Co-pyrolysis of crude palm oil and polypropylene in a stirred tank reactor to produce non-oxygenated bio-oil

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Abstract. Catalytic co-pyrolysis of crude palm oil (CPO) and polypropylene (PP) has been carried out in a stirred tank reactor to produce bio-oil at heating rate of 10 °C/min and maximum pyrolysis temperature of 550 °C with a nitrogen gas flow rate of 100 mL/min. Catalyst of ZrO₂/α-Al₂O₃-TiO₂ was used and prepared through calcination at heating rate of 7 °C/min with the maximum temperature of 1150 °C. Catalyst as much as 15% of the total feed was used. Composition of CPO and PP was varied and it was found that the feed containing 50%PP achieved the highest yield of bio-oil in which the bio-oil contains 81% volume of hydrocarbons based on GCMS spectroscopy measurement. Using pyrolysis feed containing 50% PP, compared to non-catalytic co-pyrolysis, catalytic co-pyrolysis produces nearly twice yield of bio-oil. The H-NMR and C-NMR analysis shows that bio-oil contains mostly chemical bonds of alkyl, followed by carbonyl constituting ketones and carboxylic acids and vinyl. H-NMR analysis of bio-oil and FTIR analysis of wax indicate that the catalyst is more effective in PP pyrolysis rather than CPO deoxygenation reactions to hydrocarbons with unreacted products of the deoxygenation forming wax via ketonic decarboxylation. Steric hindrance by the use of microporous catalyst may cause such incomplete deoxygenation reactions.

1. Introduction

Energy is one of the most important supporting aspects of human life. At present, petroleum is still very dominant in use, reaching 39% of Indonesia's total primary energy consumption [1]. In fact, fossil fuels are non-renewable sources of energy, and this then encourages many research and development efforts in alternative energy sources. Palm oil is still rich in oxygenate content. Therefore, the use of plastic in co-pyrolysis as a hydrogen source may reduce oxygen content in the bio-oil so that biofuel characteristics can be obtained which are almost similar to those of fossil fuels.

Hydrotreating of vegetable oils using hydrogen gas allows the formation of alkanes through decarboxylation, decarbonylation, and hydrodeoxygenation of carboxylic acids [2]. Some mechanisms have been proposed by researchers that may lead to triglyceride cleavage (CPO breakdown) including direct deoxygenation, γ-hydrogen transfer and hydrolysis [3] [4] [5]. The addition of PP plastic as a hydrogen source to the hydrotreating of triglycerides is expected to produce bio-oil which has low oxygenate content and high heating values. According to Gürbüz et al [6], the addition of plastic has an effect on increasing alkanes and alkenes in the bio-oil produced. The present work aims to obtain bio-oil with high content of non-oxygenated compounds by catalytic co-pyrolysis of CPO and PP plastic observed at different feed compositions within the range of PP content from 50 to 90%. The bio-oil is
analysed using H-NMR and C-NMR, which are rarely used for bio-oil analysis, in addition to FTIR and GC-MS, which are widely used. By the use of NMR analysis, the potential of oxygenated chemical bonds to be converted into non-oxygenated chemical bonds in further research can be estimated.

According to Ooi et al [7] mesoporous Al₂O₃-TiO₂ catalysts with 80% weight composition of Al have a capability to convert triglycerides into hydrocarbons facilitated by their Lewis acid. Medium Lewis acid strength and less coordination of monoclinic ZrO₂ improve adsorption strength carboxylic acids into ZrO₂ structure [8]. The lower the adsorption strength contributes to higher ketonisation of carboxylic acids. The oxygen vacancies in ZrO₂ activate adsorption of acid carbonyl [9]. Catalytic cracking of triglycerides of various carbon chains is not affected by steric hindrance [10]. However, the incorporation of PP plastic requires a catalyst with large surface area and high pore size due to the plastic high molecular weight and high branching [11] Therefore, in the present research catalytic co-pyrolysis of CPO and PP was carried out using high porous ZrO₂/α-Al₂O₃-TiO₂ catalyst.

