Conversion of Black Wattle to Bio-Oil and Chemicals on the Continuous Pyrolytic Reactor

Witchakorn Charusiri, Srinakharinwirot University, Thailand

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Abstract

Black wattle (*Acacia auricaliformis*) is a fasting tree which used as fuels to electrical generation plant and a feedstock to paper mill industry. Biomass residues considered as a renewable resources with highly potential for energy production while pyrolysis is application to converted biomass to bio-oil and fuels for the future. The pyrolysis of black wattle were performed in a small size reactor at 400-600 °C under feeding rate of 0.4 – 1.2 kghr^{-1} under N_2 flow with 10 °C/min heating up. The yield of char, liquid, and gas rarely investigated. Pyrolysis liquid product as a bio-oil and tar were in two separated phase with yield of 26.90 - 49.77 wt.%, bio-oil yield were obtained varied about 12.86-37.63 wt.% whereas gases and solid product were obtained. Both of liquid products were analyzed by gas chromatograph-mass spectrometry. The highest bio-oil yield of 39.00 wt.% was obtained at temperature of 550 °C for feeding rate of 0.6 kghr^{-1} whereas the highest tar yield at 12.63 wt.% at 550 °C for feeding rate of 1.2 kghr^{-1}. The bio-oil contained mainly aliphatic, substituted aromatic, nitrile and oxygenated compound at of 0.07, 1.50, 4.96, 60.03 respectively. Moreover, tar had mainly oxygenated compound with high molecular weight and phenol. The results show that the fasting tree residual can be considered as a potential renewable energy and revelant to valuable chemical feedstock.

Keywords: bio-oil, biofuels, biomass, pyrolysis, chemical feedstock

1. Introduction

As for the energy resources were depleted in the available of fossil energy resources while the increasing demand of energy response to the production on industrial sector, transportation and economic growth overconsumption in all developing countries. Many researchers look towards the best mean of studies emphasized on the alternative renewable energy sources for replacement the fossil fuels.

Thailand is an agricultural country which many agriculture products gave a residuals were not used for utilization worthily and discomposing as a waste in landfills. On the other hand, biomass now being considered as a renewable energy that can alleviate the energy consumption by direct combustion, gasification, liquefaction and pyrolysis were many technologies available to convert the biomass into higher value fuels.

Pyrolysis is one of the most promising approaches for production liquid fuels from biomass can be achieved both thermal and catalytic conversion in which biomass is composed by heat on the absence of oxygen, leading to the production of charcoal, char, gaseous, and liquid product. (Mohan et al., 2006) In slow and fast pyrolysis were mainly difference in amount of products, (William et al., 1996) on slow reaction gave char production is maximized whereas fast pyrolysis gave bio-oil as mainly liquid products is one most valuable product and can be replace conventional fossil petroleum products (Zhong et al.,2010)

In this study, Black wattle (*Acacia auricaliformis)* is the fasting tree which used as fuels to electrical generation plant and feedstock to paper mill industry while the residuals from black wattle not necessary utilized, it identified as a potential petrocrop to produced bio-oil. The emphasized of this research to report the characterization of products from thermo and catalytic conversion in small pyrolyzer were investigated the properties of bio-oil for obtaining the maximum yield of bio-oil fraction. In order to define their potential as alternative renewable energy resources for transportation vehicle fuels replacement the fossil fuels and highly potential raw materials for chemical industry, the gas chromatography – mass spectrometry to understand the natural of chemical constituents formed during pyrolysis studies. Product yield, composition of bio-oil and tar phase and the most relevant physicochemical properties were obtained.

