

PAPER • OPEN ACCESS

Thermal and catalytic pyrolysis of palm-pressed fibre (PPF) with copper oxide doped zirconia (CuO/ZrO₂) catalyst in a fixed-bed reactor

To cite this article: A R Mohamed *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **932** 012009

View the [article online](#) for updates and enhancements.

You may also like

- [Fumarate-loaded electrospun nanofibers with anti-inflammatory activity for fast recovery of mild skin burns](#)
I Romano, M Summa, J A Heredia-Guerrero *et al.*
- [Robust multi-view PPF-based method for multi-instance pose estimation](#)
Huakai Zhao, Yuning Gao, Mo Wu *et al.*
- [Poly \(propylene fumarate\)-calcium phosphate composites for enhanced bone repair](#)
Chunmeng Ma, Zhengyu Ma, Feng Yang *et al.*

UNITED THROUGH SCIENCE & TECHNOLOGY

 **The Electrochemical Society**
Advancing solid state & electrochemical science & technology

**248th
ECS Meeting**
Chicago, IL
October 12-16, 2025
Hilton Chicago

**Science +
Technology +
YOU!**

**Register by
September 22
to save \$\$**

REGISTER NOW

Thermal and catalytic pyrolysis of palm-pressed fibre (PPF) with copper oxide doped zirconia (CuO/ZrO₂) catalyst in a fixed-bed reactor

A R Mohamed¹, Awang A N¹, D M Hassan, N Nordin and R Ahmad²

¹Department of Chemical Engineering Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis, 02100 Padang Besar, Perlis, Malaysia

²School of Environmental Engineering, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

E-mail: alina@unimap.edu.my

Abstract. The utilization of agriculture solid waste such as palm pressed fibre (PPF) in pyrolysis reaction is an alternative way in converting the solid waste into bio-oil. In this research, thermal and catalytic pyrolysis of PPF was conducted using a tubular fixed bed reactor. A series of CuO/ZrO₂ catalysts were prepared using the aqueous sol-gel technique. The catalysts were calcined at 400, 600 and 800 °C for 17 hours. The thermal and catalytic pyrolysis of PPF were carried out at 500 °C pyrolysis temperature for 5 minutes holding time using PPF particle size of 250-500 µm. The pyrolysis results showed that 44.35% bio-oil was obtained under thermal condition and their yields reduced to 41.07%, 35.45% and 38.18% respectively when CuO/ZrO₂ catalysts calcined at 400, 600 and 800 °C were incorporated in PPF pyrolysis. The bio-oil was analyzed by using fourier transform infrared (FTIR) spectroscopy for the determination of functional groups. It was found that bio-oil from thermal and catalytic conditions possessed oxygenated functional groups such as aldehyde, ketone and carboxylic acid. In addition, the bio oil from catalytic conditions CuO/ZrO₂ catalysts calcined at 400 and 600 °C showed the presence of saturated hydrocarbon.

1. Introduction

In Malaysia, palm oil industry is one of the main contributor to the economy over the years. The production of crude palm oil produced abundant amount of biomass solid waste such as empty fruit bunch, palm-pressed fibre (PPF) and frond. Palm-pressed fibre is a mixture of several solid waste such as palm mesocarp fibre, kernel shell and crushed kernel [1]. PPF is a potential biomass source which can be useful in thermochemical processing technology. Biomass thermochemical processing technology such as pyrolysis and torrefaction are preferred for the production of either biochar or torrefied biomass, bio-oil and gas. Torrefaction of biomass were reported which indicated the prominency of torrefaction process for the production of torrefied biomass with improved calorific value [2-5]. Pyrolysis is a thermochemical processing that allows process manipulation to produce desired products such as bio-oil or bio-char [6]. A number of research has been focused on the thermal pyrolysis of biomass in terms of the evaluation of product distribution yields quantitatively and optimization on the process parameters (7-13).

¹ To whom any correspondence should be addressed



Catalytic pyrolysis is considered to be the most attractive way to assist either liquid yield or to promote several deoxygenation reactions of biomass during pyrolysis process [14-15]. It was reported that catalytic pyrolysis of EFB with alumina showed a slightly higher bio-oil yield compared to under non-catalytic condition [16].

