

Catalytic Pyrolysis of Oil Palm Frond (OPF) Using Graphite Nanofiber (GNF) As Catalysts

Cheah Kin Wai, Suzana Yusup*, Nazratul Zaheera Abdul Kapor, Calvin Chok

Biomass Processing Lab, Centre of Biofuel and Biochemical, Green Technology, Mission Oriented Research, Chemical Engineering Department, University Technology PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia.
drsuzana_yusuf@petronas.com.my

This paper focuses on exploring the application of Graphite Nanofiber (GNF) as a carbon allotropes catalyst in thermal pyrolysis of Oil Palm Frond (OPF) with the hope of breakthrough in replacing conventional Zeolite ZSM-5 catalyst. The present study primarily highlights on the bright potential of GNF catalyst in producing high quantity of bio-oil, along with excellent thermal decomposition performance as a carbon based catalyst. In this paper, the thermal pyrolysis is conducted in a semi batch pyrolysis reactor which externally heated by an electrical vertical split tube furnace. 15 g of OPF biomass is thermally decomposed at three distinct temperatures of 573K, 673K and 773 K and catalyst loadings of 1 wt%, 5 wt% and 12 wt%. The nitrogen gas flow rate and heating rate are kept constant at 60 mL/min and 20 °C/min. Comprehensive evaluation of the catalyst performances in term of pyrolysis oil yields are performed at various reaction temperatures and catalyst loadings in thermal pyrolysis of OPF. The superior results obtained revealed OPF biomass can be an excellent biomass feedstock in producing excellent quantity of bio-oil with oil yield as high as 46.04 ± 1.77 wt% at a mild reaction temperature of 673K and catalyst loading of 1 wt%. On the other hand, the highest solid residue yield is obtained at 5 wt% catalyst loading and temperature of 573 K, mainly due to incomplete decomposition of the biomass structure. In conclusion, as the pyrolysis temperature increases, the bio char yield decreases with significant trend, leaving high pyrolysis oil yield and low quantity of char residue.

1. Introduction

In light of diminishing fossil fuel supply and soaring energy demands from various industrial and transportation application, development of biomass derived fuels as an alternative energy source has becoming essential. Bio-fuels could be a promising prospective fuel of tomorrow due to its excellent reproducibility, resource universality and benign environmental protection (Zhang et al., 2013). The renewable fuel production can be facilitated through flash pyrolysis, which has been recognized as one of the most feasible routes up today. It is a densification technique where both mass and energy densities increased by treating raw biomass at mild temperatures from 573 K to 873 K. As the consequences of high heating rates and short residence times, a dark brown liquid with a distinctive smoky smell is formed, which commonly known as bio-oil or pyrolysis oil. It is a complex mixture of several hundreds of organic compounds, mainly consists of low molecular weight oxygenated molecules such as ketones, aldehydes, esters, alcohols, acids, and phenols. It is readily served as a substitute for fuel oil or diesel in many static applications such as boilers, furnaces, engines and turbines for electricity generation.

Virtually any type of biomass is compatible with pyrolysis, ranging from forestry biomass to agricultural residues as well as energy crops. However, abundance availability of cheap biomass resource is a major consideration closely associated to the feasibility of commercializing such fuels production as raw material cost can reach up as high as 75 % of the total bio-fuel production expenditures (Phan and Phan, 2008). To circumvent such issue, local production of bio-fuels seems to be the most viable solution, providing the biomass resource can be obtained locally and available in bulk quantities. With national government's policy on crop diversification as well as intensification, accelerated growth in palm oil industry makes Malaysia as the world's largest producer and exporter of palm oil up today. However, such enormous

production scale resulted a mass output of fibrous biomass waste, Oil Palm Frond (OPF). It has been estimated that an average of 54.43 Mt/y of oil palm fronds will be available in the years of 2007 to 2020 (MPOB, 2004). Utilization of such abundant resource as feedstock in the production of bio-fuel has a bright potential in satisfying the local bioenergy feedstock demand due to its vast availability and sustainability in Malaysia. Despite the abundant OPF waste available in Malaysia, little research works have been attempted on using OPF as the pyrolysis feedstock in producing bio-fuel, specifically bio-oil. Therefore, an attempt on using OPF as the feedstock in thermal pyrolysis process is carried out with the hope of improving the yield of bio-oil produced from conventional biomass resources.

