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The effects of potassium on distributions of bio-oils obtained from fast pyrolysis of agricultural and forest biomass in a fluidized bed

Huiyan Zhang*, Yuna Ma, Shanshan Shao, Rui Xiao*

Ministry of Education of Key Laboratory of Energy Thermal Conversion and Control, School of Energy and Environment, Southeast University, Nanjing 210096, PR China

HIGHLIGHTS

- Potassium effects during pyrolysis of agricultural and forest biomass was studied.
- K increases furans and phenols yields, decreased aldehydes, esters and sugars yields.
- K converts anhydrosugars to linear aldehydes and then to 5-hydroxymethylfurfural.
- More polyphenols produced from small polymers with the assistance of K.
- Reaction pathway of potassium influence on biomass pyrolysis was proposed.

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ABSTRACT

Potassium, due to its strong catalytic effects on biomass pyrolysis vapors, has great influence on the components of the obtained bio-oil. In this work, fast pyrolysis of acid washed and potassium salts impregnated feedstocks (camphor branch, corn cob and walnut shell) were carried out in a fluidized bed. The effects of potassium and the ash in biomass on yields and selectivities of bio-oil compounds were studied. The results showed that the walnut shells yielded the greatest amount of phenol and acids. Potassium promoted the conversion of large molecular compounds (such as levoglucosan) to furans. The existence of potassium reduced the yield of aldehydes and enhanced that of furfural. With the assistance of potassium, the selectivity of monophenols (phenol, methyl phenol, dimethyl phenol, etc.) decreased significantly to around half, while that of polyphenols (ethyl phenol, 2-allylphenol, 4-(2-propenyl)-phenol, 2-allyl-4-methylphenol, etc.) increased obviously. Finally, a possible reaction pathway indicating potassium influences on biomass pyrolysis was proposed according to the experimental results.

1. Introduction

The development of renewable energy technologies is one of the possible ways to address the major issues of fossil reserves depletion and environmental pollution. Biomass, which attracts much attention recently, is considered as an environmental friendly energy since it is renewable and CO₂ neutral [1–4]. Fast pyrolysis is one of the most promising technologies for biomass utilization, which can convert biomass into liquid fuels (bio-oil) within several seconds [5–10]. The yields of bio-oil can reach up to 70 wt% on biomass, depending on different reactors, process conditions and feedstocks [11,12]. Several reactors, such as bubbling fluidized bed, circulating fluidized bed, transported bed, auger, vacuum, rotating cone and ablative moving beds, have been developed for biomass fast pyrolysis during last decades [7,13–15]. Bubbling and circulating fluidized bed reactors are

regarded as the easiest reactors for commercialization. Bubbling fluidized beds have the advantages of simple operation and efficient heat transfer to biomass particles. The Dynamotive in Canada built the largest bubbling fluidized bed of biomass fast pyrolysis with a capacity of 8000 kg/h [16]. The main drawback of this type of reactor for scaling up lies in the heat transfer to the bed materials (sand). Circulating fluidized beds have the advantage of a direct heat transfer from pyrolysis char combustion to sand and then to biomass by recirculating of sand. The Ensyn plants in the USA [17] and a 4000 kg/h plant in Canada [18] are the large scale setups in the world. However, the hydrodynamics of the circulating fluidized bed for biomass fast pyrolysis is complex and the obtained bio-oil contains a lot of fine char. This char contains ash which catalyzes the bio-oil and make it unsteady.

Bio-oil, which is a complex mixture of oxygenated compounds (i.e. ketones, phenols, furans, acids, aldehydes, etc.), can be used directly in

* Corresponding authors.

E-mail address: ruixiao@seu.edu.cn (R. Xiao).

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Table 1
Ultimate analysis, proximate analysis and chemical properties of different biomass feedstocks.

	Camphor branch	Corn cob	Walnut shell
<i>Proximate analysis (wt.%)</i>			
M	9.8	8.2	6.5
VM	74.1	75.1	55.8
FC	15.3	15.3	36.1
Ash	0.8	1.3	1.6
<i>Ultimate analysis (ad, wt.%)</i>			
Carbon	42.5	40.8	46.6
Hydrogen	5.1	5.4	6
Oxygen	41.3	43.5	38.3
Nitrogen	0.4	0.7	0.9
Sulfur	0.1	0.08	0.06
<i>Chemical properties</i>			
Cellulose	37.9	40.2	22.1
Hemicellulose	22.6	32.6	18.9
Lignin	23.8	13.5	46.1

traditional boilers, and also can be upgraded into high-grade transportation oils and chemicals [4,8,19–22]. However, contributed to abundant different kinds of feedstock, there is a great diversity in physical and chemical properties of the bio-oils obtained, which finally depress the universal applicability of the bio-oil's upgrading methods and utilization modes. Except for the difference contents of cellulose, hemicellulose and lignin in feedstocks, ash is also one of major factors that lead to the great diversity of pyrolysis products [10,12]. Ash is one of the main factors which influence the quality of the obtained bio-oils. Even trace amount of certain ash components (< 0.1%) can change both the thermal degradation rate and chemical reaction pathways during fast pyrolysis [23,24].

