Co-pyrolysis of rice straw and polypropylene using fixed-bed pyrolyzer

N I Izzatie[1], M H Basha[1], Y Uemura[2], M A Mazlan[2], M S M Hashim[2], N A M Amin[1], M F Hamid[3]

[1] Mechanical Engineering Programme, School of Mechatronic Engineering, Universiti Malaysia Perlis, Pauh Putra Campus, 02600 Arau,Perlis,Malaysia.

[2] Centre for Biofuel and Biochemical Research, Universiti Teknologi PETRONAS, Malaysia.

[3] School of Mechanical Engineering, Universiti Sains Malaysia.

E-mail: hafifbasha@unimap.edu.my

Abstract. The present work encompasses the impact of temperature (450, 500, 550, 600 °C) on the properties of pyrolysis oil and on other product yield for the co-pyrolysis of Polypropylene (PP) plastics and rice straw. Co-pyrolysis of PP plastic and rice straw were conducted in a fixed-bed drop type pyrolyzer under an inert condition to attain maximum oil yield. Physically, the pyrolysis oil is dark-brown in colour with free flowing and has a strong acrid smell. Co-pyrolysis between these typically obtained in maximum pyrolysis oil yields up to 69% by ratio 1:1 at a maximum temperature of 550 °C. From the maximum yield of pyrolysis oil, characterization of pyrolysis product and effect of biomass type of the composition were evaluated. Pyrolysis oil contains a high water content of 66.137 wt.%. Furfural, 2-methylnaphthalene, tetrahydrofuran (THF), toluene and acetaldehyde were the major organic compounds found in pyrolysis oil of rice straw mixed with PP. Bio-char collected from co-pyrolysis of rice straw mixed with PP plastic has high calorific value of 21.190 kJ/g and also carbon content with 59.02 wt.% and could contribute to high heating value. The non-condensable gases consist of hydrogen, carbon monoxide, and methane as the major gas components.

1. Introduction

Fossil fuels such as coal, petroleum, and natural gas are considered as non-renewable resources and not sustainable because their formation takes billions of years. Thus, many researchers found alternative ways by replacing biomass such as palm kernel shell wastes [1], bagasse [2], rice straw [3], rice husk [4], corn stalk [5], wheat straw [6], corncobs [5], and sunflower residue [7] as energy source. In Malaysia, rice milling factories generated bulk quantities of rice straw and rice husk as by-products every year. Traditionally, to control rice straw diseases, rat infestation and to eliminate sources of insect pests, straw burning is the simple way to overcome farmer's problems and also to save time for land management for the next crop season [8]. However, open burning of rice straw releases a lot of

air pollutants that can cause a hazard to air quality, human health, and climate [9]

A negligible concentration of nitrogen, sulphur, and ash and lower emission qualifies biomass as a clean energy source compared to the conventional of fossil fuels [9-10]. Polymer wastes such as plastics that are used in our daily life have increased every year which causes a serious threat to the environment and the organisms living around. Most of the plastics are non-biodegradable that takes a long time to get decomposed. Incineration is an economic way for plastics wastes management but highly toxic pollutants were released and will cause environmental problems. Studies from literature revealed that pyrolysis of biomass can produce pyrolytic oil, char, and non-condensable gas. Rice straw biomass have less lignin since it is non-wood biomass and high attractive content which can generate more yield and great quality with a high energy content of pyrolytic oil [11-12]. Pyrolysis oil has similar composition and properties to the petroleum-derived fuels and does not contain hazardous gases that increase emission of greenhouse gases [14].