In fast biomass pyrolysis, the lignocellulosic organic compounds are thermally decomposed at a relatively high temperature of 450 °C in the absence of oxygen, producing a mixture of organic vapours, pyrolysis gases and residue char. Typically, Zeolite-ZSM 5 has been widely recognized as an active catalyst in producing high quantity of liquid bio-oil (Mihalcik et al., 2011). However, there are still abundant rooms for further exploration on others potential new catalyst in improving the production of bio-oil. GNF is one of the carbon allotropes that has a wide range of applications in electronics, energy storage, catalysis and gas sorption, but still has not been used as a catalyst in bio oil production in any previous study. The lightweight and stable carbon based materials possess high surface area and flexible functionality which offer a great scope in studying the performance of the carbon based catalyst in thermal pyrolysis of biomass.

2. Materials and methods

The aim of present experimental study is to investigate the applicability of Graphite Nanofiber (GNF) as a carbon based catalyst in producing high quantity of pyrolysis oil through catalytic pyrolysis of Oil Palm Fiber (OPF). The catalyst performances at varies pyrolysis temperatures (573 K, 673 K, 773 K) and catalyst loadings (0 wt%, 1 wt%, 5 wt%, 12 wt%) were assessed and evaluated based on the yields of pyrolysis oil and char residue produced. Identification of phenolic compounds present in the oil was performed under Gas Chromatographic coupled with Mass Spectrometry (GC-MS). In additional, the relationships of reaction temperatures and catalyst loadings on the oil and char yields were investigated and discussed as well.

2.1 Feedstock Preparation and Characterization

Raw OPF was collected from FELCRA Berhad Nasaruddin, Bota, Perak, Malaysia. Prior to the experiment, the raw biomass were ground and sieved to a particles size of < 300µm before they are dried in the oven at 105 °C for 24 h. By using Thermogravimetric analyzer EXSTAR TG/DTA 6300, proximate analysis was experimentally done on the dried OPF covering studies of moisture content, ash content, volatile matter and fixed carbon. Furthermore, ultimate analysis was performed to determine the elemental composition of dried OPF such as carbon, hydrogen, nitrogen, sulphur and oxygen contents under CHNS Analyzer, LECO (Model 932) based on ASTM D5291 standard. Oxygen content was computed from the difference of the CHNS analyses values and the high heating value was measured using IKA C5000 Bomb Calorimeter. The dried OPF properties are displayed in Table 1:

Table 1: Characteristic of Oil Palm Fronds (OPF)

Proximate Analysis (wt%)		Ultimate Analysis (wt%)	
Moisture	5.30	Carbon, C	43.60
Volatile Matter	71.00	Hydrogen, H	4.76
Fixed Carbon	16.80	Oxygen, O	50.56
Ash	6.90	Nitrogen, N	0.57
High Heating Value, HHV (MJ/Kg)	20.20	Sulphur, S	0.52

2.2 Catalyst Preparation and Characterization

The catalysts employed in this work were Graphite Nanofiber (GNF) obtained from *Platinum Green Chemical Sdn.Bhd.* To ensure its activeness, the catalyst materials were calcined under nitrogen flow at a temperature of 773 K for 5 h in a tube furnace reactor. From running down of the N₂ adsorption-desorption isotherms, *Brunauer–Emmett–Teller* (BET) specific surface area and micropore volume of as-prepared samples were determined at 77 K by using *Surface Area Analyser Micromeritics ASAP 2021*. Morphology and particle size of the porous samples were observed under Field Emission Scanning Electron Microscopy (FESEM, Zeiss Supra 55 VP) analyser and Transmission Electron Microscopy (TEM) on a FEI instrument which is subjected to an acceleration voltage of 200 kV.

