19.9 wt%, respectively. The other products were formed at the yield of 17.7 wt% water, 9.9 wt% CO, 9.4 wt% CO₂, 1.9 wt% hydrocarbons, and 14.8 wt% char.

As shown in Table 6, the light oxygenates had high oxygen content of around 50 wt % and were a mixture with water. Therefore, no further analysis was conducted for the light oxygenates and the effect of the catalysts on the bio-oil product was studied.

Fig. 5 Comparison of product yield for Ni₂P/SiO₂, Ni/SiO₂ and Pd/C upgrading (0.5 g/min dry cedar chips, 20 g catalyst) at (a) 300 °C and (b) 350 °C.

Table 6 Characteristics of light oxygenate product obtained at atmospheric pressure after 60 min of the reaction (0.5 g/min dry cedar chips, 20 g catalyst)

Temperature / °C	Catalyst	Yield /wt%	Element/ wt%			
			O	C	H	N
300	Ni ₂ P/SiO ₂	17.2	49.7	43.1	5.7	1.4
	Ni/SiO ₂	18.9	48.5	42.4	7.7	1.4
	Pd/C	6.3	69.0	30.5	0.4	0.2
350	Ni ₂ P/SiO ₂	12.6	50.5	46.8	2.6	0.1
	Ni/SiO ₂	16.5	51.1	44.0	4.7	0.2
Without catalyst		19.9	48.6	46.9	4.5	0.0

The Pd/C catalyst showed high activity for gasification and almost all of the bio-oil was decomposed to gases after the upgrading. As shown in Table 7, the oxygen content in the refined bio-oil was 31.2 wt%, indicating no deoxygenation occurred compared to the bio-oil obtained without catalyst which had oxygen content of 29.7 wt%. This result is in agreement with a previous study on model compounds which reported that Pd/C had high hydrogenation activity, but its ability was poor for deoxygenation [39].

A decrease in the refined bio-oil yield and an increase in the gas yield were also observed for Ni₂P/SiO₂ and Ni/SiO₂, particularly in the CO yield for the Ni₂P/SiO₂ catalyst. On the other hand, the oxygen content decreased to 21.0 wt% and 24.2 wt% for Ni₂P/SiO₂ and Ni/SiO₂, respectively, in contrast to the case of Pd/C catalyst. The oxygen content in the

refined bio-oil obtained via $\text{Ni}_2\text{P}/\text{SiO}_2$ upgrading was lower than that via Ni/SiO_2 upgrading though the yield was slightly higher in the latter case. Therefore, it was indicated that the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst eliminated oxygen from the oil more effectively than the Ni/SiO_2 catalyst, in agreement with the results shown in the experiments using the model compound 2-MTHF. The viscosity also decreased significantly from 2400 cP to 30 cP after upgrading with $\text{Ni}_2\text{P}/\text{SiO}_2$. Furthermore, the increased production of CO gas with $\text{Ni}_2\text{P}/\text{SiO}_2$ is deemed to be a desirable result because the CO is considered as a hydrogen source through the water gas-shift (WGS) reaction, in which CO reacts with water to produce CO_2 and H_2 [40]. It should be noted that Ni is not particularly active for the WGS [41], and separate studies by our group also show that Ni_2P is minimally active. To utilize the CO in the WGS would require the addition of a component such as Fe-Cr that could carry out the transformation.

When the temperature in the catalytic reactor was raised to 350 °C, product yields and refined bio-oil properties changed as shown in Fig 5(b) and Table 7. After $\text{Ni}_2\text{P}/\text{SiO}_2$ upgrading, the yield of bio-oil decreased to 5.3 wt% and simultaneously, the oxygen content decreased to 17.9 wt%. That means that, compared to the level without catalyst of 29.7%, the Ni_2P is able to reduce the oxygen level by $(29.7-17.9)/29.7 = 40\%$. However, the yield and oxygen content of the refined bio-oil produced after Ni/SiO_2 upgrading did not greatly change even if the temperature increased. This might be because of coking on the catalyst.

Table 7 Characteristics of bio-oil product obtained at atmospheric pressure after 60 min of the reaction (0.5 g/min dry cedar chips, 20 g catalyst) Ni₂P reduces oxygen level from 29.7% to 17.9% or by 40%.

