



Pt/Al₂O₃-catalytic deoxygenation for upgrading of *Leucaena leucocephala*-pyrolysis oil



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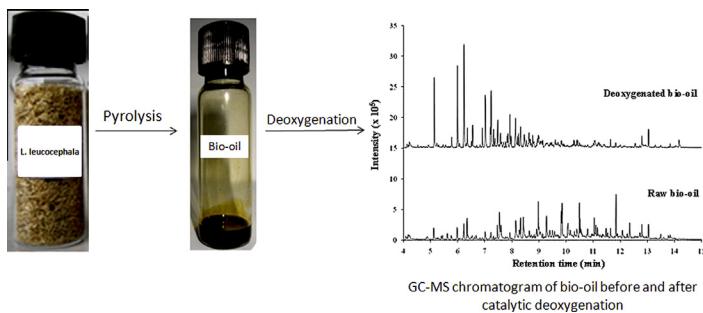
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HIGHLIGHTS

- Pt/Al₂O₃-catalytic deoxygenation could upgrade real bio-oil from biomass pyrolysis.
- O/C value of deoxygenated bio-oil from *L. leucocephala* trunks pyrolysis was 0.14.
- Phenolic compounds in bio-oils from woody biomass were difficult to be eliminated.
- Catalytic deoxygenation reduced O/C of bio-oil from microalgae pyrolysis to 0.06.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to improve the quality of bio-oil produced from the pyrolysis of *Leucaena leucocephala* trunks via catalytic deoxygenation using Pt/Al₂O₃ (Pt content = 1.32% (w/w)). The minimum molar ratio of oxygen/carbon (O/C) at 0.14 was achieved when the amount of catalyst was 10% (w/w, bio-oil) and was applied under 4 bar of initial nitrogen pressure at 340 °C for 1 h. The reaction mechanism of the catalytic deoxygenation, in terms of reforming, water–gas shift and dehydration reactions, was proposed. To consider the effect of different biomass types on the efficiency of catalytic deoxygenation, the bio-oils obtained from the pyrolysis of sawdust, rice straw and green microalgae were likewise evaluated for direct comparison.

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1. Introduction

The world's energy consumption is annually increasing due to the increase in the global population, economics and level of technologies. This induces high depletion rate of the non-renewable fossil fuels. Moreover, the use of such levels of fossil fuels leads to the release of carbon dioxide (CO₂), one of greenhouse gases, at higher volumes than can be autotrophically fixed (Bulu-

shev and Ross, 2011). For agricultural countries, the biomass of crop plants left after harvesting has high potential to be used as a sustainably renewable energy source with low cost and high production efficiency by converting the oil component to biodiesel (fatty acid alkyl esters) and the carbohydrate component to small organic compounds and especially to alcohols like ethanol or propanol, or by the direct combustion of the biomass in electricity generation and other thermal processes (Dam et al.,

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2008; Wang et al., 2010). Moreover, the utilization of such waste agricultural biomass as an alternative energy source promotes a net zero CO₂ emission and so does not directly contribute to the global warming problem. One attractive process for the transformation of biomass into alternative liquid fuels is pyrolysis, which is a simple and highly efficient thermochemical conversion process involving the degradation of solid materials as liquid and gaseous products under an oxygen-free atmosphere (Bulushev and Ross, 2011).

In this study, four different biomass feedstocks, comprised of two woody ones (*Leucaena leucocephala* (*L. leucocephala*) trunks and sawdust obtained from furniture industry) plus two non-woody sources (rice straw and green microalgae), were used for bio-oil production. Among of these four biomass types, *L. leucocephala* trunks was selected for study because it is an energetic crop with a high growth rate of both foliage and woody mass and it is also a good nitrogen fixing legume capable of growing in relatively poor soils. Thus, it is suitable for the mass-scale production for bioethanol, quality livestock fodder, paper, charcoal and firewood, amongst other uses (Al-Mefarrej et al., 2011; Feria et al., 2011). Accordingly, *L. leucocephala* has also been considered as a suitable biomass source to generate alternative liquid fuels ("bio-oil") via pyrolysis. However, the bio-oil obtained from biomass pyrolysis is normally inappropriate for direct combustion since it contains a high proportion of oxygenated compounds (35–40% (w/w)) produced from the depolymerization and fragmentation of the cellulose, hemicellulose and lignin in the biomass during pyrolysis (Yakovlev et al., 2009; Zhang et al., 2007). These compounds are found in diverse chemical forms, such as acids, alcohols, aldehydes, esters, ketones, guaiacol, syringol, phenols and their derivatives (Fisk et al., 2009; Zhao et al., 2011), precluding their simple removal. However, these oxygenated compounds impart to the bio-oil having undesired properties: high viscosity, corrosiveness, thermal instability and low heating value (Xu et al., 2009; Zhang et al., 2007).

The quality of bio-oil could be improved by catalytic deoxygenation to eliminate the oxygenated compounds in the bio-oil. The catalysts normally selected for this process consist of noble transition metals, such as Pt, Ni, NiMo, CoMo and sulfided-CoMo (CoMoS), supported on alumina (Al₂O₃) (Centeno et al., 1995; Fisk et al., 2009; Xu et al., 2009; Bu et al., 2012). The catalytic deoxygenation via the aqueous-phase reforming (APR) process has been reported to convert oxygenated hydrocarbons to hydrogen (H₂) and CO₂ using supported Pt or Ni catalysts through the cleavage of C–C bonds and C–H and/or O–H bonds (Davda et al., 2005; Fisk et al., 2009). However, most of these reports have focused on the catalytic deoxygenation of a single or a mixture of just a few oxygenated-model compounds that are normally found in the crude bio-oil, such as anisole, guaiacol, furfural and phenol (amongst others), to avoid the complexity of the diverse mixture of these oxygenated compounds in the real bio-oil (Centeno et al., 1995; Fisk et al., 2009; Yakovlev et al., 2009; Zhao et al., 2011).

