Utilizing Tobacco Residues to Generate Bio-oil and Biochar via Ablative Pyrolysis

Lalita Chumsawat[a], Nakorn Tippayawong[b],*

[a]Graduate Degree Program in Energy Engineering, Faculty of Engineering, Chiang Mai University.
[b]Department of Mechanical Engineering, Faculty Of Engineering, Chiang Mai University, Chiang Mai, 50200, Thailand.
 n.tippayawong@yahoo.com

Tobacco industry in Thailand uses tobacco leaves for cigarette production. About 10 % of the processed leaves consisting of midribs and dust was generated as waste. These residues may be utilized as energy source. In the present study, the tobacco residues were analyzed for physico-chemical properties. Proximate and ultimate analyses for moisture, volatile matter, fixed carbon, ash and chemical elements (C, H, O, N, S) as well as analysis for lower heating value were carried out. It was found that the residues contained high carbon and volatile matter, with the heating value in the range of 11 - 14 MJ/kg. Results with the detergent method showed fairly high amount of lignocellulose content in the range of 24 - 31 %. The tobacco residues were also thermally treated via ablative pyrolysis process. The highest yield of pyrolysis liquid was about 54 % with the heating value was 30 MJ/kg. Properties of the pyrolysis products were shown to have high potential for energy application. From spectroscopic analysis of the products, there were carboxyl compounds, carbonyl compounds and aromatic compounds present. It was clear that alternative energy and fuel products can potentially be generated from the thermal processing of these tobacco wastes.

1. Introduction

The energy needs in the world is based largely on fossil fuels (oils, natural gas, coal), of which the reserves are finite. Given the growing world population, the energy consumption per capital, the evidence of global warming, and the need for alternative energy sources in the long term is explicitly increasing (Jahirul et al., 2012). Biomass is an environmentally friendly renewable energy source, appropriate and consistent with the current energy situation. Biomass utilization in energy uses is receiving great attention due to environmental considerations and the increasing energy demands worldwide (Zhang et al., 2007). Biomass is recognized as an important renewable resource for agricultural countries around the world. For Thailand, most energy sources are derived from processing of fossil fuels for use as fuels in industrial sector, transportation sector, and power generation sector. At present, Thailand imports crude oil on average 977,000 barrel/d (Ministry of Energy, 2018). There are many agricultural wastes created annually. Their disposal is problematic in many areas, mainly due to limited landfill areas and increased public anxiety with environmental pollution (Wongsiriamnuay and Tippayawong, 2015). This tendency led to increased public concern for the management of these wastes.

Adoption of thermochemical conversion to store carbon is cutting the cycle of returning carbon to the atmosphere. This approach is accepted by the United Nations as a tool to reduce global warming. On-going efforts are important to change the low carbon emissions in Asia (Lee et al., 2018). Using biomass residues from the agricultural sector via thermal processes may help with the energy issues. These thermal routes such as torrefaction (Onsree et al., 2019), gasification (Homdoung et al., 2019), slow pyrolysis (Tippayawong et al., 2018), fast pyrolysis (Jaroenkhasemmeesuk and Tippayawong, 2015), and combustion (Sittisun et al., 2015) have been shown to be suitable for the agro-residues. Pyrolysis is a simple, inexpensive technology for processing a wide variety of biomass feedstocks and very flexible in the process and products. The liquid product as a source of liquid fuel for direct use, biofuels and source of chemicals.

In northern Thailand, tobacco is a popular secondary crop grown after paddy rice harvest. Major production is usually managed by the Thai tobacco monopoly. In its central processing plant, all cured dry leaves in the

north of the country are transported to Denchai redrying plant in Phrae for extraction and processing of tobacco leaves into cigarettes. About 10 % of the processed leaves consisting of midribs and dust was generated as waste. It was estimated that there are more than 6,000 t of tobacco waste left unharnessed each year. From this quantity, the tobacco residues may be used as alternative biomass energy source via various thermochemical conversion methods. Environmental sustainability can be benefited through the waste (solid, water, heat) recovery (Fan et al., 2019). From the existing literature, reported works on physico-chemical properties and lignocelulosic composition of tobacco residues remain scarce. To the authors' knowledge, no report is yet available on applying ablative pyrolysis to tobacco residues to generate bio-oil and biochar. Ablative technique enables fast pyrolysis to generate high yield of liquids at relatively large sized biomass.

