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Bio-oil Production from Vacuum Pyrolysis of Palm Empty Fruit Bunch: Effect of Operating Conditions and Process Energy Balance

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Abstract: This study investigated the effect of temperature, heating rate and particle size on the yields of pyrolysis products from palm empty fruit bunch (EFB). Experiments were carried out in a lab-scale fixed bed pyrolysis system under vacuum condition. Under all conditions studied, the liquid product or known as bio-oil appeared to be dominating. The total liquid (organic + water) yield reached its maximum at 550°C with around two-third being organic and the rest being water. Increasing the particle size generally increased gas yield and decreased liquid yield. However, the catalytic effect of inorganic matters could also have some role during pyrolysis. Higher heating rates increased the yield of organic fraction and overall pyrolysis conversions. The mass and energy balance analysis showed that about two-third of the energy from biomass was concentrated in the liquid product. If not being able to utilize the product char due to the high content of alkalis and only the product gas was used to provide energy for pyrolysis reactions, the net efficiency of the process will largely be affected by the required process energy consumption and the import of external energy may be needed.

Keywords: Bio-oil; Vacuum pyrolysis; Palm empty fruit bunch; Energy balance.

1. Introduction

Biomass is a potential source of renewable energy in Thailand. Being an agricultural country, a large amount of waste is generated each year from agricultural and agro-processing industry. One of the major industries in Thailand is palm oil industry. The oil palm is mainly grown in tropical climate regions including Thailand and other Southeast Asian countries. In Thailand, the plantation of oil palm has been increasing steadily during the past decade. In 2010, the plantation area reached over 0.6 million ha, which produced about 8.2 million tons of palm fresh fruit bunch (FFB) and 1.5 million tons of crude palm oil [1].

From the palm oil processing, a vast amount of biomass wastes is generated, including palm fibre, palm shell and palm empty fruit bunch (EFB) at 11-18%, ~6-8% and 20-25% based on the weight of fresh fruit bunch (FFB) processed, respectively [2-3]. The palm fibre and palm shell are fully used as fuel for boiler to provide the process steam and produce electricity, while the more abundant EFB is used with a limited ratio. Apart from the naturally high moisture content and fibrous nature of EFB, its unacceptably high alkali and chlorine content often causes ash deposition problems during combustion even when EFB is used in low proportion for boiler fuels mixed [4].

The bio-oil production by pyrolysis is considered as one of pretreatment methods to eliminate or reduce unwanted fractions that are the major cause of problems and alternative utilization of biomass. During pyrolysis, the feedstock material is heated under atmosphere in absence of oxidizing agent, producing solid char, bio-oil and combustible gases. The product distribution depends on the operating conditions used. By using material with very small particle size and short residence time of pyrolysis product vapour, the bio-oil yield can be maximized [5]. Major advantages that can be realized by converting solid biomass into bio-oil include the increased energy density, reduced alkali content since they are preferentially retained in the solid char, more flexibility for application in existing oil/gas fired boilers [6].

In an ideal situation, pyrolysis for bio-oil production is operated under the atmosphere of sweeping inert gas, i.e. nitrogen or helium, as used in laboratory-scale studies [7-9]. In such cases, external heat supply to maintain the operating temperature is required. For large and commercial-scale operations, air is typically applied to allow partial oxidation of biomass to provide heat for all the endothermic pyrolysis reactions. No expensive source of inert gas is needed, but this in turn produces low yield of bio-oil. Similarly to the introduction of the inert sweep gas, operating under vacuum atmosphere also provide a suitable condition for bio-oil production. Not only vacuum keeps the atmosphere inside the reactor vessel non-reacting, but also continuously sucks the evolving volatile vapours out away from the reaction zone. As compared to atmospheric pyrolysis under sweeping inert gas, the typical residence time inside the reactor of vacuum pyrolysis is shorter and hence undesirable reactions can be reduced [10]. Vacuum pyrolysis even at low or medium heating rate is capable of producing bio-oil product [11-12]. A study of rice husk pyrolysis by Pipatmanomai [13] showed that pyrolysis under vacuum gave a slightly higher total volatile yield but much higher increased bio-oil yield compared to that derived from the condition under a forced sweeping N_2 gas. GC-MS analyses of the product oil also revealed that vacuum pyrolysis generally yields chemical species with smaller molecular masses than does the pyrolysis under inert sweeping gas. These advantages of pyrolysis under vacuum atmosphere over the atmosphere of sweep inert gas have been realized and some commercial applications based on vacuum pyrolysis technology have been developed especially for tires such as Pyrovac [14].

