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IMPROVING BIO-OIL QUALITY THROUGH CO-PYROLYSIS OF CORN COBS AND POLYPROPYLENE IN A STIRRED TANK REACTOR

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ABSTRACT

Bio-oil produced by biomass pyrolysis contains high oxygenates, namely, carboxylic acids, alcohols, and ketones resulting in low calorific fuel, and therefore bio-oil requires upgrading to sequester these oxygenates. By conducting the co-pyrolysis of biomass and plastic feed blend, the donation of hydrogen by plastic free radicals to the oxygen of biomass free radicals may sufficiently reduce oxygenate compounds in the bio-oil and increase its yield. Therefore, the synergetic effects are functional. Currently, co-pyrolysis reactors have high aspect ratios (ratio of height to diameter) of 4 or more and small diameters (maximum 40 mm), in which the heat transfer from the furnace to the feed blend is immaterial even though the plastic material has low thermal conductivity. However, in large-scale reactors, such a design restricts the bio-oil's capacity due to the heat transfer constraint. To resolve the latter and to improve bio-oil quality, in the present work, the co-pyrolysis of corn cobs and polypropylene (PP) is conducted in a stirred-tank reactor with a low aspect ratio (2). PP composition in the feed blend was varied from 0–100% weight with a 12.5% weight interval, heating rate of 5°C/min, and final temperature of 500°C. The results show that by increasing the PP composition in the feed blend from 37.5% to 87.5%, the bio-oil yield increased from 25.8% to 67.2% feed weight. An analysis of bio-oil quality shows that there was a favorably abrupt increase of non-oxygenate composition in the bio-oil from less than 5% to more than 70% as the PP composition in the feed blend was increased from 37.5% to 50% and more.

Keywords: Co-pyrolysis; Corn cobs; Polypropylene; Stirred tank reactor; Synergistic effect

1. INTRODUCTION

Indonesia is blessed with large reserves of biomass residues that can be harnessed as renewable energy feed stocks. Through pyrolysis, biomass can be converted into various types of fuels, such as gas, char, and liquid. The bio-oil produced from the pyrolysis process has great potential for use as a fuel or chemical; nevertheless, its high oxygen content means that there a few challenges inherent in its application, caused by its low calorific value, corrosion problems, and instability due to its high content of oxygenate compounds (Lu et al., 2009). The addition of plastic to biomass pyrolysis may allow a reduction of the bio-oil's oxygenate content, while also increasing the bio-oil yield through a mechanism of hydrogen donation by plastic free radicals to biomass free radicals in the vapor phase of the pyrolysis process. Free radicals' interaction during co-pyrolysis may also prevent phase separation, a condition that is most likely to emerge when oils from separate pure feedstock pyrolysis are co-mixed (Abnisa & Wan

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Daud, 2014).

In this study, corn cobs were considered due to their highly abundant waste in Indonesia. According to the country's Ministry of Agriculture, within a five-year span (2011-2015), Indonesia harvested corn grains in areas covering about 4 million hectares, with production increasing from 17.6 to 19.6 million tons (Ministry of Agriculture, 2016). In broad terms, the weight ratio of the corn cobs to the grains harvested is about one sixth (Zynch, 2008); therefore, it is estimated that the cobs produced in 2015 amounted to as much as ± 3.3 million tons. The consumption of diesel oil in Indonesia was 32.67 million kiloliters in 2014, or 27.18 million tons (Ministry of Energy and Mineral Resources, 2016). If 60% of the corn cobs harvested can be converted into bio-fuel, then the country could produce 1.96 million tons of bio-fuel or 7% of its diesel oil consumption. The other reason for selecting corn cobs was their high combined cellulose and hemicellulose content. Clark and Lathrop (1953) and Foley (1978) found that corn cobs contain 32.3–45.6% cellulose, 39.8% hemicellulose (mostly composed of pentosane), and 6.7–13.9% lignin. According to Yang et al. (2006), cellulose and hemicellulose have high potential to produce volatile matter from which bio-oil and non-condensable gas can be produced. Therefore, about 72.1–85.4% of corn cobs could be converted into bio-oil and non-condensable gas. Wannapeera et al. (2008) succeeded in extracting from such volatile matter as much as 78.7% of corn cobs' weight. PP plastic was selected, as there is very high demand for it in Indonesia. In 2009, the volume of PP plastic required was about 800,000 tons, a quantity that is steadily increasing year-on-year (Indonesian Commercial Newsletter, 2010). PP plastic also has a high weight ratio of hydrogen to carbon (H/C) (Paraschiv et al., 2009). These authors conducted an ultimate analysis of a typical plastic PP to find that the mole ratio of H/C was 2.03. In comparison, Wannapeera et al. (2008) found that the corresponding ratio for corn cobs was 1.64. This higher H/C mole ratio of plastic PP compared to that of corn cobs allows hydrogen donation from free radicals of plastic PP to those of corncob pyrolysis in the vapor phase, resulting in the sequestration of oxygen in bio-oil (Oyedun et al., 2013).