2. Experimental

2.1 Materials and characterization

The raw materials used were residues from black wattle biomass in agricultural fields which fed to paper mill industry. This residues were obtained by crushed and sieved to particle size from 0.5 to 5 mm. represented about of 18 %wt of Black wattle tree to paper mill industry. This raw material were oven dried at 100 ^{o}C during 5 hr to reduced the moisture content before experiment, proximate and ultimate analysis following the procedure by ASTM. Oxygen levels in feedstock were calculated by difference method of ultimate analyzed (Oasmaa et al., 2001)

2.2 TGA measurement

In order to investigate thermal decomposition behavior of black wattle residues, the studies performed thermal gravimetric analysis (Netzch 409 Simultaneous STA) under heating up rate of 5°C/min to determine the correlation between time and weight loss of the residue were recorded

2.3 Pyrolysis

The bio-oil fraction and tar fraction in liquid product were obtained from the pyrolysis under N_2 atmosphere to avoid oxidative degradation on a continuous pyrolyzer. Figure 1 show schematic diagram for this experiment, it consisted of under-screw feeding reactor which was made from stainless 316 of 120 cm. length and covered by an insulation device. Under screw feeder carried the biomass residues and weight of dolomite as catalyst of 1-5 %wt inside pyrolyzer with nitrogen gases flow rate of 2 to 6 mL/min. The temperature of pyrolysis was explored under the temperature of 400 to 600 °C, the heating up rate of 10°C/min from room temperature to be the final temperature of desired and kept constant during for 15 min using a PID controller. A cold trap was used to separate the gaseous form the entrained lighter and the gaseous product. The detention time was controlled by reactor screw feeder at feeding rate of 100 to 300 rpm. The higher speed (rpm) cause the lower detention time and conversely.

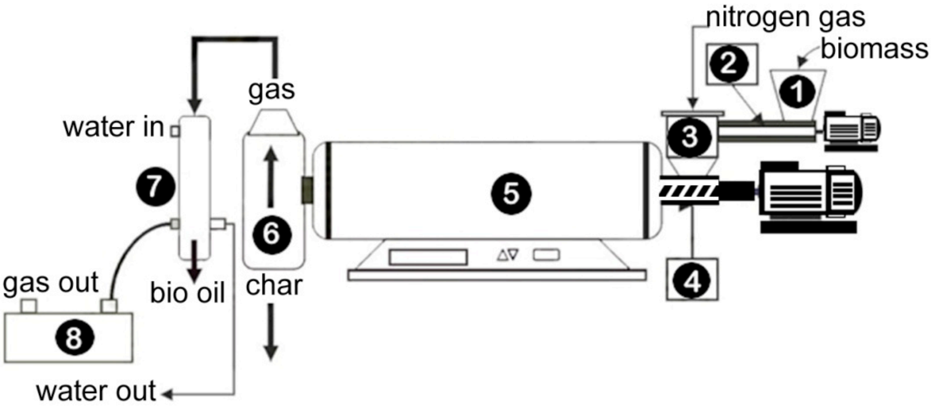

Figure 1: Schematic diagram for the continuous pyrolyser
1) Hooper1 2) Nitrogen gas feeding 3) Hooper2 4) under-screw feeder
5) Pyrolyzer 6) Gas Chamber 7) Condenser 8) Gas collector

2.4 Experimental design and mathematical model

The statistical method of factorial design of experiments (DOE) eliminates the systematic errors with an estimate of the experimental error and minimizes the number of experiments. 2k experimental design is an effective method to determine how various reaction parameters affect the system. It is very useful in the primary experiment study when there are many factor effects to determine. The main parameters in the pyrolysis of black wattle residues are temperature of reaction (A) residence time (B) N2 gas feed rate (C) and amount of dolomite catalyst (D) and each is considered at three levels, namely low(-1), central(0), high(+1) as shown in table 1. For the two level factorial design, the yield of bio-oil and tar fraction, amount of aromatic content, and acidity were defined as the response by a change on the level of these factors. The treatment combination is standard order can be written as (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd. The experiments were designed to run a double replicate to obtain the response data as the yield of bio-oil, aromatic content, and acidity represented in table 2

Accordingly, 35 experiments were conducted with the first 32 experiments organized in a factorial design and the remaining 3 involving the replication of the central points for each stage. Model terms were selected or rejected based on the P values with 95% confidence level. Variance, normality and residual test were analyzed by Design Expert^{TM} software

2.5 Product characterization

The yield and conversion were calculated by the equation as following

Yield (wt%) = Liquid Phase/feedstock x 100 .....1)
Conversion (wt%) = amount of products/feedstock x 100 .....2)

The analytical procedure involved measuring the yield of each product, identifying the various compounds using GC-MS, elemental determination using CHN analyzer. The total liquid phase was physicochemical analysis for density, water, ash content, acidity and heating value compared to those of diesel fuels.