Generally speaking, the content of ash is higher in agricultural biomass, up to 10% in rice husk [25], while forestry biomass contains less ash, the contents of ash in pine wood is less than 1% [12,26]. Though the amounts of alkaline metal (K, Na, etc.) and alkaline earth metal (Ca, Mg, etc.) elements are much smaller than that of silicon in ash, they play a crucial role in biomass pyrolysis [27–29]. When the biomass particle was heated, pyrolysis reaction happened from outside

to inside along with heat transfer. The surface of the particle carbonized first with almost all the metal elements remained in the shell [30]. When the vapors of particle interior diffused, the vapors come through the coke shell and be catalyzed by metal elements [31]. Potassium is the most influential metal element on pyrolysis product distribution. By observing the yield of levoglucosan, the effect trend of different positive metal ions was obtained: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ [24,32]. Potassium can significantly promote the secondary reactions of vapors, which reduces the yield of bio-oil remarkably with the formation of char and gas [33,34]. At the same time, potassium leads to variation of the product distribution, especially the liquid products. Some studies have investigated the liquid components derived from the potassium-catalyzed pyrolysis with different biomass species and pyrolysis conditions. Fuentes et al. studied the effects of individual ash components (K, Mg, Ca, Fe, and P) on willow pyrolysis by using TGA and Py-GC/MS [35]. Their results showed potassium strongly catalyzed the overall thermal degradation and altered the bio-oil composition. Wang et al. studied the pyrolysis of pine wood in a slow heating fixed-bed reactor, showing that K_2CO_3 demonstrated a notable catalytic effect on decomposition of hemicellulose, cellulose and lignin [36]. However, there are rare studies about the effect of potassium aimed at the product distribution of biomass pyrolysis in a real fast heating system such as a fluidized bed reactor. In this type of reactor, biomass particles are heated very fast (heating rate is more than 1000 °C/s) and always moving in the whole pyrolysis process, the vapors release and reaction process with other particles are different with that in fixed bed.

In this work, fast pyrolysis of three kinds of feedstocks (camphor branch, corn cob and walnut shell) with different pretreatment conditions (acid washing and K impregnated) were carried out in a fluidized bed reactor. The liquid product bio-oil was analyzed by gas chromatography/mass spectrometry (GC/MS). The compounds of bio-oil were categorized in groups. Based on the yields and selectivity of compounds, the effects of potassium and ash on pyrolysis product distribution were studied in detail. Finally, a possible reaction pathway of potassium influence on biomass pyrolysis was proposed according to the experimental results.

Table 2
Ash composition of raw and pretreated biomass feedstocks.

Compound	Peak area percentages in all detected compounds (%)								
	Camphor branch			Corn cob			Walnut shell		
	A [ⓐ]	R [ⓑ]	K [ⓐ]	A [ⓐ]	R [ⓑ]	K [ⓐ]	A [ⓐ]	R [ⓑ]	K [ⓐ]
SiO ₂	49.2	73.85	12.9	33.5	89.68	22.4	29.4	90.31	24.2
Al ₂ O ₃	9.5	14.6	2.6	6.1	6.3	1.7	2.75	3.4	1
Fe ₂ O ₃	8.6	9.4	1.6	2.6	2.4	0.73	2.66	2.8	0.8
CaO	17.3	1.6	0.3	15.28	0.6	0.24	16.28	1.2	0.11
MgO	1.2	0.02	0.01	4.7	0.3	0.12	10.85	0.8	0.25
SO ₃	2.4	0.02	0.01	4.3	0.08	0.05	1.65	0.02	0.003
Na ₂ O	0.7	0.01	NA	1.4	0.05	0.04	1.15	0.03	0.01
K ₂ O	10.2	0.2	82.5	30.7	0.26	74.6	32.06	0.52	73.427
P ₂ O ₅	0.9	0.3	0.08	1.3	0.3	0.12	3.1	0.9	0.2
TiO ₂	NA	NA	NA	0.12	0.03	0.02	0.1	0.02	NA
SiO ₂	49.2	73.85	12.9	33.5	89.68	22.4	29.4	90.31	24.2
Al ₂ O ₃	9.5	14.6	2.6	6.1	6.3	1.7	2.75	3.4	1
Fe ₂ O ₃	8.6	9.4	1.6	2.6	2.4	0.73	2.66	2.8	0.8
CaO	17.3	1.6	0.3	15.28	0.6	0.24	16.28	1.2	0.11
MgO	1.2	0.02	0.01	4.7	0.3	0.12	10.85	0.8	0.25
SO ₃	2.4	0.02	0.01	4.3	0.08	0.05	1.65	0.02	0.003
Na ₂ O	0.7	0.01	NA	1.4	0.05	0.04	1.15	0.03	0.01
K ₂ O	10.2	0.2	82.5	30.7	0.26	74.6	32.06	0.52	73.427
P ₂ O ₅	0.9	0.3	0.08	1.3	0.3	0.12	3.1	0.9	0.2
TiO ₂	NA	NA	NA	0.12	0.03	0.02	0.1	0.02	NA

Note: A[ⓐ], Acid washing sample; R[ⓑ], Raw biomass; K[ⓐ], K impregnated sample; NA, Not detected.

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