2. Experimental

2.1 Catalyst Preparation
Mix ZrO₂, α-Al₂O₃, and TiO₂ in a beaker glass. Add NaCl and NaHCO₃ used as a pore-forming agent and ethylene glycol used as a binder to the mixture above. Add 100 g of distilled water to the mixture, then stir the mixture using a stirrer for 10 min. Take the precipitate from the solution using a membrane. Dry the catalyst at 120 °C for 12 h in the oven. Cool to room temperature, then carry out calcination at 500 °C in a muffle furnace for 1 h to remove low temperature pore-forming and reheat to 1150 and 1300 °C then keep at these temperatures respectively for 2 h. Cool the ZrO₂/α-Al₂O₃-TiO₂ catalyst mixture to maintain the stability of the catalyst.

2.2 Catalytic Co-Pyrolysis Experimental
Feedstocks of co-pyrolysis, i.e. CPO liquid and PP granules, that have passed the pre-treatment stage, with total weight of 200 g and catalyst of 30 g weight were put together in a reactor. The feed blend was varied at 50%PP without catalyst (non-catalytic co-pyrolysis), 0, 50, 60, 75 and 90%PP all with catalyst (catalytic co-pyrolysis). The co-pyrolysis process was carried out in a stirred tank reactor with nitrogen gas as a carrier gas at flow rate of 100 mL/min. The mixture was stirred at a revolving speed of 80 rev/min with pyrolysis heating rate of 10°C/min. The mixture was held for 10 min at temperature 550 °C. In this process two bulb condensers in series were used to condense vapour from the reactor. Cooling was done by using cold water as a cooling fluid which was in counter-current flow to maximize the heat transfer. The bio-oil collected in an Erlenmeyer flask can be regarded as biofuel produced by co-pyrolysis of triglycerides and PP plastic. Non-condensable gas came out of the hose and was allowed to go outside. While the wax and tar settled in the condenser. After the pyrolysis process completion, the produced bio-fuel was taken and analysed.

3. Results and Discussion

3.1 Characterization of ZrO₂/α-Al₂O₃-TiO₂ Catalyst
Table 1 shows the comparison of surface area, pore size and pore volume of ZrO₂/α-Al₂O₃-TiO₂ catalyst in various conditions. It can be seen that the pores were of microporous size with the size less than 2 nm. The catalyst sample prepared with maximum heating temperature of 1150 °C and heating rate of 7 °C had the largest surface area, pore size and pore volume compared to those of other samples. Catalyst surface area affects the activity of the catalyst. Sun et al [12] suggested that higher surface area of catalyst boosts the activity of catalysts Such microporosity may be disadvantageous to the deoxygenation of CPO as indicated by Ooi et al [7].

The diffractogram in Figure 1 shows there are the monoclinic and tetragonal structure crystals of ZrO₂, whereas the peaks of α-Al₂O₃ or TiO₂ are not visible due to their small contents and their small particle diameters to be detected by XRD technique [13]. Foraita et al [9] found that adsorption of carboxylic acid group on an oxygen vacancy of ZrO₂ and the abstraction of alpha-hydrogen atom with
elimination of oxygen atom to produce an olefin is the governing mechanism to the kinetics of conversion of carboxylic acids to olefins. They also found that high concentration of oxygen defect on monoclinic phase is more active compared to tetragonal phase of ZrO$_2$ crystalline. According to Ding et al [8], high concentration of monoclinic phase as shown in Figure 1 is advantageous for deoxygenation of carboxylic acids produced by CPO breakdown. Using Scherrer equation, crystallite size can be determined and the result is presented in Table 2.