Co-pyrolysis is one of a technique that can produce high-grade pyrolysis oil from biomass that involves two or more different materials as feedstocks. Co-pyrolysis of polymers and biomass will enhance the quality of biomass pyrolytic oil [13]. Biomass has high oxygen and carbon whereas plastics are rich in hydrogen and carbon. Many researchers have argued that co-pyrolysis with plastics produce high yield and enhanced the quality of pyrolysis oil such as waste polystyrene co-pyrolyzed with Karanja and Niger seeds [13], woodchip with block polypropylene [15] and Kemal Pasua with low-density polyethylene[16]. Polypropylene (PP) plastic is a thermoplastic polymer use for various applications including packaging, stationery, textiles, and automotive components. PP has a short life span of packaging and most of these thermoplastics end up in landfills as wastes. In 2010, a research study by Feng Gao [17] found about 84.2 wt% condensed liquid products, 15.7 wt% non-condensable gas and less than 0.25 wt% of char were obtained from pyrolysis of PP. Based on the analysis of PP pyrolysis oil, most dominant components which account for 21 wt% in PP pyrolysis oil is 1,3,5-trimethyl-cyclohexane (C_9H_{18}) oligomers with 3 propene units.

In this work, a fixed bed drop type pyrolyzer is used to collect the pyrolysis products. The objective of this study is to investigate the effect of reaction temperature (450,500,550,600°C) on the oil yield of co-pyrolysis of rice straw and polypropylene plastics. Additionally, to determine the physical and chemical components of the proposed method, the product yield is analyzed.

2. Materials and methods
2.1. Raw materials
Rice straw and polypropylene (PP) plastics were used as feedstocks in the present study. Rice straw was collected from the rice mill in Kangar, Perlis. Rice straw biomass was dried ground and sieved to the size 0.50mm-2.0mm. PP plastics of food containers was collected and cut in size 3.0mm x 3.0mm. The materials were stored in an air tight container to prevent an imbalance of moisture in biomass.

2.2. Co-pyrolysis experiment apparatus
A drop type fixed-bed pyrolyzer is used to carry out co-pyrolysis of rice straw and PP plastics. Figure 1 shows the schematic diagram of the pyrolyzer. The setup consisted of a stainless steel cylindrical reactor with 53mm internal diameter and 166mm height. The pyrolyzer was installed inside an electrical heater with water jacket and insulation to enable high heating reaction in reactor up to 600°C. Nitrogen and vacuum lines used to purge nitrogen gas to achieve inert conditions in the pyrolyzer. The co-pyrolysis temperature in the reactor was controlled by a K-type thermocouple that was inserted in the pyrolyzer. Two condensers that which were immersed in a cooled ethylene glycol bath were connected to the reactor to condense the pyrolysis vapour at below -10°C. 3L of gas sampling bag was connected to the outlet of vapour trap to accumulate the non-condensable gases (NGC).
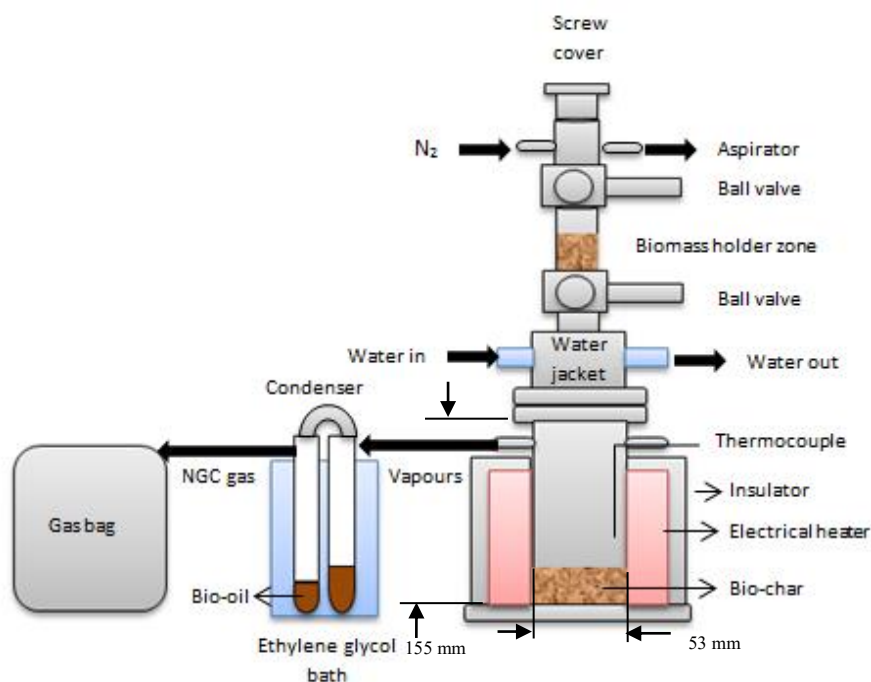
Figure 1. Schematic diagram of the fixed bed drop-type pyrolyzer

