Thermogravimetric Study on Rice, Corn and Sugar Cane Crop Residue

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Abstract: Vietnam is recognized as an agricultural country and there is a potential of biomass resources originated from residues of agricultural section. Rice husk, rice straw, corn cob and bagasse are main biomass of agricultural residues. In this study, proximate and ultimate analyses of biomass samples were investigated. Thermogravimetric analysis of biomass was carried out to understand its thermal behavior in inert and air environment from ambient temperature to 800°C at the heating rate of 10°Cmin^{-1}. It is observed that all the four biomass samples displayed similar weight loss trend. In nitrogen environment, three reaction zones corresponding to the dehydration, first decomposition that generated volatile and second decomposition of the char. In air environment, three reaction zones are corresponding to the dehydration, devolatilisation and combustion of char.

Keywords: biomass agricultural residues, thermogravimetric analysis.

1. Introduction

Vietnam has over 84 million people with a nominal GDP capital of US$1540 in 2012. Vietnam is endowed with several energy resources including coal, oil, natural gas, hydro, and renewable and it has generally been an energy-self-sufficient economy. In 2007, total domestic energy production was 49.4 MTOE while the corresponding primary energy demand in that year was 31 MTOE, making a positive balance of 18.4 MTOE [1]. Vietnam would become a net energy importer around 2015 and by 2025, Vietnam will have to import 46.7 MTOE. Aware of the matter, the Government decision No 1855/QD-TTg of December 27, 2007 approving Vietnam's national energy development strategy up to 2020 with 2050 vision is to assure national energy security. One of the targets is to boost the development of new and renewable energies, bioenergy in order to meet the requirements of socio-economic, with increasing the proportion of new and renewable energies to about 3% of the total amount of commercial primary energy by 2010; about 5% by 2020 and 11% by 2050.

Vietnam is an agricultural country and it possess abundant biomass resources which can be more efficiently utilized to substitute an important part of the fuel and electricity needs of the country. Rice husk, rice straw, bagasse and corn cob are main residue of agricultural biomass resources in Vietnam. It is estimated that about 70% of rural population in Vietnam are currently relied on biomass as a daily cooking fuel. Biomass is also used to produce thermal energy in various industries such as the traditional brick, lime and pottery kilns, and some sugar refiners use bagasse for power generation.

Efficiency using biomass resources for energy purpose required the knowledge of biomass chemical and physical properties and appropriate energy conversion technology for utilization of biomass. Extensive research for biomass properties and their energy application has been investigated. However, there is not much works mentioned for the potential of biomass, their characterization and even their application for energy demands in Vietnam. In this paper, the geographical distribution of some agricultural residues was mentioned and proximate, ultimate analysis and thermal behaviors of biomass was discussed.

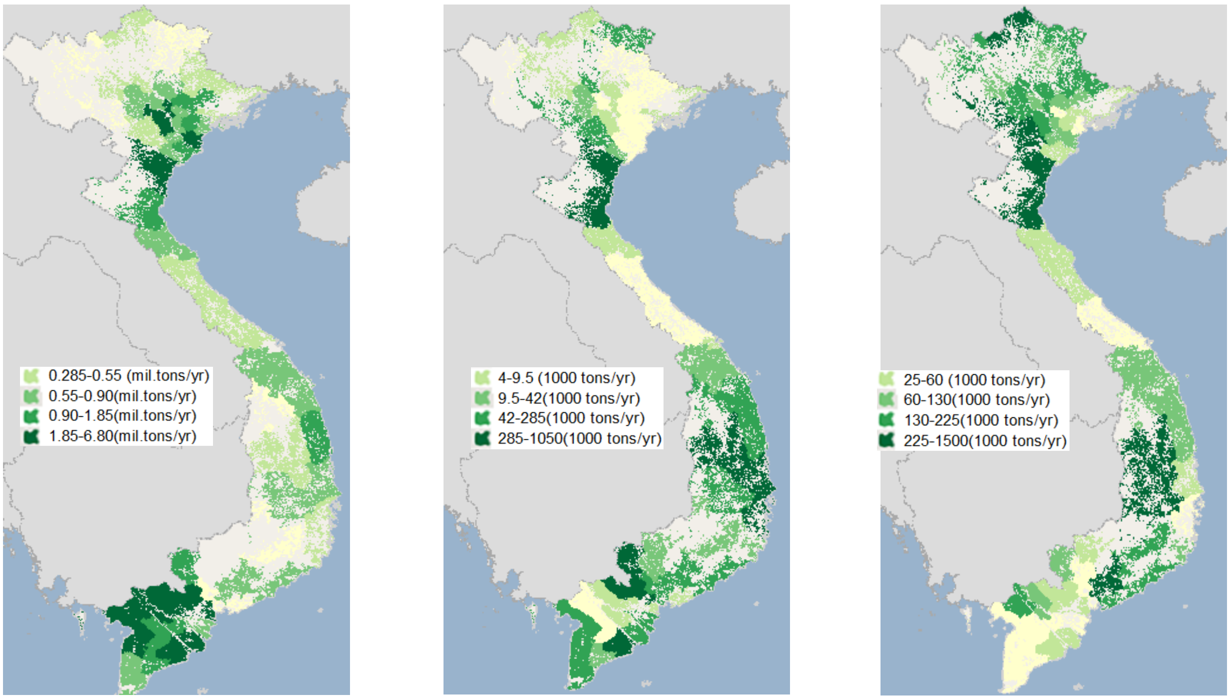
2. Potential of biomass agricultural residues