In this study, vacuum pyrolysis of palm empty fruit bunch (EFB) was carried out to investigate the effect of temperature, heating rate and particle size of EFB on the yield of the pyrolysis products, namely char, bio-oil and gas. The understanding of these parametric effects will provide the useful basic information for further system design and operation of bio-oil production from palm EFB. Finally, the energy balance for the EFB derived bio-oil production was discussed.

2. Experimental

2.1 Sample preparation and analyses

Palm empty fruit bunch (EFB) was air-dried to reduce the residual moisture content and then the particle size was reduced by an ultra centrifugal ball mill before being sieved to three particle size fractions: <106 μm, 250-425 μm and >500

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µm. The samples were dried under vacuum at 70°C for 24 hours before experiments. The proximate analysis was carried out by using a thermogravimetric analyzer or TGA (Perkin Elmer, Pyris 1 TGA). The ultimate analysis of sample was carried out using an elemental analyzer (Thermo Finnigan, Flash EA 1112) to determine the principle elemental content: C, H, N and S. The oxygen content was determined by difference. The calorific value was measured using a bomb calorimeter (LECO, AC 350).

The preparation of biomass samples for ash analysis was conducted following ASTM E 1755 (the standard test method for ash in biomass). About 30 grams of biomass was placed in the stainless steel reactor (5 cm. O.D.) which was externally heated up in air with heating rate of 10°C min^{-1} to 575°C and held for 24 hours to ensure complete combustion. The relatively low temperature ashing was employed to ensure that any alkali compounds present would not evaporate and be preferentially retained in the solid residue or ash. The laboratory prepared ashes were then sent for analysis by X-Ray diffraction (XRF) (Philips PW 2400) to determine the oxide composition.

2.2 Vacuum pyrolysis experiments

The schematic diagram of the vacuum pyrolysis system is shown in Figure 1. The pyrolysis reactor was a 5 cm. O.D. stainless steel reactor, which was externally heated up by an electrical furnace. The desired heating rate and final temperature were achieved by the programmable temperature controller, which received the signal from a K-type thermocouple inserted inside the reactor very near to the sample bed level.

To conduct the vacuum pyrolysis experiment, about 10 grams of EFB was loaded into the reactor. The EFB bed was located at the level as indicated in Figure 1 by the support of quartz wool. After the reactor was sealed, the vacuum pump was started. The heating furnace was switched on after the vacuum level reached 66 kPa. It was found that further decrease of vacuum level did not affect the pyrolysis product yields. Therefore, experiments at much below 66 kPa, as is typically used in other studies and pilot plants [15], were not carried out in this study. The reactor was heated up at the heating rate of 10, 30 and 50°C min^{-1} to temperatures in the range of 400-600°C. The holding time of 60 min was applied to ensure a maximum capture of condensable volatile fraction. In the separate tests carried out to investigate the effect of holding time at 450°C, no further gain in volatile yield and liquid yield was observed when extending the holding time longer than 60 min.

During pyrolysis, the gas phase volatile was sucked out from the reaction zone by vacuum through the bottom exit of the reactor and subsequently passed through a series of ice-water cooled condenser traps, where the liquid product (including organic compounds and water) was condensed and collected for the yield measurement. The water content in the liquid product was analysed by the Karl Fischer titration before it was subtracted from total liquid to obtain the yield of organic fraction. Non-condensable gases escaped the condenser traps and finally collected in the gas bag for composition analysis. After each experiment, the reactor was left to cool down naturally to room temperature and the vacuum pump was stopped. The reactor was dismantled and the solid residue or char was collected for the yield and property analyses. The % yields of char and bio-oil are determined by the weights of char and condensing liquid normalized to the weight of original sample. Since the complete collection of char particles from the quartz wool after the experiment is not possible, the char product and quartz wool are always weighed together and is subtracted by the original weight of quartz wool. A series of blank tests (quartz wool without sample) were also conducted to ensure that all the weight losses occur were attributed to the EFB pyrolysis. For bio-oil yield, the direct weight measurement of the condensing traps before and after experiment is used. A 4-digit sensitive balance is used for weight measurement. The % yield of pyrolysis gas is determined from the overall mass balance. Experiments were carried out in at least 3 repetitions for each set of conditions. The mean errors for solid and liquid yield were within 2% and 3%, respectively. All the % yields are reported on the dry weight basis.