The acidity of catalyst was analysed by ammonia TPD analysis, with results being shown in Table 2. According to Sari [14], low acidity is required for decarboxylation and hydrogenation of triglycerides, and ZrO$_2$ is deemed to be suitable to generate low acidity [15]. The amount of total acidity per gram of catalyst in the present work was 36.2 mole/g. This figure is much lower than that measured by Wang et al using similar catalyst, which reaches 221 mole/g [16] and by Sari using Pd/Si-C catalyst which reaches 120-1530 mole/g [14]. In their studies, Wang et al and Sari used the catalysts to convert triglycerides into diesel fuel.

SEM-EDX data presented in Table 1 show that element composition data produced by EDX confirm the presence of elements Zr, O, Al and Ti. It is found that the Zr to O atomic number ratio is 1: 2.66, which is close to the ratio of 1: 2 in molecule of ZrO$_2$. The rest of oxygen atoms are part of molecules of $\alpha$-Al$_2$O$_3$ and TiO$_2$. This analysis indicates that the mole fractions of $\alpha$-Al$_2$O$_3$ and TiO$_2$ in the catalyst were much smaller than that of ZrO$_2$.

### Table 1. BET Surface Area Characterization of ZrO$_2$/$\alpha$-Al$_2$O$_3$-TiO$_2$ Catalyst

| Sample  | Heating Rate ($^\circ$C/min) | Calcination Temp. ($^\circ$C) | Surface Area (m$^2$/g) | Pore size (nm) | Pore Volume (cc/g) |
|---------|-----------------------------|-----------------------------|------------------------|----------------|-------------------|
| Sample A | 5                           | 1150                        | 2.199                  | 1.5792         | 0.002             |
|         |                              | 1300                        | 2.659                  | 1.6348         | 0.004             |
| Sample B | 7                           | 1150                        | 3.792                  | 1.6290         | 0.005             |
|         |                              | 1300                        | 2.891                  | 1.5820         | 0.002             |
| Sample C | 9                           | 1150                        | 2.745                  | 1.5814         | 0.002             |
|         |                              | 1300                        | 2.967                  | 1.5767         | 0.004             |

**Figure 1.** XRD Characterization of ZrO$_2$/$\alpha$-Al$_2$O$_3$-TiO$_2$ Catalyst
3.2 Yields of Pyrolysis Products
Table 3 shows that the use of catalyst decreases the yield of wax. FTIR analysis data on wax shows that the wax contains mostly C-H bend, C=O and C=C bend (see Table 4) which indicate that the wax may contain long saturated carbon chain of PP pyrolysis fragments. Wax may also contain long carbon chain ketones as a result of reactions between two compounds of carboxylic acids in the presence of catalyst of ZrO$_2$ [17] [18]. Gomez et al [19] found that support of ZrO$_2$ on the catalyst of CrOx improves C-H and C-C scissions. It is expected that the presence of catalyst of ZrO$_2$ improves C-H scissions in carbon chains favourable to generate hydrogen radicals.

Comparison of yields of wax by catalytic co-pyrolysis at different PP feed compositions shows that co-pyrolysis using PP feed composition of 50% produces the highest yield of bio-oil and the lowest yield of wax. Higher wax obtained by catalytic co-pyrolysis using feeds containing PP more than 50% may indicate less sufficient cracking of PP leading to more formation of wax and consequently to less sufficient donation of hydrogen radicals. According to Kruse et al [20], pyrolysis of PP compounds, which have high branching of methyl, leads to steric hindrance effect to allow more hydrogen abstraction, leading to more oligomeric products. In order to produce more liquid products, Li et al [21] suggested to use mesoporous catalyst. In fact, in the present work, the catalyst used is of microporous so that the cleavage of C-C and C-H bonds in PP pyrolysis is very difficult leading to more formation of wax and less formation of hydrogen radicals. The radicals are used to proceed to hydrodeoxygenation, decarboxylation and decarbonylation of carboxylic acids to form alkanes and alkenes [15]. With insufficient presence of hydrogen radicals in the reactant mixture, carboxylic acids tend to combine to form long carbon chain ketones which have high melting point and form wax.

