



BIO-OIL FROM PYROLYSIS OF PRE-TREATED EMPTY PALM FRUIT BUNCH (EPFB)

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ABSTRACT

The pyrolysis of four EPFB samples, one without pretreatment and three pre-treated with enzymes (LiP, MnP and LiP+MnP) were performed to investigate the differences in product compositions among the feeds. Heavy and lighter fractions in the bottom and upper layers were produced for all samples. The chemical compounds were classified into four categories, namely hydrocarbon compounds, oxygenated, nitrogenated and others. All the three treated EPFB (LiP-treated, MnP-treated and LiP+MnP-treated) produced high yield of hydrocarbons as compared to the original untreated substrate. The highest hydrocarbon yield was obtained when the two enzymes LiP and MnP were combined. The yield being 49.5% was 2.7 times higher than the untreated EPFB. Both LiP and MnP-treated samples gave yields of 43.1% and 34.9%, respectively, which is 2.3 and 1.9 times higher than the untreated samples. The untreated sample however produced higher yield of oxygenated and nitrogenated compounds. The yields were approximately 60% and 20%, respectively. GC-MS analysis demonstrated that the pyrolysis of enzyme-treated EPFB has increased the production of hydrocarbons significantly with the major compounds to be aromatics. The highest aromatics yield at 39.5% was observed with the LiP + MnP treated sample. The pre-treatment method offers a promising means of biofuel production for industrial application due to the simplicity of the pretreatment process and the enhanced hydrocarbons production.

INTRODUCTION

The lignocellulosic materials can be converted into important chemicals via pyrolysis technology. Due to the complex structure, the compounds are hardly degraded at the typical biomass pyrolysis temperature (300-500 °C) (Aguado *et al.*, 2006, Boateng *et al.*, 2006, Lappas *et al.*, 2007). One of the most promising alternatives is for the raw materials to be pretreated before thermo-chemical conversion or pyrolysis takes place. Intentionally, modification of EPFB structure is required to alter or modify lignocellulosic structure. Besides disassembling the biomass chain, it may also be able to increase the accessible surface area of the lignocellulosic material for conversion during pyrolysis.

In recent years, there have been many studies on the pretreatment of lignocellulosic biomass materials either chemically or physically (Mosier *et al.*, 2005). One of the most effective chemical pretreatment alternatives is by using ammonia. In previous study, soybean straw pretreated by ammonia showed an increase of about 70.27% cellulose while hemicellulose and lignin decreased by 41.45% and 30.16% respectively (Xu *et al.*, 2006). In another study, cellulase, xylanase, lignin peroxidase (LiP), and manganese peroxidase (MnP) isolated from *C.ligniaria* NRRL 30616 resulted in losses of about 75% hemicelluloses, 50% cellulose and 40% lignin contents in semisolid cultures (Lopez *et al.*, 2007). Lignin peroxidase was recognized as the most effective peroxidase where it can oxidize phenolic and non-phenolic compounds, amines, aromatic ethers, and polycyclic aromatics (Perez *et al.*, 2002). Manganese peroxidase (MnP) on the other hand, was found to only attack phenolic compounds of lignin, but not for the non-phenolic units.

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Generally, pyrolysis is a thermal degradation process in the absence of an externally oxidizing agent. Its products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char (Boateng *et al.*, 2006). In order to achieve a better selectivity, zeolite such as HZSM-5 has been used as catalysts for cracking and commercially in synthetic fuels (methanol to gasoline), petrochemicals (alkenes isomerization, toluene disproportionation, and benzene alkylation) and in petroleum refining (lube and distillate dewaxing) (Xu *et al.*, 2006). The main objective of the present research is to evaluate the potential of biological pretreatment on empty palm fruit bunch (EPFB) for biofuel production. Lignin Peroxidase and Manganese Peroxidase enzymes were used in this study. The enzymes performances were evaluated by comparing the products produced during the pyrolysis reaction.

EXPERIMENTAL

EPFB was obtained from Felda Bukit Besar, Kulai, Johor. Lignin peroxidase and Manganese Peroxidase enzyme were supplied from Fluka (Germany), while commercial HZSM-5 (50) catalyst was supplied by Zeolyst International (USA).

