



vol. 17 / 2023



The 7th International Conference on Science Technology

organized by
Faculty of Social Science and
Law Universitas Negeri Manado and
Consortium of International Conference
on Science and Technology

The Innovation Breakthrough in Digital and Disruptive Era

Bio-oil production from pyrolysis of Polypropylene using dolomite catalyst

Yorinda Buyang^{1*}, *Yenni Pintauli Pasaribu*¹, *Paulus Mangera*², *Dina Kartika Maharani*³ and *Novike Bela Sumanik*¹

¹Department of Chemistry Education, Faculty of Teacher Training and Education, Musamus University, Merauke, South Papua, 99600, Indonesia

²Department of Electrical Engineering, Faculty of Engineering, Musamus University, Merauke, South Papua, 99600, Indonesia

³Department of Chemistry, Faculty of Mathematics and Natural Sciences, Surabaya State University, Surabaya, 60231, Indonesia

Abstract. Polypropylene is converted into bio-oil through catalytic pyrolysis using dolomite as a catalyst. The purpose of this study was to determine the effect of using dolomite directly without prior treatment on the bio-oil produced from the pyrolysis of propylene plastic. The amount of loading catalyst used is 5%. Increasing the pyrolysis temperature from 350 to 450 °C increased bio-oil from 35.56 wt% to 64.84 wt% by reducing gas to 21.08 wt%. In thermal pyrolysis, the production of bio-oil is 85 wt% with 19.30 wt% char. In the GC-MS analysis of bio-oil from thermal and catalytic pyrolysis, the most dominant alcohol composition was obtained. Based on the result of the analysis, it can be concluded that the bio-oil obtained can be further developed into fuel.

* Corresponding author: buyang@unmus.ac.id

1 Introduction

The production and use of plastic in various aspects of modern life continue to increase. The high consumption of plastic is due to its light weight, corrosion resistance, low price, and energy efficiency [1]. However, the impact of using plastic on the environment is very dangerous because it's difficult to degrade.

Several studies on polypropylene (PP) have been reported by [2] at 480 °C to produce light naphta (C₅-C₇) hydrocarbons of around 13.1% and 16.7% and heavy naphta (C₈-C₁₂) of between 69.1% and 87.2%. In addition, [3] reported that co-pyrolysis of Delonix Regia, Polyalthia leaves, and PP increased the heating value of bio-oil from 22.55 MJ/kg to 34.06 MJ/kg with an increase in PP from 0 wt% to 50 wt%. Ko *et al* [4] also investigated the pyrolysis of PP into fuel at four different temperatures: 450, 488, 525, and 600 °C. Based on the research result, the maximum temperatures were obtained, namely 488 and 525 °C, with a maximum yield of 81–93 wt%. The liquid fuel obtained is in the range of the gasoline fraction, with high heating values (HHVS) of 41 and 46 MJ/kg.

Pyrolysis is thermal cracking carried out at moderate temperatures (400–800 °C) to convert plastics into hydrocarbons in an economically feasible way. Several studies have been conducted to convert plastic waste into fuel using the co-pyrolysis method [5,6], microwave assisted technology [7], and vacuum [4,8]. Catalytic cracking is proposed as an effective and selective process that supports the creation of valuable materials compared with thermal pyrolysis. Catalytic pyrolysis is the best technique to transform PP palstict into bio-oil. In catalytic pyrolysis, catalyst play significant role, particularly in the transformation of plastic to reduce coke and increase the aromatic content [9].

Dolomite [CaMg(CO₃)₂] is an abundant rock in nature, consisting of calcium, magnesium, and a few impurities. The use of dolomite as a catalyst has been widely reported because it is easy to obtain, non-toxic, and low-cost. Buyang, *et al* [10] used dolomite directly as a catalyst in the pyrolysis of *Reutealis trisperma* oil to produce a liquid yield of 77.39%. The basic site composition of CaO and MgO contained in dolomite is able to support the deoxygenation reaction through pyrolysis and increase hydrocarbons, increasing their cracking into lighter and heavier organic fractions [11]. The ketonization reaction of carboxylic acid converts it into a ketone and some oromatic and phenolic compounds. This causes the bio-oil produced to have low acidity, be rich in hydrocarbons, and increase the heating value [12]. The high activity of dolomite can be attributed to its Fe₂O₃ contents.