Thus, the aim of this research was to improve the quality of real bio-oil samples obtained from the pyrolysis of *L. leucocephala* trunks via catalytic deoxygenation using Pt/Al₂O₃. The effect of the catalyst dosage, reaction temperature, initial nitrogen (N₂) pressure and the H₂ content in the reaction atmosphere on the product yields, molar oxygen/carbon (O/C) ratio and composition in the deoxygenated bio-oil was investigated. The amount and species of gaseous products generated during the catalytic deoxygenation were also evaluated. Furthermore, the influence of three other different biomass feedstocks, one woody (sawdust) and two non-woody (rice straw and green microalgae), on the efficiency of catalytic deoxygenation of their bio-oils was investigated

for direct comparison with the bio-oil obtained from the *L. leucocephala* trunks pyrolysis.

2. Experimental

2.1. Materials

The 99.995% trace metal of tetraamineplatinum (II) nitrate was purchased from Sigma-Aldrich, Co., Ltd. (USA). Gamma alumina (γ -Al₂O₃) powder with a diameter of 150 μ m and a BET surface area of 119 m²/g was obtained from Sumitomo Chemical, (Japan). Analytical grade tetrahydrofuran (THF) from Fisher Scientific (Leicestershire, UK) and methanol (CH₃OH) from QR&C (New Zealand) were all used as received. The 99.99% purity of N₂ and H₂ gases was manufactured by Praxair Co., Ltd. (Thailand).

2.2. Preparation and characterization of biomass feedstocks

The dried biomass obtained from the *L. leucocephala* trunks, rice straw, green microalgae (obtained from PTT Research and Technology Institute, Thailand) and sawdust was milled and sieved as a powder form with a particle size of 0.5–1.0 mm. Then, the proximate analysis of the biomass powders was evaluated following ASTM D3173–D3175 to determine the contents of moisture, volatile matter, ash and fixed carbon. The ultimate analysis was performed using a CHN analyzer (LECO CHN-2000) to detect the total carbon, hydrogen and nitrogen contents of each type of biomass powder. The oxygen content was then obtained by the calculation from the percentage difference. The gross calorific value of each biomass powder was also investigated following ASTM E711.

2.3. Bio-oil production from pyrolysis of biomass

Each dried biomass powder was pyrolyzed in a stainless steel fixed bed reactor (50 g/batch) under N₂ atmosphere at a flow rate of 0.1 L/min at 450 °C with a heating rate of 27.5 °C/min. The pyrolysis vapor was then condensed in a cool-trap unit placed in the ice bath. The obtained condensate was consisted of two fractions: a bio-oil phase and an aqueous phase. The bio-oil phase was then collected and further used as a raw material for catalytic deoxygenation. Moreover, some bio-oil trapped inside the residual char and the reactor was collected by leaching with THF. In this case, the THF in the resultant mixture was separated from the bio-oil using a rotary evaporator at 400 millibar for 20 min. All obtained bio-oil was then used as a raw material for catalytic deoxygenation.

2.4. Catalytic preparation and characterization

Platinum, supported on Pt/Al₂O₃ containing 1.32% (w/w) of Pt, was used as the catalyst for deoxygenation. This was prepared via incipient wetness impregnation by using tetraamineplatinum (II) nitrate as a precursor following the method presented elsewhere (Fisk et al., 2009). After leaving in air at room temperature for 2 h, the impregnated catalyst was then dried in a rotary evaporator at 50 millibar and 80 °C and then calcined at 500 °C for 2 h in a muffle furnace.

The surface area, pore volume and average pore size of the Pt/Al₂O₃ catalyst was measured according to the BET method by N₂ adsorption using Autosorb-1, Quantachrom with bath temperature at 77.35 K. The catalyst sample was outgassed overnight at 160 °C. The result from analysis showed that the Pt/Al₂O₃ catalyst had

113.7 m²/g of BET surface area with 87.2 Å of the average pore size and 0.248 cm³/g of the total pore volume.

The acidity of the Pt/Al₂O₃ catalyst was also determined by using ammonia temperature-programmed desorption (NH₃-TPD), performed on an AutoChem II 2920 V1.00 instrument. The catalyst sample (0.06 g) in the U-shape quartz tube of sample cell was pretreated to 250 °C at a heating rate of 10 °C/min under an argon (Ar) flow rate of 50 mL/min for 1 h. After cooling to 100 °C, NH₃ adsorption was performed for 1 h under a 1:9 (v/v) NH₃:Ar at a flow rate of 10 mL/min. The adsorbed NH₃ was physically removed by blowing Ar gas at 100 °C at a flow rate of 50 mL/min for 10 min. The temperature of a sample cell was then linearly increased to 900 °C at a heating rate of 10 °C/min under a 1:9 (v/v) NH₃:Ar stream at a flow rate of 10 mL/min. The acidity of Pt/Al₂O₃ catalyst, as calculated from the peak area of the obtained NH₃-TPD profile, was 0.376 NH₃ mmol/g, catalyst.