2.3 Experimental Setup and configuration

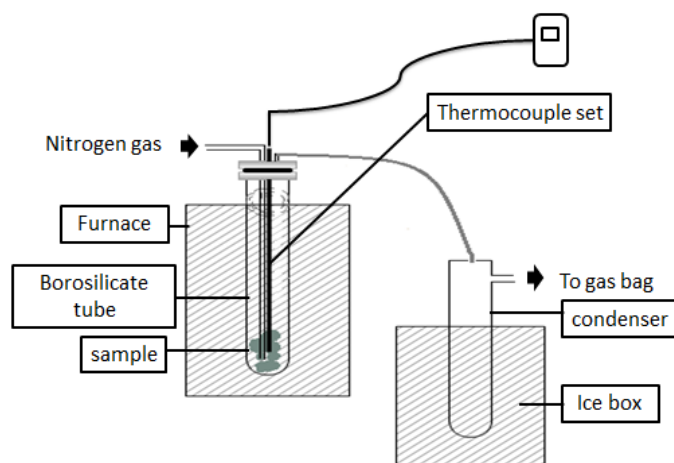


Figure 1: Semi Batch Reactor - Vertical Tube Furnace

Figure 1 illustrates the overall set up of the catalytic pyrolysis experiment. The setup consists of a semi-batch reactor which is externally heated by an electrical vertical split tube furnace and the paralysed unit is equipped together with a liquid collecting unit. A total 15 g of OPF biomass with constant particle size of < 500 μm is placed into the borosilicate tube, along with various GNF catalyst loadings (1 wt%, 5 wt% and 12 wt%) sandwiched in between two layers of glass wool. In order to measure in-situ feedstock temperature, the thermocouple set is introduced into the borosilicate tube and connected to the furnace heating system. Before heating up the paralysed unit, the paralysed unit is purged with inert nitrogen gas at a flow rate of 500 mL/min for 5 min. Nitrogen flow is then lowered to 60 mL/min once the furnace heating system started. Through the study, the nitrogen flow rate and the heating rate are kept constant at 60 mL/min, and 20 $^{\circ}\text{C}/\text{min}$. Overall, the OPF biomass is thermally decomposed at three distinct temperatures of 573 K, 673 K and 773 K and catalyst loadings of 1 wt%, 5 wt% and 12 wt% for an interval of 30 min in each run. After the completion of each run, the reactor is left to cool down to room temperature with the presence of nitrogen flow before performing the product analysis.

2.4 Bio-oil and Residue Char Yield Analysis

In this work, all product yields were reported on dry basis and each yield is basically averaged at two experiment replicates to ensure the reproducibility of the results obtained. The weight of bio-oil was computed by the weight difference of condenser before and after each run, similar to the weight of char residue formed. Comprehensive evaluation of the catalyst performance in thermal pyrolysis of OPF at various reaction temperatures and catalyst loadings was conducted in terms of bio-oil and char residue yields. With reference to Rahman et al (2014), the percentage of char and liquid product yields were defined as Eq(1):

$$\frac{\text{Weight of solid char or bio oil (g)}}{\text{Weight of dried OPF used (g)}} \times 100\% \quad (1)$$

Furthermore, the chemical compositions of 12 bio-oil samples were analyzed with an Agilent 7890A GC model Clarus 500 (60 m X 0.25 mm ID, 0.25 μm film thickness). Helium gas was employed as a carrier gas at a constant flow of 1.5 mL/min. The dilution solvent used was methanol and the dilution rate was 1:5. About 1 μL of diluted liquid bio-oil was injected into the column. The initial column temperature, 673 K, was maintained isothermally for approximately 10 min. Thereafter, the temperature was subsequently raised to 308 K at 0.90 $^{\circ}\text{C}/\text{min}$, until the final temperature reached 120 $^{\circ}\text{C}$. Finally, the final temperature of 473 K was achieved with a very steep 10 $^{\circ}\text{C}/\text{min}$ ramp. The inlet pressure of the column was 135 kPa and the scanning range was 10-300 amu.

3. Results and discussion

3.1 Catalyst Characterization

Figure 2 illustrates the microstructural and morphologies of GNF catalysts under TEM and FESEM imaging. From Figure 2(A) and (B), both TEM images revealed as-prepared samples have a hollow core coated with a cylindrical graphide like morphology layer, along the longitudinal axis of fiber. From Figure 2(C), it can be clearly seen that the graphite plane layers are stacked at a certain angle with respect to the axis of the hollow fiber and resulting fibers with exposed edge planes along the entire interior and exterior surfaces of the nanofibers. Such microstructure can be identified as “stacked cup” or “herringbone structure” which is in good agreement with the findings obtained by Klein et al., (2008). Furthermore, FESEM images of the nanostructure confirmed the width of nanofibers are in the nanorange of 100-500 nm, depending on the fiber morphology. Additionally, the surface area and pore volume of the GNF were 173.3262 m²/g and 0.422024 cm³/g.

