

Catalytic Pyrolysis of Water Hyacinth with Rice Husk-derived Silica Modified by Vanadium

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Abstract

Water hyacinth, one of the world's worst aquatic weeds, was pyrolyzed here in a 0.5 L tubular reactor to convert it into the valuable products including bio-oil, bio-char and fuel gas. Considering on the bio-oil product, it was found that the bio-oil yield of the pyrolysis was relatively low (12.5 %wt). Therefore, the catalytic pyrolysis with vanadium-modified silica (commercial, CMV) was introduced in the study to overcome that problem. This resulted in increase of the bio-oil yield almost 2 times (24.0 %wt). In addition, in order to reduce processing cost and gain benefit from agricultural residue, silica extracted from rice husk was also used as a catalyst in the pyrolysis, compared with the commercial one. It was observed that the catalytic pyrolysis with rice husk-derived silica (modified with vanadium, RHV) gave a higher bio-oil yield than the non-catalytic pyrolysis at 400 °C, but slightly lower at 600 °C. When comparing between two catalysts, it was found that RHV gave lower bio-oil yield than CMS at all pyrolysis temperatures. The bio-char obtained from the pyrolysis without further modification was applied for benzene adsorption, and exhibited a high adsorption capability. This would add value to the pyrolysis products from water hyacinth, and evidently shows the efficient utilization of this weed.

KEYWORDS: GVL; Catalytic pyrolysis; bio-oil; modified silica

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Introduction

It is expected that oil production from fossil fuel will go into terminal decline because the largest and most productive fields are becoming depleted, while new discoveries have been progressively smaller and of lesser quality [1]. Due to this depletion, renewable energy has drawn significant attention from researchers around the world. One of the interesting renewable energy sources is biomass [2] which can be converted into fuel through a pyrolysis process to obtain biofuel (solid, liquid or gaseous fuels). Thailand as an agricultural country has many sources of biomass including agricultural residues (such as rice husk and fruit peels) and natural weeds.

Water hyacinth, one of the world's worst aquatic weeds is abundantly available in Thailand causing many serious problems to people. Those problems include choking lakes, dams and irrigation channels, increasing water loss by evaporation, degrading water quality and so on [3]. The usual

control method for water hyacinth is mechanical removal from its sources and leaving it useless. Therefore, converting the removed water hyacinth into value materials such as bio-fuel is of interest [4 – 6]. However, it has been known that the bio-oil from biomass have the main drawback of relatively high acidity with pH around 2 – 3. The acidity of bio-oil could cause corrosion in engines if used as fuel thus restricting its practical application.

In general, the acidity results from different classes of oxygenated organic compounds consisted in bio-oil [7], including carboxylic acid compounds and carbonyl compounds. Deoxygenation by cracking or dehydrating the oxygenated organic compounds into the small molecules may reduce the acidity in bio-oil [8]. These reactions may be enhanced on the solid surface with acid active sites. Therefore, some catalysts with available acid sites were introduced into pyrolysis (catalytic pyrolysis) to attain the lower acidity of bio-oil. In addition, some catalysts also increased bio-oil yield by further converting the biomass into

hydrocarbon compounds (including carbon from the biomass) [9].

Various types of catalysts have been used in catalytic pyrolysis [10], including ZSM-5 [11], FCC [12], HZSM-5 [13], Y-zeolite [14] and Ca(OH)₂ [15]. For silica (SiO₂), although it has chemically inert properties, it is still used as catalyst support, or is modified with some other ingredients to achieve specific catalytic properties. In addition, silica is abundant and cheap, and can be produced from agricultural residues such as rice husk.

Therefore, in this study, the catalytic pyrolysis of water hyacinth was investigated. Two types of silica including commercial silica and rice-husk derived silica were used as a catalyst in the pyrolysis. In addition, both types of silica were modified with vanadium (V) to enhance their catalytic performance due to vanadium having been proven as an active catalyst or modifier catalyst in many works previously [16 – 18], including our work [19] which used vanadium-modified rice husk silica for the catalytic pyrolysis of Para rubber seeds and found success in production of low acidic bio-oil. The qualities of the obtained bio-oil i.e. acidity and heating values were observed. In addition, the obtained bio-char from the pyrolysis was used for benzene removal in order to add value to another pyrolysis product from water hyacinth, besides the bio-oil.