Geospatial software (GS) was innovated and developed by National Laboratory of Renewable Energy (NLRE). It is a powerful tool for evaluation and assessment of Biomass sources for specific areas. The data of GS was updated the biomass of Vietnam based on "Statistical handbook 2010". GS is focused on by product of Agricultural biomass and classified into 5 catalogues: Rice crop, corn crop, peanut crop, sugar cane crop and cassava crop residues.

Rice crop: Mekong Delta region in the South and Red River Delta area in the North are biggest cultivation areas in Vietnam. Rice production in Vietnam has increased gradually. While rice straw is mainly left in the fields after harvesting, rice husk is produced in large quantities of hundreds of thousands of rice mills all over the country. The geographical distribution of residue of paddy plantation was in figure 1a. By the software evaluation, the total of theoretical biomass residue of paddy plantation was approximately 49 million tons. This value of biomass was similarly to Arvo Leinonen work [2]. Among the mass volume of paddy biomass, only 19 million tons of paddy residue could be collected [3].

In fact, rice husk was accumulated at the rice mill and it could be used for heat and power demands. Rice husk is currently used in Vietnam in many different ways. Rice husk were used as a fuel for local ceramic and brick factory and it is the most polluted way of utilization of rice husk. Larger amount of rice husk was briquette and it was used as a fuel for boiler in industry section. For power production by utilization of rice husk, The Dinh Hai Cogen Joint Stock Company has built a rice-husk steam power plant in Can Tho City in 2006. The annual consumption of rice husk is 37.500 tons for 6000hour working per year. Unlike rice husk, rice straw is not utilized to nearly the same extent. Small amount of rice straw is used for heating demand of residential areas. Large amount of straw is burnt or decomposed in the field for soil enrichment. The combustion released carbon dioxide emission and methane is formed during decomposed and emits to the environment.

Sugar cane crop: Sugar cane is a short-term industrial plant vital to the sugar industry. The cultivated areas are mostly in the North-Central region, the South-Central coast region. The country had had 37 sugar refineries with total capacity 1.3 million ton in 2012. As mentioned, it has nearly 300,000 ha of land planted to sugarcane [4]. Geographical distribution of residue of sugar cane production was shown in figure 1b. The cane stalk is removed for processing and the leaves are stripped off and left on the field to dry to be later burned. Harvest sugarcane is transported to the factory for processing to sugar and various by-products and residues. As evaluation by Geospatial software, the total of theoretically residue of sugar cane approximately 7.8 million tons. This number was similar to the report of Arvo Leinonen [2]. It was about 64% of the theoretical value (5 million tons) sugar



a b c

Figure 1. Geographical distribution of residue of paddy plantation (a); residue of sugar cane production (b) and corn cob residue (c).

cane residue are gathered at the sugar cane factory [3]. Some of sugar mills use bagasse in their CHP boilers to supply electricity and heat for their own use. Nevertheless, most processing factories have low efficient co-combustion technologies that present opportunities for optimization.