3. Results and Discussion

3.1 Characteristics of biomass samples

The analyses of EFB are shown in Table 1. The very high volatile matter and low ash content indicates that high bio-oil yield is probable. The EFB contains high contents in both alkali metals and chlorine, with K_2O accounting for more than half of all mineral matters.

Table 1. analyses of EFB.

Proximate analysis	% wt, dry basis
Volatile matter	84.0
Fixed carbon	13.9
Ash	2.1
Ultimate analysis	**% wt, dry-ash-free basis**
C	40.7
H	5.4
N	0.3
S	1.1
O (By difference)	52.5
Heating value	**MJ/kg, dry basis**
	19.3
Oxide composition	**(% wt, dry ash basis)**
K_2O	53.2
CaO	12.5
SiO_2	16.1
Cl	4.3
P_2O_5	6.8
Fe_2O_3	3.5
MgO	2.5
Traces	1.2

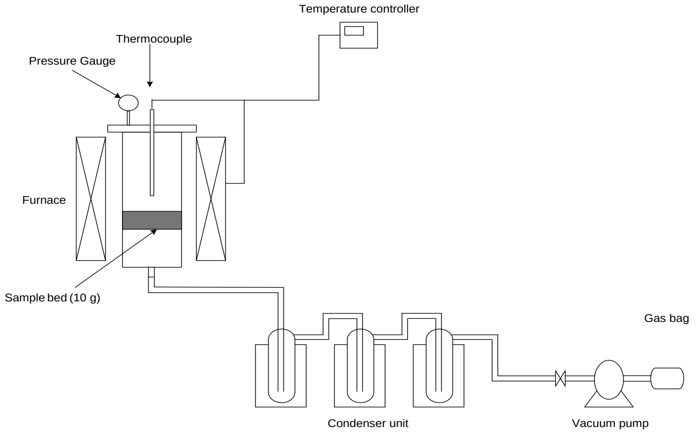


Figure 1. Schematic diagram of the vacuum pyrolysis system.

3.2 Effect of temperature on the yields and properties of pyrolysis products

Samples having a particle size in the range 250-425µm was pyrolysed at the heating rate of 30°C min^{-1} to the final temperature of 450-600°C. The yields of organic, water, char and gas products at different pyrolysis temperatures are shown in Figure 2. The effect of the pyrolysis temperature on the product distribution could be clearly observed. Under all conditions studied, bio-oil appears to dominate the product from vacuum pyrolysis. The total liquid yield as well as the organic yield had an increasing trend with temperature and reaching its maximum at 550°C. The moisture content, which could be resulting from the original moisture in the biomass feedstocks and as a product of the dehydration reactions occurring during pyrolysis, was about one third of the liquid for all conditions. The relatively high yield of organic yield, compared to that obtained from other biomass feedstocks under similar conditions, is thought to be contributed not only to the products from degradation of its chemical structure (i.e. cellulose and lignin) but also the organic components after the crude palm oil processing remaining inherent with the incoming EFB feedstocks. Nevertheless, the water removal prior to utilization of the liquid product is highly necessary to improve the combustion stability and prevent phase separation.

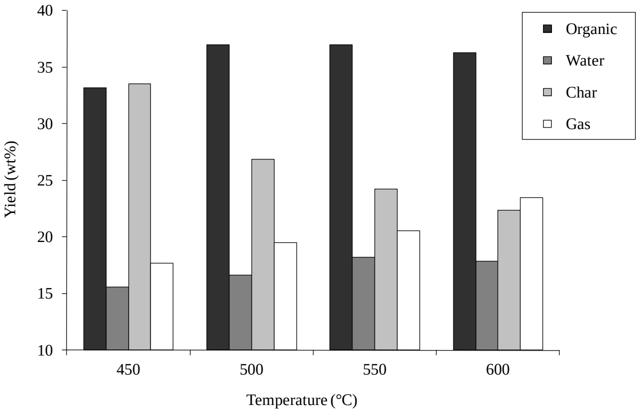


Figure 2. Effect of temperature on distribution of pyrolysis products.