Transition metal oxide catalysts are viewed as prominent candidate to increase the biomass pyrolysis oil yield as well as reducing the oxygenated compounds such as carboxylic acids content in the bio-oil. This is because transition metal would affect the mode of oxygen rejection by producing more carbon dioxides and more water making that way more hydrogen available for incorporation in hydrocarbon [17]. Zirconia is a well-known metastable support with acidic catalytic active sites [18]. Catalytic pyrolysis of biomass with ZrO_2 - TiO_2 have been reported that showed good performance towards producing selective products and higher organic liquid yields [19]. ZrO_2 - TiO_2 catalyst was also reported to have positive effect in reducing the phenols, acid and sugar content in bio-oil from the pyrolysis of poplar wood [20]. It is obvious ZrO_2 requires the presence of another metal oxide or dopant to assist the catalytic action. Copper oxide is a transition metal oxide catalyst active towards oxidation reaction [21]. The utilization of copper alumina (Cu/Al_2O_3) in catalytic pyrolysis of tomato waste produced higher yield of 26.68% at 5 wt% catalyst loading [22]. The Cu/Al_2O_3 catalyst was also being tested in the catalytic pyrolysis of paper in a thermogravimetric analyzer. It was reported that at 30 wt% catalyst loading, the devolatilization temperature of paper has occurred at a much lower temperature [23]. These studies indicate that copper oxide catalyst as dopant in zirconia could be a promising catalyst system which has good effect in biomass pyrolysis. Most of the studies above reported about the effect of catalysts at different catalyst loading. There is scarce information that reports the effect of CuO/ZrO_2 catalyst at different calcination temperature in biomass pyrolysis. Therefore, the objective of this study is to report the pyrolysis of PPF under thermal and catalytic condition with CuO/ZrO_2 catalyst at different calcination temperature towards the distribution of bio-oil, bio-char and gas yields. The identification of functional groups exist in bio-oil from CuO/ZrO_2 catalyzed reaction were investigated with fourier transform infra-red (FTIR) spectroscopy.

2. Materials and methods

2.1 Biomass preparation

The palm pressed fibres (PPF) were obtained from palm oil mill North Star Palm Oil Mills which is located in Kuala Ketil, Kedah, Malaysia. The PPF sample was air-dried for 24 hours. Then, the sample was placed in the oven at 40 °C for 24 hours for homogeneous mild drying. Then, the sample was crusher using a lab-scale crusher and sieved using Retsch sieve shaker to several particle sizes [2-5].

2.2 Catalyst preparation

10.0 g zirconium oxy chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) is weighed and dissolved in distilled water for 30 minutes. Then, copper nitrate 2.5 hydrate of corresponding stoichiometric ratio is weighed and dissolved in distilled water for 30 minutes. The solutions containing copper nitrate and zirconium oxychloride are mixed and stirred for another 30 minutes and given moderate heat treatment in the oven at 70 °C for 24 hours to obtain solid phase. Further calcination at temperature of 400 °C, 600 °C and 800 °C was carried out in the furnace yielded black powder metal oxide catalysts.

2.3 Catalytic and thermal pyrolysis experiments

The PPF pyrolysis catalytic and thermal experiments were conducted using a fixed bed reactor system. The major components of the reactor system include a reactor tube, furnace, gas cylinder (N_2), condenser and thermocouple to monitor reaction temperature and a cooling circulation unit. The reactor system is connected to a computer for the data login system using a programmable controller.

For each thermal pyrolysis, 5.0 g of PPF weighed and placed inside the reactor tube. For catalytic pyrolysis run, 0.5g CuO/ZrO₂ catalyst was weighed and mixed with PPF and fed into the reactor tube. The furnace temperature and its holding time were set at 500 °C for 5 minutes using a programmable controller. The reactor tube containing the biomass was located in the furnace. The nitrogen gas was purged to the system at flowrate of 100 ml/min for 10 minutes before furnace ignition. The furnace temperature increased from room temperature to the desired temperature once it is ignited at a ramp rate of 50°C/min. The products were obtained after the holding process which took about 30 minutes [16].

