ORIGINAL PAPER 원저

돈분과 돈슬러리의 성분이 열분해공정에 의한 바이오오일 생산효율에 미치는 영향

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Effect of Pig Feces and Pig Waste Mixture Compositions on Bio-oil Production by Pyrolysis Process

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ABSTRACT

Pyrolysis is recently used as one of alternative methods of animal waste treatment. In this study bio-oil was produced at 550℃ in an auger reactor through pyrolysis process. Two pig waste mixtures were used, pig feces mixed with rice husks and pig feces mixed with sawdust. The main compositions of hemicellulose, lignin, cellulose, protein, and fat were analyzed chemically. Based on the main composition results obtained, the contents of holocellulose (the sum of hemicellulose and cellulose) and lignin had a significant positive effect on bio-oil production, and there was a significant negative effect of ash content on bio-oil yield. The interactions between the different feedstocks were evaluated, and it was concluded that the interaction between pig feces and rice husks was minimal, whereas the interaction between pig feces and sawdust was significant.

Keyword : ash, bio-oil, holocellulose, lignin, pig waste mixture, pyrolysis

초 록

바이오매스를 바이오오일로 전환시키기 위하여 오거형의 반응조를 설계, 제작하여 실험하였다. 10.2L의 반응조는 550℃를 유지하며 Batch식으로 운영하였다. 돈분뇨 혼합물, 돈분・왕겨혼합물, 돈분・톱밥혼합물 등 세 가지 혼합물을 대상으로 주(主) 구성성분인 헤미셀루로즈, 리그닌, 셀루로즈, 단백질, 지질(脂質) 등을 화학적으로 분석하였다. 실험결과에 의하면 전섬유소 (holocellulose = hemicellulose + cellulose),

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리그닌(lignin)의 함유량이 클수록 바이오오일 생산량은 많았으나, 회분(ash)함량은 현저한 감소를 나타내었다. 본 연구에서는 다양한 바이오매스기질을 평가하였으며, 돈분과 왕겨의 상관성은 거의 나타나지 않았으나 돈분과 톱밥의 상관성은 매우 높게 나타났다.

핵심용어 : 회분, 바이오오일, 호로셀루로즈, 리그닌, 돈분혼합물, 열분해

1. Introduction

The increasing depletion of currently available energy sources has revitalized interest in converting solid wastes to fuel. Many processes, including anaerobic digestion, hydro gasification, pyrolysis, and partial oxidation, have been developed to recover energy from organic solid wastes. Pig manure represents a renewable source of energy and is available in huge quantities. On a dry basis, pig manure has a carbon content of 38 – 48 wt % and a heating value of 15–17 MJ/kg. If it could be economically converted to fuel, the demand for limited fossil fuels would be considerably reduced.

Due to the combined advantages of weight/volume reduction and energy recovery, thermal treatments for pig manure are considered as one of the most effect methods for energy recovery. Pyrolysis is the basis of almost all available thermochemical processes, and pyrolysis studies have been widely conducted for converting energy from animal waste. Kim et. al. (2003) successfully converted up to 70% of swine manure solids to oil and reduced manure chemical oxygen demand by up to 75%. Keri et. al. (2007) reviewed the important role of thermochemical conversion in livestock waste–to–energy treatments. In the preliminary study of Stephane (2009), bio–fuel was produced from swine manure solids by vacuum pyrolysis. Deepak and Mohammad (1981) investigated the gas yield, composition, and product heating values resulting from the pyrolysis of bovine waste. Yoshiyuki and Yutaka (2003) reported the physical and chemical properties of pyrolytic products from cow biosolids. The kinetic parameters during the pyrolysis of chicken litter were studied by Kim and Agblevor (2007). However, few studies are available on the pyrolysis of pig feces or pig waste mixed with rice husks or sawdust. This study mainly focuses on 1) analysis of the main compositions of pig feces and pig waste mixtures, and 2) the pyrolysis characteristics of pig feces and pig waste mixtures, consisting of pig feces and rice husks or sawdust, to discuss the effects of the major components on pyrolysis.

