Effect of feed composition of co-pyrolysis of corncobs–polypropylene plastic on mass interaction between biomass particles and plastics

D Supramono¹, M A Nabil¹, Setiadi¹ and M Nasikin¹
¹Department of Chemical Engineering, Universitas Indonesia, Kampus Baru UI Depok 16424, Indonesia

Email: setiadi@che.ui.ac.id

Abstract. Polypropylene plastic (PP), which has higher hydrogen content compared to that in biomass, is potential to be used as a cheap hydrogen source for pyrolysis of biomass, such as corncobs, to remove part of oxygen content in the biomass pyrolysis oil. By charging these two materials, synergistic effects will appear that improve quality and quantity of bio-oil produced. The aim of the present work is to investigate possible mass interaction between biomass and plastic materials leading to the synergistic effects using slow co-pyrolysis. The experiment was performed in a displacement reactor. Feed composition was varied at 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, and 87.5% weight of PP. This phenomenon was observed through expansion-contraction of the reactor prior to large mass decomposition of the reactor feed. In experiment involving biomass-dominated feeds, i.e. PP contents < 50% (regime 1), there was reactor bed contraction due to slight biomass decomposition followed by no-displacement of reactor piston. During the contraction, it is estimated, there was low velocity ejection of biomass volatile matter, while during no-displacement stage, there was a phase change of plastic granules to plastic melt. In experiment with plastic-dominated feeds, i.e. PP ≥ 50% (regime 2), the reactor bed underwent contraction due to phase change of plastic granules which reduced the bed volume, followed by bed expansion due to the swelling of biomass particles estimated in the presence of hydrogen bonding in the phenolic environment in biomass material. The last stage of co-pyrolysis in regime 2 was the bed contraction and it is predicted that there was high velocity gas ejection through the small pores which intensified interaction of biomass-plastic radicals in hydrogen-rich environment favourable for exerting synergistic effect.

1. Introduction
Energy is an important supporting aspect of human life. In fact, widely-used fossil fuels are derived from non-renewable energy sources, and this disadvantage encourages various research and development efforts of finding alternative energy sources. One way of these efforts is by conducting co-pyrolysis of biomass and plastics especially those with high hydrogen content, such as polypropylene (PP). The addition of plastics to the co-pyrolysis at sufficient amount will decrease the oxygenated compounds in the bio-oil product and improve the bio-oil yield [1]. The quality improvement of bio-oil is induced by hydrogen donation from free radicals of plastic pyrolysis to those of biomass to remove oxygen from pyrolysis volatile matter and form more non-oxygenate compounds in bio-oil [2]. The quantity improvement of bio-oil occurs as a result of bonding of small radicals into larger molecules which increases bio-oil yield [1]. Synergistic effect occurs if the yield of bio-oil or non-polar phase of bio-oil as a result of oxygen removal produced by co-pyrolysis of 2
materials is higher than that obtained by summing yields of pyrolysis of pure materials. Therefore, synergistic effect improves both quantity and quality of bio-oil.

There are 2 different feeds which affect yields of bio-oil and non-polar phase, i.e. biomass-dominated feeds (regime 1) where the PP plastic provides no sufficient hydrogen to remove any oxygen radicals from bio-oil and plastic-dominated feeds (regime 2) where PP plastic provides enough hydrogen to remove part of oxygen radicals of biomass pyrolysis. In regime 1 no synergistic effects have been observed both on bio-oil and non-polar phase yields in co-pyrolysis, while in regime 2 they occur [3]. It is suspected that there is mass interaction between biomass and plastic materials which governs the bio-oil and non-polar phase yields. However, there has been no research in co-pyrolysis of biomass-plastic investigating what possible mass interaction occurs affecting the yields. It seems that Fei et al (2012) investigated for the first time relationship between swelling-shrinking phenomena of bituminous coal and synergistic effect in co-pyrolysis of lignite and bituminous coal [4]. They observed combined effect of swelling of bituminous coal particles and calcium content in lignite particles. They explained that the swelling assists coal fluidity and improves contact area between lignite and coal particles, while calcium could provide catalytic effect on tar yield of bituminous coal so that the bituminous coal particles shrink. Therefore, calcium in lignite particles are favourable for synergistic effect on bio-oil yield. This synergistic effect mechanism may have been different for the case of co-pyrolysis of biomass-plastic in the present work. Biomass may undergo swelling due to the presence of hydrogen bonding [5]. This physical character of biomass particles may influence synergistic effects on bio-oil and non-polar phase yields in co-pyrolysis of biomass-plastic.

The aim of the present work is to investigate possible mass interaction between biomass and plastic materials leading to the synergistic effects. The experiment was carried out in a displacement reactor to perform slow co-pyrolysis. To investigate the swelling-shrinking of biomass particles in the environment of plastic melt attributed to the mass interaction, the present work has used in a small tubular reactor of 24mm diameter and 60mm height filled with a feed blend of corn cob particles and PP plastic granules to simulate the swelling-shrinking of biomass particles leading to synergistic effects in a stirred tank reactor for larger yield of bio-oil. The independent variable used is feed compositions of corn cob and polypropylene plastic in the feed. The swelling-shrinking of the biomass particles was investigated in relationship with the synergistic effects.

