

STUDY OF CATALYTIC PYROLYSIS PROCESS OF PHYSIC NUT WASTE USING DROP TUBE REACTOR

Sarawut Rungjang, Duangduen Atong, Viboon Sricharoenchaikul

Abstract— Production of biodiesel from Physic nut (*Jatropha curcas L.*) extraction creates agricultural waste. In this study, utilization of this waste was investigated as a potential source of energy while reducing the costly management and control of this waste which may otherwise result in land and water pollutions. The objectives of this work were to investigate the effects of catalysts and pyrolysis conditions, such as reactor temperature, and residence time, on catalytic pyrolysis of Physic nut waste by using a drop tube reactor. Particle size of raw material and temperature of the reactor were varied from 0.425-1 mm. and 600-900°C, respectively while nitrogen carrier gas flow was kept at 2 L/min. The catalytic effect on liquid yields was identified by comparison with non-catalytic (NC) pyrolysis and char-catalytic (CC) pyrolysis. The distribution of gas, liquid and char with non-catalytic (NC) and char-catalytic (CC) were 50.20, 15.07, 34.73 wt% and 61.21, 18.73, 20.07 wt%, respectively at 800°C during 30 min of pyrolysis experiments. Condensed product was further analyzed using GC-MS to determine the chemical components of this complex product.

Keywords—Pyrolysis, Catalyst, Physic nut, Thermal conversion

I. Introduction

Biomass fuels and residues could be converted to more valuable feedstock such as gas, liquid, and solid by thermochemical process, pyrolysis and gasification. Thailand, biodiesel may be extracted from physic nut that produced approximately 50% of solid wastes after the process. Moreover, 20% of physic nut wastes were reported as residue oil that cannot be directly extracted. Thus, bio-oil production from physic nut wastes obtained from biodiesel process via fast pyrolysis process is one of viable pathway. There have been reports investigating the effects of biomass types and pyrolysis conditions, such as reactor temperature, residence time and effective catalyst, on catalytic pyrolysis of physic nut waste by using a drop tube reactor [1-3].

Pyrolysis process with short residence time of decomposition, fast pyrolysis, has been usually applied to produce liquid fuel from cellulosic feedstock. Proportion of liquid yield depends on the temperature, particle size, and heating rate.

However, liquid fuel obtained from pyrolysis process contain oxygenated compound which reduced quality and engine performance. Thus, in-situ catalytic process was studied to improve the quality of produced fuel. Bio-oil can be upgraded in a number of ways, physic, chemical, thermal and catalytic. Before considering catalytic upgrading of bio-oil, it is important to appreciate firstly that biomass contains very active catalysts within its structure. The most active is potassium followed by sodium which cause secondary cracking of vapors and alter the property of liquid yield and depending on the concentration, the effect can be more severe than char cracking [4-6].

In this work, fast pyrolysis of physic nut wastes was carried out by drop tube updraft pyrolyzer in order to produce quality bio-oil via catalyst addition. Effect of particle size, operating temperature, and type of catalysts on yield of bio-oil, quality, and product distribution were discussed. Additionally, basic properties of bio-oil and char analyzed and compared with literature data.

II. Experimental

A. Raw materials

Physic nut waste sample acquired from local oil extraction plant were ground and sieved to 0.425-1 mm and dried in an oven at 105°C for 24 hr prior to experiments. Generally, the main elemental compositions of biomass are carbon, hydrogen, nitrogen and oxygen. The elemental analysis of physic nut waste was reported in Table 1. From the results, composition of small particle size is very close to the larger one that observed carbon as the main composition with higher than 50%. Nitrogen and sulfur of physic nut is lower than 5% and 0.4%, respectively, indicated the possibly low NO_x and SO_x production from thermal conversion processes. Higher heating value of physic nut was carried out by bomb calorimeter as displayed in Table 1. which are approximately 22 MJ/kg and are slightly different due to atomic ratios, (H/C) and (O/C). Due to a large number of complex organic compounds found in biomass, the composition of the fuel as well as its energy content are needed for thermal design of a biomass utilization system.