This research work focuses on characterization of tobacco industry residues and subsequent generation of bio-oil and biochar via ablative pyrolysis. Analyses for chemical compositions, heating value, thermal decomposition characters and lignocellulosic components were performed. Comparison of the bio-oil and the char against the original tobacco waste via FT-IR spectra was made for a number of basic functional groups at various frequencies.

2. Materials and methods

2.1 Raw material

The raw material used was tobacco residues from extraction and processing of tobacco leaves into cigarettes at the Denchai redrying plant in Phrae. The moisture content of the samples was about 10 - 15 %. The samples were sent to laboratories for physico-chemical properties analysis. Results are shown in Table 1. The tobacco residues received were in the form of 0.5 - 5 cm long slice which were directly fed to the pyrolysis system.

Table 1: Comparison of chemical composition and properties of tobacco residues from previous works in Spain (Encinar et al., 1997), Turkey (Pütün et al., 2007), Turkey (Akalin and Karagöz, 2011) and Brazil (Tuzzin, 2016).

%	Spain residues	Turkey residues	Turkey stem	Brazil dust	stem	This work (Thailand) Virginia	Burley
Extractives	-	16.84	-	-	46.53	-	-
Hemicellulose	-	44.25	-	-	1.86	7.46	7.61
Cellulose	-	-	-	-	20.85	8.15	15.74
Lignin	-	9.20	-	-	6.39	9.11	7.10
Moisture	-	7.74	12.30	5.20	-	19.99	14.95
Volatile matter	74.4	67.67	72.75	68.80	-	71.01	68.32
Fixed carbon	19.2	13.43	1.69	6.10	-	11.69	7.84
Ash	6.4	11.16	13.26	19.90	20.78	17.30	23.81
C	47.8	51.65	42.39	44.48	-	38.96	31.80
H	5.9	6.20	6.49	6.04	-	4.71	3.81
O	45.6	40.10	48.48	45.59	-	36.91	36.61
N	0.6	2.05	2.23	2.77	-	1.95	3.90
S	0.1	-	0.14	0.43	-	0.17	0.07
HHV (MJ/kg)	15.6	19.57	14.98	15.59	-	14.53	11.14

2.2 Pyrolysis reactor setup

Biomass is rapidly heated to a high temperature in the absence of oxygen in the fast pyrolysis process. The reactor is the heart of any pyrolysis process, and it has been the subject of considerable research (Jareonkhasemmeesuk et al., 2018). The basic characteristics of the fast pyrolysis process are high heat transfer and heating rate, very short vapour residence time, rapid cooling of vapours and aerosol for high bio-oil yield and precision control of reaction temperature (Demirbas and Arin, 2002). Reactors of pyrolysis designs have been explored to optimize the pyrolysis performance and to produce high yields of bio-oil. Each reactor type has specific characteristics, bio-oil yielding capacity, advantages and limitations.

In this work, the pyrolysis experiments were carried out at 450-600 °C in a laboratory scale, externally heated, ablative vacuum reactor, shown in Figure 1.

Ablative pyrolysis offers good control over vapour residence and able to utilize larger size biomass (Khuenkaeo and Tippayawong, 2018). About 50 g was fed into the reactor using a feed valve installed at the top. The pan shape reactor (inner diameter of 25 cm and height of 4 cm) was heated by a gas stove and the