All liquid and gases products were analyzed by conventional gas chromatography in Algilent 7820 with a flame ionization detector. Tar fraction on was separated from liquid product and dissolved at 10%wt in methanol to perform this analysis together. Bio-oil phase was performed by gas chromatography-mass spectrometry (GC-MS) in Algilent GC7890/GCMS5978. The GC was fitted with a 30 m x 0.25 capillary column coated with 0.25 mm thick film of 10% Dimethylpolysiloxane (HP-5MS) mass selective and the chromatographic peaks were obtained using response factor for each of the chemical groups were identified with NIST mass spectral data library.

3. Results and Discussion

3.1 Characterization of feedstock

The properties of black wattle residue shown in Table 1, the analysis in proximate, ultimate and composition of the residues were obtained which show high lignocellulosic material. The content of oxygen is relatively high therefore higher heating value (HHV) are low value.

Table 1: Characterization of Black Wattle residue (dry basis)

Proximate Analysis	(wt%)
Moisture	6.07
Volatile matter	64.46
Fixed carbon	20.15
Ash	9.32
Ultimate Analysis	(wt%)
Carbon	29.74
Hydrogen	5.16
Nitrogen	1.75
Oxygen	63.35
Composition	(%)
Lignocellulosic	84.16
Lignin	16.63
Cellulose and hemicellulose	67.53
Higher Heating Value (HHV)	19.85 MJ/kg

3.2 Themal Gravimetic Analysis

TGA thermogram and the mass loss rate of this residues, which was began to loss mass at 348 ^{o}C to 576^{o}C, this behavior of slightly mass loss due to the moisture removing and thermal decomposition of volatile matter from cellulose at ranging of 400^{o}C

3.3 Product yield in the pyrolysis.

This study were investigated the effect of temperature, feeding rate of feedstock, flowing rate of N_2 gas, and %wt of dolomite catalyst which produced bio-oil through fast pyrolysis. The liquid products consisted of two phase made up of a large number of compounds representing various chemical group derived from lignocellulosic component of biomass residues. It mainly depend on the reaction of temperature and time of residence by feeding speed rate of feedstock whereas, the N_2 flow rate and %wt of dolomite catalyst have not a significant effect on the product fraction. The variation of the liquid yield over the long residence time of slow feeding rate at of 0.6 kghr^{-1} shown in Figure 2. The results show that the liquid product is mainly a bio-oil fraction reached a maximum at 550^{o}C, whereas the tar fraction was constantly proportional with temperature increased. Furthermore, the highest bio-oil yield was obtained at the temperature of 550 ^{o}C. The explanation for this results implies that the feedstock fed into pyrolyzer at high temperature, thermal effect is mainly effect to promote devolatilization of cellulose and hemicelluloses in the black wattle residue to bio-oil (Demira et al., 2011; Xiong et al., 2013) whereas oxygen content had been substituted to the oxygenate compound in tar fraction were occurred (Bertero et al., 2012) Moreover, at high temperature favored the reaction which contributed to the increase in gas yield product. Figure 3 show the variation of the yield at the optimum temperature of 550^{o}C, the yield of liquid product decreased with increasing feeding rate. At feeding rate of 0.6 kghr^{-1} shows the highest liquid yield depending on suitable long residence time.