2.3. Co-pyrolysis procedure

In the co-pyrolysis of rice straw and PP plastics experiment, a constant ratio of 1:1 with 10g of feedstocks was put into the biomass holder zone with ball valves closed. The screw cover was tightened and nitrogen gas was purged into the apparatus to remove air in the system. The reactor was heated until the desired temperature is achieved. For this work, the reaction temperature was set to 450°C, 500°C, 550°C and 600°C respectively. After the desired temperature was achieved the feedstock was dropped down to the reactor to start the reaction. The experiment was done in a close environment. Duration of the experiment was held at that temperature for 20 minutes until no significant release of brownish gas was observed. The reactor was then cooled and bio-chars formed inside the reactor were collected.

2.4. Characterizations of the feedstock and products.

The elemental analysis of the feedstocks; rice straw and polypropylene (PP) plastics were carried out using a Perkin Elmer 2400 CHNS Analyzer. The amount of carbon, hydrogen,nitrogen and sulphur was determined and the oxygen content was calculated by difference. The calorific value the feedstocks, pyrolysis oil and bio-char was measured using an IKA-WERKE C2000 bomb calorimeter. The water content of bio-oil was measured by a volumetric Karl Fischer titrator (Mettler Toledo, V30) with Combititrant 5 Keto (Merck) as a titrant and CombiSolvent Keto as a solvent. All the analyses were repeated twice to verify the results and average. The composition of non-condensable gases was detected by Thermal Conductivity Detector (GC-TCD) with a Davidson Grade 12 Silica Gel packed column for CO_2 detection and a Molecular Sieve 5A packed column to detect CO, CH_4, H_2, and O_2. Quantitative analysis of some organic compounds in the bio-oil was performed using a gas chromatography/flame ionization detector (GC-FID). The analysis was executed on a SHIMADZU GC-2014 model A BPX-5 capillary column with 30 m, 0.25 mm, and 0.25 μm of length, internal diameter, and film thickness, correspondingly was used. Oven temperature was held at 35 °C for 2 min. Then, the temperature was raised to 250 °C with a heating rate of 20 °C/min and held for 20 min. The injector and detector temperatures were set constant at 280 °C. A 1.1 mL-NTP/min column flow

rate of nitrogen with 99 % purity was used as a carrier gas. Methanol was utilized as a solvent and n-dodecane as the internal standard.

3. Result and discussion

### 3.1. Characteristics of feedstocks

The proximate and elemental analyses were done and the results are listed in Table 1. The result shows the rice straw has high moisture content compared to PP. The moisture content of feedstocks must be lower than 10 wt% because high moisture content can reduce the feedstock's effectiveness as a fuel [18]. PP contains a high calorific value with 46.339 wt% due to polymer composite structure in high content of carbon and hydrogen. By calculating the difference, rice straw had high oxygen content which can low the calorific value of the products yields [19].

Table 1. Proximate and elemental analysis of rice straw and PP plastic.