2.5. Catalytic deoxygenation of bio-oil

For the typical catalytic deoxygenation procedure, the bio-oil derived from the pyrolysis of the biomass powder obtained from the *L. leucocephala* trunks was selected to study the effect of the reaction parameters on the product distribution and oxygen removal efficiency. Bio-oil (20 g) containing 10–30% (w/w, bio-oil) of Pt/Al₂O₃ catalyst loading was charged into a 300 mL-high pressure reactor equipped with a glass liner. The reaction system was flushed with N₂ gas several times to ensure that the oxygen was removed. The catalytic deoxygenation of bio-oil was then initiated under 2–8 bar of initial N₂ pressure at 300–420 °C. At 2 bar of initial pressure, the effect of the partial to total replacement of N₂ with H₂ in the fed gas stream on the molar O/C ratio of the deoxygenated bio-oil was also investigated. The stirring speed and reaction time were kept constant at 400 rpm and 1 h, respectively. Once the reactor was cooled to room temperature, gaseous products generated during the catalytic deoxygenation were taken for analysis before disassembly of the reactor. The deoxygenated products, which consisted of an aqueous phase and a solid residue, were separated accordingly. The solid residue was then leached using THF to extract the trapped deoxygenated bio-oil, and the THF was then removed from the pooled THF extracts using the rotary evaporator at 65 °C and 400 millibar for 20 min to leave the deoxygenated bio-oil. The extracted solid residue was weighed and subtracted from the amount of applied Pt/Al₂O₃ catalyst to obtain the solid yield after catalytic deoxygenation. The efficiency of catalytic deoxygenation using Pt/Al₂O₃ was evaluated via monitoring the molar O/C ratio of the deoxygenated bio-oil.

2.6. Characterization of bio-oil before and after catalytic deoxygenation

The total carbon, hydrogen and nitrogen contents in the bio-oil before and after catalytic deoxygenation and the gross calorific value were examined using a similar method as that for the biomass evaluation (Section 2.2.). The overall water content generated during catalytic deoxygenation was determined as the weight of both the aqueous phase and the water trapped in the bio-oil, the latter being detected using a Karl's Fisher Titrator. The composition in the bio-oil before and after catalytic deoxygenation was identified by gas chromatography-mass spectrometry (GC-MS, Shimadzu-2010) equipped with a DB-5 column. Helium was employed as the carrier gas at a flow rate of 1.52 mL/min. All the bio-oil samples were diluted to 75 mg/mL in CH₃OH (1 mL of CH₃OH contained 75 mg of bio-oil) before analysis. Each sample (1 µL) was injected into the GC with a split ratio of 1:10. The initial oven temperature was held at

40 °C for 2 min, and then increased to 200 °C at a heating rate of 15 °C/min and held at this temperature for 8 min. The injector and detector were maintained at a constant temperature at 230 °C.

2.7. Analysis of gaseous products

The gaseous products produced during catalytic deoxygenation were examined by GC equipped with a thermal conductivity detector (TCD) and a unibeads C packed column (Shimadzu – 2014). The column temperature was heated from 50 to 180 °C and the injection temperature in the GC was kept constant at 120 °C. The composition in the gaseous product was calculated based on the exclusion of N₂.

3. Results and discussion

3.1. Characterization of biomass feedstocks and distribution of their pyrolysis products

Table 1 shows the results from the proximate and ultimate analysis, heating value and pyrolysis yields of *L. leucocephala* trunks compared to those for rice straw, green microalgae and sawdust. Based on the weight of dried biomass, the proximate analysis showed that all the dried biomass samples had a small residual amount of moisture in the level of 0.3–3.7% (w/w) with a high content of volatile matter (68–77% (w/w)). The amount of ash was highest in the green microalgae, followed by that in the rice straw (21.1% and 11.4% (w/w), respectively) compared to the low levels found in the woody biomasses of *L. leucocephala* and sawdust (1.2% and 3.2% (w/w)). The green microalgae also had the lowest fixed carbon content (10.1% (w/w)). These results for the green microalgal biomass were similar to that previously reported for *Chlorella* sp. algae with a high level of ash (9.5% (w/w)), possibly derived from the inorganic salt content (Babich et al., 2011). From the results of ultimate analysis, all four biomass samples had a high oxygen content (44–53% (w/w)), especially the rice straw, which at ca. 53% (w/w) was higher than that of other woody biomasses (Lee et al., 2005). Moreover, the nitrogen content in the green microalgae at 6.7% (w/w) was 7.4- to 22.4-fold higher than that of the other biomass feedstocks. This could be explained that algae are a relatively rich source of proteins (Babich et al., 2011; Becker, 2007; Du et al., 2011), which contain nitrogen atoms in the amino acid residues. In terms of the gross heating value of these biomass feedstocks, the two woody biomasses (*L. leucocephala* and sawdust) were 1.16- to 1.27-fold higher than that of the two non-woody biomasses (rice straw and green microalgae).

With respect to the biomass pyrolysis products, these could be classified as liquid, char and gas fractions. The liquid product was comprised of both oil and aqueous phases, with all four evaluated biomass samples yielding a broadly similar amount of oil phase (10–16% (w/w, dried biomass)). However, the molar O/C ratio of each bio-oil was 1.2- to 1.3-fold higher in the two non-woody biomasses (rice straw and green microalgae) than in the woody biomasses (*L. leucocephala* and sawdust), and was seemingly dependent on the amount of oxygen and carbon contents in the biomass powder. Moreover, the pyrolysis of green microalgae also showed the highest amount of char (1.3- to 1.5-fold), reflecting the highest ash content. It was also found that the water content in the bio-oils was depended on the O/C value. Thus, the bio-oils derived from the pyrolysis of rice straw and green microalgae with a high O/C value, and so a high polarity, contained higher amounts of water at 21.2% and 28.5% (w/w, bio-oil), respectively.

Table 1

Characterization of biomass feedstocks, yields of their pyrolysis products and molar O/C ratio including water content of the obtained bio-oils.