The char yield decreased while the gas yield increased consistently with increasing pyrolysis temperature. As the pyrolysis reaction rate is largely driven by the temperature, the volatile (oil + gas) yield increased while the char yield decreased with rising temperature [16]. However, the secondary cracking of the pyrolysis vapours into gas, which is favoured by high temperatures, resulted in a decrease in the oil yield while the gas yield rose further.

3.3 Effect of particle size and heating rate on pyrolysis products of EFB

The particle size and heating rate are known to influence the pyrolysis product yields. Here, the effect of particle size was investigated on the three EFB particle size fractions: <106 µm, 250-425 µm and >500 µm. Pyrolysis experiments were carried out at 550°C and heating rate of 30°C min^{-1}.

The influence of particle size on the product yields is shown in Figure 3. Within the particle size range of study, the differences in char yields were considered insignificant (within the range of experimental errors), while the yields of other products were clearly affected. As the particle size was increased, the gas yield continuously increased. This is likely due to the catalytic cracking of tars (in volatiles) on the char surface during the release of volatiles inside a larger particle and may produce secondary char and light gases [17]. Although the total liquid yield consistently decreased as the particle size was increased, the highest yield of organic fraction was obtained at the particle size 250-425 µm, which also coincided with the lowest yield of pyrolytic water. Based on this observation, it is speculated that the catalytic effect of inorganic matters could have some role during pyrolysis. Abdullah and Gerhauser [8] conducted pyrolysis experiments on palm empty fruit bunch (EFB) with various ash contents prepared by particle sizing. More inorganic matters were preferentially found in the smaller particle size fraction. A substantial increase in organics yield was found by lowering the ash content. The ash, and particularly potassium, which is generally accepted to be catalytically active and favours secondary reactions [6], was believed to explain the reduction in organics yield and corresponding increases in reaction water, gas and char yields. However, further investigations are needed to prove the occurrence of such catalytic effect.

The EFB at particle size 250-425 µm was selected for further investigation of the heating rate effect on pyrolysis yields and the results are presented in Figure 4. Higher heating rates significantly increased the yield of organic fraction and pyrolysis conversions, especially from 10 to 30°C min^{-1}. A further increase of heating rate to 50°C min^{-1} increased the organic fraction to about 40%, an additional by only a few more percentages. At low heating rates, the rate of mass or heat transfer in the complex matrix of biomass is low, which allows intraparticle cracking. Extended exposure times resulted from low heating rates favour secondary reactions such as cracking, repolymerization and recondensation of radical components leading to the formation of char with limited oil and gaseous products [18]. The results are in a good agreement with other studies regardless of the range of heating rates and biomass feedstocks, e.g. [9, 18-21].

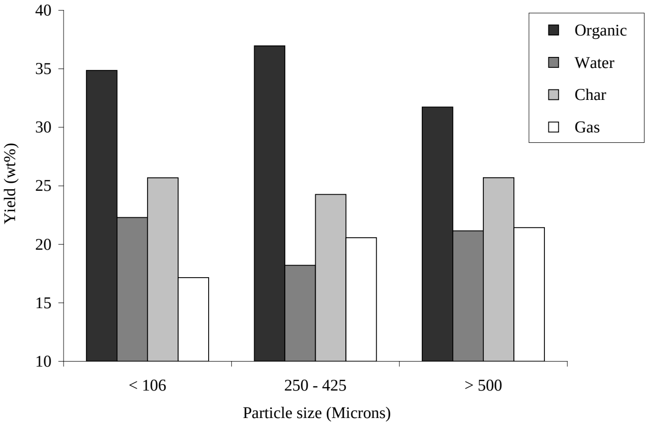


Figure 3. Effect of EFB particle size on the distribution of pyrolysis products.

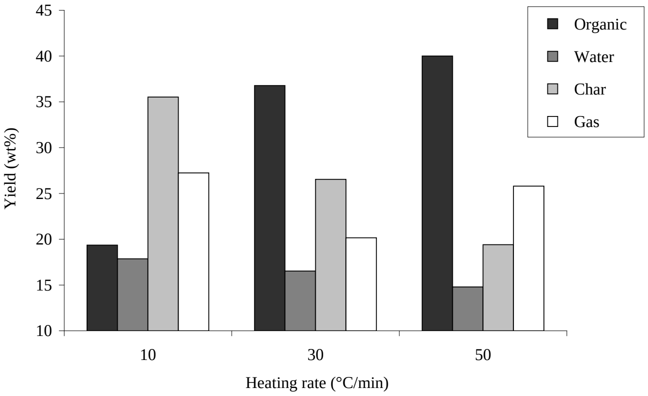


Figure 4. Effect of heating rate on the distribution of pyrolysis products.

