Low Acid Bio-Oil from Para Rubber Seeds Produced via Catalytic Pyrolysis with V-modified Silica Catalyst

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Abstract

Bio-oil produced from pyrolysis of biomass is considered one of the most important renewable fuels due to wide availability, cheaper cost compared to fossil fuels, reduction of waste in landfills and carbon neutrality. In this study, bio-oil from Para rubber seeds (shell and flesh) was produced via a conventional pyrolysis with a 0.5 L batch reactor at various temperatures (400–600°C). It was found that the temperature affected the bio-oil yields of both shell and flesh pyrolysis but in different manners. For shell pyrolysis, the bio-oil yield increased with increasing temperature from 400 to 500°C and decreased when the temperature reached 600°C. For flesh pyrolysis, the bio-oil yield increased with increasing temperature until 600°C. However, the obtained bio-oil from those processes has low quality with high acidity (pH 2.6–5.0) which causes corrosion to an engine if used as fuel. In order to improve its quality, catalytic pyrolysis with rice-husk derived silica modified with vanadium (SiO_2/V) was introduced. It was found that the catalytic pyrolysis produced the bio-oil with a lower acidity (pH 8). It was due to SiO_2/V leading to the reactions which reduce acidic compounds occurring in the pyrolysis system, thus decreasing acidity in the bio-oil. The catalytic pyrolysis here also provides bio-oil yield slightly higher than those from the non-catalytic pyrolysis at the same temperature (44.1 and 43.6 wt%), but lower heating value (36.4 and 37.3 MJ/kg). With further modification, it is plausible that the obtained bio-oil from the catalytic pyrolysis in this study could be comparable to the commercial diesel fuel which pH is between 5.5 and 8.0, and heating value is roughly 45.5 MJ/kg. Thus, the bio-oil from pyrolysis of rubber seeds could be a potential candidate for renewable fuel.

Keywords: Catalytic pyrolysis, Bio-oil, Modified silica

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1. Introduction

The shortage of energy is a growing problem in modern society because the world's energy resources decreased continuously, especially fossil fuels which are non-renewable energy. This promotes the development of renewable fuels.

Bio-oil produced from pyrolysis of biomass is considered one of the most important renewable fuels due to wide availability, cheaper cost compared to fossil fuels, reduction of waste in landfills and carbon neutrality (Kukreja, 2017). Thailand as an agricultural country has many sources of biomass including Para rubber trees which provides a high amount of rubber seeds leaving in fields. It has been reported that about 109,000 tons of Para rubber seeds are produced annually, and only 50% are used for the next agricultural cycle while the rest are discarded to be waste (Chaiya and Reubroycharoen, 2013).

Therefore, producing bio-oil from Para rubber seed is an interesting way for reduction of waste and addition value to agricultural residues. Chaiya and Reubroycharoen (2013) studied the pyrolysis of Para rubber seed which produces bio-oil with flash point higher than those of the other referred bio oil types and also in range of bio diesel standard. Other studies were also conducted with rubber seeds as a biomass material for pyrolysis. However, the bio-oils obtained in the mentioned studies have the main drawback of relatively high acidity with pH around 2–3. The acidity of bio-oil could cause corrosion in engines if used as fuel thus restricting its practical application. This undesirable property results from different classes of oxygenated organic compounds consisted in bio-oil (French and Czernik, 2010), including carboxylic acid compounds and carbonyl compounds. In order to reduce those compounds, catalytic pyrolysis or pyrolysis with catalysts having specific properties was introduced into the production of bio-oil. Pyrolysis in the presence of catalysts makes the volatiles released by pyrolysis underwent various reactions including decarboxylation and decarbonylation.