Table 3. Comparison of yields of different phases of co-pyrolysis products

| %PP in Feed | Crude Palm Oil (% weight) | Yield Bio-oil (% weight) | Yield Coke (% weight) | Yield Wax (% weight) | Yield Non-Condensable Gas (% weight) |
|-------------|--------------------------|-------------------------|-----------------------|----------------------|-------------------------------------|
| 50% Non-Catalytic | 50 | 27.50 | 0.60 | 51.52 | 20.38 |
| 50 | 50 | 50.00 | 13.50 | 23.70 | 12.80 |
| 60 | 40 | 39.05 | 12.40 | 26.70 | 21.85 |
| 75 | 25 | 42.45 | 13.15 | 28.45 | 15.95 |
| 90 | 10 | 34.50 | 15.30 | 35.72 | 14.48 |

Table 3 shows that the introduction of the catalyst unfortunately generates much coke in the reactor. The existence of coke in co-pyrolysis may be initiated by the aromatic formation. Fung and Wang [22] found that aromatisation rate is correlated with the site density of acid and base sites. Their result shows that n-paraffin is first adsorbed on the pair of the acid-base sites followed by abstraction of hydrogen atoms by the catalyst. The adsorbed molecules undergo cyclisation and desorption from the sites as aromatics is formed. Zheng et al [23] suggested that weak acid sites facilitate the formation of aromatics, while medium acid sites the formation of coke. Sistani et al [24] found that the incorporation of ZrO$_2$ improves both acid and basic strength due to amphoteric nature of ZrO$_2$. However, such improvement is not sufficiently high to improve acidity of the catalyst as shown by Table 2.
Table 4. FTIR Characterization of Wax Bio-oil Using Catalyst

| Compound       | Wavenumber (cm\(^{-1}\)) | % Transmittance |
|----------------|---------------------------|-----------------|
| C-H Bend       | 2914.71                   | 74              |
| C=O Stretch    | 1699.77                   | 77              |
| C=C Bend       | 938.77                    | 86              |

3.3. Characteristics of Bio-oil

Table 5 shows FTIR data of bio-oil at different feed compositions from 50 to 90%PP prepared by catalytic co-pyrolysis and at the feed composition of 50%PP by non-catalytic co-pyrolysis. Comparison of FTIR data of bio-oil obtained by co-pyrolysis using feed containing 50%PP shows that bio-oil prepared by catalytic co-pyrolysis has similar transmittances for C-H, higher transmittance for C=C bends and lower transmittance of C=O compared to those measured on bio-oil prepared by non-catalytic co-pyrolysis. C=C may be part of PP fragments and aliphatic carbon chains of CPO while C=O from aliphatic carbon chains of CPO. Higher transmittance of C=C in bio-oil prepared by catalytic co-pyrolysis means that the pyrolysis is able to saturate double bonds of C=C due to the availability of hydrogen radicals. On the other hands, in case of C=O transmittance, the presence of hydrogen radicals provided by catalytic co-pyrolysis is unable to reduce oxygen content in bio-oil. Referring to modelling of PP pyrolysis suggested by Kruse et al. [20] and deoxygenation of fatty acids involving no hydrogen gas suggested by Rogers and Zheng [15], products of PP pyrolysis contain much olefins while the intermediate products of CPO pyrolysis contain olefins if the deoxygenation is preceded by dehydration. It seems that hydrogen radical donation works on saturation of olefins produced by PP pyrolysis rather than on saturation of olefins by CPO pyrolysis. As consequences, the use of catalyst ZrO\(_2\) encourages ketonic decarboxylation, which produces long carbon chain ketones and goes to wax during condensation of pyrolysis product vapour [17].