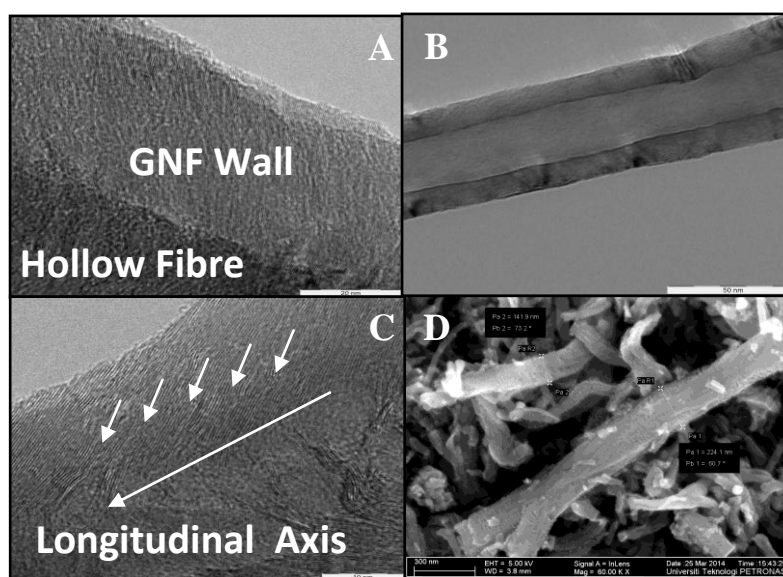


Figure 2: (A) TEM image at higher magnification (400 kX), (B) TEM image of GNF at low magnification (31.5 kX), (C) TEM image of GNF, (D) FESEM image of the structure (60 kX)

3.2 Effect of Catalyst Loadings and Temperatures on Bio-Oil Yield

In the absence of catalysts, the thermal pyrolysis of OPF yielded a maximum liquid product of 44 wt% at 673K before it dropped back to less than 43 wt% at 773 K. Similar trend can be observed at catalyst loading of 1 wt%. Both trends are in good agreement with the findings reported by Abdullah et al. (2010), Abdullah et al.(2008) and Sulaiman et al. (2011). This is possibly due to competition of hydrolysis and repolymerization as hydrolysis causes decomposition of biomass and formation of small molecules compounds. The small compounds rearrange through condensation, cyclization and polymerization to form new compounds (Qu et al., 2003). Another reason behind such trend could be secondary cracking of pyrolysis oil into gaseous products. Increment of temperature has made the rate of thermal cracking reaction of the pyrolysis vapors becomes faster, thus resulting in the release of non-condensable compounds such as carbon dioxide and carbon monoxide. However, at high catalyst loadings, it is noticeable that the liquid yields increases proportional with pyrolysis temperature. This could be attributed to the strong tangled agglomeration structures of CNF as such mesopore structure promotes an open pore volume which reduces diffusion limited transfer and provides a higher surface area for chemical adsorption and reactant conversion (Van et al., 2014). Furthermore, catalytic pyrolysis of OPF using GNF offers a higher liquid yield in contrast to that without any aid of catalysts. Such results appear to contradict with other pyrolysis studies as the use of catalyst materials does not favour in the production of liquid bio-oil (Aresta et al., 2012). This is mainly attributed to low secondary cracking of organic material due to low acidity of GNF materials. In overall, the bio-oil yields produced from catalytic pyrolysis of OPF using GNF are generally higher than that produced from H-ZSM 5 catalysts with the use of rice husk, empty fruit bunch and others (Abu Bakar, 2012). It can be seen that the maximum liquid yield obtained was 46 wt% at mild temperature of 673 K and low catalyst loading of 1 wt%.