To obtain a high yield of bio-oil from biomass pyrolysis, the use of high heating rates (10–200 K/second) is recommended. Under fast pyrolysis conditions, the yield of liquid products could reach 50–75% wt with 12–25% wt of solids and 8–20% wt of gaseous product, depending on the biomass type used (Jahirul et al., 2012; Dynamotive Energy Systems Corporation, 1999). However, plastic pyrolysis must undergo relatively low heating rates (slow pyrolysis) to obtain a higher oil yield (Gao, 2010). Consequently, to allow the contribution of plastic pyrolysis to the liquid products' content, the conditions of co-pyrolysis should be controlled by those of plastic pyrolysis. The synergistic effect depends on the extent of the contact between materials and is more likely to occur when pyrolysis is carried out in a fixed-bed reactor than in a fluidized-bed reactor (Fei et al., 2012). A study by Martinez et al. (2014) showed that an auger reactor produces a higher liquid yield than can be gained from fixed-bed reactor. However, the complexity of an auger reactor makes it an undesirable one.

Gao (2010) pointed out that the low thermal conductivity of plastics results in a large temperature gradient in the batch process and prevents the decomposition of plastic, thereby resulting in more wax. The use of reactors with a high aspect ratio (ratio of height to diameter) and small diameter, such as tubular reactors, exhibits non-constraint of heat transfer from the furnace to the feed blend (Frasson, 2014; Brebu et al., 2010). A high aspect ratio of 4 or more is required to yield a large volume for the gas phase above the feedstocks' surface, which sustains a sufficient residence time for synergistic effects to occur (Martinez et al., 2014; Abnisa & Wan Daud, 2014). Brebu et al. (2010) showed that by using a tubular reactor with an aspect ratio of 10 and diameter of 30 mm with feedstocks of biomass pine cone and different plastics, the bio-oil yield can reach up to 64% of the weight of the feedstocks. However, when using batch reactors for commercial purposes, their diameter should be large enough to accommodate the large capacity of reactor feedstocks. The present work proposes a co-pyrolysis of corn cob and PP using a stirred tank reactor in which the aspect ratio is low, i.e. 2, and the reactor diameter is 96 mm, but which is equipped with nitrogen flow to enhance the convective heat transfer from the reactor wall, on which a heater is installed, to the plastic feedstock to overcome the low thermal conductivity of plastic PP. Nitrogen bubbles in the plastic melt can reduce its viscosity and, as a result, the convective heat transfer would be upgraded (Chen et al., 2006).

This study is aimed to produce bio-oil by co-pyrolysis of corn cobs and PP plastics in a stirred tank reactor equipped with nitrogen flow at a low heating rate. The reaction was expected to create a synergistic effect that would improve the quantity and quality of the bio-oil produced.

2. EXPERIMENTAL SETUP

Corn cobs obtained from an agricultural waste dump in Bogor, West Java were ground and sieved to a particle size of 500μm−1mm. The particles were then dried in an oven so that the moisture content reached ≤ 10%. Meanwhile, the polypropylenes used in the experiment were 80 mesh-recycled PP plastic waste pellets without additives. Unlike the corn cobs, the PP plastics did not undergo any pre-treatment prior to pyrolysis. Some characterization studies were carried out for all raw materials; the results in terms of the properties and composition of the materials are given in Table 1.

Before the co-pyrolysis was conducted, about 10 mg of feedstocks of pure corn cob particles, pure PP plastic, and that of 50% weight of corn cob and 50% weight of PP plastics were pyrolyzed in a thermogravimetric analyzer (TGA) in a nitrogen atmosphere to evaluate their solid mass loss during heating. The flow rate of the nitrogen gas was kept at 500 ml per minute. The sample was heated from an ambient temperature to 825^{o}C, at a heating rate of 5^{o}C per minute. The changes to the mass of the various feedstocks with rising temperature are displayed in Figure 1. This figure shows that a maximum temperature of 500^{o}C is appropriate to attain minimum remaining solid masses in pyrolysis of biomass, plastic, and mixed biomass and plastic. This maximum temperature in the TGA would be used for setting the maximum temperature in the co-pyrolysis.

To perform the co-pyrolysis of corn cob and polypropylene particles in the stirred tank reactor, pure feedstocks and a feedstock blend of corn cobs and PP plastic with PP compositions in the feedstock were used at 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%, and 100%. A schematic of the co-pyrolysis process is shown in Figure 2. In all, 100 grams of feedstock were used under heating at the rate of 5^{o}C/minute from ambient temperature to 500^{o}C, with a holding time of 10 minutes to allow further pyrolysis of the remaining solid at 500^{o}C. See Section 3.1 for the reasons for taking the final temperature at 500^{o}C. The flow of nitrogen gas was maintained at 500 ml/minute, which has been proven to obtain maximum oil yield using plastic feedstock. A faster flow of nitrogen is likely to lead to a shorter residence time in the vapor phase for interaction between free radicals of biomass and plastic to attain a synergetic effect. Conversely, if the flow rate of nitrogen is too low, it could trigger a secondary pyrolysis reaction in the reactor due to an excessively long residence time (Bridgwater, 2012; Kato et al., 2016). The rotation rate of the two-blade stirrer was 50 rpm. The resulting pyrolysis vapor was condensed in a series of two water-cooled bulb condensers and the bio-oil produced was collected in a vacuum flask. Cooling water at 15^{o}C was used in the condensers. At the end of each experiment run, the liquid product, char residue, and wax were collected after the completion of the holding time and weighed.