Corn cob: Corn cultivation has been increasingly grown over the past 10 years. There was 1,172,000 hectares under corn farming with total output reaching 5.5 million tons in 2013. Corn farming is extensive in Northeastern, Northwestern, Central highlands, Southeastern provinces, Red River and Mekong Delta (figure1c). Corn productivity is lower than other countries. Corn is primarily used as food by highland people and as animal feed. There were 124 animal feed factories with a total capacity of 10.5 million tons/year. In 2013, the country had to import 2.2 million tons of maize for animal feed production. The primary uses of maize residues include animal feed and domestic fuel. Small amount of corn cobs are used at village level as a cooking fuel, however, in the main growing areas of the country dumping of corn cobs post-harvest is still common and can present an environmental issue. At the moment, there is absent of technology for conversion of corn cob to energy in Vietnam.

The theoretical potential that mentioned above represented the theoretical maximum of biomass for energy purposes, but did not account for technical limitations. When such factors are considered the amount of biomass available for energy production is called the technical potential. At this moment, there is not so much information relating to the technical potential of biomass in Vietnam.

3. Thermogravimeric study on biomass agricultural residues

The agricultural residues was collected from field and dried for a period of 2-3 weeks. The samples were kept in closed polyethylene bags to avoid contamination prior to carrying out the tests. The samples were milled to powder and sieved to a particle size less than 1 mm before carrying out the tests. Moisture content was determined using the ASTM E871 standard. The proximate analysis was used to determine the volatile matter, fixed carbon and ash content. Volatile matter was measured by following procedures described in ASTM standard E872. Carbon and hydrogen were determined according to standard ASTM E777 and oxygen was calculated by difference. The heating value of the samples was measured using Parr 1266 Bomb Calorimeter followed standard ASTM 5865-04. The ash of biomass was prepared according to ASTM 1755, biomass samples were burned in the oven at 575°C until the weight unchanged. Metal oxide of biomass ash was analyzed by ICP-MS (IRIS-INTREPID, PE Optimal 7300DV). Thermogravimetric analysis (TG/DTA) with PerkinElmer PYRIS Diamond model was used for both pyrolysis and combustion analysis. 10 mg sample was loaded into an alumina crucible and heated at programmed temperature by the rate of 10°C min^{-1} in nitrogen or air environment. The weight loss and DTA signal was recorded during the analysis process.

Fuel properties of biomass can be conveniently grouped into physical, chemical, thermal properties Important chemical properties of biomass relates to ultimate analysis, proximate analysis, heating value, ash composition and ash fusion temperature. Proximate analysis of a biomass fuel sample involves the determination of moisture, volatile matter, ash and fixed carbon content. Ultimate analysis relates to the C, H and O composition of biomass. The proximate analysis, ultimate analysis, ash composition and LHV of biomass samples were shown in table 1.

In air dry condition, the moisture of rice straw was 13.13% and it higher than rice husk 2.5%. The rice straw and rice husk has high ash content and it value in a range of 12-13%. The volatile of rice husk was 68.69% and of rice straw was 58.34%. Fix carbon of both samples was approximately 15%. The proximate analysis of rice husk was similar to that reported by S.J. Yoon [5]. For corn cob samples, the moisture of air dry was 7.77% and of bagasse was 13.17%. Both samples had similar volatile matter was approximately 74% and very low ash content. The fix carbon of corn cob was 15.6% and of bagasse was 9.43%. Ultimate analysis of biomass, i.e carbon, hydrogen and oxygen was listed in table 2. Obtained results shows that the carbon content of biomass lower than 50% and their composition owned large amount of oxygen. The high proportion of oxygen leads to the reduction of calorific value. According to previous studies [6-7], the nitrogen and sulfur content are 0.3% and 0.08% for corn cob, 0.3% and 0.07% for bagasse, 0.3% and 0.09% for rice husk, and 0.6% and 0.10% for rice straw. As evaluated, the amount of nitrogen and sulfur were very low, so that, they were all neglected in our studies.