2. Experimental

Figure 1 shows schematic design of the displacement reactor. The movement of the piston reactor was observed to measure the expansion-contraction of the reactor piston at the top of the reactor using a ruler in which swelling-shrinking of biomass feed may have occurred in the reactor. The cylindrical reactor and its piston are made of stainless steel (SS 316). When the piston was placed into the reactor, there was a very narrow gap between the rim of the piston and the inner wall of the reactor to allow the release of volatile matter and the free up and down movement of the piston when the biomass particles swelled and shrank. On the side of the reactor, there is a ruler to measure the displacement during co-pyrolysis.

The reactor feed composition was varied at 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, and 87.5% weight of PP and the feeds were charged into a displacement reactor at different batches. In each batch, the co-pyrolysis process was carried out at a slow heating rate (slow co-pyrolysis) of 5°C/min from room temperature to temperature just before the mass decomposition occurred estimated by TGA curves [6]. When the co-pyrolysis process took place, the magnitude of reactor piston displacement was measured every 1 minute. The initial total feed weight and final temperature of heating for each composition are given in Table 1.

To investigate possible relationship between the swelling-contraction of the biomass particles and synergistic effect, SEM image of char surface of each co-pyrolysis regime has been taken and compared to that taken from pyrolysis of pure biomass particles. All batches were conducted prior to large mass decomposition of the co-pyrolysis to observe how synergistic effects were prepared.
Tab
le 1. Initial total feed weight and final temperature of heating

| Composition (Corncob : PP Plastic) | Total Feed Weight (gr) | Final Temperature of Heating (°C) |
|-----------------------------------|------------------------|----------------------------------|
| 87.5%:12.5%                       | 12.00                  | 215                              |
| 75%:25%                           | 12.00                  | 220                              |
| 62.5%:37.5%                       | 12.00                  | 225                              |
| 50%:50%                           | 10.83                  | 300                              |
| 37.5%:62.5%                       | 8.96                   | 310                              |
| 25%:75%                           | 8.05                   | 315                              |
| 12.5%:87.5%                       | 7.44                   | 320                              |

Figure 1. Schematic displacement reactor

Figure 2. Biomass temperature vs % displacement in regime 1

3. Result and discussion

For biomass-rich co-pyrolysis feeds (regime 1), i.e. those with PP < 50% weight, the piston displacements during co-pyrolysis are shown in figure 2. The figure shows negative displacements (contraction) in the reactor followed by no displacement. These indicate that there was only shrinking of biomass particles. It was observed that during the contraction, the release of vapour was seen from the reactor. Figure 2 shows that the contraction ends at maximum temperature of 125°C. The measurement of melting point of PP granular in the present work shows that it started at 130°C. Therefore, contraction of all samples occurred before the melting of PP granules occurred and the heating of biomass particles were still in gas environment. In such a condition, heat radiation was predominant during biomass particle shrinkage and the feed with higher biomass composition received higher heat flux of radiation from the reactor wall. Consequently, the feed with higher biomass composition or lower PP content started shrinking at lower surrounding temperature as shown in figure 2 due to the less required temperature driving force. The contraction occurred mostly due to the decomposition of cellulose and hemicellulose to form vapour phase starting at low temperature [7]. All the contraction curves end before the plastic melted.

During the contraction stage, where the heat radiation was predominant, the heat sensed by the biomass material depended on the depth of heat penetration. Because the density of biomass is low, the radiative heat can penetrate into the inner part of the biomass [8]. Therefore, cellulose and hemicellulose, which were more susceptible to crack by heating than lignin [9], decomposed into smaller molecules, while lignin may have been still intact because delignification could occur in the presence of small molecule carboxylic acid such as acetic acid and formic acid as pyrolysis products of hemicellulose starting at 200°C [10]. To support the explanation of the above displacement mechanism, it is necessary to observe the surface morphology of the biomass particles by taking a char morphology image through a Scanning Electrone Microscope (SEM) test on the char. As representation of regime 1, the char tested was of co-pyrolysis using 25% PP feed. In addition, for
comparison, char morphology by SEM originating from pyrolysis of pure biomass particle surfaces was also observed. These two char samples were taken from pyrolysis runs at temperatures prior to large mass decomposition according to the TGA curves measured by Miranda (2017) [6], which temperature data are presented in Table 1. Pure biomass char of pyrolysis results was taken from a pyrolysis run ending at 205°C, while char derived from 25% PP feed co-pyrolysis was taken from a pyrolysis run ending at 220°C. SEM images of both char samples are shown in figures 3a and 3b. SEM images show that the morphology of both char samples are similar wherein they exhibit sufficiently large char pores allowing vapor phase of pyrolysis to come out easily. The dark parts of the SEM images show the pore locations, while the light parts the char surface. It is expected that vapour phase ejection from large-sized pores occurred at low velocities.