3.4 Mass and energy balance

In order to analyze the potential of bio-oil production from EFB pyrolysis for further development, the energy aspect of the system is an important issue to consider. Therefore, a mass and energy balance of the system was conducted.

The data for the mass and energy balance analysis were selected at the optimum pyrolysis temperature 550°C with heating rate of 30°C min^{-1} and particle size 250-425 μm. The energy contents of liquid and char were obtained from direct heating value measurement as higher heating value (HHV). The energy content of gas was calculated from the dry gas composition (H_2, CO, CO_2 and CH_4) obtained from GC analysis as given in Table 2 and their individual heating values (HHV) [22]. All derived pyrolytic water was assumed to be condensed with the organic fraction in the condenser. Table 3 summarizes the mass and energy distribution in pyrolysis products of EFB, which shows that not only the pyrolysis of EFB (provided the condition used in this study) gave high bio-oil yield, but the derived bio-oil also had a high heating value. As a result, the energy distribution shows that about two-third of the energy is concentrated in the liquid product.

To conduct an energy balance of a pyrolysis system for bio-oil production, a simple schematic diagram of a continuous system with material mass flow based on 100 kg/hr of dry EFB is constructed and presented in Figure 5. Yield and quality of pyrolysis products obtained from the batch experiments in this study are assumed for the proposed continuous system. The non-condensable gas product after the condenser is combusted with air to generate the hot flue gas, all of which is recycled to the pyrolysis process to provide heat-up to 550°C. Considering the heating value of the product char, it has potential as energy source but the energy recovery is not recommended because of the likely ash deposition problem induced by high alkali content concentrating in the char. Alternatively, char, which is also rich in carbon, can be used as a bio-fertilizer to improve soil quality [23].

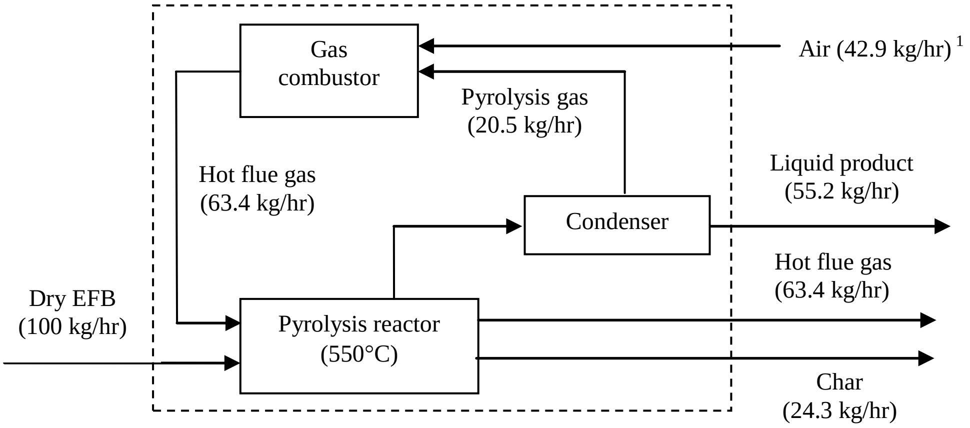
The energy balance of the system is shown in Figure 6. Since pyrolysis is an endothermic reaction; in operating pyrolysis, energy is required to achieve the desired process temperature. Based on the difference in energy in EFB and pyrolysis products from the batch experiments indicates that the energy needed to operate pyrolysis at the desired process temperature is 252.8 MJ/hr or 13.1% of the energy in feed biomass. This value is higher than that reported by Leibbrandt et al. [24] based on AspenPlus analysis. However, in their study the vacuum pyrolysis system was operated at a lower temperature, i.e. 350°C, for which the process energy demand for pyrolysis reactor and gas heating was 9% of the feed biomass energy. As mentioned above, the pyrolysis gas is utilised as fuel to provide heat for the proposed continuous system and therefore significantly reduces the energy required from an external source.

Table 2. Relative composition of gas products from EFB pyrolysis at their optimum conditions.

Gas species	H_2	CO_2	CH_4	CO
Relative yield (% dry gas volume basis)	2.5	26.9	4.9	54.1

Table 3. Mass and energy distribution of products from EFB pyrolysis at optimum condition for bio-oil production.

