Appl. Chem. Eng., Vol. 29, No. 4, August 2018, 474-478
https://doi.org/10.14478/ace.2018.1068

Article

우슬(*Achyranthes* Root) 탕제 후 얻어진 폐한약재 부산물의 열분해

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(2018년 7월 3일 접수, 2018년 7월 5일 심사, 2018년 7월 9일 채택)

Pyrolysis of Waste Oriental Medicine Byproduct Obtained from the Decoction Process of *Achyranthes* Root

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(Received July 3, 2018; Revised July 5, 2018; Accepted July 9, 2018)

Abstract

Thermal decomposition of waste *Achyranthes* Root (WAR) emitted from its decoction process was investigated using a TG analyzer and a fixed-bed reactor. The WAR had the larger C and fixed carbon content than fresh AR (FAR) due to the extraction of hemicelluloses from FAR during decoction process. Thermogravimetric (TG) analysis results also revealed the elimination of hemicellulose by its decoction. Relatively high contents of the cellulose and lignin made high contents of their typical pyrolyzates, such as acids, ketones, furans, and phenols, in the pyrolysis of WAR using the fixed-bed reactor. The increase of pyrolysis temperature from 400 to 500 ℃ increased yields of oil and gas due to the more effective cracking efficiency of WAR at a higher temperature. The chemical composition of product oil was also changed by applying the higher pyrolysis temperature, which increased the selectivity to furans and phenols.

***Keywords**: waste oriental medicine, Achyranthes root, bio-oil*

1. Introduction

Owing to the rapid industrialization, the use of fossil fuels were dramatically increased and made the potential crisis, such as fossil fuel shortage, global warming, and climate change[1-3]. Many countries are focusing on making the sustainable society which can develop each country with the minimum use of natural resource. One of the solution is a recycling which can reduce the amount of natural resource for manufacturing products by the use of resources recovered from wastes. The other is the use of renewable source, such as biomass, for the production of energy or chemical feedstocks. The use of biomass is meaningful because of its large abundance, carbon neutrality, and CO_2 reduction effect on its growth[4]. Although other technologies, such as solar, wind, geothermal, water power generation systems, can be effectively applied on the production of energy, it is difficult to produce liquid fuels or chemical feedstock by these methods. One of the possible way to produce liquid fuels or chemical feedstock from renewable energy is the conversion of biomass. By applying various kinds of technologies, such as fermentation, torrefaction, pyrolysis, gasification, and so on, large amounts of chemical products can be produced and the relative yields of gas, liquid, and solid are differentiated depending on not only the property of biomass but also the applied biomass conversion technology[5].

Pyrolysis is a thermal decomposition process of polymeric materials by applying medium high temperature, mainly at the range of 400 and 600 ℃ to biomass, under non-oxygen atmosphere. Compared to other thermal conversion technologies, biomass pyrolysis can produce larger amount of liquid product which can be easily stored and transported. During recent decades, many kinds of biomass, such as woods, waste lignins, fruit peels, waste papers, and so on, were applied on the pyrolysis to produce liquid product and actual commercialization of biomass pyrolysis was also been successfully achieved in several countries [6]. Although many kinds of biomass, mainly woods, can be applied on pyrolysis feedstock, they also can be used in wide industrial area, such as a feedstock for furniture, wood-plastic composites, and so on [7], Therefore, many countries, such as Korea or Japan, having limited biomass source due to its small harvesting area, need to maximize the use of waste biomass having limited recycling ratio as the pyrolysis feedstock.

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pISSN: 1225-0112 eISSN: 2288-4505

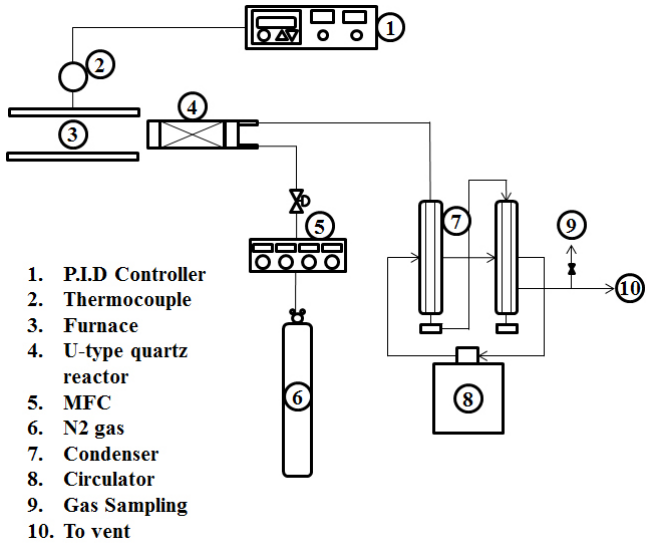


Figure 1. Schematic diagram of a fixed-bed pyrolysis reactor used in this study[11].