Table 1 Result of feedstock proximate and ultimate analysis (Air-dried basis)

Analysis Parameter	Corn Cobs	Polypropylene	Unit
Proximate			
Air-Dried Moisture	11.02	0.11	%
Ash	5.07	0.00	%
Volatile Matter	69.31	99.89	%
Fixed Carbon	14.60	0.00	%
Ultimate			
C	41.07	87.18	%
H	6.54	12.70	%
N	0.76	0.03	%
Total Sulphur	0.09	0.07	%
O*	46.47	0.02	%
H/(C+H+O+N) mole ratio	0.07	0.13	

* by difference

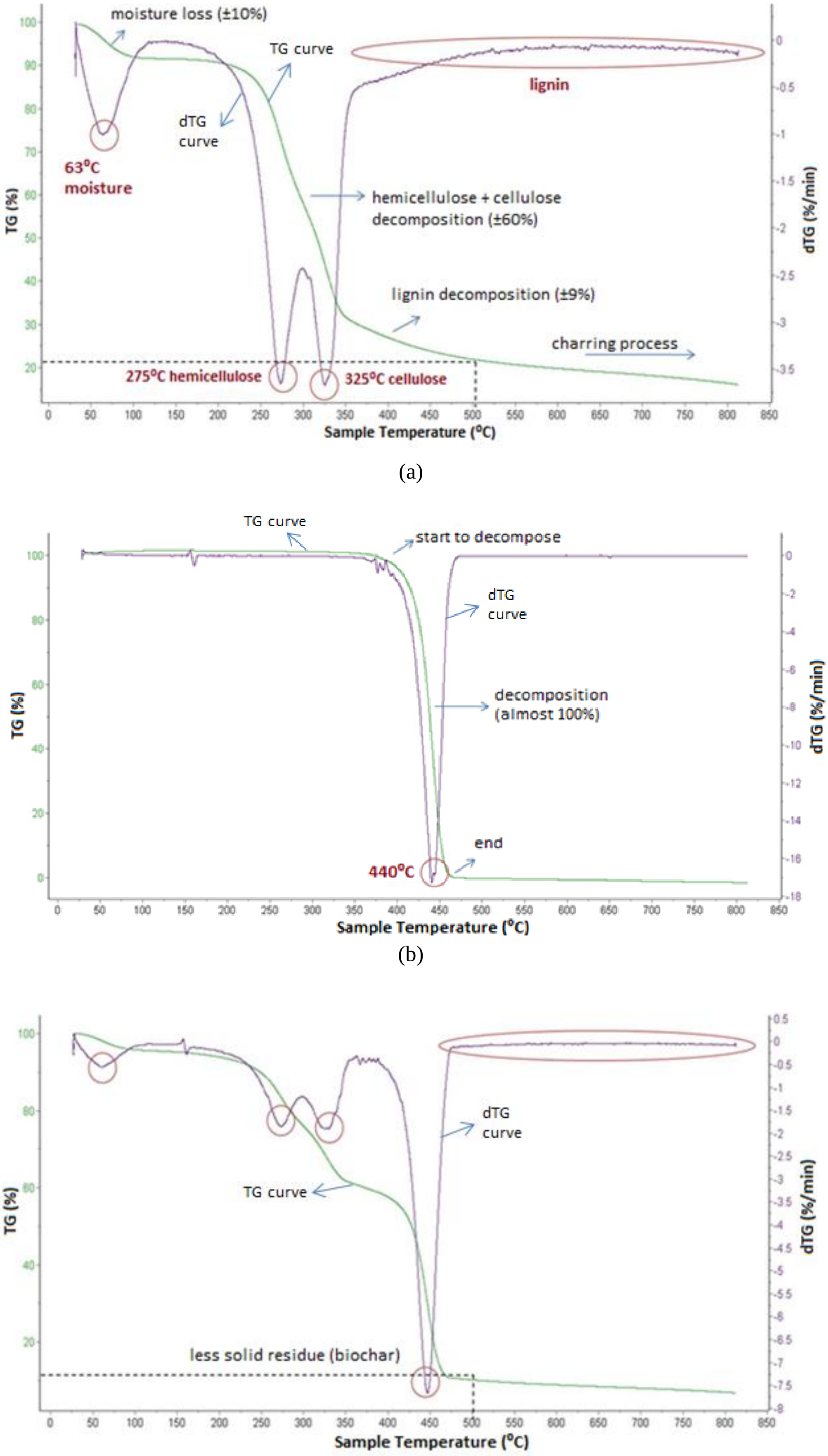
3. RESULTS AND DISCUSSION

3.1. TGA Results

Unlike PP plastics, which experience a sudden release of volatiles or mass reduction at a certain temperature in a narrow range, corn cobs decompose in a wide range of temperatures that are contributed to by the varying decomposition characteristics of their three main constituents: hemicellulose, cellulose, and lignin (Oyedun et al., 2013). According to Collard and Blin (2014), the decomposition of hemicellulose occurs at a temperature range of 200-350^{o}C with the highest mass loss rate occurring around 290^{o}C (for xylan) and 310^{o}C (for glucomannan), while that of cellulose occurs at 300–390^{o}C, with the highest mass loss rate occurring between 330–370^{o}C. Meanwhile, lignin undergoes decomposition and conversion over a wide temperature range from 200–800^{o}C with the highest mass loss rate typically occurring between 360 and 400^{o}C. At temperatures up to 380^{o}C, lignin begins to experience the process of char formation (charring process).