Proximate analysis gives the composition of the biomass in terms of gross components such as moisture, volatile matter, ash and fixed carbon. The volatile matter of a fuel is the condensable and non-condensable vapor released when the fuel is heated. Its amount depends on the rate of heating and the temperature to which it is heated. Ash is the inorganic

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solid residue left after the fuel is completely burned. Fixed Carbon this represents the solid carbon in the biomass that remains in the char in the pyrolysis process after devolatilization. Fixed carbon includes elemental carbon in the original fuel, plus any carbonaceous residue formed while heating.

Table 1. Elemental analysis of physic nut waste and char from activate carbon and other fossil fuels

Raw material	%Weight					HHV (MJ/kg)
	C	H	N	S	O	
Physic nut waste	53.14	7.17	3.09	0.23	29.84	22.10
Char of physic nut waste	57.98	3.78	11.75	0.10	23.55	21.60
Char of cassava stalk [7]	54.80	2.50	1.00	-	10.30	20.30
Sewage sludge [8]	29.20	3.80	4.10	0.70	19.90	16.00
PRB coal [9]	65.80	4.88	0.86	1.0	16.20	26.44
Petcoke [9]	86.30	0.50	0.70	0.80	10.05	29.87
Anthracite [9]	90.70	2.10	1.00	7.60	11.40	29.96

The major components of biomass are cellulose (15.31%), hemicelluloses (60.90%) and lignin (23.79%). Moreover, decomposition of each component depends on heating rate, temperature and the presence of contaminants to different molecular structure. Hemicellulose would be the easiest one to be pyrolyzed, followed by cellulose, while lignin would be the most difficult to be decomposed. Interestingly, both lignin and hemicelluloses could affect the pyrolysis characteristics of cellulose while they could not affect each other obviously in the pyrolysis process. Bio-oil mainly derived from the cellulose component of biomass (around 500°C), whereas the solid residue (bio-char) came from the lignin. This is also evident from the composition of bio-char, which has an element composition close to that of lignin. Therefore, pyrolysis of biomass with a high percentage of lignin can produce better bio-oil yields. This is because of the different physio-chemical characteristics of cellulose, hemicellulose and lignin.

B. Pyrolysis process

For each run, physic nut with 0.425-1 mm size was fed from the top of the reactor with feed rate of 1 g/min and carried gas at 2 L/min of N₂. Pyrolysis temperature was carried out at 600, 700, 800 and 900°C. Gas products including CO₂, CO, H₂ and CH₄ was measured by online-gas analyzer. For catalytic pyrolysis, 5 g of catalysts was mixed with 25 g of SiC and was supported by quartz wool as catalytic unit. The catalytic unit was placed inside the reactor where reaction between catalyst and reactive gas were occurred. Therefore, the liquid product was collected in two sequential steps. The first cooling unit is a jacked tubular condenser cooled by water to reduce the gas yields temperature and condensable products were collected. The second condenser was cooled by liquid nitrogen in order to trap hydrocarbon compound, liquid yields. Permanent gas stream was cleaned up by filtration unit prior to measure by online gas analyzer. The experimental was carried out for 30 minutes until equilibrium state was reached. Liquid yields was analyzed using SHIMADZU Gas Chromatograph Mass Spectrometer model GCMS-QP2010 Plus. Identification of the compounds was achieved by comparing the mass spectrum (m/z distribution) with Wiley and NIST mass spectral database and literature data [10].

C. Characterization of catalysts

An X-ray diffractometer was used to investigate the surface inorganic components of the prepared activated carbons. The X-ray patterns were recorded under the scan rate of 0.1°/min. Textural Characterization. The surface area and the porous texture of activated carbons were characterized using adsorption of nitrogen at -196°C with the accelerated surface area and porosimetry system (ASAP 2020: Micro Merities). The N₂ adsorption-desorption isotherms were used to determine the following parameters: BET surface area, total pore volume, total micropore volume, and total mesopore volume. The surface characteristics of samples were analyzed using scanning electron microscopy (JSM 5410, JELO) [11].