Oriental medicine business is a big medical industry in Asian country, such as China and Korea, and about 90,378 tons of biomass was harvested and used to extract the effective natural components from medical biomass in 2012 and most of them are being emitted as wastes[8]. Although some of waste medical biomass can be used as soil fertilizer, it is necessary to be used as a feedstock for the production of value added products.

Achyranthes Root is being intensively used as an oriental medicine due to the high content of steroid, saponin, and triterpenoid compounds, carbohydrate, benzonoid, and protein related substances[9]. Owing to the increased use of *Achyranthes* root as a medicine in Korea, the amount of waste *Achyranthes* root, obtained after the extraction of herbal ingredients, was also being increased. Although some of them used as agricultural compost or animal feed, most of them was dumped without additional recycling.

Therefore, the pyrolysis of waste *Achyranthes* root (WAR) was investigated to know its potential for the production of bio-oil in this study. Fresh *Achyranthes* root (FAR) was also been used as a reference feedstock for the pyrolysis reaction. For the experiments, the pyrolysis of WAR and FAR were performed using a fixed bed reactor at different temperatures, 400 and 500 ℃ under nitrogen atmosphere. The yields of gas, oil, solid residue and their detailed chemical compositions were evaluated to know the feasibility of the pyrolysis of WAR.

2. Materials and Methods

2.1. FAR and WAR

Physico-chemical properties of WAR and FAR, was evaluated according to the procedures already reported in previous literatures[10].

2.2. Thermogravimetric (TG) analysis

6.0 ± 0.1 mg of WAR or FAR in TG sample cup was non-isothermally heated from ambient temperature to 900 ℃ under 60 mL/min of nitrogen atmosphere using a TG analyzer (Perkin Elm, Pyris 1).

Table 1. Analysis Condition of GC/MS

GC	
Instrument	7890A Gas Chromatography, Agilent Technologies
Column	Ultra alloy-5 (30 m × 0.25 mm × 0.25 μm)
Carrier gas	Helium
Flow rate	1 mL/min
Inlet	320 ℃, 20 : 1
Oven program	40 ℃ (5 min) → 5 ℃/min → 320 ℃ (10 min)
MS transfer line	300 ℃
MS	
Instrument	5975C Inert Mass Spectral Detector, Agilent Technologies
MS source temperature	230 ℃
MS quadruple temperature	150 ℃
Ionization voltage	70 eV
Scan range	29-550 amu
MS library	NIST05a and F-Search

2.3. Fast pyrolysis and its product analysis

A fixed bed reactor, shown in Figure 1[11], was used for the fast pyrolysis of WAR and FAR. After loading the specific amount of WAR (3.0 ± 0.1 g) and purging the inside of reactor with nitrogen (30 minutes) to eliminate the residual air, the fast pyrolysis was performed by sliding the preheated furnace (400, 500 ℃) to the sample position and the product vapor was condensed at -30 ℃. Uncondensed gas products were collected using a gas sampling bag.

The yields of solid and liquid were obtained by measuring the actual weights of residual solid inside the reactor and condensed liquid in two stage condensers. The yield of gas was calculated by subtracting the summed yields of solid and liquid products from the total yield (100%). The product oil and gas were analyzed using a gas chromatography/mass spectrometry (GC/MS) and GC-flame ionization detector/thermal conductivity detector (GC/FID/TCD), respectively. The detailed operation system for GC/MS and GC/FID/TCD were shown in Table 1 and 2.

3. Results and Discussion

3.1. Physico-chemical properties of WAR and FAR

Table 3 shows the ultimate analysis and proximate analysis results of WAR and FAR. Compared to FAR, WAR revealed the smaller content of volatiles (74.5%) together with the higher fixed carbon contents (11.4%). This indicates that considerable carbohydrates, hemicellulose or cellulose, was extracted during decoction, hot water extraction process of oriental medicine[12]. The contents of oxygen in WAR was also decreased together with the increase of carbon content by decoction