	<i>L. leucocephala</i> trunks	Rice straw	Algae	Sawdust
<i>Proximate analysis, % (w/w, dried biomass)</i>				
Moisture	3.7	0.3	0.5	3.4
Volatile matter	77.0	68.8	68.3	70.3
Ash	3.2	11.4	21.1	1.2
Fixed carbon	16.1	19.5	10.1	25.1
<i>Ultimate analysis, % (w/w, dried biomass)</i>				
C	46.2	40.8	40.6	49.8
H	5.8	5.2	5.7	5.6
N	0.7	0.9	6.7	0.3
O ^a	47.3	53.1	47.0	44.3
Gross heating value, MJ/kg	18.4	15.8	15.9	19.3
<i>Yield of pyrolysis products, % (w/w, dried biomass)</i>				
Oil phase	16.0	10.7	15.0	12.0
Aqueous phase	30.8	29.6	10.8	24.8
Char	33.5	38.4	61.8	48.2
Gas ^a	19.7	21.3	12.4	15.0
Molar O/C ratio of bio-oil	0.43	0.54	0.52	0.40
Water content in bio-oil, % (w/w, bio-oil)	17.3	21.2	28.5	14.4

^a Determined by difference.

3.2. Catalytic deoxygenation of bio-oil derived from pyrolysis of *L. leucocephala* trunks

Due to the high growth rate and relatively abundant availability of *L. leucocephala* as mentioned in the introduction, the bio-oil produced from the pyrolysis of *L. leucocephala* trunks was selected as a raw material for upgrading via catalytic deoxygenation using the Pt/Al₂O₃ catalyst. The univariate analysis with a center condition at a 10% (w/w, bio-oil) of Pt/Al₂O₃ catalyst loading under 2 bar of N₂ atmosphere at 340 °C for 1 h was applied to investigate the effect of reaction parameters (catalyst concentration, reaction temperature, initial N₂ pressure and the replacement level of N₂ with H₂ in the fed gas stream) on the product distribution, degree of molar O/C ratio in the deoxygenated bio-oil and gaseous composition.

3.2.1. Effect of catalyst concentration

The effect of the Pt/Al₂O₃ catalyst dosage (0–30% (w/w, bio-oil)) on the product yields derived from the catalytic deoxygenation of bio-oil and the molar O/C ratio of the obtained deoxygenated bio-oil is shown in Fig. 1 and Table 2, respectively. This reaction was carried out at 2 bar of initial N₂ pressure and 340 °C for 1 h. Without the use of catalyst, some 23.7% (w/w, bio-oil) of deoxygenated bio-oil with 0.21 of molar O/C ratio (Fig. 1a and Table 2) was obtained. Thus, the thermal process reduced the O/C value of bio-oil by ca. 50% (molar O/C ratio of raw bio-oil = 0.43). Moreover, the solid product (33.5% (w/w, bio-oil)) was also generated from the thermal-induced polymerization (Fisk et al., 2009). Increasing the catalyst dosage from 0% to 30% (w/w, bio-oil) increased the deoxygenated bio-oil content from 23.7% (w/w, bio-oil) without a catalyst up to 24.4% and 27.8% (w/w, bio-oil) at 10% and 30% (w/w, bio-oil) catalyst loading, respectively, and with a dose-dependent decrease in the molar O/C ratio (0.16–0.18). At a 20% and 30% (w/w, bio-oil) catalyst loading, the proportion of solid product decreased (1.16- and 1.29-fold, respectively), whilst the water content increased 1.2-fold at a 30% (w/w, bio-oil) catalyst loading. It is possible that the Pt-catalyst promoted the cleavage of C–O bonds in light oxygenated compounds to form hydrocarbons with water (Fisk et al., 2009) and so accordingly decreased the ability of re-polymerization of oxygenated compounds in the bio-oil to form solids.

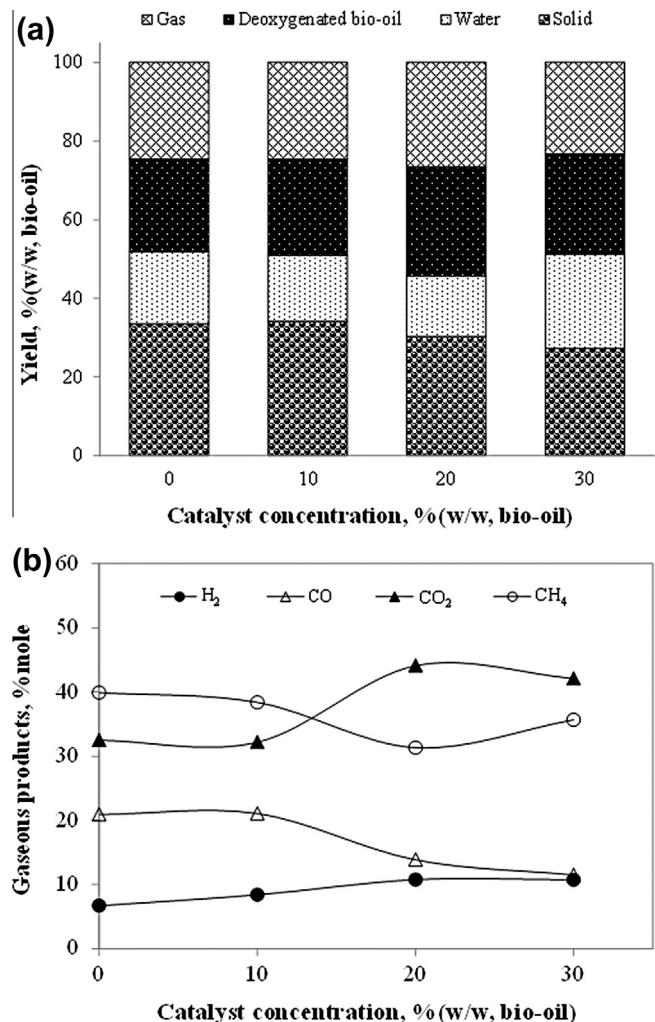


Fig. 1. Effect of the Pt/Al₂O₃ catalyst concentration on the (a) product yields and (b) gaseous products obtained from catalytic deoxygenation of the bio-oil derived from the pyrolysis of *L. leucocephala* trunks under 2 bar of initial N₂ pressure at 340 °C for 1 h.