A range of catalysts have been utilized in catalytic pyrolysis (Miandad *et al*., 2016), including ZSM-5 (López *et al.,* 2011), FCC (Lee, 2009), HZSM-5 (Hernández, 2007), Y-zeolite (Lee, 2012) and $Ca(OH)_2$ (Sarker, 2011). For silica (SiO_2), it may not be suitable for use as a catalyst because of chemically inert properties. However, this makes it not degrade or react when it comes in contact with acids, contaminants, volatile organics or solvents. Therefore, it is usually used as catalyst support, or is modified with some other ingredients to achieve specific catalytic properties. In addition, silica is so abundant and low cost material, and can be locally obtained from agricultural residues like rice husk. Utilization of silica from rice husk also conforms to an environmental issue consistent in producing bio-oil from agricultural residues.

Hence, in this study, silica extracted from rice husk first modified with vanadium (V) was used as a catalyst for the catalytic pyrolysis of Para rubber seeds. The vanadium was chosen due to being proven as an active catalyst or modifier catalyst in many reactions previously. The Para rubber seeds were separated into shell and flesh to investigate the effect of both parts on pyrolysis. The pyrolysis was first conducted without the catalyst (non-catalytic pyrolysis) and then with the catalyst, to compare between two systems. The effect of temperature varied from 400–600°C was also studied here.

2. Materials and Methods

2.1 Materials

Para rubber seeds were supplied from Kanchanaburi province in Central of Thailand. Rice husk was obtained from the local rice mill in Nakhon Pathom Province, Thailand. Hydrochloric acid (HCl) and ammonium metavanadate (NH_4VO_3) were obtained from QRëC, New Zealand.

2.2 Preparation of V-modified catalyst

At first, silica was synthesized from rice husk soaking the raw rice husk into the water for 2 days, filtered and then soaked in the solution of hydrochloric at 80°C for 1 h. The soaked rice husk was washed, neutralized and dried overnight in the oven. The prepared rice husk was then calcined under atmosphere at 700°C for 5 h to obtain the powder-like ash which was silica. The silica was then modified with vanadium by incipient wetness impregnation with solution of NH_4VO_3, dried at 120°C for 1 h and then calcinated at 565°C for 7 h. The vanadium-modified silica was obtained, and kept in a desiccator until use.

2.3 Pyrolysis of Para rubber seed

Para rubber seeds were separated into shell and flesh. Each part was then pyrolyzed with various temperatures from 400–600°C with heating rate of 10°C/min, and holding at the reaction temperature for 1 h. The pyrolysis process was conducted in 0.5 L batch reactor as illustrated in Figure 1. N_2 was used as carrier gas with flow rate of 170 mL/min. For the catalytic pyrolysis, the catalyst was impregnated with flesh of para rubber seed at concentration of 10 wt.%.

Products from pyrolysis included of 3 phases: liquid (bio-oil), solid (char) and gas. The percentage of product yield was calculated as follows;

$$\text{Product yield} = \frac{\text{weight of each phase x 100}}{\text{weight of total product}}$$