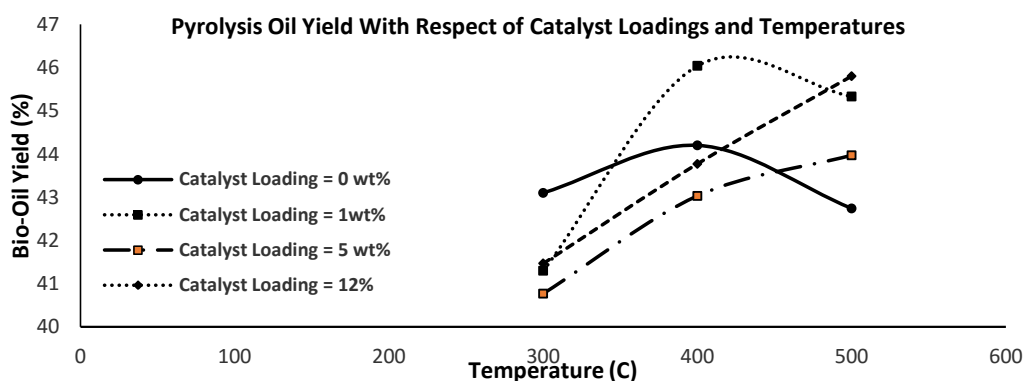


Figure 3: Pyrolysis Oil Yield

3.3 Effect of Catalyst Loadings and Temperatures on Char Yield

In general, biomass pyrolysis can be divided into four distinct stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition (Yang et al., 2007). At 573 K, the solid residue yields are significantly higher than 673 K and 773 K. Such high yields can be due to partial decomposition of biomass structure. Previous studies of Siti Sabrina, et al (2013) in pretreatment of OPF showed that the cell wall of raw OPF are rich in hemicellulose, cellulose and lignin. It was also revealed that OPF has the highest composition of hemicellulose compared to coir, pineapple, banana and even soft and hardwood fibres (Khalil, et al., 2006). Thus, it can be seen that at low catalyst loadings, the maximum bio-char yields mostly occurred at intermediate temperature of 673 K and this could be attributed to the complete decomposition of hemicellulose at the temperature interval of 573 K and 673 K (Wang, 2014). With shorter polysaccharide chain and simpler sugar monomer units present in hemicellulose, the hemicellulose is more easily to decompose than cellulose at low temperature. However, despite its simplicity in physical structure, the resultant decomposition residue contributes a higher solid residues yield than the latter. When the pyrolysis temperature is higher than 673 K, nearly all of the cellulose was pyrolyzed with a very low solid residue left. This elucidated on the sudden sharp drop in the bio-char yield at 673 K (Yang et al., 2007). As the pyrolysis temperature increases, the bio char yield decreased but with significant pattern. Volatiles matter are released from the biomass structure which results in the decrease in the weight of solid products. The decrease in char yield with an increase of temperature could be also due to primary decomposition of OPF at high temperature or by secondary decomposition of the char residue. Studies by Rahman et al. (2014) on pyrolysis of Oil Palm Fronds indicated the same trend as well. The lowest yield of bio-char is obtained at 673 K without any aid of the catalyst, while the lowest bio-char residue from catalytic pyrolysis is 27.50 wt% at temperature of 773 K and catalyst amount of 5 wt%, which is slightly lower than the quantity of bio-char yielded at the optimum parameter of highest bio oil yield.

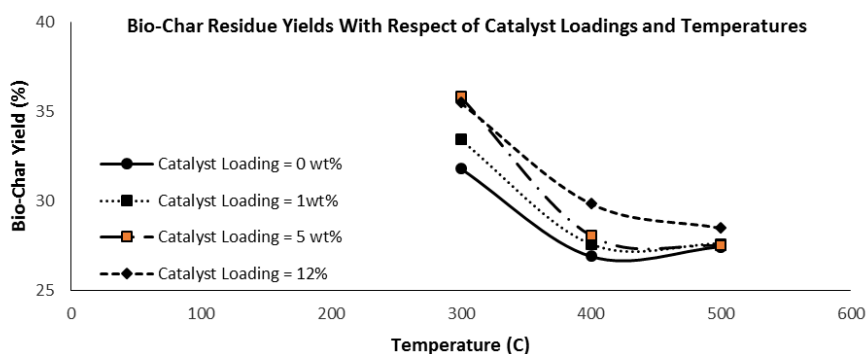


Figure 4: Bio-Char Yield

3.4 Composition of Bio-Oil

GC-MS analysis was performed to identify the composition of bio-oil from the catalytic pyrolysis of OPF at temperatures of 573 K, 673 K and 773 K. A total of 40 chief organic compounds were identified and the analysis revealed the presence of furfural, phenols, aromatic hydrocarbons, aliphatic hydrocarbon, furan