Table 2

Effect of reaction parameters of catalytic deoxygenation on the molar O/C ratio of deoxygenated bio-oil.

Catalyst concentration % (w/w bio-oil)	Reaction temperature (°C)	Initial N ₂ pressure (bar)	Molar O/C ratio of deoxygenated bio-oil
0	340	2	0.21
10	340	2	0.18
20	340	2	0.18
30	340	2	0.16
10	300	2	0.18
10	380	2	0.16
10	420	2	0.15
10	340	4	0.14
10	340	6	0.16
10	340	8	0.14

With respect to the formation of gaseous products, increasing the catalyst loading to 30% (w/w, bio-oil) did not significantly affect the net proportion of gaseous products formed, but it did influence the composition of the gaseous pyrolysis products (Fig. 1b). Increasing the catalyst loading from 0% to 30% (w/w, bio-oil) increased the amount of H₂ (~1.7-fold) and CO₂ (1.3-fold),

but decreased the amount of carbon monoxide (CO) (~1.8-fold). This phenomenon could be explained that Pt metal of the applied catalyst had high activity to promote the cleavage of C–C bonds of organic molecules in the bio-oil ($C_xH_yO_z$) (Davda et al., 2005) to generate CO and H₂. Some of the CO fraction might be utilized by reacting with the residual water contained in the starting bio-oil (17.3% (w/w, bio-oil)) to form CO₂ and H₂ via a water-gas shift reaction. Moreover, increasing the catalyst loading enhanced the amount of CO₂ and H₂ formed by the reforming reaction of oxygenated compounds and water (Trane et al., 2012; Huber and Dumesic, 2006). Increasing the catalyst content from 20% to 30% (w/w, bio-oil) also promoted some methane (CH₄) (Fig. 1b) and water (Fig. 1a) formation, presumably by the reaction of CO or CO₂ and H₂ (Nikoo and Amin, 2011; Panagiotopoulou et al., 2008).

3.2.2. Effect of temperature

To study the effect of the reaction temperature on the degree of catalytic deoxygenation and the product yields of the bio-oil, 10% (w/w, bio-oil) Pt/Al₂O₃ catalyst loading under 2 bar of N₂ atmosphere for 1 h of reaction time was applied. With respect to the obtained product yields (Fig. 2a), the net solid, water and gaseous products generated during the catalytic deoxygenation all increased as the reaction temperature was increased from 300 to 420 °C, with a 1.13-, 1.13- and 2.1-fold increase, in the net solid, water and gaseous products, respectively. However, the deoxygenated bio-oil yield markedly decreased with increasing reaction temperature to reach a threefold reduction at 420 °C compared to that at 300 °C. It is likely that the acid sites of the γ-Al₂O₃ cooperated with the Pt to promote the polycondensation or re-polymerization of oxygenated hydrocarbons to form coke on the catalyst surface at the high reaction temperatures (Fisk et al., 2009; Sint Annaland et al., 2001) and generated water as a co-product (Venderbosch et al., 2010). Moreover, the increase in the reaction temperature from 300 to 420 °C enhanced the net gaseous products, whilst the solid and water contents leveled off at ca. 35% and 18% (w/w, bio-oil), respectively in the temperature range of 340–420 °C. Since Pt catalyst had a high efficiency for H₂ production by reforming of oxygenated compounds (Davda et al., 2005), it was possible that the H₂ generated during the catalytic deoxygenation stabilized the bio-oil and so inhibited the solid product formation (Venderbosch et al., 2010).

For the effect of the reaction temperature on the deoxygenation efficiency of the catalyst, increasing the reaction temperature from 300 to 420 °C decreased the amount of oxygenated compounds in the bio-oil in a temperature-dependent manner by decreasing the molar O/C ratio from 0.43 (untreated bio-oil) to 0.18 at 300 °C down to 0.145 at 420 °C (Table 2). Although the deoxygenated bio-oil with the lowest amount of oxygenated compounds was produced at 420 °C, the deoxygenated bio-oil yield was also decreased to 14.8% (w/w, bio-oil) under this condition. Thus, the high reaction temperature simultaneously promoted the cracking reaction and reforming of bio-oil to form gaseous products.

To compare the gaseous composition (Fig. 2b), the level of CH₄ increased with increasing the reaction temperatures almost 2.2-fold as the temperature increased up to 420 °C, whilst the amount of CO was decreased almost four-fold as the reaction temperature was increased above 340 to 420 °C. The amount of CO₂ was decreased 1.4-fold as the reaction temperature was increased above 300 to 340 °C and then remained almost constant with further increases in temperature. In contrast, the level of H₂ production was not significantly altered. Accordingly, it is likely that the higher reaction temperatures promoted the methanation of CO and CO₂. Although the methanation derived from the reaction of CO or CO₂ with H₂ is exothermic ($\Delta H_{298} = -206.2$ and -165 kJ/mol , respectively), the thermodynamic analysis indicated the positive magnitude of $\ln(K)$ vs. reaction temperature obtained