In this study, we conducted research on the use of dolomite directly without treatment or calcination. The effect of temperature on thermal and catalytic pyrolysis on liquid, char, and gas yields was investigated for optimal oil yields. The chemical components of bio-oil are classified and analyzed based on their structure and carbon number. This research will help address the

serious environmental problems caused by plastic waste.

2 Materials and method

2.1 Materials

Poplypropylene plastic as feedstock was collected from a trash bank in Malang. Prior to the pyrolysis process, the PP plastic was washed in clean water and dried in the sun for two days. After that, it was then cut into small pieces with an irregular shape (with sizes approximately 1 cm x 0,5 cm). Dolomite was obtained in Bukit Jaddih, East Java, Indonesia. The dolomite was ground and sieved to get uniform particles. The sieved dolomite was dried in an oven at 105 °C for over night. The photograph of feedstock and product liquid it can be seen in Figures 1.

2.2 Pyrolysis of polypropylene

The degradation of PP plastic to produce bio-oil by pyrolysis using a semi-batch reactor. The reactor consisted of a stainless-steel chamber (dimensions: 59 cm wide x 61 cm long) with 10 kg of total volume capacity. The thermal and catalytic pyrolysis temperatures of PP plastic varied between 350 and 450 °C. For thermal and catalytic pyrolysis, a total of 1500 g of PP was poured into a stainless-steel chamber reactor. The amount of catalytic loading was 5% of the total feedstock polypropylene for catalytic pyrolysis. Dolomite was dried in an air oven at 105 °C for 24 hours before being mixed with PP. The reaction of polypropylene plastic was carried out at 350 and 450 °C at atmospheric pressure. Monitored the temperature using a thermocouple installed after the pyrolysis process ended. The bio-oil obtained was analyzed by GCMS.

2.3 Characterization of bio-oil

The composition of compounds contained in bio-oil from the pyrolysis of polypropylene was characterized. The chemical composition of bio-oil was analyzed using spectroscopy (HP 6890 GC) with a capillary column HP-5MS (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm). The GCMS inlet temperature was kept at 250 °C, and the oven was programmed at 65 °C for 8 minutes. The yield of each pyrolysis product was calculated by equations (1-3):

$$\text{Liquid yield (\%)} = \frac{\text{weight of bio-oil}}{\text{weight feedstock}} \times 100 \quad (1)$$

$$\text{Char yield (\%)} = \frac{\text{weight of char}}{\text{weight of feedstock}} \times 100 \quad (2)$$

$$\text{Gas yield (\%)} = 100 - (\text{oil yield} + \text{char yield}) \quad (3)$$

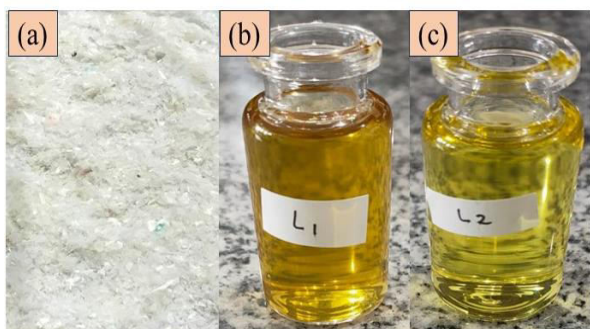


Fig. 1. Photograph of polypropylene (a) and product liquid pyrolysis (b,c) (L1: thermal pyrolysis liquid and L2: catalytic pyrolysis liquid)

3 Result and discussion

The thermal and catalytic pyrolysis of PP plastic feedstock was investigated. The main product is liquid, gas and char. All experiment were carried out with 1500 g PP in both thermal and catalytic conditions. In catalytic pyrolysis, the catalyst used is dolomite. the loading catalyst is 5% to the total feedstock. The result of pyrolysis products (liquid, char and gas) was produced within 350 and 450 °C. From the degradation of polypropylene pyrolysis was calculated using Eqs. (1)-(3).