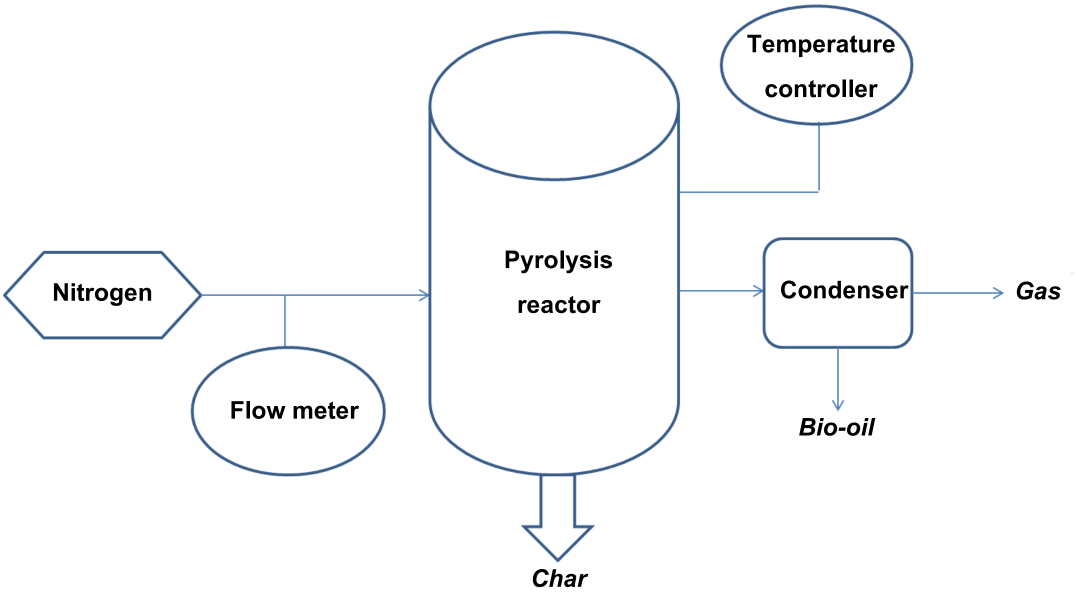


Figure 1 Pyrolysis process.

2.4 Characterization of catalyst

X-ray fluorescence (XRF): the composition of the silica was measured with a PANalytical MiniPal 4 EDXRF spectrometer, equipped with a 30 kV rhodium anode tube with a helium purge facility. A high-resolution silicon drift detector was used to count x-rays intensity. Matrix corrections were made by using either a ratio to the Compton peak or theoretical alpha coefficients, using minipal 4 software.

Fourier transform infrared spectroscopy (FTIR): the functional groups of the catalyst and also the bio-oil were determined by a Nicolet 6700 FTIR spectrometer. Infrared spectra were recorded with and range of scanning from 400 to 4,000 cm-1 with scanning times of 64.

2.5 Characterization of bio-oil

Acidity of bio-oil was determined using pH meter (Index, MA40), and heating value was determined with bomb calorimeter (Parr Instrument, IL61265) equipped with water bath and oxygen.

3. Results and Discussion

3.1 Catalyst characterization

The rice-husk derived silica was modified with NH_4VO_3 to obtained the V-modified silica for use as a catalyst in the catalytic pyrolysis. From an X-ray fluorescence (XRF) result shown in Table 1, it was found that the introduced vanadium was formed into vanadium oxide (V_2O_5) present in the catalyst in an amount of 3.789 wt.%. The different oxide species in the catalyst induces different electronic properties between two phases leading to more acidity, which favors the production of high quality bio-oil.

An FTIR measurement was used here to determine the functional group changed after the rice-husk silica had been modified. The FTIR spectra of two silicas shown in Figure 2 exhibited similar patterns suggesting that there were no significant changes of the functional groups in the catalyst. This was due to the vanadium was introduced to the silica in the small amount. However, the FTIR program still reported the difference between two silicas i.e. the addition of some inorganic oxide in the modified silica which was not clearly observed in the spectra.

Table 1 XRF analysis of vanadium-modified silica catalyst

Component	SiO_2	SO_3	CaO	V_2O_5	MnO	Fe_2O_3	CuO	NiO	ZnO
Weight (%)	95.25	0.551	0.316	3.798	0.012	0.056	0.007	0.003	0.007