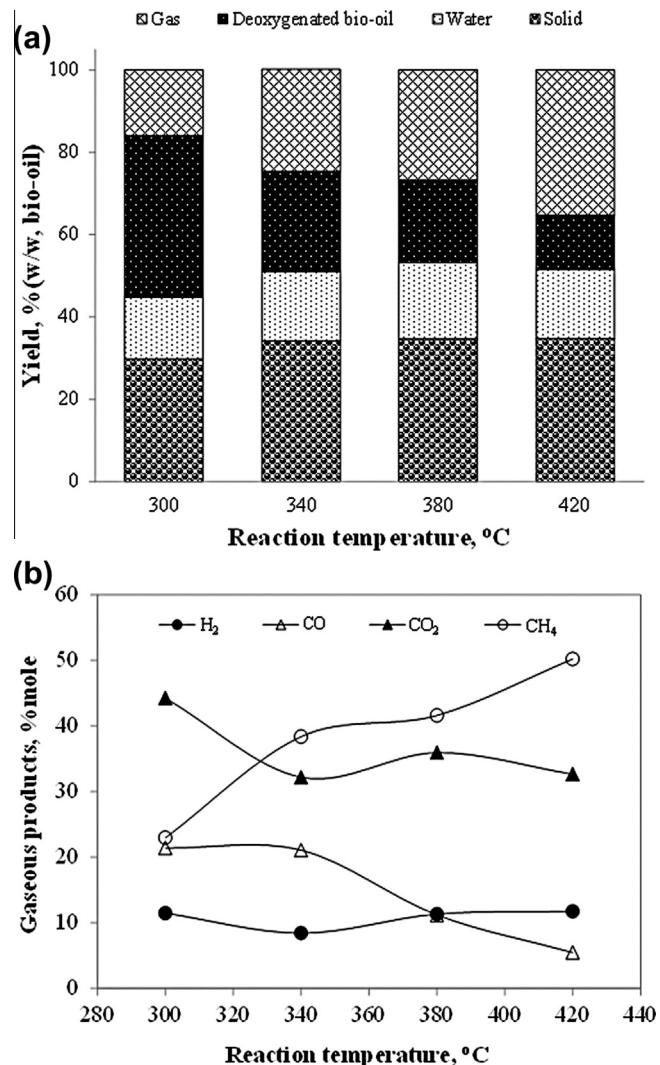


Fig. 2. Effect of the reaction temperature on the (a) product yields and (b) gaseous products obtained from the catalytic deoxygenation of the bio-oil derived from the pyrolysis of *L. leucocephala* trunks using 10% (w/w, bio-oil) of Pt/Al₂O₃ catalyst loading under 2 bar of initial N₂ pressure for 1 h.

from $K = \exp(-\Delta G_f^0/RT)$ at temperatures below 800 K (527 °C) (Nikoo and Amin, 2011).

3.2.3. Effect of initial N₂ pressure

To evaluate the effect of the initial N₂ pressure, the catalytic deoxygenation of bio-oil was performed with 10% (w/w, bio-oil) Pt/Al₂O₃ catalyst loading under an initial N₂ pressure in the range of 2–8 bar at 340 °C for 1 h. Although the increase in the initial N₂ pressure in this range did not significantly affect the yield of the obtained deoxygenated bio-oil (20–24% (w/w, bio-oil)) (Fig. 3a), it decreased the molar O/C ratio from 0.18 to 0.14 (Table 2). It was possible that the higher initial N₂ pressure facilitated the adsorption of oxygenated hydrocarbons onto the catalyst surface (Szczygiet and Szyja, 2006), which further induced the C–C and C–O cleavage and catalytic cracking of these oxygenated compounds.

With respect to the net solid, water and gas product formation levels, the solid and water contents were decreased ~1.13- and 1.2-fold, respectively, whilst the amount of gaseous products increased ~1.4-fold as the initial N₂ pressure increased from 2 to 6 bar. At 8 bar of N₂ pressure, the gaseous fraction was then decreased 1.5-fold from that at 6 bar, whilst the amount of water

and solid products were increased 1.33- and 1.13-fold, respectively. This explanation would be that the gas-generating reaction was preferred at a lower pressure and inhibited at higher pressures where condensation or re-polymerization of the bio-oil occurs to retard the gas generation as defined by the Le Chatelier principle, resulting in the higher contents of water and solid products. This phenomenon has also been observed in the pyrolysis of coal as reported by Tao et al. (2010). Although the high N₂ pressure is also likely to inhibit the cracking in the gas phase (Mayerhofer et al., 2012), as seen by the slightly reduced the amount of H₂ and CO (Fig. 3b), it was found to slightly increase the water-gas shift reaction of CO to slightly increase the amount of CO₂ (Hla et al., 2009).

3.2.4. Effect of the replacement of N₂ with H₂ in the reaction atmosphere

The effect of the partial or total replacement of N₂ atmosphere by using H₂ on the resultant product yields and molar O/C ratio of the obtained deoxygenated bio-oil is shown in Table 3. The catalytic deoxygenation of bio-oil was performed using 10% (w/w, bio-oil) Pt/Al₂O₃ catalyst loading under a total initial pressure of 2 bar at 340 °C for 1 h. Partial replacement of the N₂ atmosphere with H₂ gas did not significantly influence the amount of solid

and gas products (Table 3). Thus, the excess H₂ from the partial N₂ replacement could stabilize the bio-oil to inhibit char formation (Venderbosch et al., 2010) and suppress the generation of gaseous products. However, the total replacement of N₂ atmosphere with H₂ decreased the deoxygenated bio-oil yield 1.24-fold, whilst the water content was increased as 1.10-fold due to the effect of methanation. Considering the molar O/C ratio of the deoxygenated bio-oil, the total replacement of the N₂ atmosphere with H₂ at 2 bar decreased the molar O/C ratio from 0.18 to 0.14 possibly due to the H₂-rich atmosphere promoting the catalytic hydrogenation and hydrocracking of some oxygenated compounds in the bio-oil to form water (Fisk et al., 2009).