Materials and Methods

Materials

Water hyacinth was collected from local water sources in Nakhon Pathom, Thailand. Proximate analysis result of water hyacinth is shown in Table 1. Hydrochloric acid (HCl, 37%) was purchased from RCI Limited, New Zealand. Ammonium metavanadate (NH₄VO₃, 99.5%), sodium hydroxide (NaOH, 97%), silica (SiO₂, 98%) were purchased from Ajax finechem, Australia.

Table 1 Proximate analysis of water hyacinth.

Material	Moisture	Volatile matter	Ash	Fixed carbon
Water hyacinth	16.12	15.27	66.50	2.11

Preparation of silica

Two types of silica were used in the study. The first one was commercial silica. The second was rice husk-derived silica which was prepared with methods as follows. It was started with soaking the raw rice husk into the water for 2 days, filtered and then soaked in the solution of

hydrochloric at 80 °C for 1 h. The soaked rice husk was washed, neutralized and dried overnight in the oven. The prepared rice husk was then calcined under atmosphere at 700 °C for 5 h to obtain the powder-like ash which was silica.

Preparation of catalyst

Both silicas were modified with vanadium by incipient wetness impregnation with solution of NH₄VO₃, dried at 120 °C for 1 h and then calcinated at 565 °C for 7 h. The vanadium-modified silica catalysts were obtained, and kept in a desiccator until use. The vanadium-modified commercial silica was designated as CMV, while the vanadium-modified rice husk silica was designated as RHS.

Pyrolysis of water hyacinth

Water hyacinth was pyrolyzed with temperatures at 400 and 600 °C with heating rate of 10 °C min⁻¹, and holding at the reaction temperature for 1 h. It was due to the pyrolysis of water hyacinth conducted between 400 – 600 °C (400, 500 and 600) having been studied previously in our research group, and found that the experimental result of the pyrolysis at 500 °C was not significant. Therefore, in this study which the effect of the catalyst is mainly concerned, only the temperature at 400 and 600 °C are selected. The pyrolysis process was conducted in 0.5 L batch reactor. N₂ was used as carrier gas with flow rate of 80 ml min⁻¹. For the catalytic pyrolysis, the catalyst was impregnated with water hyacinth at concentration of 10 %wt. Products from pyrolysis included of 3 phases: liquid (bio-oil), solid (char) and gas. The percentage of product yield was calculated as follows;

$$\text{Product yield} = \frac{\text{Weight of each phase}}{\text{Weight of total product}} \times 100\% \quad (1)$$

Characterization of catalyst

X-ray fluorescence (XRF): the composition of the silica was measured with a PANalytical MiniPal 4 EDXRF spectrometer, equipped with a 30 kV rhodium anode tube with a helium purge facility. A high-resolution silicon drift detector was used to count x-rays intensity. Matrix corrections were made

by using either a ratio to the Compton peak or theoretical alpha coefficients, using minipal 4 software.

Characterization of bio-oil

Acidity of bio-oil was determined using pH meter (Index, MA40). Heating value was determined with bomb calorimeter (Parr Instrument, IL61265) equipped with water bath and oxygen. Functional groups of the catalyst and also the bio-oil were determined by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR spectrometer. Infrared spectra were recorded with and range of scanning from 400 to 4000 cm^{-1} with scanning times of 64.

Benzene adsorption of bio-char

Benzene solution (250 mg l^{-1}) of 30 ml was first prepared. The bio-char of 0.1 g was added into the solution, and then shaken at 300 rpm for 6 h. The bio-char was filtered off and the filtrate was determined for the VOCs concentration using UV vis spectrometer (UV-1601, Shimadzu) at 254 nm for benzene. The adsorption capacity of benzene and toluene was calculated as follows;

$$q = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where q is adsorption capacity (mg g^{-1}), C_0 (mg l^{-1}) is the initial concentration and C_e (mg l^{-1}) is the final concentration at equilibrium of benzene and toluene, V is volume of sample (ml), and m is amount of adsorbent (g).

Results and Discussion

Characterization of catalyst

Two types of silica including of commercial silica and rice husk-derived silica were modified with vanadium to enhance their catalytic performance. After the modification, the silica catalysts were then characterized with an X-ray fluorescence (XRF) spectrometer to determine the chemical composition as shown in Table 2. It can be observed that the amount of vanadium in oxide form (V_2O_5) were nearly similar in both catalysts. This indicates that the different types of silica did not affect the ability to be interacted with the vanadium modifier. The differences of functional groups between the two catalysts were determined using an FTIR spectrometer. However, no change of the functional groups between them was observed in the FTIR spectra (not shown).