Temperature / °C	Catalyst	Yield /wt%	Element/ wt%			
			O	C	H	N
Without catalyst		27	29.7	63.3	6.9	0.1
300	Ni ₂ P/SiO ₂	9.6	21.0	71.1	7.7	0.2
	Ni/SiO ₂	7.5	24.2	68.3	7.2	0.3
	Pd/C	0.4	31.2	61.0	7.6	0.2
350	Ni ₂ P/SiO ₂	5.5	17.9	74.4	7.4	0.2
	Ni/SiO ₂	7.6	24.2	68.3	7.2	0.3

Fig. 6 shows the GC-MS charts of the bio-oil obtained with and without catalytic upgrading. In the figure, only the six peaks with the largest GC areas are labeled to reduce clutter. The GC peak area of a compound does not give direct quantitative information, however, it is considered to be a relative quantity [42]. Therefore, the compounds corresponding to the main peaks can be compared to monitor the change of the bio-oil characteristics after catalytic upgrading.

Fig. 6 GC-MS charts of bio-oils obtained via upgrading with (a) $\text{Ni}_2\text{P}/\text{SiO}_2$, (b) Ni/SiO_2 and (c) without catalyst obtained after 60 min of the reaction at 300 °C, atmospheric pressure.

As shown in Fig. 6, the bio-oil mainly consisted of phenolic compounds. Without upgrading, main phenolic compounds containing carbonyl, methoxy, or unsaturated alkyl groups were present. Similar results have been obtained in the pyrolysis of a lignin model compound [43].

After $\text{Ni}_2\text{P}/\text{SiO}_2$ upgrading, these main compounds were demethoxylated and decarbonylated. Phenolic compounds with no carbonyl or methoxy group, or with saturated alkyl groups were the major products. On the other hand, phenolic compounds with methoxy and carbonyl groups remained after Ni/SiO_2 upgrading. Similar results were obtained in the reaction of guaiacol with $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 [44].

From the difference in the GC-MS analyses before and after the upgrading with $\text{Ni}_2\text{P}/\text{SiO}_2$, it was suggested that several reactions including decarbonylation from formyl groups, hydrolysis of alkoxy groups, hydrodeoxygenation of carbonyl groups, and hydrogenation of alkenes occurred simultaneously during the upgrading. Several possible reactions are shown in Scheme 1. Reactions include decarbonylation, which forms carbon monoxide a major gaseous product, (Scheme 1a) and hydrodeoxygenation, which eliminates oxygen as water without carbon loss (Scheme 1b), hydrogenation, which increases the H-content of the product (Scheme 1c), hydrolysis, which forms alcohols (Scheme 1d), and alkylation, which forms alkyl chains on aromatic rings

(Scheme 1e). It would be interesting to calculate the equilibrium constants of the reactions to identify the ones which are most likely to occur. However, the thermodynamics alone may not be controlling, because of the kinetics of the individual transformations and possible coupling between different reactions.

From these results, it was found that the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst was effective to remove the carbonyl and methoxy groups from the phenolic compounds and to saturate the C-C double bonds in side chains, indicative of its decarbonylation, hydrodeoxygenation, and hydrogenation activity.

Scheme 1 Possible reactions in the $\text{Ni}_2\text{P}/\text{SiO}_2$ upgrading

(a) decarbonylation, (b) hydrodeoxygenation, (c) hydrogenation, (d) hydrolysis, and (e) alkylation

FT-ICR MS was used for elemental characterization of the bio-oil. The high mass accuracy enabled the determination of the exact elemental composition (e.g. $\text{C}_x\text{H}_y\text{O}_z$) of

the bio-oil compounds [45]. Therefore, whole compounds in bio-oil can be analyzed including heavier compounds that could not be analyzed by GC.

Fig. 7 shows the negative-ion FT-ICR MS broadband spectra of the bio-oils obtained via upgrading at 300 °C with (a) $\text{Ni}_2\text{P}/\text{SiO}_2$, (b) Ni/SiO_2 , and (c) without catalyst, respectively. The region of m/z shown is 100 to 1200. Spectra for both (b) Ni/SiO_2 and (c) without catalyst show a similar distribution, centered around $m/z = 300$. On the other hand, the distribution for (a) $\text{Ni}_2\text{P}/\text{SiO}_2$ was more narrow, and was centered around $m/z = 200$.

Fig. 7 Negative-ion FT-ICR MS broadband spectra of the bio-oils obtained (a) via upgrading with $\text{Ni}_2\text{P}/\text{SiO}_2$, (b) Ni/SiO_2 and (c) without catalyst obtained after 60 min of the reaction at 300 °C, atmospheric pressure.