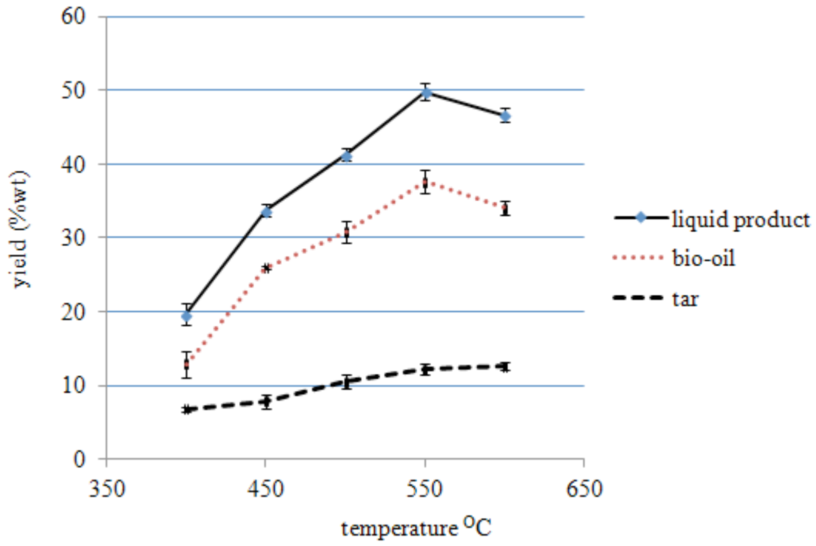

Figure 2 : the effect of temperature depended on liquid fraction

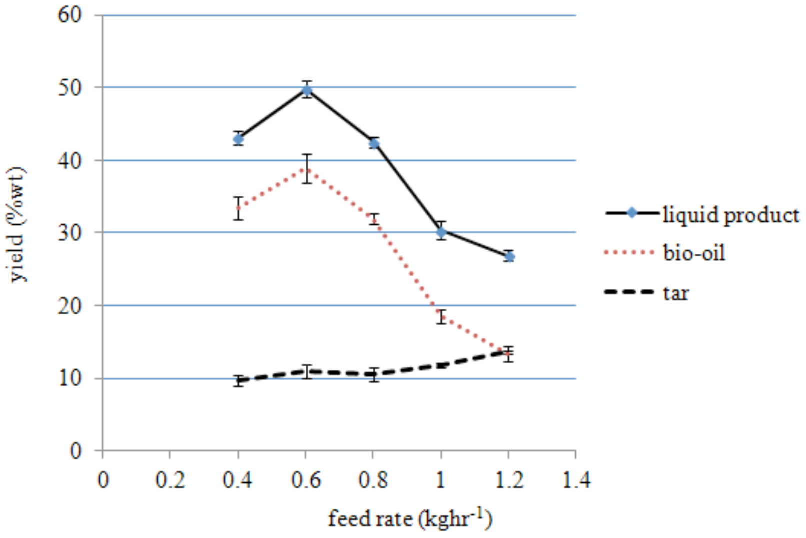

Figure 3: the effect of feeding rate depended on liquid fraction

Effect of temperature

In order to explore the effect of temperature implies that the yield of liquid products increased with temperature rapid increasing to 600 ^{o}C and was dropped because of high temperature, the pyrolysis reaction still received the effected of high temperature to pyrolyzed the composition of celluloses and fiber which composing of long chain hydrocarbon molecule and was trap-cooled into middle hydrocarbon into mixture of bio-oil and tar phases as well, while the gaseous product were made up mainly CO and CO_2 indicating a higher extent of deoxygenation through decarboxylation reaction occurred (Putun et al., 2005; Bertero et al.,2014) At temperature reached 600 ^{o}C, it seems that the gaseous were mainly product cause from high temperature effect in the pyrolyzer (Zhang et al., 2007). At 550^{o}C reaction temperature was selected as the highest liquid products yield was obtained with this temperature.

Effect of feeding rate of feedstock

In order to studies the effect of feeding rate of black wattle residues as a feedstock into pyrolysis, the yield of liquid product increased with decreasing feeding rate. It seems that lower feeding rate implied the long residence time in the pyrolyzer (Jale et al., 2007) The residue of black wattle still received the effect of high temperature for a long time, the pyrolysis reaction with the decomposition of volatile matter undergo and condensation to liquid phase. At feeding rate of 0.6 kghr^{-1} shows the highest liquid yield depending on suitable long residence time.

Table 2 : Analyzed composition of bio-oil and tar fraction at the highest yield

Composition	%wt
gases yield	38.49
solid yield	10.48
liquid yield	51.03
bio-oil fraction	40.37
tar fraction	10.48

The reactivity of various compounds representing each of the chemical fraction is presented in table 2. The product consisted of liquid, solid and gas fraction whereas the chemical properties of liquid phases were analyzed by Gas chromatography - Mass spectrometry. Figure 3 and Figure 4 show the GC-MS chromatograms of bio-oil phase and tar phase respectively.