2. Materials and Methods

2.1 Feed preparation

Bio–oil was produced by pyrolyzing pig feces in an auger reactor. The pig feces were obtained from an experimental animal farm at Seoul National University. The feces samples were air dried for two days to reduce the moisture content to less than 20% which was suitable for auger type pyrolysis system. The pig waste mixtures, which were made by mixing pig feces with either rice husks or sawdust in various mass ratios (dry matter), were also used as the feedstocks for pyrolysis. The properties of the pig feces, rice husks, and sawdust used in this study are listed in [**Table 1**].

2.2 Bench-scale auger reactor of pyrolysis

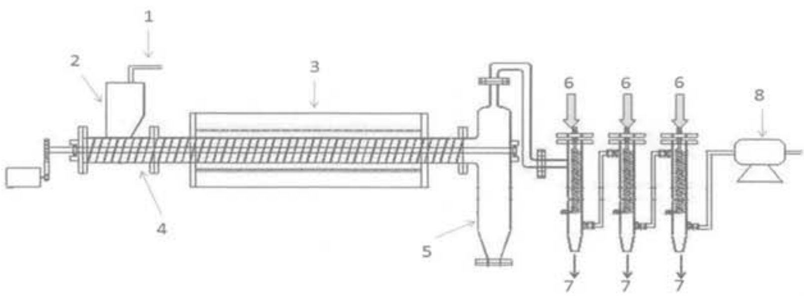
Pyrolysis of the pig waste mixture samples was conducted at a 3 kg/hr feed rate in a stainless steel auger reactor. The auger reactor was compact and operated continuously. One inlet was provided in the top of the feed hopper to supply a slow metered stream of nitrogen gas. The auger reactor pipe was 108 mm in diameter and 1,800 mm in length. A Kanthal molding electrical heating furnace (114 mm in diameter and 1,000 mm in length) was used to heat the auger reactor. The auger speed was 3 rpm at a pyrolysis temperature of 550℃. Approximately six minutes were required for the initial feed to move to the char exit point. However, as vapors or aerosols formed, they moved to the condensers within a few seconds.

Bio-oil was collected after the pyrolysis reaction for approximately one hour with continuous biomass feeding, by which time the entire process had reached a steady state. Pyrolysis produced a mixture of gases, aerosols, and some very fine char particles. A solid char residue was also formed which was moved through the reactor by the rotating auger to a removal pot. The gases and aerosols were condensed as bio-oil (entrapping some entrained fine char particles) in three consecutive condensers. Ethanol was used as the cooling liquid. A diagram of this pyrolysis system is showed in [**Fig. 1**].

The analysis of main compositions including

[Table 1] Properties of Pig Feces, Rice Husk and Sawdust

Feedstock	Proximate Analysis (wt %)		
	Moisture	Volatiles	Ash
Rice husk	9.6	74.3	16.1
Sawdust	11.9	86.2	1.9
Pig feces	18.6	74.7	6.7



[Fig. 1] Diagram of pyrolysis system: 1, Nitrogen flow; 2, Feed hopper; 3, Electric heating furnace; 4, Screw; 5, Collector of solid residue; 6, Three condensers with ethanol; 7, Liquids collector; 8, Air pump.

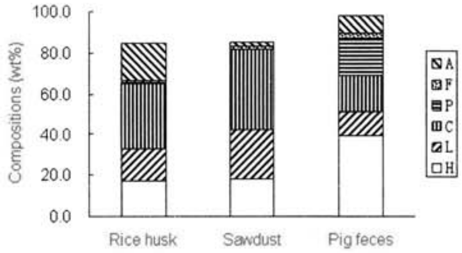
cellulose, hemicellulose, lignin, protein, fat, moisture, and ash were conducted by using AOAC (Association of Official Analytical Chemists) standard methods in this study.

3. Results and Discussion

3.1 Main compositions of rice husk, sawdust and pig feces

For organic waste, cellulose, hemicellulose, and lignin are generally recognized as the main components[4]. Protein and fat are another two important components. **[Fig. 2]** shows the major organic components in the feedstock samples employed in this study.

As can be seen in **[Fig. 2]**, cellulose is the main component in the sawdust (40.0%) and rice husks (32.4%), while in pig feces, the hemicellulose content is the highest (39.4%). Comparing the feedstocks, rice husk had the highest amount of ash (17.8%), sawdust had the highest amounts of lignin (23.0%) and cellulose, and the highest amounts of hemicellulose, protein (18.3%), and fat (2.6%) were found in the pig feces. The contents of the five main organic components vary from 17.3 ~ 39.4% for hemicellulose, 12.0 ~ 23.7% for cellulose, 17.5 ~ 40.0% for lignin, 0.1 ~ 18.0% for protein, and 1.0 ~ 2.6% for fat.