Pyrolysis of water hyacinth

The pyrolyses of water hyacinth were carried out at 400 and 600 $^{\circ}\text{C}$. The conditions of pyrolysis, product yields and some properties of the obtained bio-oil and bio-char from the pyrolysis are shown in Table 3.

The products from the pyrolysis process consisted of 3 phases including liquid (bio-oil), gas and solid (bio-char) phases. It can be seen that the product yield distribution varied with the condition used in the pyrolysis whether the

Table 2 XRF analysis of vanadium-modified silica catalysts

Catalyst	Chemical composition (% wt)								
	SiO_2	SO_3	CaO	V_2O_5	Fe_2O_3	CuO	NiO	MnO	ZnO
CMV	94.85	1.21	0.13	3.78	0.02	0.01	0.01	–	–
RHV	95.25	0.55	0.33	3.79	0.06	0.007	0.003	0.0012	0.007

Table 3 Product yields and product properties from pyrolysis of water hyacinth.

Run	Temperature ($^{\circ}\text{C}$)	Catalyst	Yield (% wt)			pH ^a	Benzene Ads. ^b (mg g^{-1})
			Bio-oil	Bio-char	Gas		
1	400	–	12.5	37.0	50.5	3.5	43.2
2	400	CMV	24.0	40.1	35.9	5.4	39.6
3	400	RHV	17.6	36.6	45.8	4.8	39.5
4	600	–	24.3	39.2	36.5	3.2	42.7
5	600	CMV	25.9	37.8	36.3	5.4	39.5
6	600	RHV	16.2	35.8	47.9	4.1	38.6

^apH of bio-oil

^bBenzene adsorption capacity of bio-char

temperature and the introduction of a catalyst into the system.

The amounts of bio-oils from the pyrolysis of water hyacinth were between 12.5 and 25.9%. These values were relatively low compared with those from the other biomass; for examples pine saw dust (62%), switch grass (49 – 53%), rice straw (44%) and sugar cane bagasse (50%) [20]. This was due to the specific composition of water hyacinth leading to the low bio-oil yield. It has been found that presence of high amount of lignin contents leads to the formation of char residue while hemicelluloses and cellulose are favorable for the bio-oil yield [21]. As a result that water hyacinth has lower contents of hemicellulose and cellulose (52.7%, [22]) compared with other biomass such as saw dust (>60%, [23]) and rice straw (61%, [24]), it gave a lower bio-oil yield as observed in the result. However, comparing among the bio-oil yields obtained from water hyacinth in various studies (24.6% [25], >30% [26 – 27]), the bio-oil yield from this study still can be comparable, particularly for the catalytic pyrolysis. The reason for increasing in bio-oil yield with a catalyst is that it inhibited gas and char production through oil as intermediates [28].

Comparing between 2 catalysts, it was found that CMV gave the higher bio-oil yield than RHV at both temperatures (400 and 600 °C). At 400°C, the catalytic pyrolysis with RHV still gave the higher bio-oil yield than the non-catalytic system but the opposite was true at 600°C. The lower bio-oil for RHV at 600°C was probably due to it increasing the rate of the cracking reactions which leads to an increase in the yield of gases as shown in the result with a reduction in liquid oil yield [10]. It was also observed that the lower bio-oil yield occurred at the higher pyrolysis temperature. In general, increasing pyrolysis temperature could increase the bio-oil yield with enhancing the reaction rate of the first pyrolysis reactions such as decomposition and depolymerization of biomass. This is in consistent with the result of bio-oil yields of the non-catalytic systems at 400 and 600 °C. The presence of RHV could alter this event. Therefore, to develop the rice-husk silica to be appropriate for the pyrolysis should be conducted.

Characterization of bio-oil

The quality of bio-oil can be evaluated using the acidity which can be determined as pH or as TAN (total acid number) [29]. The pH is a representation of how corrosive the oil may be. The pH of bio-oils from untreated biomass is low, typically 2.5 – 3. It can be seen from Table 3 that

the pH of the obtained bio-oils from the non-catalytic systems (run 1 and 3) were low at 3.5 and 3.2, close to the typical range. The catalytic pyrolysis in the presence of the vanadium-modified silica catalyst reduced the acidity of the bio-oil as seen for both catalysts (CMV and RHV) at 400 and 600°C with the pH ranging from 4.1 – 5.4. The catalysts may enhance deoxygenation of oxygenates compounds such as carboxylic acid compounds and carbonyl compounds which causes acidity in the bio-oil. Carlson et al. who conducted fast pyrolysis of cellulose in pyro probe reactor with the commercial ZSM-5 [30] suggested that the strong acidity of the ZSM-5 might be the reason for higher deoxygenation. The introduction of vanadium and sulfate into the silica based catalyst had been proven to increase Brønsted acidity to the catalyst as reported by Lee et al. [31]. Therefore, the reduction of acidity of the bio-oil (increase of pH) was probably resulted from the vanadium-modified catalysts which posed high Brønsted acidity, thus enhancing deoxygenation of oxygenates compounds in the bio-oil.