3.1 Product yield

The temperature is one of the important factors in the pyrolysis process for producing bio-oil. The effect of pyrolysis temperature was observed at temperatures of 350 and 450 °C. Figures 2 (a) and (b) show the thermal and catalytic pyrolysis products (liquid, char, and gas). In thermal pyrolysis (Figures 2b), when the temperature is 350 °C, the resulting liquid yield is 54.3 wt%, which increases to 85 wt% when the temperature is increased to 450 °C. On the other hand, at 350 °C,

gas and char products were obtained at 22.4 and 19.3 wt%, respectively. Meanwhile, gas and char produced at a lower temperature of 450 °C were 9.06 and 5.94 wt%, respectively. Based on these results, it can be concluded that high temperatures have a significant impact on increasing liquid yield.

The higher liquid obtained in thermal pyrolysis is due to the branched chemical structure of PP plastic, which makes it easy to decompose [13]. In addition, the proportion of tertiary carbon present in the PP chain is high enough to cause thermal cleavage of C-C bonds [14] and encourage the formation of carbocations during the process of thermal degradation [15]. This is the reason to achieve maximum PP degradation without a catalyst.

We also observed a similar trend in catalytic pyrolysis at 350 and 450 °C with dolomite as a catalyst. There are three products produced: liquid, gas, and char. The product yield by catalytic pyrolysis is shown in Figures 2b. The temperatures of the catalytic pyrolysis are 350 and 450 °C. The liquid yield obtained was 35.56 wt% at 350 °C. The increase in liquid yield occurred when the temperature was increased to 450 °C, with a liquid yield of 64.84 wt%. The change in char and liquid gas yields from 38.95 wt% and 25.49 wt% at 350 °C decreased to 21.08 wt% and 14.07 wt% when the temperature was increased to 450 °C. The high yield of char obtained at low temperatures can be attributed to the imperceptible cracking process and unstable heating. As reported [16], a low reaction can increase the yield of char. When the temperature increased to 450 °C, the PP plastic decomposition process occurred properly, causing an increase in liquid yield. Based on the thermal and catalytic yields, similar results were obtained for the liquid yield. Similar results have also been reported previously [17].

3.2 Product component

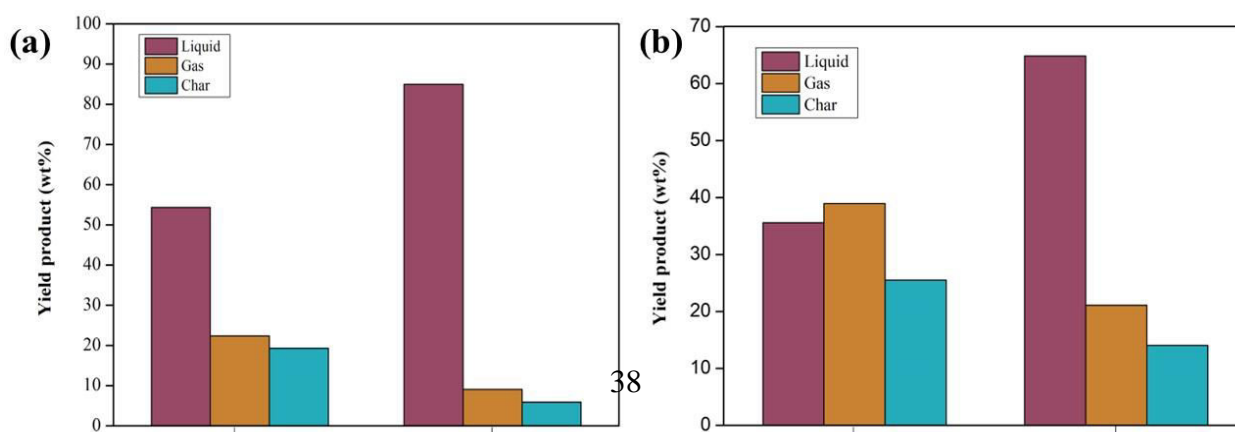


Fig. 2. Yield product at thermal (a) and catalytic (b) pyrolysis

Figures 3 shows the bio-oil component produced from the thermal pyrolysis of PP at 350 °C and 450 °C. Based on the GC-MS analysis, there are eleven functional groups present in the pyrolysis liquid. There are three main functional groups produced: hydrocarbons (218.46 g), alcohols (485.1 g), and cyclics (100.5 g). The other 8 functional groups are found in relatively a small, such as esters (33.81 g),