[Fig. 2] The contents of main compositions in feedstock. A is ash, F is fat, P is protein, C is cellulose, L is lignin, and H is hemicellulose.

3.2 Pyrolysis of pig waste mixture

Analysis of the above-mentioned mixtures shows that there are high amounts of ash in rice husks and high amounts of cellulose and lignin in sawdust. Therefore, in pig waste mixtures, rice husks could be used for adjusting ash content, while cellulose and lignin contents could be adjusted with the use of sawdust. In order to quantitatively elucidate the effects of the main components on the pyrolysis characteristics of pig waste, the pig waste mixtures were produced by mixing rice husks or sawdust with pig feces in various mass ratios. **[Table 2]** and **[Table 3]** show the bio-oil yield from the pyrolysis processes of the pig waste mixtures with rice husks and sawdust, respectively. In the mixture of rice husks, the contents of moisture, hemicellulose, protein, and fat had a positive effect on bio-oil yield, while the ash, lignin, and cellulose contents had a negative effect. However, the results were very different in the sawdust mixture: the bio-oil production as positively related to lignin and cellulose content and negatively related with the contents of moisture, ash, hemicellulose, protein, and fat.

Of the 13 feedstock mixtures, the correlations between the composition of feedstock and bio-oil yield are given in **[Table 4]**, where holocellulose represents the sum of hemicellulose and cellulose. In all mixtures, there is no significant correlation between bio-oil yields and hemicellulose or cellulose content, however, the content of holocellulose had a significant positive effect on the yield of bio-oil. A similar result was reported by Raveendran et al.[8]. Furthermore, the bio-oil

[Table 2] Bio-oil Yield from Pyrolysis of the Mixture of Pig Feces with Rice Husk

Mixture[1]	Moisture (wt %)	Composition[2] (dry matter basis, wt %)						Bio-oil yield (wt %)
		A	H	L	C	P	F	
PF:R=1:0	18.6	8.2	39.4	12.0	17.5	18.3	2.6	32.7
PF:R=3:1	16.4	10.6	33.9	12.9	21.2	13.9	2.2	31.1
PF:R=2:1	15.6	11.4	32.1	13.1	22.5	12.5	2.1	30.6
PF:R=1:1	14.1	13.0	28.4	13.7	25.0	9.6	1.8	30.1
PF:R=1:2	12.6	14.6	24.7	14.3	27.4	6.6	1.5	29.3
PF:R=1:3	11.9	15.4	22.8	14.6	28.7	5.2	1.4	28.4
PF:R=0:1	9.6	17.8	17.3	15.4	32.4	0.8	1.0	26.6

[1]PF is pig feces ; R is rice husk.
[2]A is ash, H is hemicellulose, L is lignin, C is cellulose, P is protein, F is fat.

[Table 3] Bio-oil Yield from Pyrolysis of the Mixture of Pig Feces with Sawdust

Mixture[1]	Moisture (wt %)	Composition[2] (dry matter basis, wt %)						Bio-oil yield (wt %)
		A	H	L	C	P	F	
PF:S=1:0	18.6	8.2	39.4	12.0	17.5	18.3	2.6	32.7
PF:S=3:1	16.9	6.7	34.1	14.9	23.1	13.8	2.3	32.7
PF:S=2:1	16.4	6.2	32.4	15.9	25.0	12.2	2.2	32.9
PF:S=1:1	15.3	5.2	28.9	17.9	28.8	9.2	1.9	33.1
PF:S=1:2	14.1	4.1	25.3	19.8	32.5	6.2	1.7	33.2
PF:S=1:3	13.6	3.6	23.6	20.8	34.4	4.7	1.6	33.4
PF:S=0:1	11.9	2.1	18.3	23.7	40.0	0.1	1.2	38.0

[1]PF is pig feces; S is sawdust.
[2]A is ash, H is hemicellulose, L is lignin, C is cellulose, P is protein, F is fat.