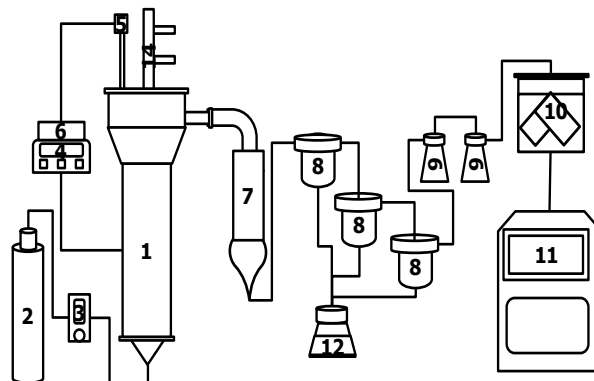


Figure 1. Schematic of drop tube reactor reactivity testing apparatus showing: (1) reactor, (2) carrier gas, (3) flow control, (4) temperature controller, (5) thermocouple, (6) temperature display, (7) water condenser, (8) liquid nitrogen, (9) washer, (10) flowmeter, (11) online-gas analyzer, (12) liquid yields.

III. Results and discussion

A. Characterization of pyrolysis products

The catalytic effect on liquid yields was identified by comparison between non-catalytic (NC) pyrolysis and char-catalytic (CC) pyrolysis, as shown in Table 2. For the char-catalytic, activate carbon from pyrolysis of physic nut waste at 800°C with the size of 0.425-1 mm was used without thermal treatment and activation. The liquid yields were highest at 13.03-18.73% for reaction temperature of 700-800°C with char-catalytic (CC). Low production of gas and liquid yields for 600°C was observed due to lesser degradation of physic nut at low temperature. Observation of unburned physic nut was also found in these cases. Increasing temperature to 700 and 800°C resulted in much higher degradation of raw material and increasing of gas yield. From these results, the optimum condition for liquid production is 800°C with char as catalyst while highest gas yields with low liquid yields were achieved at the temperature of 900°C.

The product distribution of pyrolysis experiments was presented in Table 2. During pyrolysis, large complex hydrocarbon molecules of biomass break down into relatively smaller molecules. Most of the reduction in the liquid yields can be explained by the reduction in the yields of this fraction.

The partial destruction of biomass cellular structure during the preparation of small biomass particle may also be responsible for the high liquid yields from the small particles. Therefore lower process temperatures and longer vapor residence times favor the production of solid. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures and short vapor residence time are optimum for producing liquids.

Table 2. Product distribution obtained from pyrolysis between NC and CC

Temperature (°C)	Product distribution (%wt)					
	Non-Catalytic			Char-Catalytic		
	Liquid	Solid	Gas	Liquid	Solid	Gas
600	4.20	49.23	46.57	6.66	74.27	19.07
700	7.50	34.40	58.10	13.03	53.77	33.20
800	15.07	34.73	50.20	18.73	20.07	61.21
900	12.17	27.83	60.00	11.57	29.3	59.13