2.4 Relevant calculations

The products such as bio-char, bio-oil and gas yields obtained in the pyrolysis reaction were calculated on weight basis according to Equation 1, Equation 2 and Equation 3.

$$\text{Bio - char yield (wt\%)} = \frac{\text{mass of bio - char (g)}}{\text{mass of PPF feed (g)}} \times 100\% \quad (1)$$

$$\text{Bio - oil yield (wt\%)} = \frac{\text{mass of bio - oil (g)}}{\text{mass of PPF feed (g)}} \times 100\% \quad (2)$$

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

2.5 FTIR Analysis

The fresh bio-oil obtained 30 minutes after thermal and catalytic pyrolysis experiments were analysed by Perkin Elmer 65 Fourier Transform Infrared (FTIR) to identify the presence of functional groups. In each analysis, 4 scan was performed on each bio-oil sample from wavenumber 4000-650 cm⁻¹.

3 Results and discussion

3.1 Catalytic and thermal pyrolysis of PPF

The product distribution such as the bio-oil, bio-char and gas yields from thermal and catalytic PPF pyrolysis with CuO/ZrO₂ are shown in Figure 1.

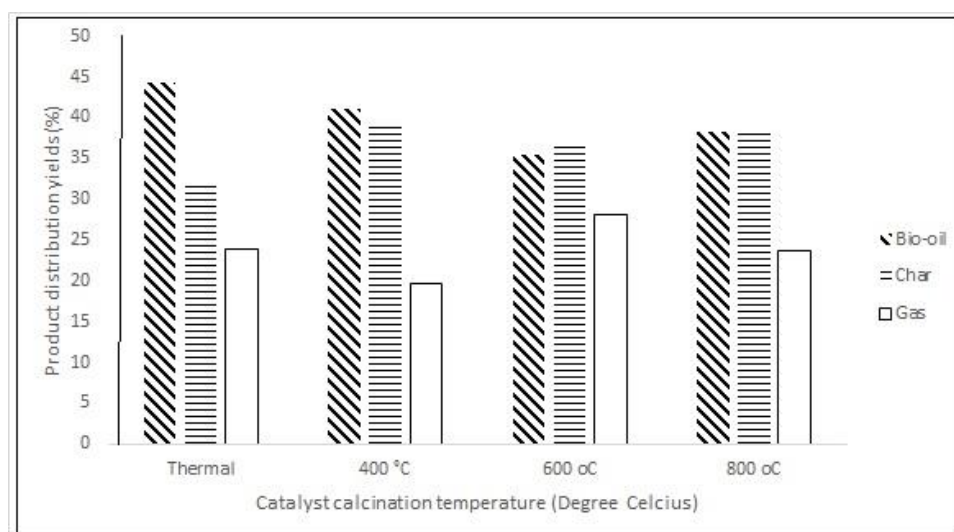


Figure 1. The production of bio-oil, bio-char and gas under thermal and catalytic PPF pyrolysis with CuO/ZrO₂ catalysts calcined at 400, 600 and 800 °C.

The bio-oil yields were 44.35 wt%, 41.07 wt%, 35.45 wt% and 38.18 wt% respectively for the thermal and catalytic PPF pyrolysis by CuO/ZrO₂ catalysts calcined at 400, 600 and 800 °C. This indicated that the bio-oil yield showed reduction with the utilization of CuO/ZrO₂ catalysts regardless of calcination temperature. The results are in good agreement with reported studies by [19]. The reduction of bio-oil yield occur when the cracking and polymerization of volatiles occur into char and gas. Meanwhile, the bio-char yield was in the range of 31.78-39.28 wt % for thermal and catalytic pyrolysis. This indicated that the presence of catalyst has no significant effect towards the bio-char yield. The catalytic pyrolysis of biomass can be generally divided into two main processes. The first process is the devolatilization of biomass particles into organic volatiles which are commonly oxygenated compounds. The second process is the catalytic cracking and reformation of the volatiles into desirable hydrocarbon and aromatics components [24].