Pyrolysis products	Mass (%wt)	Energy content (MJ/kg)	Energy (%)
Bio-oil	55.2	25.3	64.0
Char	24.3	22.5	25.0
Gas	20.5	11.7	11.0



[1] Air supplied at 10% higher than the stoichiometric air requirement for pyrolysis gas with composition based on Table 2

Figure 5. Mass balance of the pyrolysis system for bio-oil production.

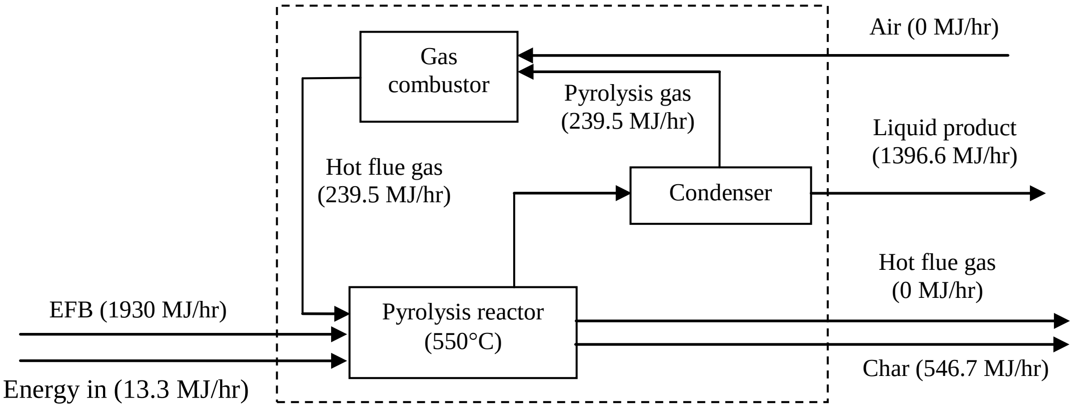


Figure 6. Energy balance of the pyrolysis system.

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Nevertheless, the energy self-sufficiency of the system in practice depends also on other energy consuming major equipment, such as pumps, cooler, and so on, as well as feedstock drying and grinding, the extent of which depends on the characteristics of the feed biomass used.

4. Conclusions

This study investigated the effect of temperature, heating rate and particle size on the yields of pyrolysis products from palm empty fruit bunch (EFB). Experiments were carried out in a lab-scale fixed bed pyrolysis system under vacuum condition.

Under all conditions studied, bio-oil appeared to dominate the product from vacuum pyrolysis. The total liquid (organic + water) yield as well as the yield of organic fraction had an increasing trend with temperature. Under the heating rate of 30°C min^{-1} and EFB particle size 250-425 μm, the organic yield reached its maximum of around 37% at 550°C. The char yield decreased while the gas yield increased consistently with increasing pyrolysis temperature. Increasing the particle size did not have a significant effect on char yields, but increased the gas yield continuously. Although the total liquid yield consistently decreased as the particle size was increased, the highest yield of organic fraction was obtained at the middle particle size range, i.e. 250-425 μm, which also coincided with the lowest yield of pyrolytic water. Based on this observation, it is speculated that the catalytic effect of inorganic matters could have some role during pyrolysis. Higher heating rates significantly increased the yield of organic fraction and overall pyrolysis conversions, especially from 10 to 30°C min^{-1}. A further increase of heating rate to 50°C min^{-1} slightly increased the yield of organic fraction. The mass and energy balance analysis showed that about two-third of the energy from biomass was concentrated in the liquid product. The product char is not recommended for energy recovery due to the high content of alkalis and, therefore, only the product gas can be used to provide energy for pyrolysis reactions. The net efficiency of the process will largely be affected by the required internal energy consumption and the import of external energy may be needed.

This study has shown that the bio-oil production from pyrolysis, especially under vacuum atmosphere, has a good technical potential and competitive with other pyrolysis techniques. However, various aspects of studies to further develop it towards the commercial scale production and utilization are needed. The two major aspects for further studies include the techno-economic feasibility study of system design for vacuum pyrolysis and the development to reduce cost of bio-oil upgrading process.

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References

[1] The Joint Graduate School of Energy and Environment, *Strategic Evaluation of Biomass Utilization for Energy Concerning Energy Benefit Ratio and Life Cycle CO_2, Final report* (2012).