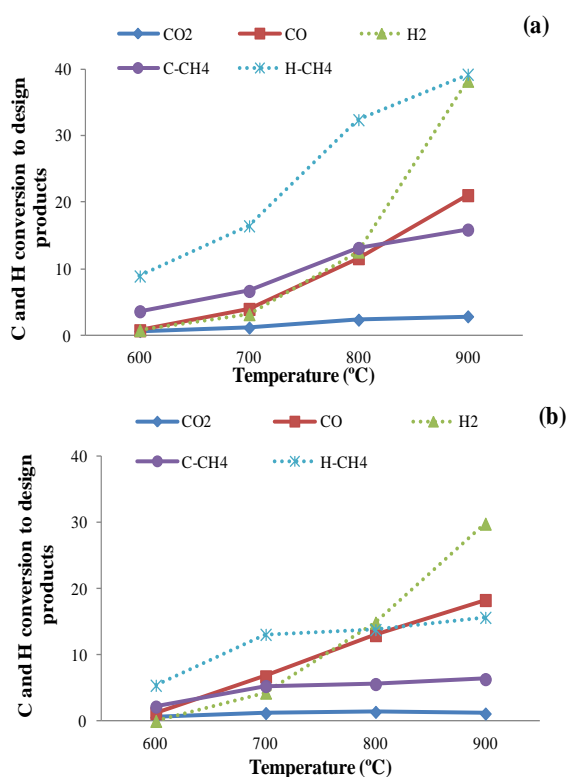


Figure 2. Carbon and hydrogen conversion obtained from reforming reaction(a) pyrolysis with non-catalytic, (b) pyrolysis with char-catalytic

B. Effects of gas conversion

The effect of temperature on gas product derived from pyrolysis in drop tube reactor was calculated by conversion of carbon and hydrogen in biomass to measured gas including CO₂, CO, H₂ and CH₄ as presented in Figure 2. The C-CH₄ and H-CH₄ reduced with the case of char-catalytic runs while CO₂, CO and H₂ stable when temperature increases. The results indicated that hydrogen and carbon in physic nut were induced to convert to liquid form when applied char as catalysts. The gas products from pyrolysis decreased according to liquid yields increase from 700-800°C for the case of char-catalytic runs. Reducing of C-CH₄ and H-CH₄ was due to the secondary vapor cracking with the case of char-

catalytic. Residence time in the reaction zone of vapor increased due to pores and morphology in catalytic unit resulted in greater liquid yields.

C. X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM)

It is generally accepted that pore structure is influenced by many factors, including inorganic impurities and the initial structure of the carbon. XRD pattern Figure 3. of solid residue obtained from 900° C appeared a broad peak at the 2° of 28° indicated the presence of silica.

Generally, the wood surface has a relatively smooth structure with some pores and occasional crevices and also covered with silica agglomeration. However, in this work, the physic nut residue was obtained from an oil-extraction process using a twin screw extruder; thus, there was rupturing of wood tissues in the waste structure. During pyrolysis, the char may be evolved through a liquid phase. The surface showed relatively smooth regions as well as cracked and pitted morphology. The presence of small pore on the surface showed that char was starting to develop an elementary pore network Figure 4. It can be clearly seen that physical activation resulted in a porous structure and the opening of pore on the surface of all activated carbon, pores on activated carbons are classified by their sizes. For physical activation, to increase the surface area, the carbon is activated by the action of carbon dioxide. The oxidizing gas attacks the more readily oxidizable portion of the char, resulting in the development of the porous structure and the extensive internal surface area. Typically, the reactions may be presented by

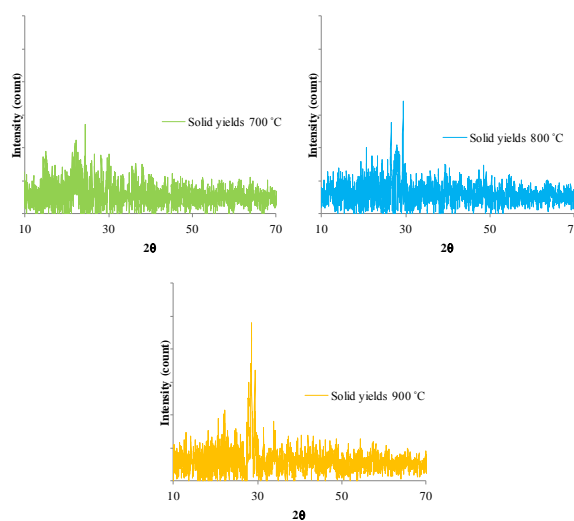
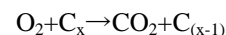
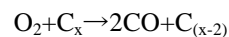
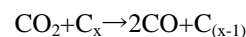