derivate, ketones, aldehyde and some cresols as well as trace quantity of guaiacols. The presence of such organic compounds are mainly attributed to the lignocellulosic biopolymer textures such as hemicellulose, cellulose and lignin within the OFP structure. In contrast to catalytic pyrolysis, the most abundant organic species found in non-catalytic pyrolysis are primary oxygenates which mainly composed of ketones, acids, alcohols and phenolic compounds. However, its content significantly reduced at higher pyrolysis temperature and catalyst loadings. The reduction of oxygenates and acids in catalytic pyrolysis indicates the instability of the bio-oil was significantly improved under the presence of carbon based catalyst.

4. Conclusion

GNF is an excellent carbon based nanocatalyst in thermal pyrolysis of OFP as it is capable to produce bio-oil yield as high as 46 wt% at mild temperature of 400 °C and low catalyst amount of 1 wt%. Such high bio-oil yield strengthened the fact that OFP can be employed as the potential feedstock in producing excellent quantity of bio-oil fuel, char and vapour. The oil from such biomass resource could be a great sustainable fuel source in near future.

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References

- Abdul Khalil H.P.S., Siti Alwani M., Mohd Omar A.K., 2006, Chemical composition, anatomy, lignin distribution, and cell wall structure of Malaysian plant fibers, *Bioresources*, 2(1), 220-232.
- Aresta M., Dibenedetto A., Dumeignil F., 2012. *Biorefinery: From Biomass to Chemicals and Fuels*, Walter de Gruyter & Co, New York, USA.
- Sulaiman F., Abdullah N., 2011, Optimum conditions for maximizing pyrolysis liquids of oil palm empty fruit bunch. *Energy*, 15, 2352-2359.
- Khor K., Lim, K., Zainal Alimuddin, 2010. Laboratory-scale pyrolysis of oil palm trunks. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 32(6), 518-531.
- Klein, K. L., Melechko A.V., McKnight T.E., Retterer S.T., Rack P.D., Fowlkes J.D., Joy D.C., Simpson M.L., 2008, Surface characterization and functionalization of carbon nanofibers. *Journal of Applied Physics*, 103(6), 061301.
- Bakar M.S.A., Titiloye J.O., 2013, Catalytic Pyrolysis of Rice Husk for Bio-Oil Production, *Journal of Analytical and Applied Pyrolysis*, 103, 362-368.
- Abdullah N., Gerhauser H., 2008, Bio-oil derived from empty fruit bunches, *Fuel*, 87(8), 2606-2613.
- Phan A., Phan T., 2008, Biodiesel production from waste cooking oil, *Fuel*, 87, 3490-3496.
- Qu Y., Wei X., Zhong C., 2003, Experimental Study on the Direct Liquefaction of *Cunninghamia Lanceolata* in Water. *Energy*, 28(7), 597-606.
- Rahman A.A., Abdullah N., Sulaiman F., 2014, Temperature effect on the characterisation of pyrolysis products from oil palm fronds. *Advance in Energy Engineering (AEE)*, 2, 14-21.
- Siti Sabrina M.S., Roshanida A.R., Norzita N., 2013, Pretreatment of Oil Palm Fronds for Improving Hemicelluloses Content for Higher Recovery of Xylose, *Jurnal Teknologi*, 62(2), 39-42.
- Van T.D.N., Sufian S., Mansor N., Yahya N., 2014, Characterization of Carbon Nanofibers Treated with Thermal Nitrogen as a Catalyst Support Using Point-of-Zero Charge Analysis, *Journal of Nanomaterials*, 6, 1-6.
- Wang L., 2014, Biomass Pyrolysis and Bio-oil Utilization, In: Wang D.L. (ed.), *Sustainable Bioenergy Production*, CRC Press, Taylor & Francis Group, 362, 727-735.
- Yang H., Yan R., Chen H., Lee D.H., Zheng C., 2007, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel*, 86, 1781-1788.
- Zhang L., Liu R., Yin R., Mei Y., 2013. Upgrading of bio-oil from biomass fast pyrolysis in China: A review, *Renewable and Sustainable Energy Reviews*, 24, 66-72.