When comparing between two catalysts, it was found that CMV had the higher ability to reduce acidity in the bio-oil than RHV. Even though it was seen from the XRF result that both catalysts had nearly similar amount of vanadium, their acidity may be different due to the difference in rearrangement of crystal structure caused by the presence of two different components between vanadium and silica. Nevertheless, RHV which prepared from agricultural residues like rice husk still exhibited a good potential to be used as catalyst with acid reducing property.

To identify functional groups inside the bio-oil which can relate to the chemical compounds present, an FTIR spectrometer was employed here. The FTIR spectra of the bio-oil obtained from various pyrolyses at 600 °C are shown in Fig.1. All spectra exhibited similar patterns except the peaks between 2800 and 3000 cm^{-1} which are apparently higher in the bio-oils from the catalytic pyrolyses than that of the non-catalytic pyrolysis. These peaks attributed to the C-H stretching vibrations along with the C-H deformation vibrations between 1350 and 1475 cm^{-1} indicate the presence of alkanes [32]. This suggests the higher fraction of alkanes in the bio-oils from the catalytic pyrolysis. The alkanes may be derived from deoxygenation of furan over catalyst acid sites forming methyl-, ethyl- and propyl- cyclohexanes [33]. From the finding of Wang et al. [34], cellulose-derived furanic compounds arise from either the catalytic

dehydration, decarbonylation or decarboxylation (RA) of light compounds formed from cellulose decomposition, or directly from the five-member carbon rings present in hemi-cellulose. Therefore, the high fraction of alkanes as seen in the bio-oil from the catalytic pyrolysis points to roles of the catalyst in the reaction such as dehydration, decarbonylation and decarboxylation. The occurrence of these mentioned reactions are also in accordance with the reduction of acidity in the bio-oils from the catalytic pyrolysis.

The other FTIR peaks of the three bio-oil consisted of; the O-H stretching vibrations between 3200 and 3400 cm^{-1} indicating the

presence of phenols and alcohols, C=C stretching of alkenes between 1600 and 1700 cm^{-1} , C-O stretching and O-H deformation vibrations between 950 and 1100 cm^{-1} attributed to the primary, secondary and tertiary alcohols. All these peaks are usually found in the bio-oils as reported by many studies [32, 35 – 36]. The peak attributed to alcohols (950 – 1100 cm^{-1}) of bio-oil produced from the pyrolysis with CMV was highest among those of all bio-oil indicating to the high amount of alcohols inside this bio-oil. This should be another factor leading to the higher pH value of bio-oil produced from CMV as observed.