Table 1. Proximate, ultimate and elemental analyses of Vietnam agriculture residues.

Characteristics	Rice husk	Rice straw	Corn cob	Bagasse
Proximate analysis				
Moisture (%-air dry)	2.50	13.13	7.77	13.17
Volatile matter (%-dry basic)	68.69	58.34	74.86	76.03
Ash (%-dry basic)	12.85	13.47	1.77	1.36
Fixed carbon (%-dry basic)	15.86	15.06	15.60	9.43
Ultimate analysis				
Carbon (%-dry basic)	40.53	33.13	49.50	49.80
Hydrogen (%-dry basic)	2.71	4.92	4.90	5.90
Oxygen (%-dry basic)	43.30	49.90	43.85	43.91
LHV	15.50	14.80	17.00	17.36
Ash (% mass)				
SiO_2	91.86	71.26	51.88	87.85
Al_2O_3	0.25	0.67	1.32	3.63
Fe_2O_3	0.91	0.89	4.27	3.87
CaO	3.13	7.05	4.17	2.12
MgO	0.12	1.46	1.85	0.61
Na_2O	0.29	0.98	0.37	0.14
K_2O	1.54	15.62	29.58	0.52
Other	1.90	2.07	6.56	1.26

The main compositions of rice husk were SiO_2, CaO and K_2O while Al_2O_3, Fe_2O_3, MgO just appearance with small amount. The content of SiO_2 significantly hold 91.86% mass of rice husk ash, CaO and K_2O was 3.13% and 1.54%. The main composition of metal oxide contain in ash of rice hush was similar with the results of S. Fukuda [8]. For rice straw, the composition of SiO_2, CaO and K_2O were also the main ingredient however their proportion was difference with rice husk which the content SiO_2, CaO and K_2O in ash were 71.26%, 7.05% and 15.62%, respectively. For the corn cob sample, the SiO_2 content is smaller than of an above samples and the content of K_2O was approximately 29.58% of the ash and its high compared with those of agricultural residues. The ash content with high composition of alkaline oxide has a major impact on the trouble-free operation of a biomass gasifier or combustor. The danger lies not only in their influence to lower the fusion temperature of the ash but in their vaporization at temperatures prevailing inside a biomass gasifies/combustor and subsequent deposition on cold surfaces.

Our results showed that among all analyzed samples, bagasse had the highest calorific value 17.36 $MJkg^{-1}$ and corn cob, rice straw and rice husk were 17.00, 15.50 and 14.80 $MJkg^{-1}$, respectively. These results due to relate with element composition of rice husk, rice straw, corn cob and sugarcane, especially carbon and hydrogen content that has highest value in bagasse.

Thermogravimetric study is one of the precious analysis for studying the combustion or pyrolysis of biomass. As described detail by Van for thermal analysis of biomass in the inert environment, there are three separate stages occurred [9]. The first stage is water removal of biomass and it regular completes below 150°C. The second stage is in the rage of 200-400°C and it is the initial decomposition of biomass and directly related to the formation of volatile. The last stage is the continuously decomposition of char at higher temperature. In case of thermal analysis of biomass in the air environment, there distinct zone are occurred during the thermal process. The water removal is the initial process and it is completed below 150°C. The second stage is a decomposition of biomass for generation of volatile and the combustion of volatile also occurred. In the last stage, there is continually combustion of char at higher temperature in the air environment. In this investigation, discussions of thermal behaviors of some biomass were mentioned.