Characteristics	Rice straw	Polypropylene (PP) plastic
Proximate analysis (wt.%)		
Moisture	5.935	0.003
Calorific value	15.036	46.339
Elemental analysis (wt.%)		
C	36.02	87.85
H	6.63	10.58
N	1.12	0.23
O (by difference)	55.85	0.48
S	0.38	0.86

3.2. Effect of pyrolysis temperature on products yields

Figure 2 show the result of total product yields (wt.%) for different reaction temperature of co-pyrolysis rice straw mixed with PP. At temperature 550°C, a maximum yield of pyrolysis oil was obtained which is 69 wt%. However, the yield of pyrolysis oil and bio-char decreased at temperature 600°C assuming the decreasing trend continues and the yield of non-condensable gases increases due to continuous volatilization reaction.
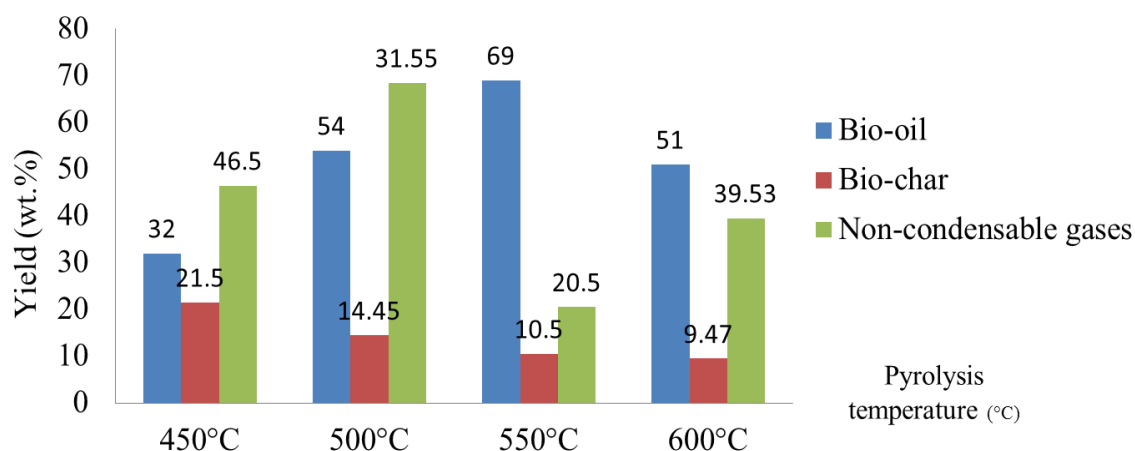

Figure 2. Effect of reaction temperature on the product yield of co-pyrolysis of rice straw and PP

Table 2. Proximate and elemental analysis of the co-pyrolysis products yields at temperature 550°C.

Feedstock	Pyrolysis oils	Bio-chars
Elemental analysis (wt%)		
C	87.090	59.050
H	10.450	3.120
N	0.470	1.150
S	0.400	0.260
O	1.590	36.450
(by difference)		
Calorific value (kJ/g)	12.007	21.190
Water content (wt%)	66.137	

The proximate and elemental analyses of the pyrolysis oil are presented in Table 2. Typical pyrolysis oil has high water content and a few of suspended solids from biomass. Approximately 66.137 wt% of water content had been detected in pyrolysis oil of rice straw mixed with PP. Cracking of bigger molecules in a longer residence time will form smaller organic compounds at the high temperature was a cause of sudden increased the water content [1]. The high amount of water can cause phase separation and reduced its behaviour as a fuel especially in combustion as delay the ignition, reduced the combustion rates and lowers the heating value of bio-oil [22]. In addition, long periods of time in storage and high storage temperature (60°C) will increase the water content and favour existed in a homogenous phase of water content on the top part and bottom part of bio-oil [23]. Thus, freezer or cold room were suitable conditions to store bio-oil liquids for long storage time.