Fig. 8 shows 3D plots of the contributions between oxygen number and carbon number based on the composition formula in the bio-oil estimated by the results of data analyses of the negative-ion FT-ICR MS spectra. The X and Y axes respectively represent the number of carbon (α) and oxygen (γ) atoms in a given compound ($C_\alpha H_\beta O_\gamma N_\delta$). The Z axis indicates the frequency of compounds which have the given carbon and oxygen numbers. The distribution of oxygen-carbon number became narrow and the average value became smaller after Ni_2P/SiO_2 upgrading. In contrast, those after Ni/SiO_2 upgrading were not greatly changed. The respective distribution of oxygen and carbon molecules in the bio-oil is shown in the supporting information (Fig. S7), indicating the change after Ni_2P upgrading clearly. These FT-ICR MS results confirm that upgrading of the bio-oil as a whole by Ni_2P/SiO_2 occurred.

(a) $\text{Ni}_2\text{P}/\text{SiO}_2$

(b) Ni/SiO_2

(c) Without catalyst

Fig. 8 Oxygen-carbon number contributions in the estimated compounds for the refined bio-oils obtained (a) via upgrading with $\text{Ni}_2\text{P}/\text{SiO}_2$, and (b) Ni/SiO_2 (c) without catalyst obtained after 60 min of the reaction at 300 °C, atmospheric pressure.

From the above results, it can be concluded that the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst had better activity for upgrading of biomass fast pyrolysis vapors than the Ni/SiO_2 catalyst. The hydrodeoxygenation activity of nickel phosphides reported in previous research over model compounds was possibly responsible for the reduction of the oxygen content in the actual bio-oils.

The effect of catalyst amount and upgrading temperature for $\text{Ni}_2\text{P}/\text{SiO}_2$ was also determined by using different catalyst amounts. Experiments with 5 g, 10 g and 20 g were conducted at 350 °C and with 10 g, 20 g, and 30 g at 300 °C.

As shown in Table 8, with increasing catalyst weight from 10 g to 30 g, the oxygen content in the bio-oil slightly decreased to from 21.9 wt% to 20.6 wt% at 300 °C. The yield of the bio-oil also decreased from 11 wt% to 5.2 wt%. The bio-oil yield decreases because of side reactions that produce light oxygenates and retrograde reactions such as cracking that form gases.

When the temperature was raised to 350 °C, the oxygen content in the bio-oil decreased with increasing catalyst amount. When the catalyst weight was increased from 5 g to 20 g, the oxygen content in the bio-oil decreased from 25.8 wt% to 17.9 wt%. The yield of the bio-oil also decreased from 12 wt% to 5.5 wt%. These results indicated that the deoxygenation activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ was enhanced at higher T.

Table 8

Effect of the upgrading temperature and Ni₂P/SiO₂ amount to the characteristics of the refined bio-oil obtained at atmospheric pressure after 60 min of the reaction

Upgrading temperature / °C	Ni ₂ P/SiO ₂ amount / g	Yield / wt%	Element / wt%			
			O	C	H	N
300	10	11	21.9	70.5	7.4	0.2
	20	9.6	21.0	71.1	7.7	0.2
	30	5.2	20.6	71.3	7.9	0.2
350	5	12.0	25.8	66.9	7.0	0.2
	10	7.7	22.3	70.3	7.2	0.3
	20	5.5	17.9	74.4	7.4	0.2

In further experiments, the reaction time was changed to determine the effect of catalyst deactivation. As shown in Table 9, the oxygen content in the bio-oil was lower at shorter reaction times while the yield also decreased. This indicates that catalyst deoxygenation activity decreased in the course of reaction and deactivation took place. The deactivation likely occurred as a result of coking on the catalyst (*vide infra*). Pyrolysis and catalytic experiment beyond 90 min were not conducted. However, trends of increasing yield and oxygen content of the bio-oil can be seen with increasing reaction times of 20, 60 and 90 min. Thus, to produce bio-oil with low oxygen content, a continuous process is likely to require catalyst regeneration capabilities.

Table 9

Effect of the reaction time to the characteristics of the refined bio-oil in upgrading
obtained at 350 °C, atmospheric pressure (20 g catalyst)

Catalyst	Reaction time / min	Yield /wt%	Element / wt%			
			O	C	H	N
Ni ₂ P/SiO ₂	20	2.3	12.9	79.4	7.5	0.2
	60	5.5	17.9	74.4	7.4	0.2
	90	9.0	18.7	73.8	7.3	0.2

The effect of support was also investigated for Ni₂P catalyst. ZSM-5 zeolite (Si/Al ratio = 1800) was employed as Ni₂P support instead of amorphous SiO₂. The Ni₂P/ZSM-5 catalyst was synthesized successfully by the temperature programmed reduction method (Details shown in the Supporting Information section).