The TGA results exhibited in Figure 3 show that hemicellulose in corn cobs experienced the greatest mass loss rate at a temperature of 275^{o}C, whereas cellulose did so at 325^{o}C. Lignin is a complex macromolecule that is difficult to decompose. It experiences a mass reduction in a wide temperature range up to 800^{o}C, with a very slow mass loss rate of < 0.25% wt/min. Meanwhile, polypropylene starts to decompose at 400^{o}C with a peak mass loss temperature of 440^{o}C, where it experiences the significant loss of almost 100% of its weight (mass loss rate is about 17% wt/min). It can be noted that plastic decomposition occurs at a sufficiently narrower temperature interval than that of corn cob, necessitating a slower heating rate so that the plastic radicals have sufficient time to react with those of corn cobs and avoid secondary cracking, which otherwise produces gas that cannot be condensed. Sufficient time is provided to allow synergistic effects to occur in the co-pyrolysis process, which can increase the bio-oil yield (percentage by weight) as well as its non-oxygenate content.

The blend of PP plastic and corn cob particles in the feedstock can suppress the yield of char due to synergistic effects. Decomposition temperatures, where the highest mass loss rates occur in the feedstock blend pyrolysis, are roughly equal to those of corn cobs alone and PP alone; i.e., hemicellulose at 275^{o}C, cellulose at 325^{o}C, lignin from 380-800^{o}C, and PP plastic at 440^{o}C. However, the magnitudes of the highest mass loss rates of the feedstock blend are lower than those of the pure feedstock at similar temperatures. The highest mass loss rates of the feedstock blend are distributed at more temperature instances than those of the pure feedstock.



(a)

(b)

(c)

Figure 1 (a) TG and DTG curves of corn cobs; (b) polypropylene; and (c) the 1:1 binary mixtures

According to TG analysis, the noticeable weight losses and structural decompositions were shown to occur up to 500^{o}C. Above this temperature, only a small amount of biomass weight losses occurred, mostly due to continuous lignin degradation (Çepelioğullar & Putun, 2014), while the decomposition of PP completed at about 440^{o}C, before that of the corn cobs. Therefore, the final temperature for the batch stirred-tank reactor experiment was set at 500^{o}C.

3.2. Pyrolysis Yields

Figure 2 shows the pyrolysis yields that were calculated in the weight percentage. The result shows that by increasing the PP composition in the feed blend from 0–37.5%, the yield of bio-oil decreased from 39.3–25.8% in weight, but increased from 25.8–67.2% in weight when augmenting the PP in the blend from 37.5–87.5%. These data imply that there were two regions of co-pyrolysis; namely, one at the rich biomass composition in the feedstock (called region 1) and the other at the rich plastic composition in the feedstock (called region 2). The existence of these regions seemed to be governed by competition between heat radiation to biomass and heat convection to plastic.