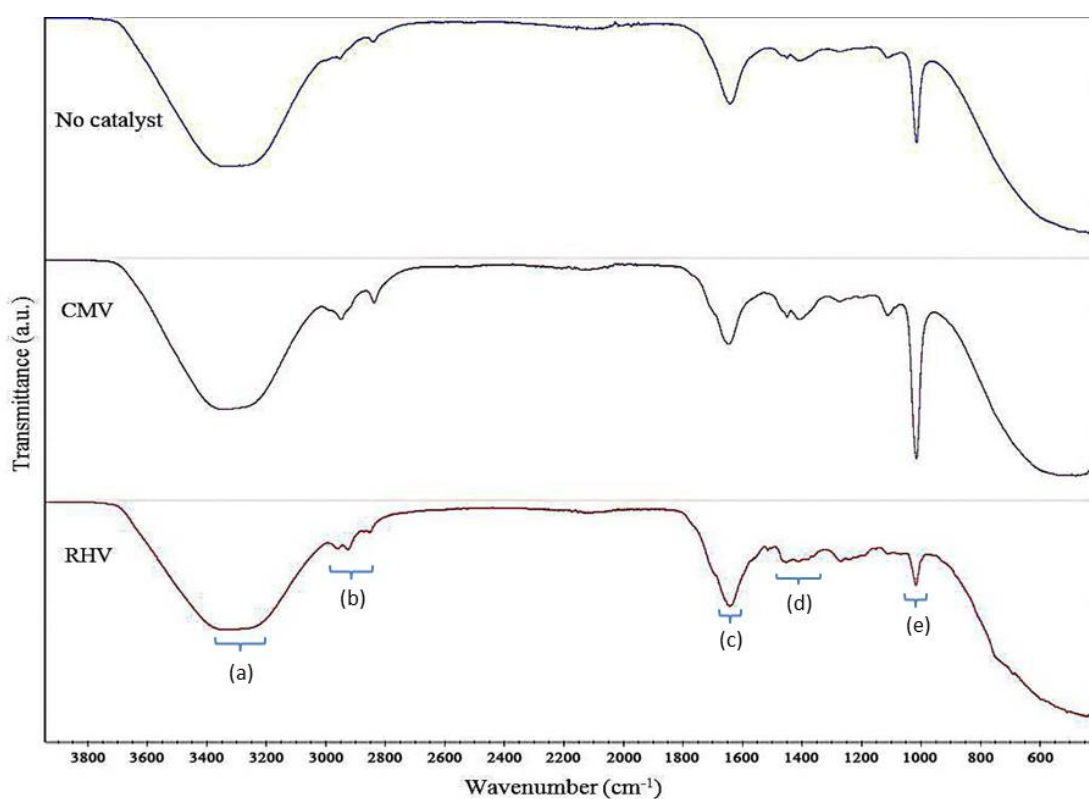


Fig. 1 FTIR spectra of the bio-oil obtained from various pyrolyses at 600 °C; (a) 3200 – 3400 cm^{-1} , (b) 2800 – 3000 cm^{-1} , (c) 1600 – 1700 cm^{-1} , (d) 1350 – 1475 cm^{-1} and (e) 950 – 1100 cm^{-1} .

The heating value can only be detected in the bio-oil obtained from the pyrolysis with CMV at 600 °C (run 5) due to the small-scale experiment, equaling to 40.29 MJ kg^{-1} . This value is almost equal to those of the standard commercial diesel (45.00 – 46.00 MJ kg^{-1}). Thus, the bio-oil from the catalytic pyrolysis of water hyacinth with the vanadium-modified silica catalyst could be a potential candidate for renewable fuel.

Benzene adsorption of bio-char

To extensively utilize the products from the

pyrolysis of water hyacinth, the obtained bio-char as a porous material was applied for benzene adsorption. From Table 3, the bio-char had the benzene adsorption capacities between 38.6 and 43.2 mg g^{-1} , which can be comparable with the other adsorbents previously studied. The activated coconut shell based carbon had the benzene adsorption capacity ranging from 14.4 to 55.4 mg g^{-1} depending on the initial concentration of benzene, and increasing to 63.0 mg g^{-1} after treating with NH_3 [37]. The bio-solid from a petrochemical wastewater treatment plant treated

with $ZnCl_2$ was also used for benzene adsorption and found that the adsorption capacity ranging from 59 – 164 $mg\ g^{-1}$ [38].

It can be observed that the bio-char from water hyacinth exhibited the moderate benzene adsorption capacity without any treatment. Therefore, improving its adsorption capacity with some treatments should be further investigated. When comparing between the bio-char from different pyrolyses, it can be seen that the ones obtained from the non-catalytic systems (run 1 and 4) exhibited the higher adsorption capacities than all catalytic systems. This was due to the bio-char obtained from the catalytic systems still contained the catalysts which had been introduced into the systems and not decomposed during the pyrolysis. The presence of the silica based catalyst with high hydrophilicity thus reduced the benzene adsorption capacity of the bio-char. Therefore, a separation process between the bio-char and the remained catalyst needs to be applied prior utilization of bio-char. In addition, the pyrolysis temperature insignificantly affected the benzene adsorption capacity of the bio-char.

Conclusion

Water hyacinth was pyrolyzed here with and without a catalyst at 400 and 600 °C. It was found that the catalysts i.e. CMV and RHV both increased the bio-oil yield at 400°C but at 600 °C only CMV increased the bio-oil yield. The presences of CMV and RHV in the catalytic pyrolysis also reduced the acidity of the bio-oil. In addition, the bio-oil obtained from the catalytic pyrolysis with CMV at 600 °C had the relatively high heating value of 40.29 $MJ\ kg^{-1}$. The bio-char obtained from the pyrolysis was applied for benzene adsorption, and exhibited the high adsorption capability. The increase of gas yield was observed for RHV at 600 °C due to it increasing the rate of the cracking reactions.

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