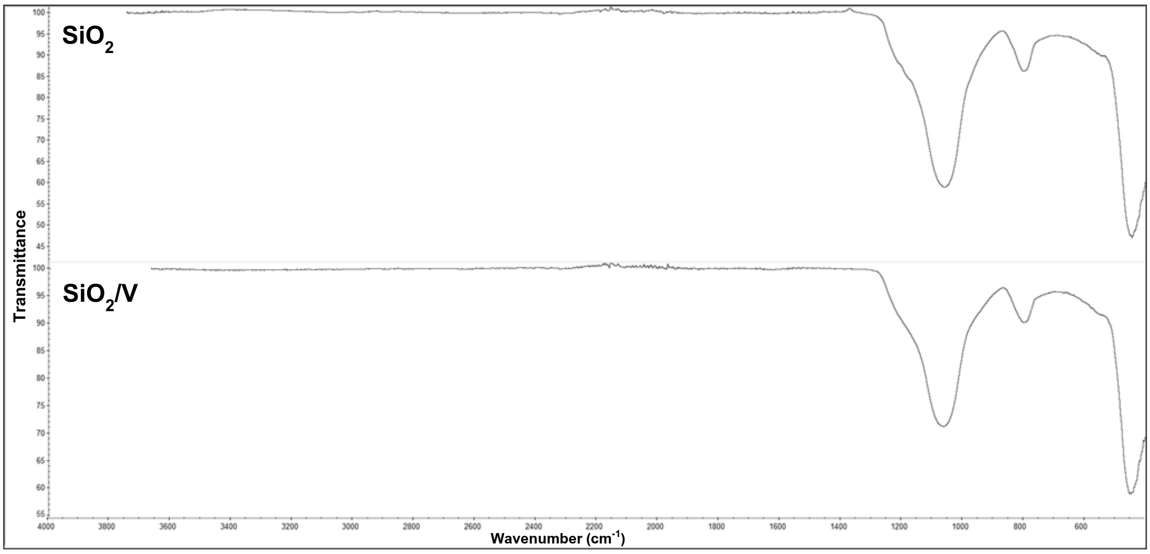


Figure 2 FTIP spectra of SiO2 and SiO2/V

3.2 Pyrolysis of Para rubber seed

The pyrolysis of Para rubber seeds which were separated into shell and flesh were carried out with 3 various temperatures i.e. 400, 500 and 600°C. The conditions of pyrolysis, product yields and some properties of the obtained bio-oil from the pyrolysis are shown in Table 2. The pyrolysis processes gave the products consisting of 3 phases including liquid, gas and solid phases. The liquid phase known as bio-oil from pyrolysis of biomass usually contains a high amount of water. Therefore, the obtained bio-oils were then subjected to be centrifuged to separate the water from the oil. The physical appearance of the bio-oils from all 6 non-catalytic pyrolysis processes (run 1–6) was shown in Figure 3. It was observed that after centrifugation only the bio-oils from flesh of rubber seeds pyrolyzed at 500 and 600°C (run 5 and 6) can be separated into 2 phases while the rest (run 1–4) were still as 1 phase. This was probably due to the bio-oils from run 1–4 consisting of the high fraction of water and polar molecular substances. Thus, regarding to the physical appearance only the bio-oils from run 5–6 are suitable to be further used as fuel or chemical feed stock for other value products.

Considering on the product yield of all pyrolysis in Table 2, it can be observed that the temperature affected the product distributions of both shell and flesh pyrolysis but in different manners. This could be resulted from the differences in composition of both parts. To better understand in product distribution arising in pyrolysis system, the conceptual model illustrated the synthetic pathway of products in pyrolysis system is displayed in Figure 4.

For shell pyrolysis, the bio-oil yield increased with increasing temperature from 400 to 500°C and decreased when the temperature reached 600°C. This was due to the higher temperature in the first range (400–500°C) leading to the higher degree of primary reactions (Pw1) making the solid biomass became more liquid bio-oil. For the second range, the higher temperature did not increase the bio-oil yield and moreover increased the char yield. This may be came from char formation promoted by secondary reactions (2b) under high pressure of vapor (Elyounssi *et al.,* 2010) which generated above reaction zone due to rapid rate of the primary reactions at high temperature (600°C).

For flesh pyrolysis, the bio-oil yield increased with increasing temperature until 600°C. This was because increasing temperature enhances both the primary and secondary reactions as seen that both bio-oil and gas yield increased. For the second range, the effect of char formation was pronounced forcing the liquid to form the solid (2b) instead of gas (2a).

The different effects of temperature on the production yields between 2 parts of rubber seeds are probably due to their different compositions. For shell, it generally contains high content of lignin which tends to generate char formation during pyrolysis, thus significantly increased the char yield and decreased the bio-oil yield in the pyrolysis at high temperature

(600°C). The char from pyrolysis of lignin is produced from the crosslinking reaction of the inner fractions in lignin, mainly the aliphatic structure in the form of propyl side (Wang and Luo, 2017). Wijayanti and Tanoue, 2013 have found that the char formation generated in the region of lignin thermal decomposition are between 630–1073°K (357–800°C) which cover the pyrolysis temperature in this study. For flesh, it contains various kinds of composition such as proteins, lipids and carbohydrates which are gradually decomposed in a broad temperature range. For example, the decomposition of proteins in distillers dried grains with solubles (DDGS) measured by thermal gravimetric analysis exhibited up to three regions of decomposition at 328 407 and 664°C (Liu and Rosentrater, 2016). Hence, increasing temperature in the pyrolysis of shell until 600°C could enhance more decomposition, and then increased the bio-oil yield.