3.3. Effect of biomass types on catalytic deoxygenation

The product yields following pyrolysis and catalytic deoxygenation of the four different types of biomass feedstocks of *L. leucocephala* trunks, rice straw, green microalgae and sawdust, along with the molar O/C ratio of each deoxygenated bio-oil are shown in Table 4. The catalytic deoxygenation of these bio-oils was performed with 10% (w/w, bio-oil) Pt/Al₂O₃ catalyst loading under 2 bar of N₂ at 340 °C for 1 h. The deoxygenated bio-oils derived from the pyrolysis of *L. leucocephala* trunks or sawdust both showed a high content of solid products at 34.2% and 27.1% (w/w, bio-oil), respectively, as expected since they are hardwoods or woody biomasses that contain a higher amount of lignin than the non-woody biomasses of green microalgae and rice straw (Al-Mefarrij et al., 2011; Gani and Naruse, 2007; Mohan et al., 2006; Veraverbeke et al., 2007). The abundance of methoxy substituted phenolic compounds in the lignin fraction could induce polymerization to form coke or solid products on the catalyst surface (Dorrestijn and Mulder, 1999; Zhao et al., 2004).

With respect to the catalytic deoxygenation of bio-oils, those derived from the pyrolysis of these biomass feedstocks yielded deoxygenated bio-oils as 24–32% (w/w, bio-oil), but this was higher in the bio-oil derived from green microalgae and sawdust than in those derived from the rice straw or *L. leucocephala*. The molar O/C ratio of the deoxygenated bio-oil obtained from the pyrolysis of green microalgae had the lowest value (0.06, an 88.1 reduction in the molar O/C ratio), whereas those from the pyrolysis of the two woody biomasses (*L. leucocephala* and sawdust) were higher at 0.18 and 0.16, respectively. The water content in the deoxygenated bio-oil obtained from the green microalgae pyrolysis (7.5% (w/w, bio-oil)) was the lowest of the four sources, with the largest amount of gaseous products (47.5% (w/w, bio-oil)). Therefore, the main reaction pathway for removing the oxygen compounds in the bio-oil obtained from pyrolysis of the green microalgae might not obey the methanation or C–O cleavage pathways to produce water as the by-product (Fig. 2). Moreover, a white crystalline solid (2.1% (w/w, bio-oil)) appeared during the catalytic deoxygenation of bio-oil derived from the pyrolysis of the green microalgae. Elemental analysis of the white crystalline solid revealed that it consisted of a large amount of oxygen and nitrogen (64.0% and 16.3% (w/w, white solid), respectively), with 13.8% (w/w, white solid) carbon and only 5.9% (w/w, white solid) hydrogen. Thus, it was possible that the elimination of oxygenated compounds in the bio-oil obtained from pyrolysis of algae might be via the formation of nitrate substances or gaseous nitrogen oxides.

3.4. Composition of bio-oils before and after catalytic deoxygenation

The compositions of each bio-oil derived from the pyrolysis of the *L. leucocephala* trunks, sawdust, green microalgae and rice straw before and after catalytic deoxygenation were analyzed by GC–MS and then compared. Remarkably, the chromatograms of bio-oil derived from pyrolysis of the *L. leucocephala* trunks before

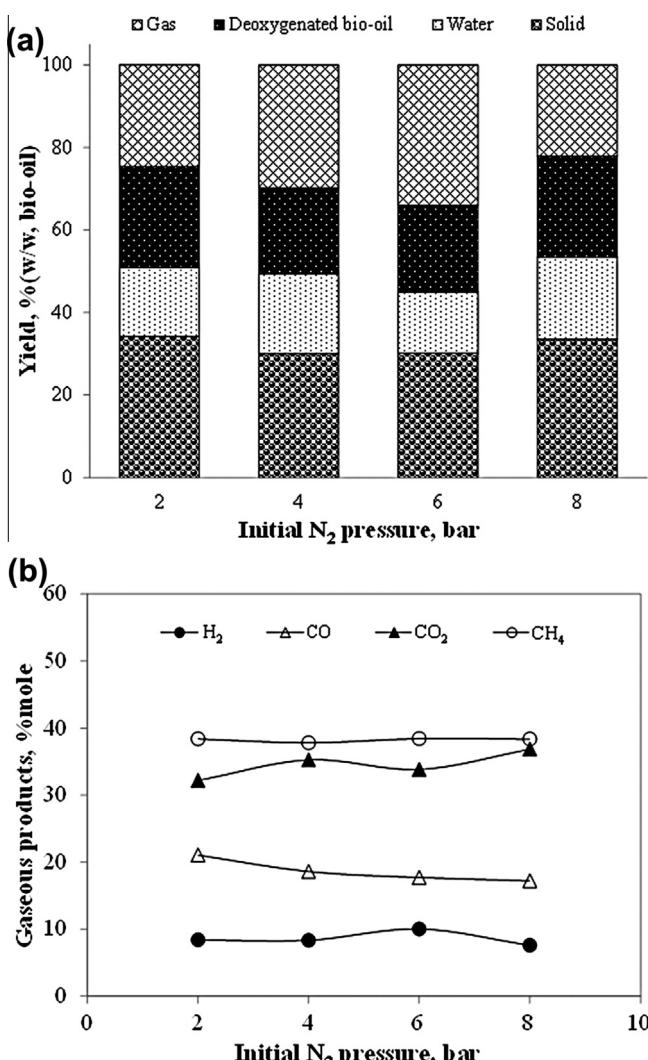


Fig. 3. Effect of the initial N₂ pressure on the (a) product yields and (b) gaseous products obtained from the catalytic deoxygenation of the bio-oil derived from the pyrolysis of *L. leucocephala* trunks using 10% (w/w, bio-oil) of Pt/Al₂O₃ catalyst loading at 340 °C for 1 h.