temperature of the hot bottom plate was controlled with a controller and a K-type thermocouple measured on the hot surface.
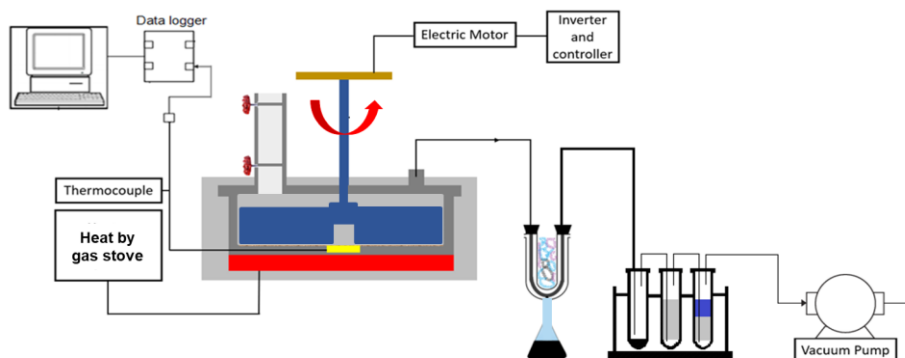

Figure 1: Schematic diagram of the ablative pyrolysis experimental installation.

During each experiment, the four-blade paddle was rotating and pressing the tobacco residues against the hot plate at a speed between 1 - 10 rpm. The volatiles release was directed through dry ice condensers and gas cleaning unit by a vacuum pump. The liquid product was collected and weighed. Gases were extracted and cooled rapidly to achieve a fast condensation. They were further cleaned in a cotton filter and silica gel traps. The yields were calculated as the relationship between the mass of the products (liquid and char) and the mass of the original tobacco residues used in each experiment, determined according to Eqs. (1) and (2) as;

$$Liquid\ Yield\ (wt\%) = \frac{m_L}{m_i} \cdot 100 \tag{1}$$

$$Solid\ Yield\ (wt\%) = \frac{m_S}{m_i} \cdot 100 \tag{2}$$

where m_L is the mass of liquid produced, m_i is the mass of initial tobacco residues and m_S is the mass of char.

2.3 Sample analysis and characterization

The tobacco residues from the redrying plant were analysed for physico-chemical properties. Proximate analyses for moisture, volatile matter, fixed carbon and ash was done using thermogravimetric analysis following ASTM D 7852 standard. Ultimate analyses for chemical element (C, H, N and O) was used following D 5373 standard. Test method for sulphur element was adopted using ASTM D 4239 standard. Standard test method for heating value (ASTM D 5865) was adopted using bomb calorimetry (Prasertpong et al., 2017). The heating value of materials were calculated from the percent of carbon, hydrogen, oxygen and nitrogen from CHON analysis according to Eq(3) (Demirbas and Arin, 2002), used for calculating Turkey tobacco residues.

$$HHV\ (MJ/kg) = 33.5(C) + 142.3(H) - 15.1(O) - 24.5(N) \tag{3}$$

where HHV is the higher heating value of material C, H, O and N are carbon, hydrogen, oxygen and nitrogen contents (wt%).

The detergent method analyzes the plant structural elements (Van et al., 1991) by extracting neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL). Virginia and Burley tobacco wastes obtained from the Denchai plant was used. They were found to have average moisture content of 10 - 15 %. They were crushed to a size of 0.5 to 1 mm and extracted with a neutral detergent solution to determine NDF. The extracted tobacco with neutral detergent was subsequently processed with a solution of acid detergent to find ADF. Difference between NDF and ADF indicated the amount of hemicellulose. The extracted with a solution of acid detergent was then reacted with 72 % H2SO4 solution for analysis of ADL. The difference between ADF and ADL was the amount of cellulose.

Table 1 shows the lignocellulosic components, proximate, ultimate analyses and HHV of the tobacco residues in Thailand compared with those given in previous literature. Raw materials from Turkey were on dry and ash free basis, while raw materials from Spain, Brazil and Thailand were based on dry basis.

The ultimate analysis was also carried out for the bio-oil and char using a Thermo-scientific Flash 2000 model C, H, N, S and O analyzer. The bio-oil and char analyzed in this section were obtained under experimental conditions that gave the maximum yield. The carbon, nitrogen, hydrogen and sulfur contents of the pyrolysis product were determined. The oxygen content was calculated by difference.