The heating values of the bio-oil from *run 5* and *6* can only be detected with the values of 40.74 and 37.28 MJ/kg. These values are almost equal to those of the standard commercial diesel (45.00–46.00 MJ/kg). Thus, the bio-oil from pyrolysis of rubber seeds could be a potential candidate for renewable fuel.

Acidity of the obtained bio-oils can be simply represented by pH value as also shown in Table 2. It was found that the bio-oils from flesh had the lower acidity than those from shell. This is due to the chemical composition of flesh which typically contains the higher protein than seed. A high amount of nitrogen (N) in protein could cause lower acidity to the bio-oil by forming nitrogen compounds such as ammonia (NH_3) which is a weak base. Chueluecha and Duangchan (2012) have also found that the high protein in cattle manure provides the obtained bio-oil from its pyrolysis with low acidity. Nevertheless, the acidity of the bio-oil from the flesh pyrolysis (4.3–5.0) was still higher compared to the standard diesel fuel with the normal pH between 5.5 and 8.0. Therefore, in order to improve this property the catalytic pyrolysis with the potential catalyst had been conducted here. The optimum condition with the highest bio-oil yield i.e. pyrolysis of flesh at 600°C was chosen to be repeated with the additional catalyst-rice husk derived-silica modified with vanadium (SiO_2/V). It was found that the bio-oil from the catalytic pyrolysis (*run 7*) had physical appearance similar to one from the non-catalytic pyrolysis at the same pyrolytic temperature (600°C) as shown in Figure 5. This indicates that the presence of the catalysts in the pyrolysis did not affect the physical appearance of the bio-oil.

The product yield and the properties of the bio-oil from the catalytic pyrolysis are also shown in Table 2. It was found that the catalytic pyrolysis produced the bio-oil yield near to that of the non-catalytic pyrolysis while the char yield was lower and the gas yield was higher. It have been reported previously that the use of catalysts increases the rate of the cracking reactions leading to an increase in the yield of gases with a reduction in liquid oil yield

(Miandad *et al.,* 2016). This is consistent with this study for the gas yield suggesting that the cracking reactions (2a) occur more intensively with the catalyst (increased from 17.9 to 27.4 wt.%), and this could reduce the liquid yield. However, as observed that the liquid yield was still the same level as the non-catalytic pyrolysis indicating that there could be more liquid generated in the catalytic pyrolysis. This may be resulted from the higher degree of thermal decomposition (1) through the catalytic system which converted solid material into liquid. Increase of the thermal decomposition may be derived from the higher heat and mass transfer (Babu, 2008) due to the presence of silica particles which were impregnated with the biomass and located all over the pyrolysis reactor.

For the acidity of the bio-oil, it can be seen that the catalytic pyrolysis produced the bio-oil with the lower acidity than the non-catalytic pyrolysis. In fact, pyrolysis in the presence of catalysts makes the volatiles released by pyrolysis underwent various reactions including decarboxylation and decarbonylation which could reduce acidity in the bio-oil.

An FTIR is an efficient equipment which can identify functional groups of the chemicals inside material. Therefore, it was used here to observe the changes in functional groups in the bio-oils obtained from the catalytic and non-catalytic pyrolysis. The FTIR spectra of both bio-oils are shown in Figure 6.