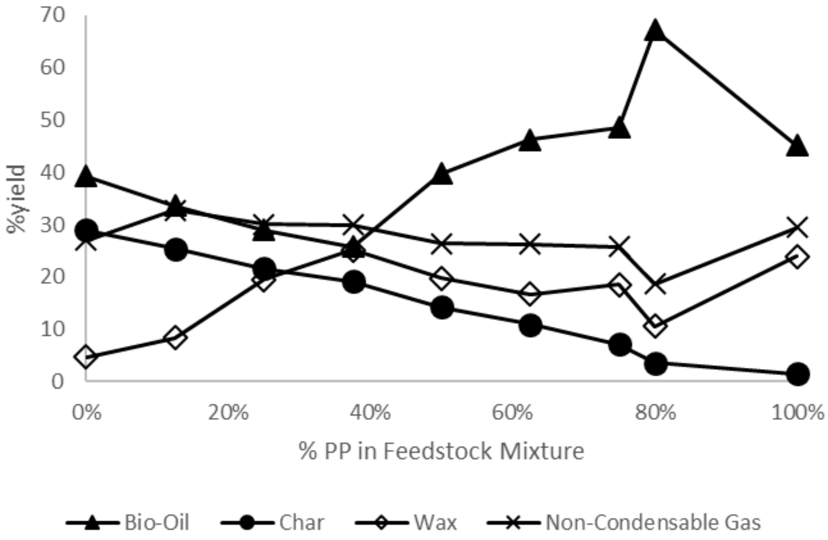


Figure 2 Yields of products of co-pyrolysis

In region 1, the yield of bio-oil reduced with the increasing composition of plastic in the feedstock, while that of the wax was bolstered. In region 2, the yield of bio-oil increased with the rising plastic composition in the feedstock, while that of the wax was downgraded. It seems that in region 1, the radiative heat transfer appeared to control the pyrolysis. In a condition where the feedstock has a high composition in biomass, which has higher emissivity when changing to char as the volatile matter evolves, it could receive a higher amount of heat from the wall of the stirred tank reactor, compared to the plastic melt and bio-oil produced, which was mostly contributed to by the pyrolysis of biomass. Biomass char emissivity can reach 0.8 (Wolfinger et al., 2001). The reduction of bio-oil yield with increasing plastic composition in the feedstock was due to the decreased content of biomass in the feedstock to contribute to it; this also reduced the char yield. A higher wax yield, with increasing composition of plastic in the feedstock, seems to be caused by the predominance of the radiative heat received by biomass particles, so that the plastic melt receives insufficient heat to complete its pyrolysis and evolves partially long carbon-chains of plastic molecules constituting wax. An insufficient pyrolysis of plastic melt seems to cause no synergetic effect, due to the supposedly high viscosity of plastic melt (Fernandez et al., 2015), as indicated by the reduced bio-oil yield with increasing plastic composition in the feedstock.

In region 2, with more plastic content in the feedstock and, consequently, lower biomass content, it appears that the plastic melt received more convective heat compared to the radiative heat received by biomass particles. With increasing plastic composition in the feedstock, more and more convective heat was received by the plastic melt and, in effect, the wax yield was exponentially reduced. The reduction of char yield with increasing plastic composition in the feedstock seems to correspond to the reduction of biomass content therein, in addition to the synergetic effect provided by sufficient hydrogen donation as generated from the pyrolysis of large amounts of plastic melt in this region. The use of nitrogen to generate bubbles in the plastic melt appears to be effective in reducing the bulk viscosity of the plastic melt, easing the convective heat transfer (Chen et al., 2006). Additionally, the use of a stirrer, which increases the shearing of the plastic melt on the reactor wall, apparently contributes to the augmentation of the convective heat transfer (Vlachopoulos & Strutt, 2002).

3.3. Bio-oil Characterization

GC-MS characterization shows that the composition of pyrolyzed bio-oil, as produced by pure waste PP plastic, was dominated by hydrocarbons as non-oxygenated compounds (82.32%), including alkanes, alkenes, cycloalkanes, cycloalkenes, and aromatics (see Figures 3 and 4). Oxygenated compounds were detected because the waste PP plastic contained oxygen atoms, as shown in the ultimate analysis result, to as much as 0.02% (see Table 1). Alkanes with carbon chain lengths of gasoline (C_7-C_{11}) and diesel chain (C_{12}-C_{16}) were found in the composition. The four compounds with the highest area percentage in descending order, as identified by GCMS, were 2,4-dimethyl-1-heptane (12.09%), methyl cyclopentane (7.74%), pentane (3.85%), and 4-methyl-heptane (3.24%).

In contrast, GC-MS characterization of bio-oil originating from pure biomass pyrolysis shows that that produced from pure corn cobs was dominated by oxygenated compounds, such as carboxylic acids, alcohols, ketones, and aldehydes (total 86%) (see Figures 3 and 4). The four compounds with the highest area percentage in descending order were identified as acetic acid (32.53%), acetol (11.89%), furfural (6.14%), and furfuryl alcohol (5.85%). Acetic acid, acetol, furfural, and furfuryl alcohol are compounds derived from cellulose and hemicellulose decomposition, while phenol is a compound derived from lignin decomposition (Collard & Blin, 2014).

In all bio-oil samples in region 2, approximately 65% of the compounds in the bio-oil could not be identified by GCMS as their confidence levels of compound detection were low (< 70%). These compounds were therefore categorized as other non-oxygenates and oxygenates. In region 2, alkenes were seen to be greater in their composition than alkanes, demonstrating that the hydrogenation process needs to be added to the co-pyrolysis procedure to ensure that the biofuel has a low alkene content.

In region 2, the total non-oxygenate compounds varied between 70% and 80% of the total feedstock weight (see Figure 4). It appears that at the lowest plastic composition in this region, i.e. 50%, the evolution of non-oxygenate compounds was mostly caused by the synergetic effect between free radicals of biomass and those of plastic. As the composition of plastic increased in the feedstock, the evolution of non-oxygenates was more greatly instigated by the pyrolysis of plastic itself, whose feedstock contained a large composition of non-oxygenates (Abnisa & Wan Daud, 2014). This pyrolysis was supposedly materialized favorably, due to the high convective heat transfer in the plastic melt in this region. This suggestion is based on the condition that a high non-oxygenate content can be achieved when the biomass particles are capable of conducting the mass transfer of their volatile matter to the surrounding plastic melt when the latter's viscosity is sufficiently low (Fernandez et al., 2015). High convective heat transfer to plastic melt enables the reduction of viscosity (Rosato et al., 2000).