The Ni₂P/ZSM-5 was tested at 350 °C and atmospheric pressure using 10 g and 20 g of catalyst. The reaction was conducted for 60 min. As shown in Table 10, the Ni₂P/ZSM-5 decreased the oxygen content in the bio-oil to 22.6 wt% (10 g of Ni₂P/ZSM-5) and 21.4wt% (20 g of Ni₂P/ZSM-5). The yields of the bio-oil were relatively high, 15.4 wt% and 14.3 wt%, respectively, compared to those of Ni₂P/SiO₂ which gave 7.7 wt% and 5.5 wt%, respectively (Table 8).

Table 10

Yield and elemental content of the refined bio-oil obtained via upgrading using

Ni₂P/ZSM-5, after the reaction for 60 min in 350 °C at atmospheric pressure

Catalyst	Catalyst amount / g	Yield /wt%	Element / wt%			
			O	C	H	N
Without catalyst	-	27.0	29.7	63.3	6.9	0.1
Ni ₂ P/ZSM-5	10	15.4	22.6	70.0	7.3	0.1
	20	14.3	21.4	71.1	7.3	0.1

3.4 Comparison of deoxygenation activity with other metal and acid catalysts

The catalytic activity of Ni₂P/SiO₂, Ni₂P/ZSM-5, Ni/SiO₂, SiO₂, silica-alumina, ZSM-5 zeolite, and FCC-catalyst was compared in terms of the refined bio-oil yield and the oxygen content of the bio-oil.

Fig. 9 shows the relationship between refined bio-oil yield and oxygen content obtained for each catalyst at 350 °C. Unless indicated, the catalyst amounts used were 20 g and reaction time was 60 min. For Ni₂P/SiO₂ and Ni₂P/ZSM-5, the results obtained at various experimental conditions which were described in the previous section are also shown in Fig. 9.

Other catalysts, Ni/SiO₂, SiO₂, silica-alumina, ZSM-5 zeolite, and FCC-catalyst, showed decreases in the yield of refined bio-oil, with slightly decreasing oxygen content. The use of a small amount of Ni₂P/SiO₂ (5 g at 350 °C) also showed a decrease in the bio-oil yield and a similar moderate deoxygenation performance to other metal and acid catalysts. However, when a larger amount of Ni₂P/SiO₂ catalyst was used, a noticeable decrease of oxygen content was observed. At a shorter reaction time of 20 min, the Ni₂P/SiO₂ catalyst showed significantly high levels of deoxygenation of the refined bio-oil. Furthermore, it was clear that the Ni₂P/ZSM-5 decreased the oxygen content in the bio-oil while maintaining the yield of the bio-oil. From these results, it was confirmed that nickel phosphide catalysts showed higher activity toward deoxygenation of bio-oil compared to conventional catalysts such as Ni/SiO₂, Pd/C and FCC-catalyst. The apparent shift of the yield curve to the right on going from the SiO₂ support to the ZSM-5 support may indicate that light oxygenates are coupling in the zeolite to produce more bio-oil product. The ZSM-5 by itself is seen to produce higher bio-oil yield, but with less HDO activity because of the lack of a metal function. This is consistent with reported behaviour in catalytic pyrolysis [46,47].

Fig. 9 Effect of the various catalysts on the oxygen content and yield of refined bio-oil (upgrading temperature 350 °C, 0.5 g/min dry cedar chips, and without annotation, reaction time 60 min, catalyst amount 20 g)

3.5 Catalyst characterization after the reaction

The properties of the $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts before and after reaction (upgrading temperature 300 °C, catalyst amount 20 g) were compared. Fig. 10 shows the Ni 2P XPS lines of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 before and after reaction. For $\text{Ni}_2\text{P}/\text{SiO}_2$, peaks corresponding Ni 2p_{3/2} (862.4 eV, 856.8 eV, 853.0 eV) and Ni 2p_{1/2} (883.0 eV, 876.6 eV) were observed before reaction. The peak at 856.8 eV can be assigned to Ni^{2+} and the 853.0 eV peak to $\text{Ni}^{\delta+}$ ($0 < \delta < 2$) in Ni_2P [48]. The peak of the fresh $\text{Ni}_2\text{P}/\text{SiO}_2$ at 853.0 eV which corresponds to $\text{Ni}^{\delta+}$ disappeared after reaction. This is likely because before reaction the Ni_2P on silica was passivated and during the reaction, the catalyst was reduced and covered with a protective layer of oil. For the C 1s peaks, which appeared at 284.2 eV, the elemental ratio was calculated from the peak area and the photoionization cross-sections of Si 2p and C 1s. For Ni/SiO_2 , the C/Si ratio was increased from 0.48 to 1.68 and for $\text{Ni}_2\text{P}/\text{SiO}_2$, the ratio increased from 0.50 to 1.39. These results suggest deposition of carbon on the surface of the catalysts.