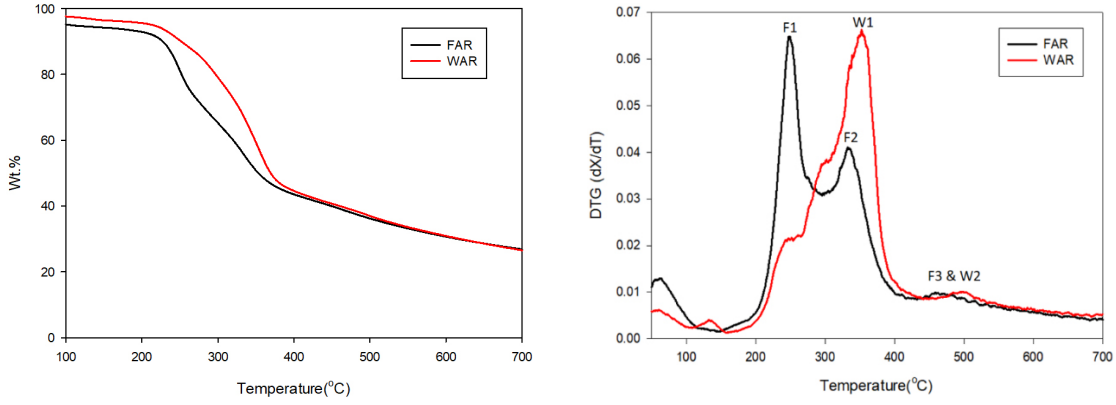
Table 2. Analysis Condition of GC/TCD and FID

	GC/TCD	GC/FID
Column	Carboxen 1000 (15 ft × 1/8 in)	HP-plot Al_2O_3/KCl (50 m × 0.32 mm × 8 μm)
Inlet	150 ℃, He: 20 mL/min	200 ℃, split ratio 10 : 1
Oven program	35 ℃ (5 min) à 15 ℃/min à 225 ℃ (10 min)	40 ℃ (5 min) à 4 ℃/min à 160 ℃ à 2 ℃/min à 200 ℃ (40 min)
Detector	150 ℃	250 ℃

Table 3. Physico-chemical Characteristics of FAR and WAR

Sample		FAR	WAR
Proximate analysis (wt%)	Water	4.5	2.8
	Volatiles	79.0	74.5
	Fixed carbon	4.6	11.4
	Ash	11.9	11.3
Elemental analysis[a] (wt%)	C	37.0	41.2
	H	5.7	5.9
	O[b]	55.0	50.6
	N	2.3	2.3
	S	-	-

[a]On a dry basis, [b]By difference.



(a) TG curves (b) DTG curves

Figure 2. TG and DTG curves of FAR and WAR at 20 ℃/min.

process due to the elimination of carbohydrates in FAR.

3.2. TG analysis results of FAR and WAR

Figure 2 shows the TG and DTG curves obtained from the non-isothermal TG analysis of FAR and WAR. Both FAR and WAR was decomposed mainly at between 200 and 400 ℃ and continued up to high temperature, up to 700 ℃. Meanwhile, the DTG peak shapes of FAR and WAR at main decomposition temperature were quite different. DTG curve of FAR had two peaks (F1 and F2), however, that of WAR had only one peak (W1). F1 and F2 can be assigned as the decomposition peaks for hemicellulose and cellulose, respectively[13]. Therefore, the absence of F1 peak on the DTG curve of WAR can suggest that the considerable amounts of hemicellulose in FAR was eliminated during decoction process. The increased peak height of W2 on the DTG curve of WAR can be explained by the relatively higher content of cellulose in WAR sample than FAR due to the elimination of hemicellulose. Interestingly, the relative contents of lignin can be increased by the hemicellulose extraction during decoction process, the peak heights of the tailing peaks (F3 & W2) on the DTG curve of WAR was similar with that of FAR. This can suggest that the decoction of FAR also can extract the lignin from FAR. According to the TG analysis results, the temperature condition for the fast pyrolysis was set up as the higher temperature than the main decomposition of both FAR and WAR.

3.3. Fast pyrolysis of WAR

Figure 3 shows the yields of gas, oil, and char produced by the pyrolysis of WAR at different temperatures. At all temperatures applied

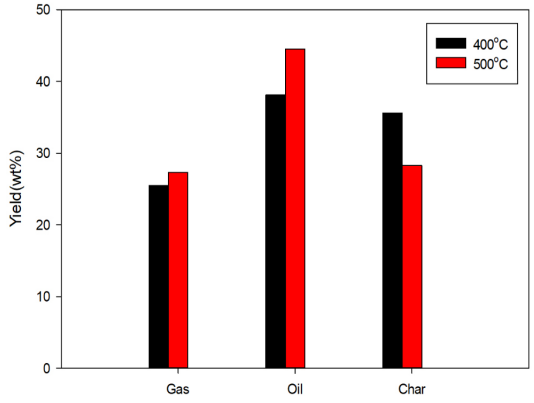


Figure 3. The yields of gas, oil, and char obtained from the fast pyrolysis of WAR at different temperatures.