Figure 2 showed the non-isothermal weight loss (TG) curves for fours biomass samples at 10°$Cmin^{-1}$ under nitrogen atmosphere. It could be said that their thermal behavior was similar to each other. Three distinct weight loss stages could be identified and it in agreement with other research. The weight loss of each stage was mentioned in table 1. The first stage is corresponding to the demoisturization of biomass. In the second stage (first decomposition), it is a rapidly devolatilisation in a narrow temperature range (approximately 200-400°C) of biomass. The devolatilisation of biomass started at 210, 216, 209 and 230°C for rice husk, rice straw, corn cob and bagasse, respectively. There was 52.7% weight loss for rice husk, 42.16% for rice straw, 56.6% for corn cob and 58.7% for bagasse residue. Hemicellulose, cellulose and lignin are the major component of biomass and the decomposition of those ingredients occurred at this temperature range. Hemicellulose decomposition take place in the range of 200-350°C, cellulose is decomposed in the range of 350-500°C and partial of lignin also decomposed in this temperature range [10]. For third stages in the range of 400-900°C (second decomposition), all biomass samples had a much lower weigh loss in comparison to the second stage. The weight loss for corn cod and bagasse was 14.6% and 17.8%, respectively. While for rice husk and rice straw, the weight loss was 12.1% and 14.9%. For this stage, Taro Sonobe *et al* reported that the char consists of the residue of lignin and some cross-linking of cellulose with lignin continues to further exothermic polymerization stage of char [11]. The explanation assumes that at the higher temperature, the polymerization of biomass char continuously occurred and the polymerization reaction is depended on the unique properties of biomass char.

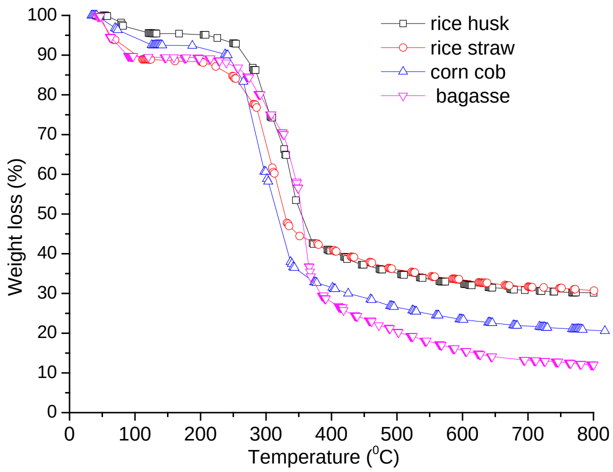


Figure 2. TG curves of biomass samples at heating rate by 10°$Cmin^{-1}$ in nitrogen environment.

The weight decrease of thermal analysis in air environment for rice husk, rice straw, corn cob and bagasse were shown in figure 3. Beside the demoisturization of biomass at lower than 150°C, clearly observed that there was two distinct stage presented. The first was the decomposition of biomass and the second one was the combustion of biomass char. The results showed that for the first stage, the cellulose component of biomass was decomposed and generated volatile. The decomposition reaction rate of the samples became faster than the pyrolysis reaction in this stage. Figure 4 was a DTA signal during the analysis, the unit of the vertical axis was adjusted to the same value of biomass sample (moisture ash free). It meant that only the combustible matter of biomass was considered. It is clearly observed similarity trend of exothermic peak in DTA curves for all biomass samples. The decomposition of cellulose and the release of volatile created the porosity of biomass char. In the analysis environments, the diffusion of oxygen into the char particle occurred resulted for the combustion of char and this phenomena caused continuously decrease in weight loss. The devolatilisation of rice husk and rice straw at the temperatures range is 208-358°C and 214-356°C, respectively whereas the temperatures range is 214-340°C and 190-369°C for corn cob and bagasse, respectively. The devolatilisation of the biomass took place in the narrow temperature range due to the rapid evolution of the volatile products. The total devolatilisation were very close for corn cob (75%) and bagasse (77%) and higher probably than rice husk (57%) and rice straw (65%)due to the higher volatile matter and lower ash contents of corn cob and bagasse (Table 1). The end of the devolatilisation zone was accepted as the beginning of the combustion of char. The combustion of char also formed the exothermic peak in DTA curves. The combustion of rice husk char occurred in the range of 358-500°C and based on the DTA curves, the combustion of char obtained the maximum value at 435°C. The combustion of char occurred in the range of 356-483°C for rice straw, in the range of 340-465°C for corn cob and in the range of 370-490°C for bagasse. Above 500°C, there is no observation of the weight loss. These results suggested that all the char was completely combusted and only the ash of biomass remain. The ash contained of biomass was identified by TG and were shown in table 3. This value was corresponding to the value of the ash that was measured by proximate analysis (Table 2).