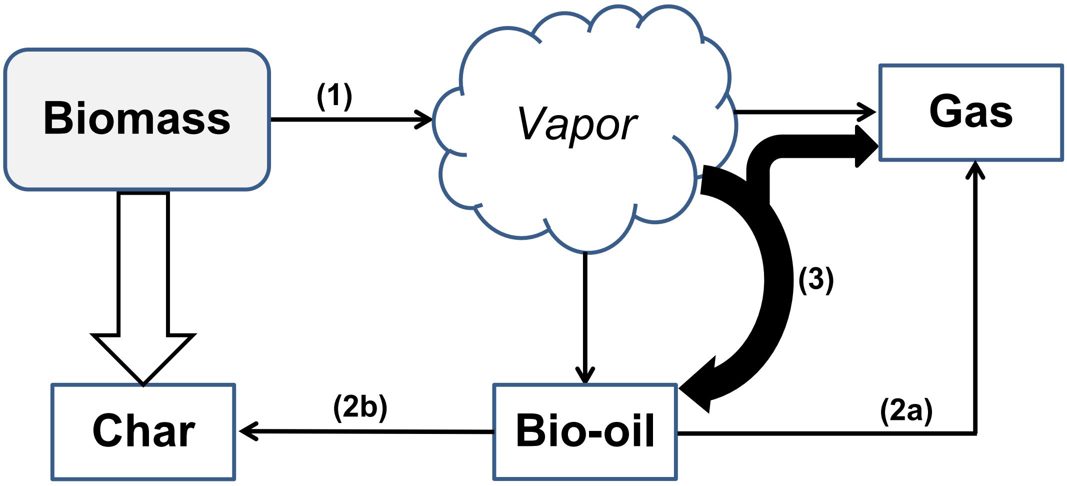
Broad absorbance peaks of O-H stretching vibrations between 3000 and 3600 cm^{-1} which indicate to water, alcohols and/or phenols in bio-oils were observed in both bio-oils but with a higher degree in the bio-oil from the catalytic pyrolysis. A higher amount of phenol compounds in bio-oil with catalysts may be conceivable in this case as previously observed by Rajic *et al.* (2013) that the zeolite modified with oxide particles (NiO and Cu_2O) yielded a pyrolysis oil with a high amount of phenols. In addition, Milovanovic *et al.* (2015) also found that increasing metal modifier content in the catalysts caused the amount of phenols higher. The significantly different peaks between 2 bio-oils were observed around 1,750–1,650 which indicate to C=O stretching attributed to ketones, aldehyde or carboxylic acids (associated with O-H stretching). The lower mentioned peaks in the bio-oil from the catalytic pyrolysis may arise from the lower amount of carboxylic acid group which concurs with the lower acidity in this bio-oil. The other peaks in 2 bio-oils were similar consisting of the C–H stretching vibrations between 2800 and 3000 cm^{-1}, the C–H deformation vibrations between 1350 and 1475 cm^{-1} indicating to the presence of alkanes (Demiral *et al*., 2008), the C-O stretching vibrations of ethers occurring between 850 and 950 cm^{-1}, and C-O stretching and O-H deformation vibrations between 950 and 1325 cm^{-1} attributed to the primary, secondary and tertiary alcohols. Therefore, it can be concluded from the FTIR result that the catalytic pyrolysis with V-modified catalyst provides the bio-oils with the higher amount of phenolic groups and the lower amount of carboxylic groups compared with the non-catalytic pyrolysis. As a matter of fact, phenols are desirable fraction of bio-oil as they have a high commercial value in industrial chemicals. In addition, the benefit of phenols in bio-oil if used as fuel is that it could act as fuel antioxidants which extend the induction period and eliminate free radical chain reactions involved in hydrocarbon oxidation. Hui-Peng *et al.,* (2009) have found that the effect of phenols on oxidation stability varied with kinds and contents of phenols. The phenol with alkyl side chains on the ortho position and para position of the phenylic hydroxyl group had positive effect on antioxidation (Hui *et al.,* 2009).

Therefore, to produce bio-oil with a high amount of phenols is another advantage of catalytic pyrolysis in this study.