The EPFB (40 g) was solubilized in 0.01 M NaOH before adjusting the pH of 5.0 with 100 mM sodium tartrate. The appropriate amount of Lignin Peroxidase (LiP) was then added to give a desired EPFB-enzyme ratio. The EPFB pretreatment using Manganese Peroxidase (MnP) enzyme was employed with a malonate buffer at pH of 4.5 and 2 mL of 0.2 mM Manganese Sulphate (MnSO_4). The pretreatment with LiP-MnP mixture, however, was performed under sodium tartrate buffer as described previously. The reaction was conducted at room temperature under stirring at 90 rpm for 6 hours. At the end of the reaction, the pretreated samples were dried overnight at temperature of 100 °C.

The pyrolysis experiments using a well-mixed EPFB (30 g) and 5 wt% of HZSM-5 were conducted in a semi-batch stainless steel reactor. The experimental system was initially purged with inert nitrogen for approximately 30 min. The reactor was externally heated by an electrical furnace at a fixed temperature of 300 °C, which is monitored by a K-type thermocouple. The experimental rig set up is illustrated in Figure 1. The vapor produced from the reaction were forced to flow through a condenser and consequently condensed into liquid bio-oil. The liquid product was collected in a round-bottomed flask while non-condensable gaseous were collected into a gas sampling port.

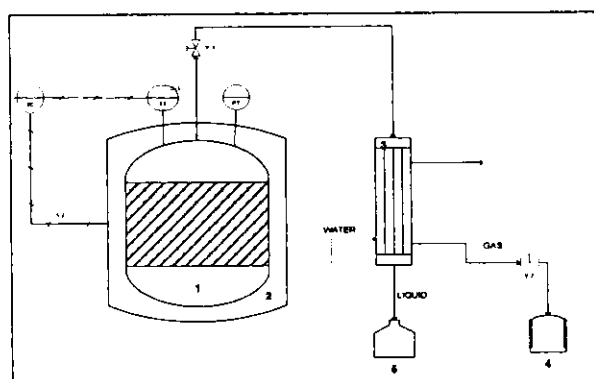


Figure 1: Experimental rig set up. 1) Semi batch reactor (EPFB and HZSM-5 placed), 2) Furnace 3) Condenser 4) Gas sampling port 5) liquid product collection

RESULTS AND DISCUSSION

The bio-oil obtained in the studies is shown in Figure 2. It was found that all of the bio-oil samples consisted of heavy and lighter fractions to form two layers of liquid phase. The upper layers appeared to be black in color, while a noticeable difference of appearance in the bottom layer in all the oil samples was observed. As can be seen, the pretreatment using LiP displayed the oil color to be darker brown, while the color of MnP-treated oil was a much lighter brown.

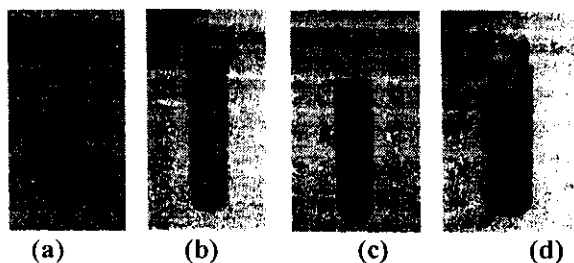


FIGURE 2: Pyrolysis oil of (a) LiP-treated, (b) MnP-treated, (c) LiP+MnP-treated EPFB, (d) untreated

Lignocellulose is complex phenolic polymers found in higher plant tissues. Lignin is the second most abundant terrestrial polymer after cellulose (Qi *et al.*, 2007). The degradation of lignin would cause significant changes in the EPFB structure which allows the EPFB to be converted into valuable components. The compound distributions in pyrolysis oil of samples were classified based on chemical functional group, and summarized in a histogram as shown in Figure 3.