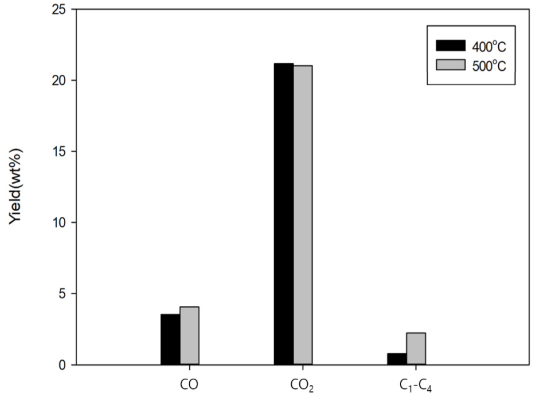


Figure 4. The yields of CO, CO_2, and Light hydrocarbons (C_1~C_4) obtained from the fast pyrolysis of WAR at different temperatures.

in this study, the yields of oil was higher than those of gas and char. At 400 ℃, the yields of char was relatively higher than that at 500 ℃ due to the incomplete decomposition of WAR, mainly lignin. By increasing the temperature from 400 to 500 ℃, the yields of char was decreased together with the increase of gas and oil products due to the additional decomposition of WAR.

Figure 4 shows the chemical composition of gas product produced from the pyrolysis of WAR at different temperatures. As expected with the increase of gas yields (Figure 4), the yields of CO, CO_2, and light hydrocarbons (C_1~C_4) were increased by applying the higher pyrolysis reaction temperatures due to the additional cracking of solid residue and secondary cracking of pyrolysis intermediates. CO and CO_2 can be produced by the effective decarbonylation and decarboxylation reactions from oxygen containing pyrolysis intermediates. Light hydrocarbons also can be produced by the dealkylation, dehydroxylation of oxygen containing pyrolysis intermediates at the high temperatures.

Figure 5 shows the chemical distributions of oil product obtained from the pyrolysis of WAR at different temperatures. At all temperatures, acids, such as acetic acid, n-hexadecanoic acid, and tetrahydroabietic acid, were occupied the largest portion in the product oil [14]. Large amount of ketones and furans, known as the main pyrolyzates of carbohydrates, were also contained in the pyrolysis oil together with the main pyrolyzates of lignin, mainly phenols[15]. These indicated that the main pyrolyzates of WAR were consisted with the typical pyrolyzates of biomass components, hemicellulose, cellulose, and lignin. By increasing the reaction temperature from 400 to 500 ℃, the amounts of ketones, furans, and phenols were increased together with the decrease of acids. Additional formation of ketones, furans, and phenols can be explained by the additional cracking of carbohydrates and lignin and the decrease of acids can be explained by the secondary cracking of acetic acid to light hydrocarbons.

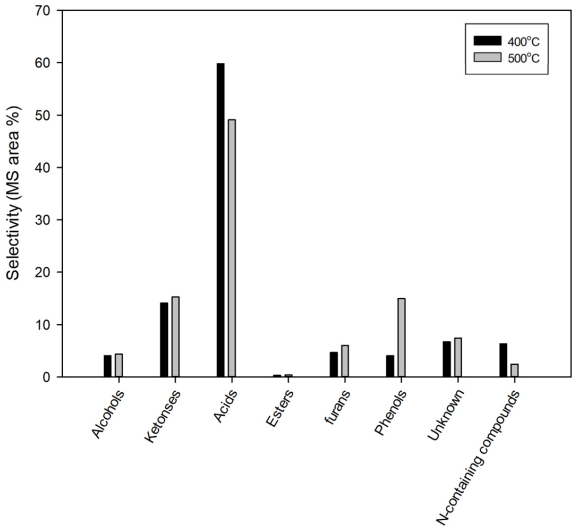


Figure 5. Chemical selectivity of the oil product obtained from the fast pyrolysis of WAR at different temperatures.

4. Conclusion

Fast pyrolysis of WAR using a TG analyzer and a fixed-bed reactor revealed the effectiveness of pyrolysis on the production of bio-oil from waste oriental medicines. Although large amount of valuable extracts was eliminated from FAR during decoction process, WAR also had the large amount of cellulose and lignin in its structure. By applying the pyrolysis to WAR, large amount of oil product consisted with acids, ketones, furans, and phenols, was obtained from WAR even at 400 ℃. The oil yield was increased by applying the higher pyrolysis temperature (500 ℃) due to the additional cracking of WAR. The yields of CO, CO_2, and light hydrocarbons were also increased by increasing the reaction temperatures due to the effective deoxygenation and additional cracking reaction. By increasing the pyrolysis temperature from 400 ℃ to 500 ℃, the relative contents of acids was decreased, however, the contents of ketones, furans, and phenols were increased.

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