Figure 3. SEM images of char (a) from pure biomass pyrolysis, (b) from co-pyrolysis with 25% PP feed (regime 1), (c) from co-pyrolysis with 75% PP feed (regime 2)

As the contraction curves end, PP granules were expected to melt because they end about the melting point of PP. Figure 2 shows no displacement stage after contraction stage describing the phase change of PP granules from solid to melt. During no displacement stage, it is expected that the heat radiation from the reactor wall to biomass material was obstructed by plastic melt surrounding the biomass material. As a consequence, the production of volatile matter from biomass decomposition was considered to be non-appreciable to the contraction of the reactor.

Figure 4 describes contraction-expansion of the displacement reactor. Contraction stage may have started from the melting point of plastic considering that there was temperature difference between surrounding gas temperature and plastic melt temperature. Exception occurred for the feed containing 50%PP which started at a temperature less than PP melting temperature because part of biomass material was not obstructed against heat radiation by PP granules. The difference in temperature ranges of the contraction stage between regimes 1 and 2 because of the difference in heat transfer mechanism. In regime 1 where the feed was rich in biomass, radiative heat transfer predominated due to its high emissivity [11], whereas in regime 2 where the feed was rich in plastic mass, the heat flux from the reactor wall to biomass was obstructed by plastic granules and heat passed through plastic melt before reaching the biomass particles. Large contraction in regime 2 may have been caused by melting of PP from PP solid granules which reduced the bed porosity inside the reactor thus contracting the feed bed volume. In this case, decomposition of biomass may have been too small to contribute to the contraction of the reactor.

Co-pyrolysis with feed comprising 50%PP is a transition one between regime 1 and regime 2. The biomass particles were partly surrounded by PP granules against heat radiation from the reactor wall. However, because mass decomposition occurred at temperatures larger than those at regime 1, the bed contraction partly contributed by biomass mass decomposition was larger than that in regime 1. The remaining contraction was contributed by phase change of PP granules to molten phases.

The contraction stage reached a point thereafter the reactor underwent expansion stage. This stage may have occurred due to the swelling of biomass induced by the presence of hydrogen bonding [12] between cellulose and lignin and between cellulose and hemicellulose [13]. Phenolic compounds as monomers produced by the first stage of lignin thermal cracking [14] contribute to strong hydrogen
bonding [5]. In terms of physical structure, lignin is located in the outer cell of biomass, cellulose is located within lignin shell and hemicellulose with amorphous structure is located within the cellulose and between cellulose and lignin [15]. This structure allows the conductive heat from plastic melt to transport heat flux in the first instance into lignin, which decomposes into phenolic compounds.

The swelling resulting from the presence of phenols inhibited the evolution of volatile matter to the surrounding plastic melt. As a consequence, with time and increased temperature, more and more cellulose and hemicellulose decompose until at a temperature that the swelling biomass could not resist the ejection of the volatile matter. When the pressure inside the biomass particle was high, the vapour would be pushed out of the swelling biomass at high velocity. The discharge of this vapour in figure 4 is illustrated by declining curves marking the second contraction.

![Figure 4. Temperature vs % displacement in regime 2](image)

To support the explanation of the presence of high velocity in regime 2, char sampled from co-pyrolysis in a stirred tank reactor involving PP 75% feed was taken and observed by SEM to image the char surface morphology. The char was taken at a temperature before the large mass decomposition based the TGA curve [6], i.e. before reaching 315°C. This high velocity ejection is indicated by the existence of small pores on the char surface (see figure 3c), which are smaller than the pores found in regime 1 (see figure 3b). This high velocity vapour phase then penetrated strongly inside the plastic melt surrounding the biomass particles. In other words, there is a strong and intensive interaction between the vapour phase of biomass pyrolysis and the plastic melt. As far as fluid dynamic point of view, this ejection would generate interface between turbulent side generated by the ejection and the laminar side exerted by plastic melt which entrains plastic melt and mixes with biomass volatile matter [16]. This entrainment through the turbulent-laminar interface enhances reactions between biomass and plastic radicals during large mass decomposition of co-pyrolysis [17]. Therefore, high velocity ejection in regime 2 where the feed blend is rich in hydrogen allows hydrogen transfer to generate synergistic effects in the co-pyrolysis of biomass-plastic [1].

4. Conclusions

The present work on co-pyrolysis of corn cob-PP plastic prior large mass decomposition has resulted in some conclusions. For reactor biomass dominated feeds, i.e. those with PP <50% (regime 1), co-pyrolysis feed bed undergoes contraction due to slight biomass decomposition prior to plastic melting, followed by no-displacement stage. For reactor plastic-dominated feeds, i.e. those with PP ≥ 50% (regime 2), co-pyrolysis bed undergoes contraction due to phase change of plastic granules to plastic melt, followed by bed expansion estimated due to the presence of hydrogen bonding in the phenolic environment in biomass material. The last stage of co-pyrolysis bed in regime 2 is the reactor bed contraction attributed to the existence of small pores on biomass sample surface and it is predicted that there is high velocity gas ejection through the small pores which intensifies interaction of biomass-plastic radicals in hydrogen-rich environment favourable for synergistic effect.
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