The heating value was calculated from the percent of carbon, hydrogen and oxygen using the modified Dulong's formula as Eq(4) (Theegala and Midgett, 2012).

$$HHV\ (MJ/kg) = \frac{33.5(C)}{100} + \frac{142.3(H)}{100} - \frac{15.4(O)}{100} \tag{4}$$

2.4 Fourier transform infrared-photoacoustic spectroscopy

Fourier transform infrared (FT-IR) photoacoustic spectroscopy was used to analyze the function of the sample via IR radiation absorption. Each functional group was allowed to vibrate at different frequencies which was reported in wave numbers. It was carried out to characterize the functional groups in the tobacco residues, the organic phase the bio-oil samples and the char.

3. Results and discussion

3.1 Product yields

Figure 2 shows physical appearances of the tobacco residues, as well as the main products from pyrolysis, bio-oil and char. The bio-oil collected was separated into two layers, organic and aqueous phase. Results of the product mass yields from pyrolysis of the tobacco residues as a function of the hot plate temperature are shown in Figure 3 for total liquid bio-oil and solid char.
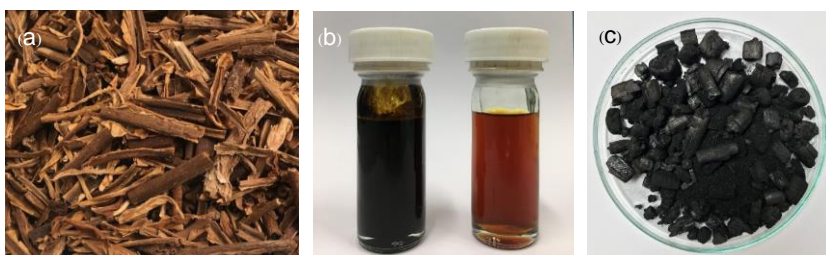

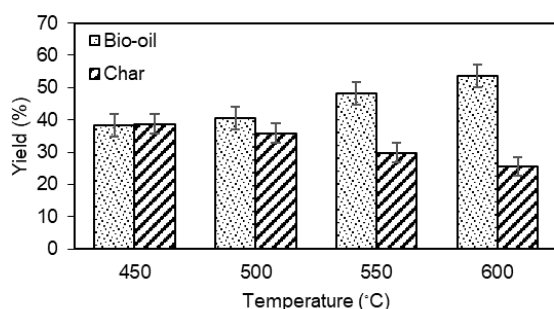Figure 2: (a) tobacco residues, and pyrolysis product (b) organic and aqueous phase bio-oil, and (c) char

Figure 3: Yields of bio-oil and char form ablative pyrolysis

The hot plate temperature was increased from 450 to 600 °C. It was found that the maximum liquid yield and the minimum solid yield occurred at 600 °C. The highest yield of the pyrolysis liquid was about 54 %. Within the pyrolysis temperatures considered in this work, it can be seen that change in temperature affected the product yields markedly. The yield of bio-oil was found to increase with increasing temperature, while the opposite was true for the char yield. It should be note that there was about 18 - 24 wt% was unaccounted for. From mass balance, it was thought that this unaccounted mass was likely to be moisture and non-condensible gases. Regarding the pyrolysis liquid yields, the values obtained here were in similar range to those reported in the previous literature (Khuenkaeo and Tippayawong, 2019).

3.2 Chemical and elemental composition

Comparison of chemical composition and properties is shown in Table 1. The results of the tobacco residues with detergent method showed that the amount of lignocellulose content were in the range of 24 - 31 %. The amount of volatile matter was between 68.3 - 71.0 %. Volatile matter represents the carbon, hydrogen and oxygen components in the biomass that turn into vapours when heated. The fixed carbon of the samples was 7.8 - 11.7 %. This small amount of fixed carbon may be disadvantage for charcoal production due to limited amount of fixed carbon in the raw materials. Ash is the non-combustible component of biomass. The tobacco residues were found to contain 17.3 to 23.8 %. High ash content and low volatile matter affected the calorific value negatively. Regarding elemental composition, the tobacco residues were found to contain high carbon and low sulphur. HHV of the Virginia and Burley tobacco were 14 and 11 MJ/kg, similar to those reported in literature for tobacco residues in Thailand.