Figure 3 shows the chemical composition of the pyrolysis oil from rice straw mixed with PP. Furfural, 2-methylnaphthalene, tetrahydrofuran (THF), toluene and acetaldehyde were the major pyrolysis organic compounds. Most of the compounds found in the analysis were aromatic groups compound represent pyrolysis of polypropylene produced benzene, propene, and toluene along with other hydrocarbons [25].
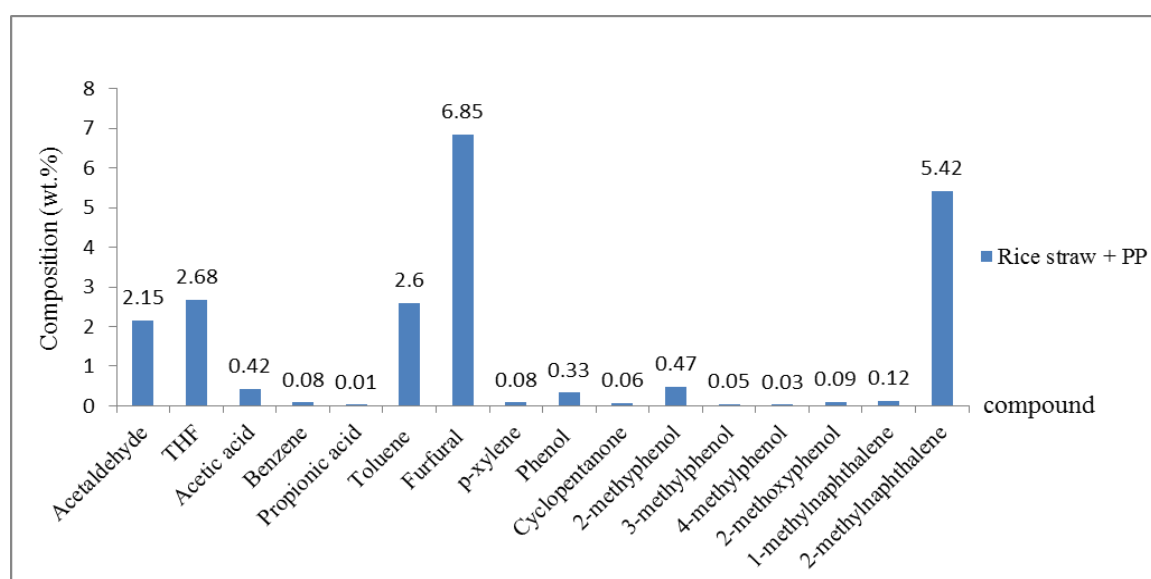
Figure 3. Organic compounds in co-pyrolysis oil of rice straw mixed with PP

Bio-char collected from co-pyrolysis bio-oil of rice straw mixed with PP plastic has higher calorific value (21.190 kJ/g) and carbon content (59.02 wt.%) contribute to higher HHV [20]. Bio-char of rice straw mixed with PP have wax-like coated represent PP presence in the reaction. A small amount of bio-char collected and more non-condensable gas (NCG) accumulated as a temperature and retention time increased.

NCG such as hydrogen, carbon monoxide, carbon dioxide, methane, and hydrocarbon was present in the co-pyrolysis of rice straw mixed with PP plastic. In order to maximize the liquid bio-oil in co-pyrolysis, the temperature and retention time should not more than 550°C and less than 20 minutes to avoid increase of volume NGC.
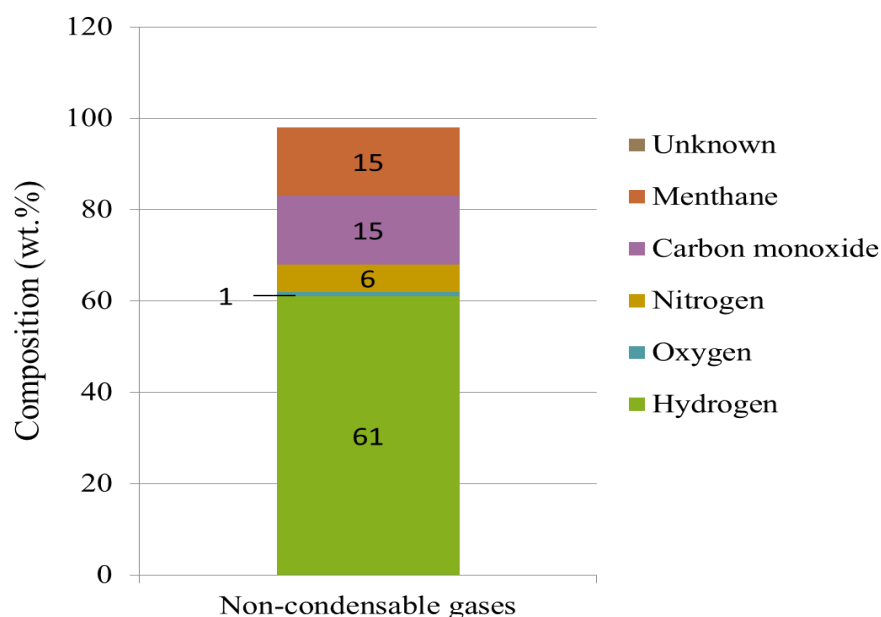