Fig. 10 XPS spectra of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts before and after reaction

The weight loss in TG analysis of $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 catalysts before and after reaction is shown in Fig. 11. Compared to the fresh $\text{Ni}_2\text{P}/\text{SiO}_2$ and fresh Ni/SiO_2 samples, which showed weight increase, the spent $\text{Ni}_2\text{P}/\text{SiO}_2$ and spent Ni/SiO_2 samples showed weight losses at a temperature around 300~700 °C. The increase of the weight of the fresh samples at 400 °C~800 °C is considered to be due to the oxidation of nickel. The fresh Ni/SiO_2 catalyst showed a faster increase in weight with increasing temperature than the fresh $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst, indicating that alloy formation with P protects the Ni from oxidation. In contrast to the fresh samples, the spent samples showed weight losses which amounted to 6.7wt% for $\text{Ni}_2\text{P}/\text{SiO}_2$ and 7.1wt% for Ni/SiO_2 . These weight losses are due to carbon removal by oxidation to CO_2 and are indicative of coke deposition on the spent catalysts.

Fig. 11 Weight loss in TG analysis of Ni/SiO₂ and Ni₂P/SiO₂ catalysts before and after reaction

3.6 Perspective

Transition metal phosphides have been investigated in the hydrodeoxygenation of various oxygenated model compounds including guaiacol [19, 44], dibenzofuran [20], 2-methyltetrahydrofuran (2-MTHF) [23, 38], methyl laurate [49], phenol [50], and 4-methylphenol [51,52]. In general it is found that Ni₂P is the most active among the phosphides of Co, Fe, Mo, and W, and has higher activity than noble metals like Pd [21,

23] and sulfides like CoMoS [19]. There is good agreement between the results with the model compound 2-MTHF and the bio-oil treated in this study. However, the deoxygenation level of Ni₂P for 2-MTHF is almost 100%, while for the bio-oil it is 40% compared to the case without catalyst. This points to the difficulty of treating a real feed like bio-oil, perhaps because of strong adsorption by some of the multifunctional organic components. Raising the pressure from 0.1 MPa to a moderate 0.5 MPa has a positive effect on the HDO reaction of 2-MTHF and greatly increases the stability of the catalyst [23, 38]. This points to the use of higher pressure in the pyrolysis bio-oil upgrading steps. Alloying studies indicate that the activity in the HDO of 2-MTHF is structure-insensitive, but that selectivity is affected by the presence of neighboring atoms, and that specifically decarbonylation requires adjacent sites [53]. The high CO production on Ni₂P in this study may be due to this phenomenon. Clearly, the control of structure by particle size or by alloying is a promising means of controlling the reactivity of phosphide catalysts.

4. Conclusions

A sequential biomass pyrolysis and catalytic upgrading was carried out. The activity of Ni₂P/SiO₂ was investigated using pyrolysis oil obtained from the thermal treatment of cedar chips at atmospheric pressure. The upgrading of the pyrolysis oil over Ni₂P/SiO₂

was moderately effective for reducing the oxygen content of the bio-oil to about half the original levels. The deoxygenation of the bio-oil was confirmed by elemental analysis and Fourier transform ion cyclotron resonance mass spectrometry analysis and gas chromatography-mass spectrometry analysis, which showed that the refined bio-oil mainly consisted of phenolic compounds. Mass spectra before and after upgrading suggested that reactions including hydrodeoxygenation, hydrogenation, decarbonylation, and hydrolysis occurred during the upgrading. The effect of the $\text{Ni}_2\text{P}/\text{SiO}_2$ amount was investigated at 300 °C and 350 °C and it was found that the oxygen content in the refined bio-oil was decreased with increasing $\text{Ni}_2\text{P}/\text{SiO}_2$ amount, especially at 350 °C. The activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ toward deoxygenation of pyrolysis oil was superior to other metal (Ni/SiO_2 , Pd/C) and acid catalysts (ZSM-5 zeolite, silica-alumina, and FCC-catalyst). Deposition of coke resulted in decreased activity of the $\text{Ni}_2\text{P}/\text{SiO}_2$ with time, so that a regeneration step will likely be needed in a continuous process.

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Cedar chips $\longrightarrow$ Pyrolysis oil $\longrightarrow$ Refined bio-oil

Pyrolysis $\quad\quad\quad$ Ni_2P Catalyst