It was observed that all treated samples (LiP-treated, MnP-treated and LiP+MnP-treated) produced high yield of hydrocarbons as compared to the original untreated substrate. The highest hydrocarbon yield was obtained when LiP and MnP were combined. It successfully produced 49.5% of the compound, which is 2.7 times higher than the untreated EPFB. Both LiP and MnP-treated samples gave 43.1% and 34.9%, respectively which is 2.3 and 1.9 times higher than the untreated sample. The untreated sample on the other hand managed to produce higher yield of oxygenated and nitrogenated compounds. The yields were approximately 60 wt% and 20 wt%, respectively. The higher yield of hydrocarbon production may be due to the pretreatment (Perez *et al.*, 2002, Mosier *et al.*, 2005, Lopez *et al.*, 2007). Pretreatment reduces biomass recalcitrance by removing or modifying lignin to make carbohydrates accessible to enzymes, and also by depolymerizing and solubilizing hemicellulose, which constitutes 20–40%w/w of the biomass (Han, 2007).

The particular chemicals produced in each functional group category are described in Figures 4 - 6 for hydrocarbon compounds, oxygenated compounds and other compound, correspondingly. Generally, all samples demonstrated similar trends of hydrocarbon production where the major compounds produced were aromatic hydrocarbons. Hydrocarbon compounds are greatly desired for the biofuel production as an alternative energy source of petroleum-derived fuel. As can be seen in Figure 4, the highest yield was produced by the LiP-treated EPFB, namely 38.1wt% followed by LiP+MnP-treated sample (29.5 wt %), MnP-treated sample (21.1) while the untreated feed was barely 14wt%. It is also important to note that, both MnP-treated and LiP+MnP-treated feed produced approximately 20wt% of alkanes yield, whereas both the LiP-treated and untreated EPFB gave just about 5% of the compound. The aromatic compounds mainly originated from lignin components of biomass. The monomers of biomass lignin are mainly as guaiacyl groups. The lignin-derived markers detected mainly guaiacyl-derived structures or methoxyl substituted compounds (Wang *et al.*, 2007).

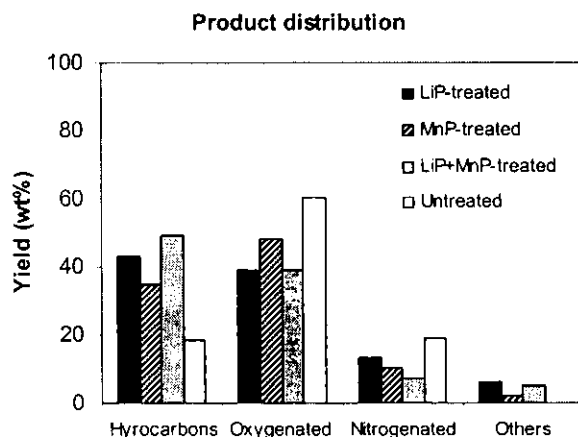


FIGURE 3: Compounds distribution for pyrolysis of untreated and pretreated EPFB

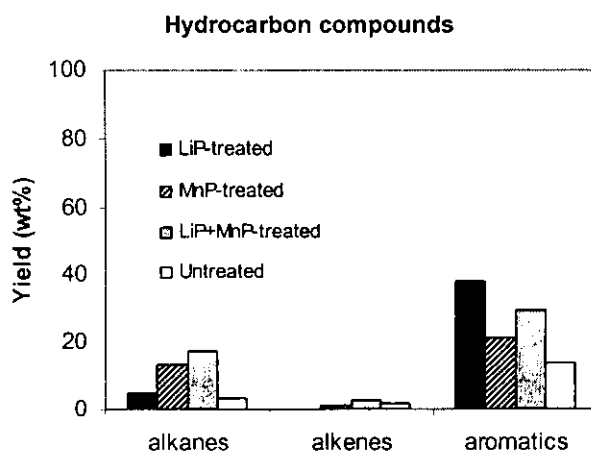


FIGURE 4: Hydrocarbon compounds produced in pyrolytic oil of untreated and pretreated EPFB

The oxygenated compounds produced consisted of phenol and its derivatives including guaiacols, acidic compounds, alcohols, ketones, aldehydes and esters as shown in Figure 5. In general, all samples demonstrated similar trends of oxygenated compound production, where the highest yield produced for each chemical compounds was approximately 20wt%. Oxygenated compounds are widely reported as the common bio-oil products either from hardwood or softwood pyrolysis oil (Demibas, 2007; Qi *et al.*, 2007). The main chemical compounds produced were phenols, ketones, aldehyde and alcohol. Interestingly, the pretreated EPFB using LiP has successfully reduced significant amount phenolic compounds from the untreated sample. These phenolic compounds are organic pollutants, highly toxic and able to cause deleterious effects to human being and living system.