Table 2 Product yields from pyrolysis of Para rubber seeds and bio-oil properties

Run	Seed	Temperature (°C)	Catalyst	Yield (%)			Bio-oil properties	
				Bio-oil	Char	Gas	pH	Heating value (MJ/kg)
1	Shell	400	-	29.5	46.1	24.4	2.6	
2		500		41.5	37.0	21.5	2.8	
3		600		29.5	50.0	20.5	2.6	
4	Flesh	400	-	19.9	54.7	25.4	4.3	
5		500		38.8	20.4	41.3	5.0	40.7
6		600		43.6	38.4	17.9	4.3	37.3
7	Flesh	600	SiO_2/V	44.1	28.5	27.4	8.0	36.4

Figure 3 Bio-oils from non-catalytic pyrolysis after centrifugation



(1) Primary reactions : decomposition, depolimerization etc.

(2) Secondary reactions : a) cracking, dehydration and b) formation etc.

(3) Catalytic reactions : decarboxylation, decarbonylation etc.

Figure 4 Conceptual model of biomass pyrolysis

Figure 5 Bio-oils from catalytic pyrolysis after centrifugation

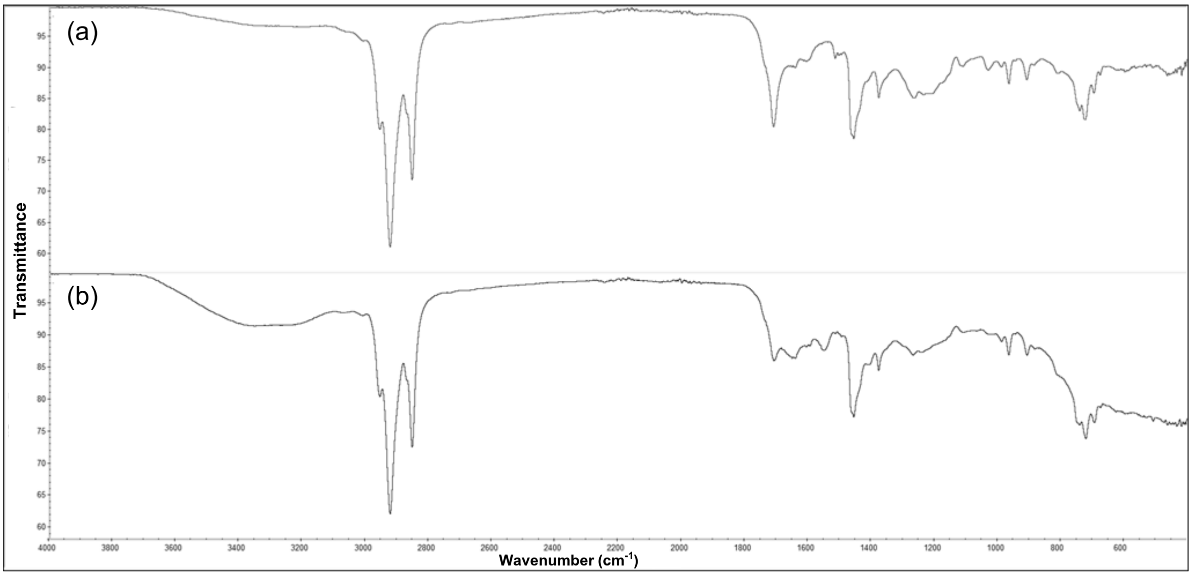


Figure 6 FTIR spectra of bio-oils from (a) non-catalytic and (b) catalytic pyrolysis

4. Conclusion

The pyrolysis of Para rubber (shell and flesh) was studied here. It was found that for shell pyrolysis, the bio-oil yield increased with increasing temperature from 400 to 500°C and decreased when the temperature reached 600°C. For flesh pyrolysis, the bio-oil yield increased with increasing temperature until 600°C. The obtained bio-oils from the non-catalytic pyrolysis were highly acidic (pH 2.6–5.0), thus improving by the catalytic pyrolysis with V-modified silica catalyst. It was found that the catalytic pyrolysis produced the bio-oil with a lower acidity (pH 8), and having heating value of 36.4 MJ/kg. The catalyst also affected the product yield distribution of the pyrolysis.

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