Table 3

Effect of the replacement of N₂ atmosphere with H₂ on yields of catalytic deoxygenation and O/C value of deoxygenated bio-oil.

% Replacement of N ₂ atmosphere with H ₂	Product yield, % (w/w bio-oil) ^a				Molar O/C ratio of deoxygenated bio-oil
	Solid	Gas	Deoxygenated bio-oil ^b	Water	
0	34.2	24.5	24.4	16.8	0.18
50	32.7	23.4	25.4	18.5	0.17
100	35.4	25.9	20.5	18.7	0.14

^a Condition: 10% (w/w, bio-oil) Pt/Al₂O₃ catalyst loading under 2 bar of initial pressure at 340 °C for 1 h.

^b Molar O/C ratio of stating bio-oil = 0.43.

Table 4

Effect of biomass types on product yields of catalytic deoxygenation and O/C value of deoxygenated bio-oils.

	Product yield, % (w/w bio-oil) ^a					Molar O/C ratio of deoxygenated bio-oil
	Solid	Deoxygenated bio-oil	Water	Gas ^b	White solid	
<i>L. leucocephala</i>	34.2	24.4	16.8	24.7	–	0.18
Sawdust	27.1	31.7	16.6	24.6	–	0.16
Rice straw	15.8	27.0	34.1	23.1	–	0.11
Algae	10.7	32.2	7.5	47.5	2.1	0.06

^a Condition: Pt/Al₂O₃ catalyst loading = 10% (w/w, bio-oil) at 340 °C for 1 h under 2 bar of N₂ atmosphere.

^b Determined by difference.

and after catalytic deoxygenation were similar to those from sawdust. Before catalytic deoxygenation, the oxygenated complexes in these bio-oils were mainly composed of methoxy phenol derivatives, acetophenone and dicarboxylic acids (ca. 9–13 min of retention time). These peaks largely disappeared or decreased in intensity after deoxygenation. The new signals attributed to small oxygenated compound molecules, such as phenol and its derivatives (2-methyl phenol, 3-methyl phenol, 2,5-dimethyl phenol and 3,4-dimethyl phenol), appeared at earlier retention times (5–8 min). This was explained by the fact that the weak phenoxy-methyl bond was possibly transformed as catechol via hydrogenolysis followed by the formation of phenol by hydrogenolysis of the aromatic C–O bonds (Centeno et al., 1995). Moreover, the coke formed on the surface of Pt/Al₂O₃ catalyst during the catalytic deoxygenation would result in the reduced catalytic efficiency to transform alkylphenols as aromatics. Indeed, it has been suggested that the elimination of these alkylphenols is the key milestone of the catalytic deoxygenation system for improving the bio-oil quality (Wang et al., 2012).

The small amount of saturated molecules, such as 2,3,3-trimethyloctane, tridecane, 3,7-dimethyldecane and 2,4,4- trimethyl hexane was found in these two deoxygenated bio-oils at 5.34, 10.3, 12.6 and 14.2 min of retention time, respectively due to the high hydrogenation activity of the Pt/Al₂O₃ catalyst (Fisk et al., 2009). Although the unsaturated compounds in the bio-oils were possibly hydrogenated, the chromatograms of deoxygenated bio-oils did not show any characteristic signals for saturated aromatic products, such as cycloalkanes. This might be due to an insufficient amount of *in situ* generated H₂ for hydrogenation and also to the complexity of the aromatic compounds presented in the bio-oil.

For the compositions of the bio-oils derived from the pyrolysis of the green microalgae and rice straw, they were different from those of the two types of woody biomass (*L. leucocephala* and sawdust). The bio-oil obtained from the pyrolysis of green microalgae showed GC–MS derived signals of various nitrogen compounds: 4-methylpentanamide (6.73 min), benzenepropanenitrile (7.92 min) and heptadecanenitrile (13.3 min) and some fatty acids: hexadecanoic acid, methyl ester and 2,4-bis [(trimethylsilyl)oxy] benzoic acid (13.5 min) including trimethylsilyl ester (11.6 min). A small amount of various phenol derivatives was also presented. After catalytic deoxygenation, new or more intense peaks from various saturated hydrocarbons: dodecane (7.56 min), pentadecane (10.3 min) and hexadecane (11.1 min) were clearly observed. After

catalytic deoxygenation, the peak intensity of carboxylic compounds: tetradecanoic acid (12.2 min) and *n*-hexadecanoic acid (13.8 min) decreased. However, the deoxygenated bio-oil obtained from the pyrolysis of rice straw showed a lower amount of phenolic compounds than that derived from *L. leucocephala* and sawdust. This could be explained that the rice straw contained the lower amount of lignin consisting of the numerous methoxyl substituted phenolic structures (Dorrestijn and Mulder, 1999).

4. Conclusions

Pt/Al₂O₃-catalytic deoxygenation could successfully reduce the oxygenated compounds in the bio-oil derived from the pyrolysis of *L. leucocephala* trunks from 0.43 molar O/C ratio to 0.14 at the selected condition. The reaction mechanism involved with the elimination of the oxygenated molecules in the bio-oil via C–C cleavage, reforming, water–gas shift and methanation reactions to form methane and water. Due to the structural complexity of woody biomass, the reduction of oxygenated compounds in the bio-oils obtained from the pyrolysis of *L. leucocephala* trunks and sawdust using Pt/Al₂O₃-catalytic deoxygenation was more difficult than that from rice straw and green microalgae.

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