3.2 Analysis on bio-oil using FTIR

The determination of functional groups in bio-oil produced from thermal and catalytic pyrolysis of PPF with CuO/ZrO₂ catalysts are shown in Figure 2 and peak assignments are simplified in Table 1. The presence of C=O are detected in all bio-oils which indicated that the bio-oil (regardless originated from thermal or catalytic PPF pyrolysis) consists mainly of oxygenated compounds such as carboxylic acids, aldehydes, ketones and ether. The strong and broad bands at approximately 3396-3384 cm⁻¹ are very characteristic of strongly H-bonded OH of carboxylic acids [25-27]. The presence of hydrocarbon at the wavenumber in the range of 2930-2800 cm⁻¹ is detected in the bio-oil originated from catalytic pyrolysis of PPF with CuO/ZrO₂ catalysts calcined at 400 and 600 °C. The peak at 1737-1701 cm⁻¹ is assigned to the existence of C=O bond of ketone or aldehyde or carboxylic acids [25]. The presence of carboxylate ion (-C-O-O group) is further confirmed by the presence of the peaks at wavenumber 1399-1365 cm⁻¹ [25]. This range of wavenumber sometimes could be misinterpreted as hydrocarbon of -C(CH₃)₂ origin. However, the -C(CH₃)₂ must give 2 symmetrical doublets at approximately 1380 cm⁻¹ [27]. Since the peak appears as singlet and not symmetrical doublet, hence it is confirmed that the peak is carboxylate ion. The bands at 1272-1270 cm⁻¹ indicates the presence of =C-O-C of ether group or oxygenated compound [25].

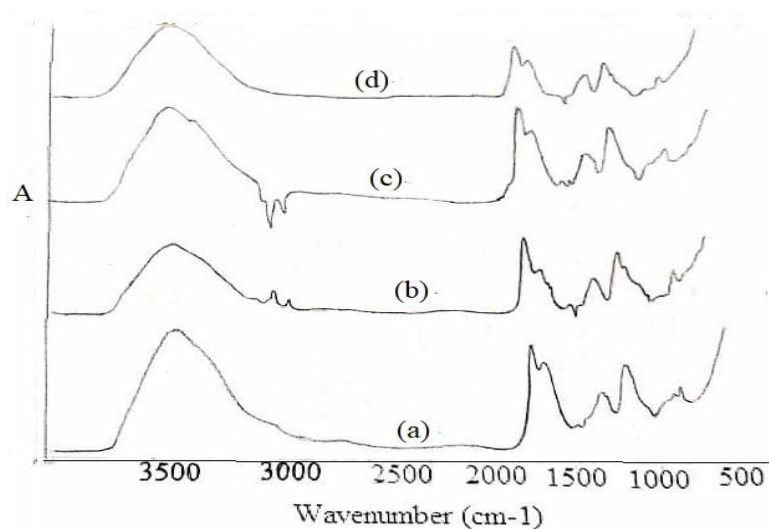


Figure 2. FTIR spectra on bio-oil from thermal reaction (a) and catalytic reactions between PPF and CuO/ZrO₂ catalysts calcined at 400 °C (b), 600 °C (c) and 800 °C (d).

Table 1. Functional groups identified by FTIR

Bio-oil (Thermal pyrolysis)	Bio-oil using catalyst calcined at 400 °C	Bio-oil using catalyst calcined at 600 °C	Bio-oil using catalyst calcined at 800 °C	Remarks
Wavenumber (cm ⁻¹)	Wavenumber (cm ⁻¹)	Wavenumber (cm ⁻¹)	Wavenumber (cm ⁻¹)	
3384	3395	3396	3394	Characteristic strongly H-bonded OH of carboxylic acid
Nil 1737	2930-2800 1710	2923-2854 1701	Nil 1714	C-H bond of alkane group C=O of ketone/aldehyde/carboxylic acid
Nil 1365	Nil 1399	1488-1464 1392	Nil 1372	C-H bond of alkane group -C-O-O ⁻ group (carboxylate ion)
1217	1271	1270	1272	=C-O-C ether or oxygenated compound

4. Conclusion

The thermal and catalytic pyrolysis of PPF with Cu/ZrO₂ catalyst at different calcination temperature were performed in a fixed bed reactor. The addition of catalyst into pyrolysis process has reduced the bio-oil yield. The reduction of bio-oil is associated with the degree of cracking and polymerization during pyrolysis reaction. The bio-oil from catalytic pyrolysis of PPF using CuO/ZrO₂ calcined at 400, 600 and 800 °C showed the presence of oxygenated compounds. However, the bio-oil from 400 and 600 °C catalyst showed the presence of hydrocarbon compounds.