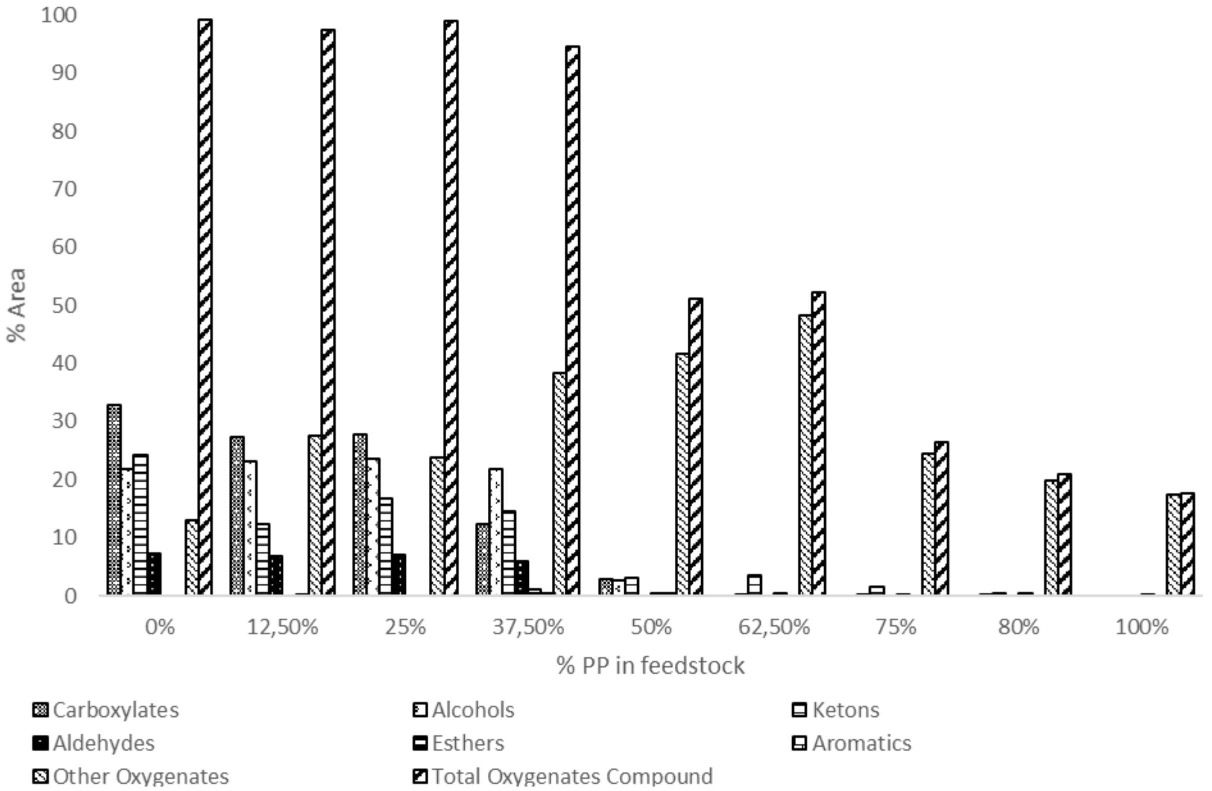


Figure 3 Compositions of oxygenated compounds in bio-oil as PP plastic composition in feedstock is varied

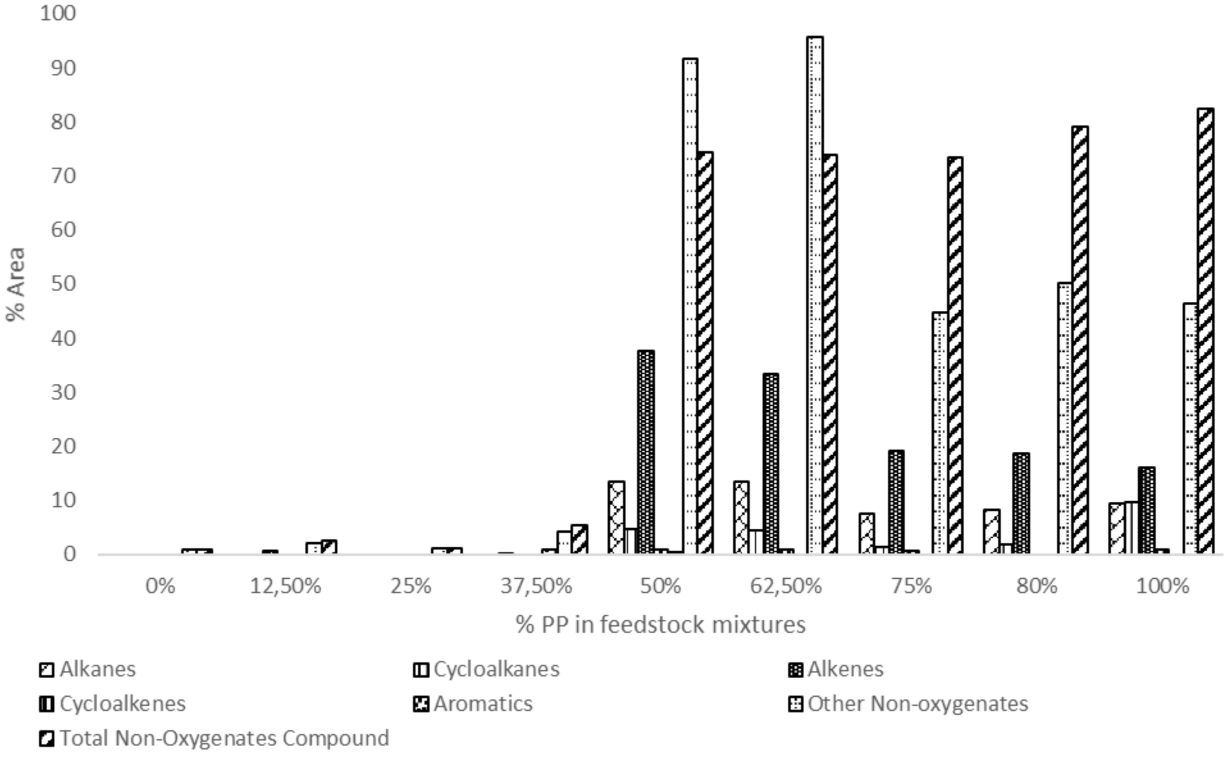


Figure 4 Compositions of non-oxygenated compounds in bio-oil as PP plastic composition in feedstock is varied