Table 5 also demonstrates that in catalytic co-pyrolysis, increasing composition of PP in feed increases the transmittance of C-O and reduces that of C=C. This indicates that more hydrogen radicals available during the reaction increases oxygen content in bio-oil and reduces unsaturated carbon-carbon bonds. Therefore, the donation of more hydrogen radicals with more PP composition in feed reverses the competition of reactions between deoxygenation of CPO and saturation of PP pyrolysis products towards less deoxygenation. This shows that more carbonyl is formed as the PP composition in feed is increased which indicates higher ketonisation of carboxylic acids. This supports the fact that wax partly is constituted by ketonic decarboxylation.

Figure 2 shows the compositions of various compounds based on functional groups measured by GC-MS spectroscopy. Different from the FTIR data which are based on qualitative analysis on chemical bonds, GCMS data are based % volume analysis of compounds which may contain either short or long carbon chains. Figure 2 shows that the presence of the catalyst increases the compositions of alkanes significantly and alkenes slightly. As FTIR analysis of bio-oil suggested, the formation of alkenes by the use of catalyst ZrO\(_2\) is more likely due to the saturation of olefins produced by PP pyrolysis.

However, the presence of the catalyst reduces the composition of alcohols significantly. In co-pyrolysis involving catalyst of ZrO\(_2\), alcohols evolve as intermediate product in the hydrodeoxygenation of carboxylic acids produced by CPO breakdown [15], in which alcohols have long carbon chains. It seems that due to small composition of hydroxyl moiety in bio-oil bonded to long carbon chain alcohols, FTIR is unable to detect its chemical bond in the bio-oil. Decarbonylation in co-pyrolysis may originate from pyrolysis of PP. The small composition of carboxylic acids, ketones and esters as products of CPO breakdown in bio-oil is more likely because most of carboxylic acids undergo ketonic decarboxylation to form long carbon chain ketones which accumulated as wax as predicted by FTIR analysis.
Table 5. FTIR Characterization of Bio-oil Using Catalyst and Without Catalyst

| Catalytic/Non-Catalytic | PP  | Compound     | Wavenumber (cm⁻¹) | % Transmittance |
|-------------------------|-----|--------------|-------------------|-----------------|
| Non-catalytic 50        | C-H Bend | 2920.67     | 79                |
|                        | C=O Stretch | 1712.16     | 86                |
|                        | C=C Bend    | 886.94      | 82                |
|                        | C-H Bend    | 2921.39     | 78                |
| Catalytic 50           | C=O Stretch | 1711.55     | 80                |
|                        | C=C Bend    | 886.95      | 85                |
| Catalytic 60           | C-H Bend    | 2919.21     | 79                |
|                        | C=O Stretch | 1711.74     | 82                |
|                        | C=C Bend    | 886.88      | 83                |
| Catalytic 75           | C-H Bend    | 2918.61     | 79                |
|                        | C=O Stretch | 1712.72     | 90                |
|                        | C=C Bend    | 886.76      | 79                |
| Catalytic 90           | C-H Bend    | 2912.73     | 81                |
|                        | C=O Stretch | 1713.22     | 87                |
|                        | C=C Bend    | 886.72      | 75                |