[2] Basiron Y, Palm oil production through sustainable plantations, *European Journal of Lipid Science and Technology* 109 (2007) 289-295.

[3] Department of Alternative Energy Development and Efficiency (DEDE) and Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ), *Best Practice Guide Eco-Efficiency in Palm Oil Industry* (2006).

[4] Konsomboon S, Pipatmanomai S, Madhiyanon T, Tia S, Effect of kaolin addition on ash characteristics of palm empty fruit bunch (EFB) upon combustion, *Applied Energy* 88 (2011) 298-305.

[5] Bridgwater AV, Renewable fuels and chemicals by thermal processing of biomass, *Chemical Engineering Journal* 91 (2003) 87-102.

[6] Chiaramonti D, Oasmaa A, Solantausta Y, Power generation using fast pyrolysis liquids from biomass, *Renewable and Sustainable Energy Reviews* 11 (2007) 1056-1086.

[7] Asadullah M, Production of bio-oil from fixed bed pyrolysis of bagasse, *Fuel* 86 (2007) 2514-2520.

[8] Abdullah N, Gerhauser H, Bio-oil derived from empty fruit bunches, *Fuel* 87 (2008) 2606-2613.

[9] Onay O, Fast pyrolysis of rape seed in a well-swept fixed-bed reactor, *Journal of Analytical and Applied Pyrolysis* 58-59 (2004) 995-1007.

[10] Zhang XH, Wang TJ, Ma LL, Chang J, Vacuum pyrolysis of waste tires with basic additives, *Waste Management* 28 (2008) 2301-2310.

[11] Wang SR, Fang MX, Yu CJ, Luo ZY, Cen KF, Flash pyrolysis of biomass particles in fluidized bed for bio-oil production, *China Particuology* 3 (2005) 136-140.

[12] Demirbas A, Pyrolysis of Ground Beech Wood in Irregular Heating Rate Conditions, *Journal of Analytical and Applied Pyrolysis* 73 (2005) 39-43.

[13] Pipatmanomai S, *Bio-oil Production from Vacuum Pyrolysis of Various Biomass Feedstocks, Final report* (2012).

[14] Roy C, Chaala A, Darmstadt H, The vacuum pyrolysis of used tires End-uses for oil and carbon black products, *Journal of Analytical and Applied Pyrolysis* 51 (1999) 201-221.

[15] Garcìa-Pérez M, Chaala A, Pakdel H, Kretschmer D, Roy C, Vacuum pyrolysis of softwood and hardwood biomass - Comparison between product yields and bio-oil properties, *Journal of Analytical and Applied Pyrolysis* 78 (2007) 104-116.

[16] Onay O, Koçkar OM, Pyrolysis of rapeseed in a free fall reactor for production of bio-oil, *Fuel* 85 (2006) 1921-1928.

[17] Boroson ML, Howard JB, Longwell JP, Peters WA, Heterogeneous cracking of wood pyrolysis tars over fresh char surfaces, *Energy & Fuels* 3 (1989) 735-740.

[18] Gerçel HF, Production and characterization of pyrolysis liquids from sunflower presses bagasse, *Bioresource Technology* 85 (2004) 113-117.

[19] Haykiri-Acma H, Yaman S, Kucukbayrak S, Effect of heating rate on the pyrolysis yields of rapeseed, *Renewable Energy* 31 (2006) 803-810.

[20] Onay O, Fast and catalytic pyrolysis of pistacia khinjuk seed in a well-swept fixed-bed reactor, *Fuel* 86 (2007) 1452-1460.

[21] Sensoz S, Olive bagasse (*Olea europea* L.) pyrolysis, *Bioresource Technology* 97 (2006) 429-436.

[22] Waldheim L, Nilsson T, *Heating value of gases from biomass gasification, IEA Biomass Agreement, Task 20-Thermal gasification of biomass* (2001).

[23] Wise J, Provin T, Husmoen D, Schnell R, Vietor D, Capareda S, Munster C, Mineral Nutrient Recovery in Co-Products of Pyrolysis for Varied Biomass Feedstocks, *ASA, CSSA, and SSSA 2010 International Annual Meetings* (2010) Oct 31 - Nov 4, 2010, Long Beach, CA

[24] Leibbrandt NH, Knoetze JH, Görgens JF, Comparing biological and thermochemical processing of sugarcane bagasse: An energy balance perspective, *Biomass and Bioenergy* 35 (2011) 2117-2126.