Apparently, nitrogenated compounds appeared to be the minor compound produced in all pyrolytic oils. There were approximately 10wt% of these compound were produced in a row. The results were illustrated in Figure 6. Brit *et al.* (1995) has reported that the composition of pyrolysis product was depending on the pyrolysis conditions such as reaction temperature, temperature, catalyst or even the employed pretreatment process. The pretreatment is highly essential in breakdown the lignin structure and disassemble the chains besides increasing the lignocellulose accessible surface area for pyrolysis (Rebecca *et al.*, 2007).

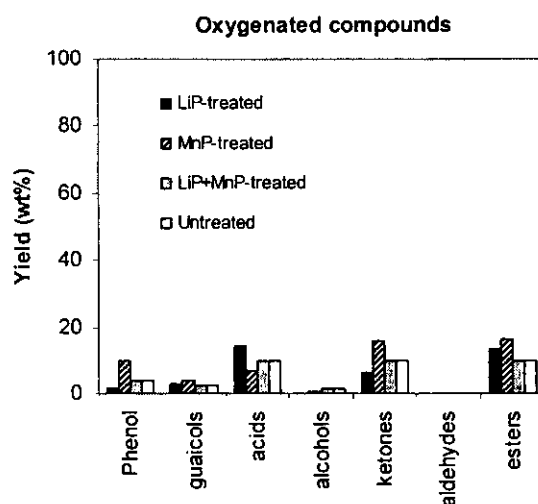


FIGURE 5: Oxygenated compounds produced in pyrolytic oil of untreated and pretreated EPFB

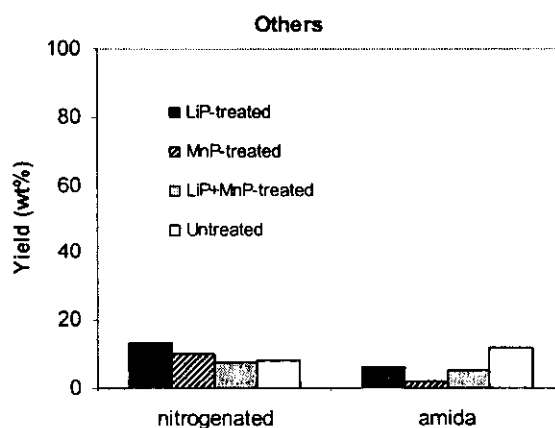


FIGURE 6: Nitrogenated and other compounds in pyrolytic oil untreated and pretreated EPFB

The use of enzyme has been widely established in lignocellulosic modification. However, the pretreatment of biomass as the means of biofuel production has never been published. Most of the enzymatic pretreatment approaches were conducted in pulp and paper industries. The lignin degradation was carried out to produce whiter and high quality paper. In another development, the enzymatic pretreatment of lignocellulosic material was also employed for the production of bioethanol (Saddler *et al.*, 1993, Karin *et al.*, 2007).

Owing to the previous studies, pyrolytic oil consisted of a complex mixture of compounds such as esters, ethers, aldehydes, ketones, phenols, carboxylic acid and alcohols (Aguado *et al.*, 2006, Dermibas, 2007). However, the production of hydrocarbons via pyrolysis was not widely established. In this work, the usage of enzyme in the pretreatment technique was found to produce high yield of valuable biofuel. Large amount of desired hydrocarbons were produced besides reducing other undesired components. Hence, this study presented a potential approach for the production of biofuel as an alternative energy source.

CONCLUSION

The biological pretreatment technique has increased the production of valuable hydrocarbons, and reduced other undesired components during pyrolysis. Pretreatment using the combination of LiP and MnP managed to produce higher hydrocarbon yield namely 49.5 % which is 2.7 higher than the original untreated EPFB. This approach provides promising technique for the production of biofuel or raw materials for petrochemical industries.

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