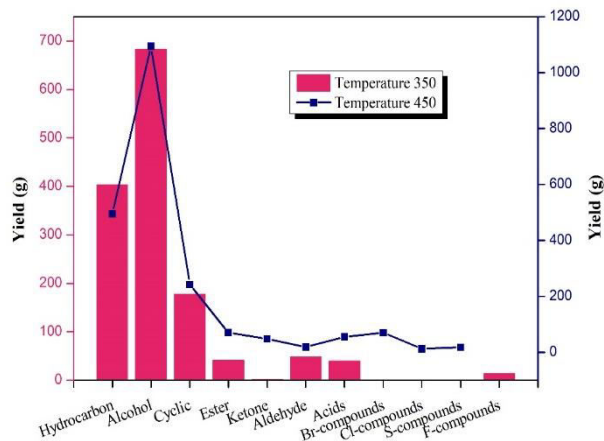


Fig. 3. Functional group obtained thermal pyrolysis (Temperature 350 and 450 °C)

ketones (21.92 g), aldehydes (26.4 g), acids (57.07g), Br- compounds (14.45 g), and S-compounds (15.37 g). At 350 °C ketones, Br-compounds and S-compounds are not found. Otherwise, at 450 °C, Br-compounds and S-compounds are found and the other hand F-compounds are not found.

The use of catalysts does not have a significant impact on the chemical composition of the bio-oil. It can be seen in Figures 4 the functional groups found in pyrolytic oil are similar to those found in liquid thermal pyrolysis: hydrocarbons, alcohol, cyclic, ester, ketones, aldehydes, acids, N-compounds, Br-compounds, and S-compounds. The dominant products obtained are hydrocarbons, alcohols, and cyclics. The use of a dolomite catalyst loading of 5% can remove Cl-compounds and F-compounds. The composition of the three chemical compounds continues to increase with increasing pyrolysis temperatures. The presence of a catalyst promotes isomerization and oligomerization reactions, thus increasing cyclic formation [18]. The alcohol groups are the most dominant products of both thermal and catalytic pyrolysis. The dominant formation of alcohol was also reported by Milea, which had an impact on increasing oxygenate. Therefore, 5% catalytic loading does not have a significant impact on the chemical composition of liquids, so it seems that it needs to be increased.

4 Conclusion

Temperature and catalyst are the most important factors in the pyrolysis of Polypropylene to produce

liquid, char, and gas. In thermal pyrolysis, the maximum production is of bio-oil (85 wt%), gas (22.4

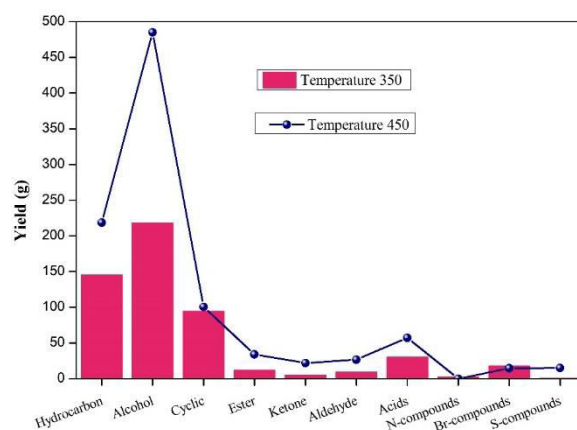


Fig. 4. Functional group obtained catalytic pyrolysis (temperature 350 and 450 °C)

wt%), and char (19.3 wt%). The catalytic pyrolysis with a 5% loading catalyst produced bio-oil (64.44 wt%), char (21.08 wt%), and gas (14.07 wt%). The GCMS analysis shows that the chemical composition of bio-oil is hydrocarbon (218.46 g), alcohol (485.1 g), and cyclic (100.5 g). Several other chemical compounds were found in small quantities, such as ester, ketone, aldehyde, acids, Br-compounds, and S-compounds (33.81 g, 21.92 g, 26.4 g, 57.07 g, 14.45 g, and 15.02 g, respectively). Alcohol is the dominant chemical found in bio-oil.