An abrupt change of non-oxygenate content from the co-pyrolysis using feedstock with 37.5% weight of PP, to that with 50% weight, appeared to be related to a transition from non-synergy to synergy conditions (see Figures 3 and 4). Recalling the analysis in Section 3.2, in region 1 near this transition, the radiative heat transfer was predominant to convective heat transfer, while in region 2, in contrast, the latter began to surpass the former. From a rheological perspective, this transition can be observed in the phenomena of swelling and contraction of the biomass particles. According to Fei et al. (2012), whose investigation on co-pyrolysis used lignite as the hydrogen donor and bituminous coal as the hydrogen receptor, the synergy is indicated by the release of pyrolyzed compounds from the lignite particles and can be adsorbed by bituminous coal particles. Consequently, the lignite particles contract after releasing their volatile matters. Comparing the present co-pyrolysis to the experiment of Fei et al. (2012), the synergy between biomass particles and the PP plastic melt would materialize if the plastic melt constitutes a favorable environment for receiving the compound fragments of the biomass pyrolysis. According to Fernandez et al. (2015), in the case of mass transfer of gas to liquid, such a transfer is restricted by an apparently higher surrounding liquid viscosity. Therefore, synergy between the biomass particles and plastic melt in co-pyrolysis is more likely to occur if the apparent viscosity of the latter is low. It is plausible that in region 1, in which the heat transfer was dominated by radiation to the biomass particles, the temperature of the plastic melt was not sufficiently high to reduce its viscosity. Therefore, the volatile matter in the cellulose and hemicellulose of the biomass particles was not released to the surrounding plastic melt, but to its surface when the particles moved there during the stirring. It is also plausible that by increasing the plastic content in the feedstock in region 1, this movement became less frequent and, consequently, the bio-oil yield was reduced. Meanwhile, when the composition of the co-pyrolysis feedstock was in region 2, in which the plastic melt received sufficient convective heat transfer, the apparent viscosity of the melt was low enough (Rosato et al., 2000) to receive the release of the volatile matter in the cellulose and hemicellulose of the biomass particles. Due to the high contact area between the biomass particles and plastic melt in this region, the synergy between the two found no resistance and, consequently, non-oxygenated compounds were produced in great amounts (Fei et al., 2012).

4. CONCLUSION

In this study, the use of a stirred-tank reactor in the co-pyrolysis of corn cob and waste polypropylene (PP) particles assisted by the flow of nitrogen produced bio-oil, wax, char, and non-condensable gas. From the results of the co-pyrolysis, it can be concluded that there were two regions of co-pyrolysis as the composition of PP plastic in the feedstock varied from 0–100%: region 1, in which the bio-oil yield reduced and wax yield increased as the plastic composition rose from 0–37.5%; and region 2, in which the bio-oil yield increased and wax yield reduced as the plastic composition in the feedstock was augmented from 37.5–87.5%. It is presumed that in region 1, the radiative heat transfer to biomass particles was predominant, while in region 2, the convective heat transfer to plastic melt began to outweigh the radiative heat transfer. There was a sharp rise in the non-oxygenated compound composition in the bio-oil from less than 5% in region 1 to more than 70% in region 2; this shows us that the synergetic effect works, as the plastic composition in the feedstock increased from 37.5–87.5%.

5. REFERENCES

Abnisa, F., Wan Daud, W.M.A., 2014. A Review on Co-Pyrolysis of Biomass: An Optional Technique to Obtain a High-Grade Pyrolysis Oil. *Energy Conversion and Management*, Volume 87, pp. 71–85

Brebu, M., Ucar, S., Vasile, C., Yanik, J., 2010. Co-Pyrolysis of Pine Cone with Synthetic Polymers. *Fuel*, Volume 89(8), pp. 1911–1918

Bridgwater, T., 2012. Upgrading Biomass Fast Pyrolysis Liquids. *Environmental Progress and Sustainable Energy*, Volume 31(2), pp. 261–268

Çepelioğullar, Ö., Pütün, A.E., 2014. Thermal and Kinetic Behaviors of Biomass and Plastic Wastes in Co-Pyrolysis. *Energy Conversion and Management*, Volume 75, pp. 263–270

Chen, X., Feng, J.J., Bertelo, C.A., 2006. Plasticization Effects on Bubble Growth during Polymer Foaming. *Polymer Engineering Science*, Volume 46(1), pp. 97–107

Clark, T.T., Lathrop, E.C., 1953. *Corn Cobs: Their Composition, Availability, Agricultural and Industrial Uses*. USDA-ARS North Regional Research Laboratory, Peoria, IL. AIC-177, 17

Collard, F.-X., Blin, J., 2014. A Review on Pyrolysis of Biomass Constituents: Mechanisms and Composition of the Products Obtained from the Conversion of Cellulose, Hemicelluloses and Lignin. *Renewable and Sustainable Energy Reviews*, Volume 38, pp. 594–608

Dynamotive Energy Systems Corporation, 1999. BioTherm™ - A System for Continuous Quality, Fast Pyrolysis Biooil. *In* Fourth Biomass Conference of the Americas.