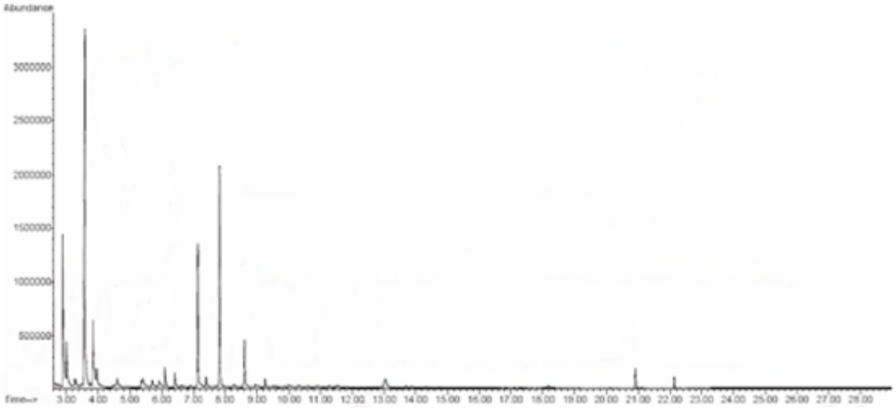

Figure 4: GC-MS Chromatograph on bio-oil fraction

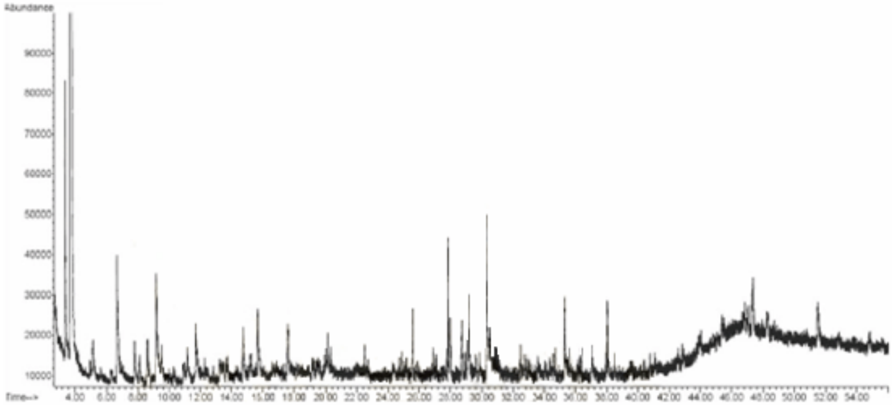

Figure 5: GC-MS Chromatograph on tar fraction

In order to determine its composition were carried out with GC-MS and the various peaks were identified by GC-MS analyzer. Table 3 shown the peak chromatograms of bio-oil, it consisted of aliphatic, substituted aromatic, ketone and other oxygenated compound. The reaction of pyrolysis shows the decarboxylation were occur in the first step through dehydration and formation of carbondioxide from the effect of high temperature, following the initial deoxygenation, hydrogenation and cyclization to formed aromatic compounds occurs (Grierson et al., 2013; Yang et al., 2014) resulting on the formation of olefins and lower molecular weight oxygenated compounds. Also alkylation and isomerization of phenol occurs to form various alkyl-substiture phenols, table 4 show the peak of tar phase, it consisted of aliphatic, aromatic, and other oxygenated compound.

Table 3: Detailed analyses of bio-oil by Gas Chromatograph – Mass Spectometry

RT (min)	Compounds	Peak area (%)
	Aliphatic hydrocarbon	
18.752	Cyclohexane, hexaethylidene-	0.07
	Substituted Aromatic	
20.912	Benzene, 1,1'-sulfonylbis[4-chloro-	1.44
21.038	Benzene, 1,1'-sulfonylbis[4-chloro-	1.44
23.336	Benzene, 1-butyl-4-	0.06
24.012	Benzene, 1-butyl-4-	0.06
	nitrile	
2.998	1H-Pyrazole, 4,5-dihydro-1,5-dimethyl-	4.13
6.112	Piperidine, 3-methyl-	0.83
	Oxygenated compound	
2.643	1-propen-2-ol	0.04
2.912	1,3-Cyclopentanedione	10.57
3.435	2-Pentanone, 4-hydroxy-4-methyl-	28.72
5.561	2-Cyclopenten-1-one, 3-methyl-	1.57
5.638	Phenol	1.16
6.439	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.35
7.714	4-Piperidinone, 2,2,6,6-tetramethyl-	10.82
8.935	.beta.-(N-tert-Butylformamido) acrolein	3.54
9.315	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	0.5
12.998	d-Allose	1.84
17.915	Hexadecanoic acid	0.17
21.967	Hexanedioic acid, bis(2-ethylhexyl) ester	0.75