References

- [1] K. Miteva, G. Bogojeva-gaceva, Catalytic pyrolysis of waste plastic into liquid fuel, **57**, 600–604 (2016).
- [2] N. Hassibi, Y. Quiring, V. Carr, F. De, L. Vernex-loset, G. Mauviel, Analysis and control of products obtained from pyrolysis of polypropylene using a reflux semi-batch reactor and GC-MS / FID and FT-ICR MS, *J. Anal. Appl. Pyrolysis*, **169** (2023).
- [3] K. Kumari, N. Kishore, S. Gupta, S. V Aravind, G. Ahmed, Current Research in Green and Sustainable Chemistry Effect of varying fraction of polypropylene waste on co-pyrolysis of Delonix regia and Polyalthia longifolia leaves, **5** (2022).
- [4] G. Ko, F. Collard, J.F. Görgens, Pyrolysis of waste polypropylene plastics for energy recovery: Influence of heating rate and vacuum conditions on composition of fuel product, **209** 36–38 (2020).
- [5] L. Melia, C. Li, J. Jing, A. Aqsha, B. Shen, A. Chun, M. Loy, B. Lai, F. Chin, D. Shidqi, N. Hameed, G. Guan, J. Sunarso, Bio-oil production from pyrolysis of oil palm biomass and the upgrading technologies: A review,

- Carbon Resour. Convers. **4**, 239–250 (2021).
- [6] J. Chattopadhyay, T.S. Pathak, R. Srivastava, A.C. Singh, Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis, *Energy*. **103**, 513–521(2016).
- [7] Y. Cui, Y. Zhang, L. Cui, Y. Liu, B. Li, W. Liu, Microwave-assisted pyrolysis of polypropylene plastic for liquid oil production, *J. Clean. Prod.* **411**, 137303 (2023).
- [8] R. Aditya, A. Nugroho, A. Faruq, W. Wang, Thermal decomposition of polypropylene plastics through vacuum pyrolysis, *Energy*. **277**, 127707 (2023).
- [9] B. Bernard, X. He, S. Wang, A.E. Abomohra, Y. Hu, Q. Wang, Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production : Recent progress and future directions elsewhere worldwide, *Energy Convers. Manag.* **163**, 468–492 (2018).
- [10] Y. Buyang, S. Suprpto, R. Edra, H. Holilah, D. Prasetyoko, Journal of Analytical and Applied Pyrolysis Catalytic pyrolysis of Reutealis trisperma oil using raw dolomite for bio-oil production, *J. Anal. Appl. Pyrolysis*. **169**, 105852 (2023).
- [11] R.M.H.R. Shahrizzaman, S. Ali, R. Yunus, T.Y. Yun-Hin, Green Biofuel Production via Catalytic Pyrolysis of Waste Cooking Oil using Malaysian Dolomite Catalyst, *Bull. Chem. React. Eng. Catal.* **13**, 489–501 (2018).
- [12] Y. Buyang, R. Edra, H. Holilah, H. Bahruji, South African Journal of Chemical Engineering Dolomite catalyst for fast pyrolysis of waste cooking oil into hydrocarbon fuel, *South African J. Chem. Eng.* **45**, 60–72 (2023).
- [13] M. Ertaş, M. Hakki Alma, Pyrolysis of laurel (*Laurus nobilis* L.) extraction residues in a fixed-bed reactor: Characterization of bio-oil and bio-char, *J. Anal. Appl. Pyrolysis*. **88**, 22–29 (2010).
- [14] J. Aguado, D.P. Serrano, J.M. Escola, E. Garagorri, J.A. Ferna, Catalytic conversion of polyole ® ns into fuels over zeolite beta, **69**, 11–16 (2000).
- [15] S. Jung, M. Cho, B. Kang, J. Kim, Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor, *Fuel Process. Technol.* **91** (2010) 277–284. <https://doi.org/10.1016/j.fuproc.2009.10.009>.
- [16] G. Duman, C. Okutucu, S. Ucar, R. Stahl, J. Yanik, Bioresource Technology The slow and fast pyrolysis of cherry seed, *Bioresour. Technol.* **102**, 1869–1878 (2011).
- [17] E. Tina, I. Christopher, F. Aibuedefe, Environmental Technology & Innovation Thermal and catalytic pyrolysis of waste polypropylene plastic using spent FCC catalyst, *Environ. Technol. Innov.* **22**, 101455 (2021).
- [18] L. Melia, M. Xin, J. Wee, J. Jing, D. Shidqi, G. Ensang, A. Aqsha, A. Saptorio, J. Sunarso, South African Journal of Chemical Engineering Co-pyrolysis of oil palm trunk and polypropylene : Pyrolysis oil composition and formation mechanism, **43**, 348–358 (2023).