Fei, J., Zhang, J., Wang, F., Wang, J., 2012. Synergistic Effects on Co-pyrolysis of Lignite and High-sulfur Swelling Coal. *Journal of Analytical and Applied Pyrolysis*, Volume 95, pp. 61–67

Fernandez, Y.B., Cartmell, E., Soares, A., McAdam, E., Vale, P., Darche-Dugaret, C., Jefferson, B., 2015. Gas to Liquid Mass Transfer in Rheologically Complex Fluids. *Chemical Engineering Journal*, Volume 273, pp. 656–667

Foley, K., 1978. *Physical Properties, Chemical Properties and Uses of the Anderson's Corncob Products*. The Andersons, Maumee, OH

Frasson, S., 2014. Thermal Degradation of Polyethylene in a Tubular Reactor for the Production of Valuable Oils. *Master Thesis*, Environmental Engineering, University of Padua, p. 60

Gao, F., 2010. Pyrolysis of Waste Plastics into Fuels. *Doctorate Thesis*, University of Canterbury Research Repository, p. 17, 19

Indonesian Commercial Newsletter, March 2010. *Development of Polypropylene (PP) Resin Industry in Indonesia*. Available online at http://www.datacon.co.id/Plastic-2010PP.html

Jahirul, M.I., Rasul, M.G., Chowdhury, A.A., Aswath, N., 2012. Biofuels Production through Biomass Pyrolysis: A Technological Review. *Energies*, Volume 5(2), pp. 4952–5001

Kato, Y., Enamoto, R., Akazawa, M., Kojima, Y., 2016. Characterization of Japanese Cedar Bio-Oil Produced Using a Bench-Scale Auger Pyrolyzer. *Springer Plus*, Volume 5, p. 177

Lu, Q., Li, W.-Z., Zhu, X.-F., 2009. Overview of Fuel Properties of Biomass Fast Pyrolysis Oils. *Energy Conversion and Management*, Volume 50(5), pp. 1376–1383

Martinez, J.D., Veses, A., Mastral, A.M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartrolí, J., García, T., 2014. Copyrolysis of Biomass with Waste Tyres: Upgrading of Liquid Bio-Fuel. *Fuel Process Technology*, Volume 119, pp. 263–271

Ministry of Agriculture Indonesia, 2016. *Produksi, Luas Panen dan Produktivitas Palawija di Indonesia, 2011-2015*. Available online at http://www.pertanian.go.id/Data5tahun/ATAP-TP2015/01-PalawijaNasional.pdf

Ministry of Energy and Mineral Resources Indonesia, Directorate General of Oil and Gas, 2016. *Consumption/ Sales of Fuels*. Available online at http://statistik.migas.esdm.go.id/index.php?r=konsumsiBbm/index

Oyedun, A.O., Gebreegziabher, T., Hui, C.W., 2013. Co-Pyrolysis of Biomass and Plastic Waste: A Modelling Approach. *Chemical Engineering Transactions*, Volume 35, pp. 883–888

Paraschiv, M., Kuncser, R., Tazerout, M., 2009. Quantitative and Qualitative Analysis of Plastic Waste Pyrolysis Product. *In:* Proceedings of the 11th International Conference on Environmental Science and Technology, Crete, Greece, 3–5 September

Rosato, D.V., Rosato, D.V., Rosato, M.G., 2000. Injection Molding Handbook, Springer Science & Business Media

Vlachopoulos, J., Strutt, D., 2002. Basic Heat Transfer and Some Applications in Polymer Engineering. *Plastics Technician's Toolbox*, Volume 2, pp. 21–33

Wannapeera, J., Worasuwannarak, N., Pipatmanomai, S., 2008. Product Yields and Characteristics of Rice Husk, Rice Straw and Corncob during Fast Pyrolysis in a Drop-Tube/Fixed-Bed Reactor. *Songklanakarin Journal of Science and Technology*, Volume 30(3), pp. 393-404

Wolfinger, M.G., Rath, J., Krammer, G., Barontini, F., Cozzani, V., 2001. Influence of the Emissivity of the Sample on Differential Scanning Calorimetry Measurements. *Thermochimica Acta*, Volume 372(1-2), pp. 11–18

Yang, W., Ponzio, A., Lucas, C., Blasiak, W., 2006. Performance Analysis of a Fixed-Bed Biomass Gasifier using High-Temperature Air. *Fuel Processing Technology*, Volume 87(3), pp. 235–245

Zynch, D., 2008. *The Viability of Corn Cobs as a Bioenergy Feedstock*. Summer Internship in Renewable Energy at the West Central Research and Outreach Center, University of Minnesota