Figure 4. Composition analysis of non-condensable gases.

4. Conclusion

In this study, co-pyrolysis of rice straw mixed with polypropylene (PP) plastic was investigated in a fixed-bed drop-type pyrolyzer to observe the effect of co-pyrolysis temperature and to characterize the product yields. The highest pyrolysis oil yield obtained was 69 wt. % at temperature 550°C with the ratio 1:1 of rice straw and PP plastic. A temperature of 550°C was suggested as the best co-pyrolysis temperature to maximize the pyrolysis oil yield from rice straw mixed with PP plastic. Besides, the pyrolysis oil produced from co-pyrolysis of rice straw mixed with PP plastic has high water content about 66.137 wt.%. The calorific value in pyrolysis oil obtained from co-pyrolysis of rice straw mixed with PP plastic was higher at 12.007 kJ/g. Furfural, 2-methylnaphthalene, tetrahydrofuran (THF), toluene and acetaldehyde were the major organic compound found in pyrolysis oil of rice straw mixed with PP. In bio-char collected from co-pyrolysis of rice straw mixed with PP plastic has a calorific value of 21.190 kJ/g) and carbon content of 59.02 wt.%. The non-condensable gases such as hydrogen, carbon monoxide, and methane were the major gas components.

References

[1]   M. Asadullah, N. S. Ab Rasid, S. A. S. A. Kadir, and A. Azdarpour, "Production and detailed characterization of bio-oil from fast pyrolysis of palm kernel shell," *Biomass and Bioenergy*, vol. 59, pp. 316–324, 2013.

[2]   I. Demiral and S. Şensöz, "The effects of different catalysts on the pyrolysis of industrial wastes (olive and hazelnut bagasse)," *Bioresour. Technol.*, vol. 99, no. 17, pp. 8002–8007, 2008.

[3]   Y. F. Huang, W. H. Kuan, S. L. Lo, and C. F. Lin, "Total recovery of resources and energy from rice straw using microwave-induced pyrolysis," *Bioresour. Technol.*, vol. 99, no. 17, pp. 8252–8258, 2008.

[4]   S. R. Naqvi, Y. Uemura, and S. B. Yusup, "Catalytic pyrolysis of paddy husk in a drop type pyrolyzer for bio-oil production: The role of temperature and catalyst," *J. Anal. Appl. Pyrolysis*, vol. 106, pp. 57–62, 2014.

[5]   O. Ioannidou, A. Zabaniotou, E. V. Antonakou, K. M. Papazisi, A. A. Lappas, and C. Athanassiou, "Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 4. pp. 750–762, 2009.

[6]   J. A. Pérez, I. Ballesteros, M. Ballesteros, F. Sáez, M. J. Negro, and P. Manzanares, "Optimizing Liquid Hot Water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production," *Fuel*, vol. 87, no. 17–18, pp. 3640–3647, 2008.

[7]   A. A. Zabaniotou, E. K. Kantarelis, and D. C. Theodoropoulos, "Sunflower shells utilization for energetic purposes in an integrated approach of energy crops: Laboratory study pyrolysis and kinetics," *Bioresour. Technol.*, vol. 99, no. 8, pp. 3174–3181, 2008.