Figure 2. Compositions of Oxygenated and Non-Oxygenated Compounds in Bio-oil

Figures 3 and 4 present the results of H-NMR and C-NMR spectroscopy analysis of bio-oil obtained from different feed compositions from 50 to 90% of PP for catalytic co-pyrolysis and the composition of 50% of PP for non-catalytic co-pyrolysis. H-NMR analysis determines the abundance of H atoms bonded to moieties of methine (CH), methyl (CH₃), methylene (CH₂), α-C at C=O, benzylic and vinyl (see Figure 3). Examining chemical structures of PP and CPO, it is most likely that methyl is chemical bond mostly forming PP chemical structures, while methylene forming CPO structures. Therefore, it is expected that H atoms bonded to methyl originates from PP pyrolysis and H atoms bonded to methylene originates from CPO breakdown.
Comparison of H abundance data between bio-oil obtained by catalytic and non-catalytic co-pyrolysis of CPO-PP shows that the presence of the catalyst significantly improves the abundance of H in methyl and slightly reduces the abundance of H in methylene. These data suggest the catalyst tends to work on PP pyrolysis rather than on CPO breakdown. Combined findings of FTIR and H-NMR analysis results suggest that the catalyst significantly works on PP pyrolysis and saturation of the pyrolysis products rather than on CPO breakdown and saturation of the breakdown products containing olefins. The reduction of H bonded to vinyl shows that the catalyst improves the saturation of double bond of C=C which, according to FTIR analysis, occurring more on olefins produced by PP pyrolysis. It seems that characteristics of the catalyst does not accommodate the breakdown of CPO and the deoxygenation and saturation of the breakdown products even though the concentration of monoclinic phase is high in the catalyst as shown by Figure 1. Table 1 shows that the pore size is within microporous range. Sari who worked on production of green diesel from triglycerides and fatty acids of vegetable oil using Pd/Si-C catalyst used mesoporous catalyst with low acidity favourable to obtain high yield of green diesel [14]. Therefore, the improvement of pore size of the catalyst in the present work is required to increase the tendency of the catalyst to adsorb carboxylic acids from CPO breakdown.

C-NMR analysis determines the abundance of C atoms bonded to moieties of primary alkyl, secondary alkyl, tertiary alkyl, residual alkyl, vinyl, ketones, carboxylic acids, and aromatics. (see Figure 4). The figure shows that carbonyl moiety in the bio-oil is predominated by ketones. According to data of GCMS analysis, ketones in bio-oil mostly consist of aliphatic of 2-heptadecanone (C_{17}H_{34}O) and cage-like structure of dioxatricyclononan-5-one (C_{7}H_{10}O_{2}). Ketones may be formed by the catalyst of ZrO_{2}, which involves oxygen vacancies [25], where carboxylic acids are converted into ketones by releasing H_{2}O. With increasing composition of PP in feed, there is reduction of ketone composition.

![Figure 3. H-NMR Characterization of Bio-oil](image)

There is competition between the conversion of carboxylic acids to ketones and the pyrolysis of PP signified by the increase of C bonded to primary alkyl as shown in Figure 4. Figure 4 also demonstrates that increasing PP content in feed from 50% to 90% reduces C bonded to secondary and tertiary alkyls, where the former form most of CPO chemical structure and the latter part of PP chemical structure. The reduction of H bonded to methylene shown in Figure 3 must correspond to the reduction of C bonded to secondary alkyl in Figure 4, where methylene and secondary alkyl are parts of CPO chemical structure. Therefore, the reduction of combined secondary and tertiary alkyls gives indication of the effect of the reduction of CPO content in the feed on the composition of secondary alkyl constituting CPO chemical structure.
4. Conclusions

The co-pyrolysis of CPO and PP plastic using microporous ZrO2/α-Al2O3-TiO2 catalyst reaches the highest bio-oil yield as the feed contains 50% PP in which the bio-oil contains 81% volume of hydrocarbons based on GCMS spectroscopy measurement. Using pyrolysis feed containing 50% PP, compared to non-catalytic co-pyrolysis, catalytic co-pyrolysis produces nearly twice yield of bio-oil. H-NMR and C-NMR analysis of bio-oil indicates that the oxygenated compounds in the bio-oil are ketones and carboxylic acids and their contents are small. H-NMR analysis of bio-oil and FTIR analysis of wax indicate that the catalyst is more effective in PP pyrolysis rather than CPO deoxygenation reactions to hydrocarbons. Unreacted carboxylic acids undergo ketonic decarboxylation reaction to form wax. The use of microporous catalyst renders steric hindrance for triglyceride access to active sites of the catalyst to proceed deoxygenation reactions.

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