5. References

- [1] Neoh, B.K., Thang, Y.M., M.Z.M and Junaidi, A 2011 *Intl. Food Res J.* **18** 746-750.
- [2] Awang A N, Mohamed A R, Salleh N H M, Hoo P Y and Kasim K K 2019 *React. Kinet. Mech. Catal.*, no. 0123456789.
- [3] Mohamed A R, Nordin N N A and Salleh N H M 2019 *J Adv Res in Eng Knowl* 6(1) 7-14
- [4] N. N. Kasim, A. R. Mohamed, M. A. M. Ishak, R. Ahmad, W. I. Nawawi, S. N. Ali and K. Ismail 2019 *J Therm Anal Calorim* **138** 343-350 doi 10.1007/s10973-019-08206-8
- [5] Kasim, N N, Ismail K, Mohamed A R, Ishak M A M, Ahmad R, Nawawi W I 2018 *Adv Science, Technol and Eng Sys J* **3(5)** 365-373
- [6] A. Demirbas 2000 *Energ Conv and Manage* **41** 633-646.
- [7] Mohamed, A R, Hamzah, Z and Daud, M Z M 2014 *Adv Mat Res* **925** 115-119.
- [8] Mohamed A R, Hamzah, Z, Daud, M Z M and Zakaria, Z 2013 *Proc Eng* **53** 185 – 191.
- [9] Mohamed, A R, Hamzah, Z and Daud, M Z M 2014 AIP Conference Proceedings 1605 1172 doi: 10.1063/1.4887756
- [10] Kasim N N, Mohamed A R., Ishak M A M, Ahmad R, Nawawi W I, Ismail K and Salleh N H M 2018 AIP Conference Proceedings, 2013 020003
- [11] Kasim N N, Ismail K, Mohamed A R., Ishak M A M, Ahmad R, Nawawi W I 2018 *Adv Science, Technol and Eng Sys J* **3(5)** 365-373
- [12] Sukiran A, Chin C M and Amer N K A B 2009 *J Appld Scien* **6(5)** 869-875.
- [13] Abnisa F, Daud W M A W, Husin W N W, Sahu J N 2011 *Biom and Bioenerg* **35(5)** 1863-1872.

- [14] Balat M, Balat M, Kirtay E and Balat H 2009 *Energ Conv Manage* **50** 3147-3157.
- [15] Mohamed A R, Li N, Sohaimi K S A, Iberahim N I, Rohaizad N M and Hamzah R 2018 *IOP Conf. Series: Mat. Sc. and Eng.* **318** 012019 doi:10.1088/1757-899X/318/1/012019
- [16] Mohamed A R and Hamzah Z 2015 *Reac Kinet Mech Cat* **114** 529–545
- [17] French R, Czernik S 2010 *Fuel Proc. Tech.* **91** 25-32.
- [18] Ross-Medgaarden E I, Knowles W V, Kim T, Wong M S, Zhou W, Kiely C J and Wachs I E 2008 *J Catal* **256** 108-125.
- [19] Stefanidis S D, Kalogiannis K G, Iliopoulou E F, Lappas A A, Pilavachi P A 2011 *Bioresour Tech* **102(17)** 8261-8267
- [20] Lu Q, Zhang Y, Tang Z, Li W-z, Zhu X-f 2010 *Fuel* **89** 2096–2103
- [21] Tidahy H L, Siffert S, Wyrwalski F, Lamonier J-F and Aboukaïs A 2007 *Catal Today* **119(1-4)** 317-320.
- [22] Ozbay N, Yargic A S, Zerrin R and Sahin Y 2018 *J Energ Instit* **91(3)** 424-433
- [23] Chattopadhyay J, Kim C, Kim R and Pak D 2009 *J Industr and Eng. Chem.* **15** 72-76.
- [24] Lu C B, Yao J Z, Lin W G and Song W L 2007 *Chinese Chem Lett* **18** 445-448.
- [25] Ahmad R, Ishak M A M, Ismail K and Kasim N N 2018 *Adv. in Sc. Technol. and Eng. Sys. J.* **3(5)** 166- 170.
- [26] Ahmad R, Hamidin N, Ali U F M and Abidin C Z A 2014 *J. of Mech. Eng. and Sc.* **7** 1134-1140.
- [27] Ahmad R, Ishak M A M, Ismail K and Kasim N N 2019 *Energy* **167** 538-547.

Acknowledgement

The authors would like to express their gratitude to the Department of Chemical Engineering Technology, Faculty of Engineering Technology UniMAP for the facility provided in conducting this research project.