Table 2 shows results from ultimate analyses and HHV of the pyrolysis products obtained from the tobacco residues. The bio-oil used was derived from the organic phase after separating the aqueous phase and char. It was shown that high carbon content of 63.69 % in the bio-oil and 41.13 % in the char were obtained. These were significantly higher than that found in the original tobacco residues. The hydrogen content was also found to increase but the oxygen content was decreased. The char appeared to contain higher oxygen percentage than the liquid bio-oil. The sulphur was found to be in the range of 0.12 - 0.81 %, less change compared to the tobacco residues. The HHV of the bio-oil was about 30 MJ/kg and that of the char was about 13 MJ/kg. As a result, it was clear that the pyrolysis process could upgrade the residues to generate higher quality fuels distinctly.

Table 2: Ultimate composition (wt%) and HHV of the pyrolysis products

Products	C	H	O	N	S	HHV (MJ/kg)
Bio-oil	63.69	7.76	10.04	3.22	0.12	30.83
Char	41.13	2.22	23.06	1.42	0.81	13.39

3.3 FT-IR analysis results

The FT-IR spectra of the organic phase bio-oil and the char are presented in Figure 4, compared against the original tobacco residues.
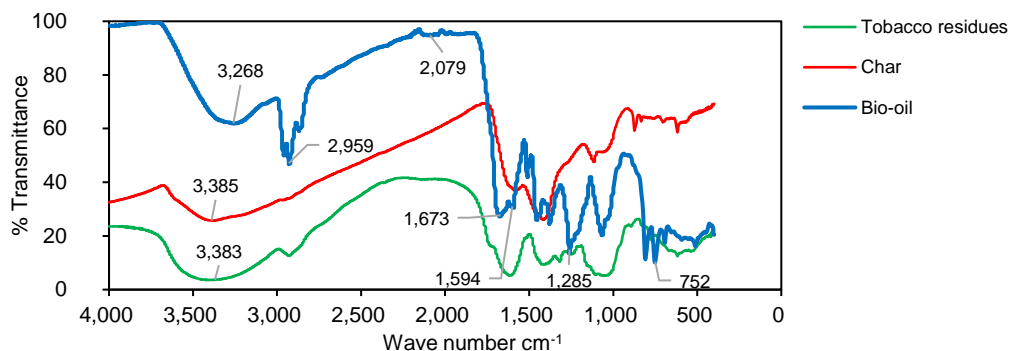

Figure 4: FT-IR spectral analysis for bio-oils and char of the pyrolysis experiments.

For the tobacco residues and the char, similar pattern was observed for a number of basic functional groups at the frequency 3,400-2,400, 1,600 and 1,475 cm^{-1} corresponding to O–H stretching and aromatic C=C. Aromatic C–H peaked at 900-750 cm^{-1} and approximately 1,020 cm^{-1} showed aliphatic C–O of organic phases. The C–O stretching vibrations between 1,680 and 1,780 cm^{-1} was because of ketones and aldehydes, whereas the O–H stretching vibrations between 3,200 and 3,450 cm^{-1} were from phenols and alcohols (Schnitzer et al., 2007). New peaks were observed, indicating that the pyrolysis products had different chemical bonds from the original tobacco residues. Various new peaks were found, indicating different bond types such as C=O, C–O, C–H, and O–H available, especially for the bio-oil.

4. Conclusions

The tobacco residues contained high carbon and volatile matter, with lower heating value in the range of 14 - 17 MJ/kg. They also contained high amount of lignocellulose content of about 24 - 31 %. Thermal conversion

via ablative pyrolysis, the bio-oil products were found to have increased carbon content of 63% and increased energetic content to 30 MJ/kg. The spectroscopic analysis results of the product showed a number of different basic functional groups. New peaks were observed, indicating that the pyrolysis products had different chemical bonds from the original tobacco residues. It was demonstrated in this work that the tobacco residues have potential for generation of carbon-negative biofuel. This way, the new added value of the tobacco wastes should be promoted for industrial use.

Acknowledgments

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