[8]   M. Z. Rosmiza, W. P. Davies, C. R. R. Aznie, M. Mazdi, and M. J. Jabil, "Farmers' knowledge on potential uses of rice straw: an assessment in MADA and Sekinchan, Malaysia," *Geogr. Malaysian J. Soc. Sp.*, vol. 10, no. 5, pp. 30–43, 2014.

[9]   D. Tipayarom and N. T. K. Oanh, "Effects from open rice straw burning emission on air quality in the Bangkok metropolitan region," *ScienceAsia*, vol. 33, no. 3, pp. 339–345, 2007.

[10] K. C. Sembiring, N. Rinaldi, and S. P. Simanungkalit, "Bio-oil from Fast Pyrolysis of Empty Fruit Bunch at Various Temperature," *Energy Procedia*, vol. 65, pp. 162–169, 2015.

[11] Q. Zhang, J. Chang, T. J. Wang, and Y. Xu, "Upgrading bio-oil over different solid catalysts," *Energy and Fuels*, vol. 20, no. 6, pp. 2717–2720, 2006.

[12] V. Kirsanovs and A. Zandeckis, "Investigation of Biomass Gasification Process with Torrefaction Using Equilibrium Model," *Energy Procedia*, vol. 72, pp. 329–336, 2015.

[13] K. P. Shadangi and K. Mohanty, "Co-pyrolysis of Karanja and Niger seeds with waste polystyrene to produce liquid fuel," *Fuel*, vol. 153, pp. 492–498, 2015.

[14] P. Basu, "Pyrolysis," in *Biomass Gasification, Pyrolysis and Torrefaction*, 2013, pp. 147–176.

[15] F. Abnisa, W. M. A. Wan Daud, S. Ramalingam, M. N. B. M. Azemi, and J. N. Sahu, "Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel," *Fuel*, vol. 108, pp. 311–318, 2013.

[16] A. Sinag, M. Sungur, M. Gullu, and M. Canel, "Characterization of the liquid phase obtained by copyrolysis of Mustafa Kemal Pasa (M. K. P.) lignite (Turkey) with low density polyethylene," *Energy & Fuels*, vol. 20, no. 5, pp. 2093–2098, 2006.

[17] F. Gao, "Pyrolysis of Waste Plastics into Fuels," *PhD Thesis*, 2010.

[18] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012.

[19] S. Czernik and A. V. Bridgwater, "Overview of applications of biomass fast pyrolysis oil," *Energy and Fuels*, vol. 18, no. 2, pp. 590–598, 2004.

[20] F. Abnisa and W. M. A. Wan Daud, "A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil," *Energy Convers. Manag.*, vol. 87, pp. 71–85, 2014.

[21] M. A. F. Mazlan, Y. Uemura, N. B. Osman, and S. Yusup, "Fast pyrolysis of hardwood residues using a fixed bed drop-type pyrolyzer," *Energy Convers. Manag.*, vol. 98, pp. 208–214, 2015.

[22] N. Ibrahim, P. A. Jensen, D. M. Johansen, R. R. Ali, and M. R. Kasmani, "Influence of Reaction Temperature and Water Content on Wheat Straw Pyrolysis," *World Acad. Sci. Eng. Technol.*, vol. 6, no. 10, pp. 10–21, 2012.

[23] F. Paradela, F. Pinto, I. Gulyurtlu, I. Cabrita, and N. Lapa, "Study of the co-pyrolysis of biomass and plastic wastes," *Clean Technol. Environ. Policy*, vol. 11, no. 1, pp. 115–122, 2009.

[24] J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö, and D. Chiaramonti, "Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass," *Applied Energy*, vol. 116. pp. 178–190, 2014.

[25] I. J. N. Zorriqueta, "Pyrolysis of Polypropylene By Ziegler-Natta Catalysts," p. 144, 2006.