Table 4 : Detailed analyses of tar by Gas Chromatograph – Mass Spectometry

RT (min)	Compounds	Peak area (%)
	Aliphatic hydrocarbon	
15.68	3-Methyl-2-(2-methyl-2-butenyl)	0.62
25.584	1-Decene, 9-methyl-	0.51
28.001	2-Hexadecene, 3,7,11,15-tetrame	0.57
	Substituted Aromatic	
35.318	Benzene, 1,1'-sulfonylbis[4-chloro-	0.81
	Nitrile	
27.864	Neophytadiene	1.13
30.575	Phenylpropanolamine acetate	0.48
	Oxygenated compound	
3.361	2-Pentanone, 4-hydroxy-	2.06
3.746	2-Pentanone, 4-hydroxy-4-methyl	84.94
6.582	Phenol	1.90
9.072	Phenol, 4-methyl-	1.82
11.651	Phenol, 3-ethyl-	0.31
28.939	Trimethylhexahydroindanone	0.86
29.345	2-Octylfuran	0.84
30.360	Hexadecanoic acid	2.02
38.175	Hexanedioic acid, dioctyl ester	1.13

Table 5 : the physicochemical of bio-oil and tar fraction

		bio-oil	tar
Ultimate Analysis	(wt%)		
Carbon		61.75	50.56
Hydrogen		8.13	11.02
Nitrogen		1.42	0.96
Oxygen		26.70	37.46
The acidity	(pH)	3.2	3.0
Higher Heating Value (HHV)		28.62 MJ/kg	20.85 MJ/kg

The properties of bio-oil do not meet standard for diesel fuels especially the higher heating values of bio-oil which contained the oxygenated compound, carboxylic acid and ketone whereas the lower temperature and short time of residence, lignocellulosic components were incompletely decomposition and depolymerization to the desired component similar to those of transportation fuels (Zhong et al., 2010; Yang et al., 2014) Furthermore, tar fraction show that the heating value is lower than bio-oil fraction. It could be explanation that high oxygen content in cellulosic component may be formed to the oxygenated compounds and given lower heating value (Oasmaa et al., 2001) The pHs of a bio-oils and tar were about of 3.2 which implied that high concentration of organic acid. This acidity makes bio-oil corrosive and not suitable direct use as fuels. (Zhong et al., 2010; Bertero et al., 2014)

Conclusion

The fast pyrolysis of black wattle (*Acacia uricaliformis*) residues produced liquid yields from 20.00 – 40.00 wt%. Each liquid product was consisted of a bio-oil and tar fraction, bio-oil fraction was obtained maximized at temperature of 550 ^{o}C and feeding rate of feedstock at about 0.6 kghr^{-1} which favor to be decomposition and depolymerization to liquid fuels while a nitrogen atmosphere and %wt of dolomite catalyst were not affected to the yield components significantly.

Liquid Products consisted of bio-oil and tar fraction, it seems that bio-oil were produced by cellulosic components via thermal decomposition of volatile matters and condensation to bio-oil phase. GC-MS chromatogram of bio-oil contain mostly aliphatic, substituted aromatic and the oxygenated compounds while tar phase consisted of aliphatic, aromatic, substituted aromatic, the oxygenated compound such as phenol, aldehyde, ketone and carboxylic acid, a very wide of complex organic chemicals. The physicochemical properties of bio-oil shown the heating value and the acidity which were not suitable to direct used as transportation fuels substitution unless it is upgraded through catalytic cracking and hydrogenation similar to petroleum diesel fuel.

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Contact email: witchakorn@swu.ac.th