4. Conclusion

Evaluation the theoretical potential of some biomass agricultural residue was done by *Geospatial software*. Proximate and ultimate analyses showed that all biomass agricultural residues are appropriated for combustion or gasification for energy and heating demand. However their ash content large amount of alkaline and alkaline earth and its melting point would be influenced. Thermogravimetric analysis (TGA) on four biomass samples (rice husk, rice straw, corn cob and bagasse) was conduct at heating rate of 10°C/min in an inert nitrogen and air atmosphere. The moisture removal occurred below 150°C. The initial decomposition of biomass in inert environment was noticed between 200°C-380°C and in air environment between 200°C-350°C. The second decomposition of biomass in inert environment continuously occurred above 400°C and the residue of rice husk and rice straw were higher than of corncob and bagasse cause of the higher ash content in their ingredient. The devolatilisation occurred in the range of 190-369°C and char combustion in a range of 340-500°C.

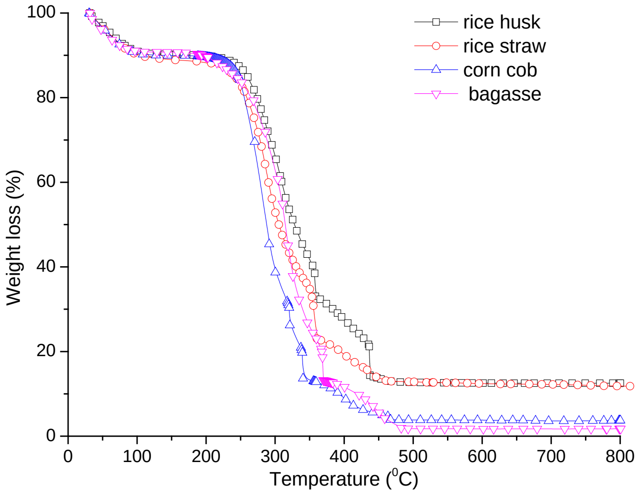


Figure 3. TG curves of biomass samples at heating rate by 10°Cmin^{-1} in air environment.

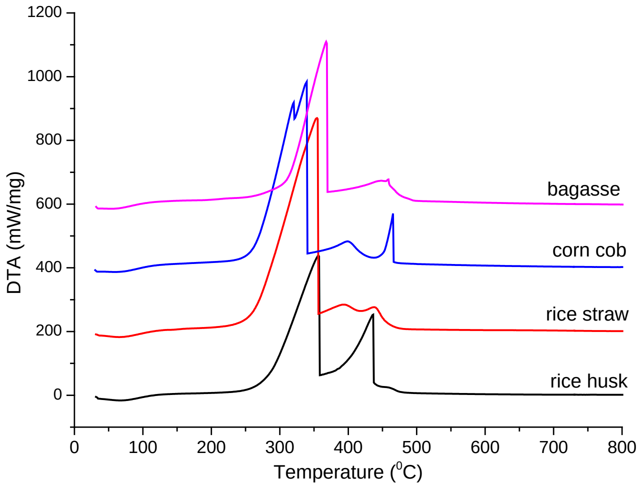


Figure 4. DTA curves of biomass thermal analysis in air atmosphere at heating rate by 10°Cmin-1.

Table 2 Thermal degradation of biomass in nitrogen environment.

Samples	Drying	First decomposition		Second decomposition		Residual weight (%)
	Water loss (%)	Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)	
Rice husk	4.3	210-377	52.7	377-800	12.1	30.1
Rice straw	11.1	216.344	42.2	344-800	14.9	30.7
Corn cob	7.2	209-351	56.6	351-800	14.6	20.8
Bagasse	10.4	230-381	58.7	381-800	17.8	12.1

Table 3. Thermal degradation of biomass in air environment.

Samples	Drying	Devolatilisation		Char combustion		Ash (%)
	Water loss (%)	Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)	
Rice husk	9.6	208-358	57	358-500	20.343	12.5
Rice straw	10.6	214-356	65	356-483	10.414	11.8
Corn cob	9.9	214-340	75	340-465	9.075	3.7
Bagasse	9.2	190-369	77	369-490	11.484	1.7

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