[Table 4] Correlation between Bio-oil Yield and the Compositions of Feedstock

Pearson Correlation	Moisture	A[1]	H	L	C	HC	P	F
Bio-oil Yield	0.337	−0.940**	0.133	0.608*	0.249	0.912**	0.058	0.238

[1]A is ash, H is hemicellulose, L is lignin, C is cellulose, P is protein, F is fat, HC is holocellulose.
*Correlation is significant at the 0.05 level.
**Correlation is significant at the 0.01 level.

yield was positively related to lignin content ($r = 0.608$) and negatively related to ash content ($r = -0.940$). Further study is necessary to reveal the mechanism of those correlations.

3.3 Interactions between pig feces and rice husk, sawdust

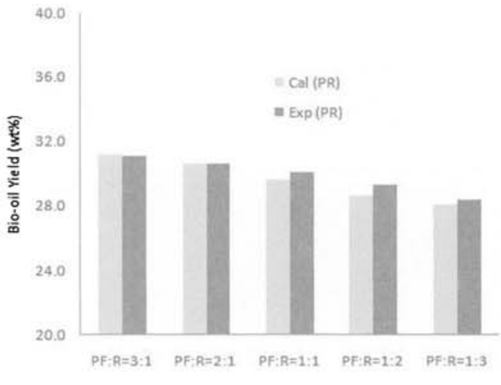
An attempt was made to reveal the possible interactions between pig feces and rice husks or sawdust. 'Exp' represents the experimental data, and 'Cal' represents the calculated data obtained by a method of weighted averages as follows:

$$X_{Cal}=\sum_{i=1}^{n} c_i X_i$$

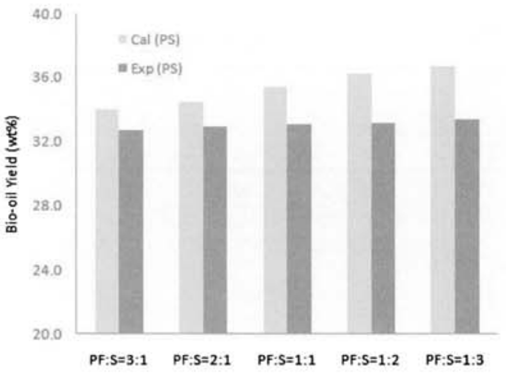
where 'c_i' was the proportion of the component X_i, and X_{Cal} was obtained under the assumption that any interaction was negligible. By comparing the 'Sum' and 'Exp' curves, it was possible to uncover the interactions between the different feedstocks. As shown in [**Fig. 3**], the 'Exp (PR)' curve matched well with 'Cal (PR)'. However, as shown in [**Fig. 4**], the 'Exp (PS)' values were all obviously lower than those of 'Cal (PS)'. Thus, it was concluded that the interaction between pig feces and rice husks was negligible. As described in [**Table 1**], there were similar volatile contents in pig feces and rice husks, which may contribute to the similar pyrolysis processes for the two materials, therefore, when they are mixed with each other, there is no change in the main reaction. However, there were some detectable interactions between pig feces and sawdust. The relatively high ash content in the pig feces could be the main reason for this result. In the sawdust, only 2% of the dry matter was ash, while the ash content in pig feces was almost four times greater. The ash in the feedstock could help fuel the gasification reaction[2], increasing the gas production, while simultaneously, reducing the bio-oil yield.

4. Conclusions

Pig waste mixtures of feces with rice husks or sawdust were used in this pyrolysis study. The main compositions of the feed materials were analyzed chemically. The major components in the feedstocks consisted of hemicellulose, lignin, and cellulose. Protein and fat accounted for less than 21% of the mixtures. The effects of those components on pyrolysis production were tested. The contents of holocellulose and lignin had significant positive effects on the bio-oil yields, while the ash contents had a negative effect on the production of bio-oil. There



[**Fig. 3**] Bio-oil yield for mixture of pig feces and rice husk. PF is pig feces, R is rice husk, PR is mixture of pig feces and rice husk.



[**Fig. 4**] Bio-oil yield for mixture of pig feces and sawdust. PF is pig feces, S is sawdust, PS is mixture of pig feces and sawdust.

were no significant effects detected from the moisture, hemicellulose, cellulose, protein, or fat on the bio-oil production. The results also suggested that there was negligible interaction between pig feces and rice husks during pyrolysis. However, the influence of sawdust when mixed with pig feces was marked. This may be caused by the relatively high ash content in the pig feces that increased the gasification reaction and reduced the bio-oil yield.

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