Figure 3. X-ray diffraction analysis of pyrolyzed solid yields

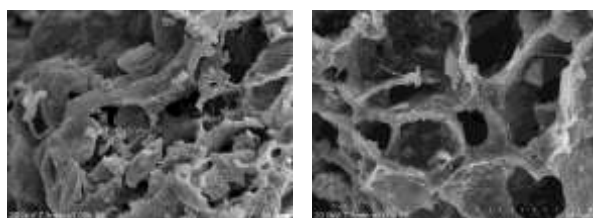


Figure 4. Scanning electron micrograph of physical activation by (a) 600°C, (b) 800°C

D. Elemental composition of solid yields obtained from pyrolysis

The residue elemental of solid yields were measured as shown in Table 3. The carbon contents of char produced in this work were in the range of 51-57 wt% which had increase by 4-6 % from 600°C to 800°C. Char is a secondary product from fast pyrolysis of physic nut waste size 0.425-1 mm and can be used as an alternative solid fuel. The hydrogen and nitrogen contents of all chars were not significantly different, but increase of nitrogen content may cause from adsorbed nitrogen gas during the experiment because char pore structure and morphology of char. However carbon residue of pyrolysis or devolatilization is not pure carbon and very active. It contains some volatiles and ash in addition to fixed carbon.

Table 3. Elemental analysis of solid yields

Temperature (°C)	Wt.% Solid yields size 0.425-1mm.					HHV (MJ/kg)
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	
600	51.38	6.36	7.77	0.32	23.97	21.10
700	56.28	5.53	10.98	0.50	23.45	21.64
800	57.98	3.78	11.75	0.10	23.55	21.60
900	55.88	2.91	19.05	0.07	19.65	21.13
Ricestraw [12]	40.98	2.37	0.35	0.32	6.08	17.00
Bamboosawdust [12]	35.50	1.81	1.16	0.02	26.91	14.00

Table 4. Elemental analysis and heating value of liquid yields

Liquid yields	%Weight				HHV (MJ/kg)
	C	H	N	S	
With non-catalytic	84.31	6.79	4.81	0.09	32.13
With char-catalytic	96.24	8.52	6.95	0.19	38.49
Wood [13]	54.00	5.50	0.20	-	19.00
Rice straw [12]	65.50	7.70	1.20	-	17.30
Rapeseed [14]	72.80	10.80	3.30	-	37.90

E. Characteristics of the liquid yields

Liquid yields obtained from pyrolysis of physic nut waste at their optimum temperature were analyzed by GC-MS technique in order to identify their chemical compounds. In general, the chromatograms look similar and are difficult to differentiate. The outstanding 50 peaks were shown in Figures 5. Peaks chromatograms differ because were cracked of chemical compound in case char-catalytic, by cracking higher molecular weight compounds into lighter hydrocarbon products. Table 4. also provides the elemental content of liquid yields. The main elemental compositions of the liquid yields were similar to the literature data, but higher carbon for the case with char-catalytic. The heating value calculation showed that the HHV of liquid yields produced from pyrolysis reactions for char-catalytic trials were in the value around 38.49 MJ/kg, which are somewhat higher than those of wood

and rice straw. With the high energy content, the liquid yields produced in this work may be used as an alternative fuel.

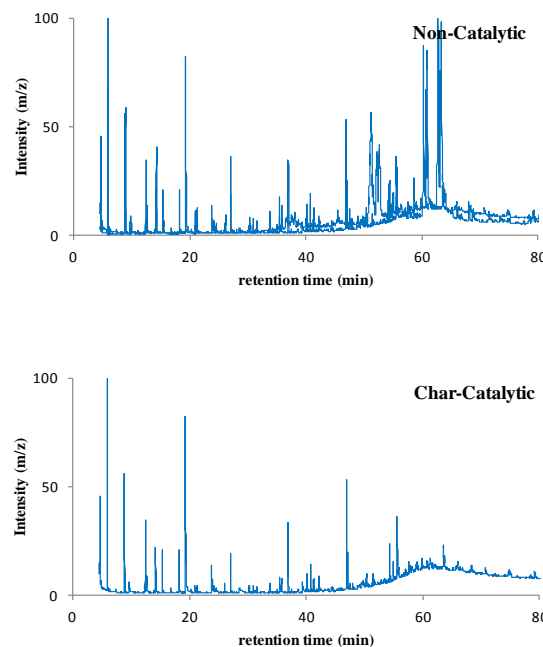


Figure 5. The distribution chromatograms of liquid yields with non-catalytic (NC) and char-catalytic (CC)

F. Characteristics of major chemical functional groups

The chemical composition of liquid yields was studied using GC-MS. Due to the enormous number of compounds and the difficulty to analyze each one individually, they were classified into 8 categories based on their major chemical functional groups which are aromatic, phenol, alcohol+ketone, ether, acid+ester, aliphatic, N-compound, and others. The catalytic effect on liquid yields was identified by comparison between non-catalytic pyrolysis and char-catalytic pyrolysis, as shown in Figures 6. The results indicated that oxygenated species present in large amount are those of phenol group which accounts to 34.64% for non-catalytic case while addition of char-catalytic significantly alters product distribution as seen on the same figure. It is obvious that char-catalytic promotes formation of aromatic compounds through effective deoxygenation of acid fractions. As much as 70.41% of measured product peak areas are exclusively aromatic hydrocarbons compose of only hydrogen and carbon atoms in their structures. Oxygenated compounds including phenol greatly reduced while large amount of N-compounds are measured indicating that more effective catalysts with denitrogenation capability is still required in order to produce acceptable quality pyrolysis liquid from physic nut waste.

These differences in the appearance of the liquid yields could be due to effect of char-catalytic including inorganic impurities and the initial structure of the carbon precursor.

Thus, property of chemical functional groups affect liquid yields quality to be used bio-oil fuel.

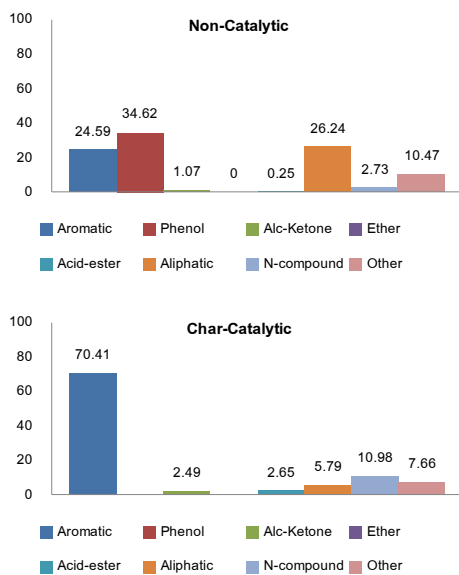


Figure 6. Effect of liquid yields of major chemical functional groups from pyrolysis with catalysts at 800 °C

Conclusion

In this study, pyrolysis of physic nut waste was performed with catalyst in a drop tube reactor. The optimum liquid yields of 18.73wt% was obtained at a pyrolysis temperature of 800°C, particle size of 0.425-1 mm and nitrogen gas flow rate of 2 L/min. The catalytic effect on liquid yields was identified by comparison with non-catalytic cases. The species distribution chromatograms of liquid yields indicated significant cracking of higher molecular weight compounds into lighter products through deoxygenation, oligomerization, cyclization, aromatization, alkylation, isomerization and polymerization. Also, the aromatic hydrocarbons of liquid yields increases in case of char-catalytic in which their chemical functional groups are relatively similar to biofuel. These char catalytic also improves the properties of liquid yields from pyrolysis. Finally, effective upgrading of liquid fuel from pyrolyzed wastes would promote the usage of alternative fuel, and reducing problems associate with management of agricultural residue which may otherwise result in land and water pollutions.

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