Pertanika J. Sci. & Technol. 30 (4): 2589 - 2602 (2022)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Effect of Process Conditions on Catalytic Hydrothermal Oxidation of *p*-Xylene to Terephthalic Acid

Mohamad Zarqani Yeop[1], Kamariah Noor Ismail[2] and Ahmad Rafizan Mohamad Daud[2]*

[1]School of Chemical Engineering, Universiti Teknologi MARA, 81750 UiTM, Masai, Johor, Malaysia
[2]School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, 40450 UiTM, Shah Alam, Selangor, Malaysia

ABSTRACT

This study investigates the influence of hydrothermal process conditions on the yield of terephthalic acid (TPA). Deionised water was employed as a green reaction medium substitute for acetic acid solvent widely used in the Amoco oxidation process for TPA production. Utilising the unique properties of water at elevated temperature and pressure, TPA was synthesised from *p*-xylene under subcritical (250 °C, 300 °C and 350 °C) and supercritical (400 °C) water conditions in a 10 mL micro-bomb batch reactor. Process conditions, including hydrogen peroxide (H_2O_2) oxidant concentrations, manganese bromide ($MnBr_2$) catalyst and water loadings, were varied at a fixed reaction time of 60 minutes. The *p*-xylene conversion and TPA yield were determined using high-performance liquid chromatography (HPLC). In addition, the presence of chemical functional groups and chemical compositions of the reaction products were examined using Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometer (GC-MS), respectively. It was found that an optimum TPA yield of 94.56% was observed at 350°C with hydrogen peroxide, deionised water and manganese bromide catalyst set at 1.5 mL, 2.5 mL, and 2 mL, respectively. Other major reaction products identified were *p*-tolualdehyde and 1,4-hydroxymethyl benzaldehyde.

Keywords: Hydrothermal, oxidation, sub-and supercritical water, terephthalic acid

INTRODUCTION

Terephthalic acid (TPA) is an important petrochemical intermediate used in manufacturing polyester (Lee et al., 2021). Almost 70% of the global terephthalate

ARTICLE INFO

Article history:
Received: 04 October 2021
Accepted: 19 January 2022
Published: 21 September 2022

DOI: https://doi.org/10.47836/pjst.30.4.16

E-mail addresses:
zarqani@uitm.edu.my (Mohamad Zarqani Yeop)
knoor@uitm.edu.my (Kamariah Noor Ismail)
ahmad2057@uitm.edu.my (Ahmad Rafizan Mohamad Daud)
* Corresponding author

ISSN: 0128-7680
e-ISSN: 2231-8526

feedstocks are industrially synthesised from *p*-xylene via an Amoco oxidation process (Tomás et al., 2013; Walt, 2020). In this process, *p*-xylene is oxidised with air at around 175-200 °C and 15-30 bar using soluble cobalt (Co)/manganese (Mn) catalyst, a bromide (Br) promoter and acetic acid (AcOH) solvent (Tomás, 2013). Although the process is highly efficient, applications of AcOH as a solvent to facilitate the reaction has led to health, safety, and environmental concerns. The AcOH reacted with the bromide catalysts to produce hazardous methyl bromide (CH_3Br) gas. Moreover, the formation of undesired bromide associated liquid products also reduces the concentration of bromine catalysts in the reaction system and causes serious corrosion to the process equipment.

Over the years, attempts have been made to develop a safer and greener synthesis route for TPA, including the elimination of purification steps via a new spray concept (Li et al., 2013), development and use of new types of homogeneous catalysts involving bromide salts of manganese, cobalt and copper (Holiday et al., 1998; Pérez et al., 2011), N-hydroxyimide (Falcon et al., 2010), heterogeneous cobalt-based catalysts (Xu et al., 2020; Vakros, 2021) and application of high-temperature liquid water to replace AcOH solvent (Dunn & Savage, 2002; Fraga-Dubreuil & Poliakoff, 2006).

The high-temperature, high-pressure water reaction conditions (>100 °C, >1 atm) known as hydrothermal have received increasing attention because of the ability to fine-tune the water physicochemical properties by pressure and temperature adjustments (Byrappa & Yoshimura, 2012; Carr et al., 2011; Cocero, 2018; Savage, 2009;). Around the critical conditions (T_c 374 °C, P_c:22.1 MPa, ρ_c:320 kg.m^{-3}), water characteristics such as diffusivity, viscosity, dielectric constant, and solvation properties change dramatically with small changes in pressure due to large compressibility of critical fluids. Consequently, favourable reaction kinetics and mechanisms (Brunner, 2014; Kwak et al., 2009), as well as an increase in the dissolution of oxygen and functionalised aromatic compounds (Kruse & Dinjus, 2007a) can be obtained to support various types of organic and aromatic chemical reactions (Eckert & Chandler, 1998; Daud et al., 2021; Kruse & Dinjus, 2007b) through free radical and ionic reactions (Kruse & Dinjus, 2007b; Jiang et al., 2020). From a chemical process perspective, hydrothermal is regarded as safe, non-toxic, environmentally benign, and easy to handle (Cocero, 2018; Dunn & Savage, 2005).

Holiday et al. (1998) demonstrated that selective *p*-xylene conversion to the TPA in a good yield of around 60% could be achieved in subcritical water. Thus, following this work, catalytic hydrothermal oxidation (Dunn & Savage, 2002 & 2005; Dunn et al., 2003; Fraga-Dubreuil & Poliakoff, 2006; Osada & Savage, 2009a; Osada & Savage, 2009b; Pérez et al., 2011) and non-catalytic hydrothermal oxidation (Kim et al., 2002) of *p*-xylene under hydrothermal conditions have been investigated. Generally, the *p*-xylene hydrothermal oxidation pathway mimics the AcOH solvent-based Amoco process pathway. From the outset, efforts have been directed at bypassing the rate-limiting step of *p*-toluic acid oxidation to 4-carboxybenzaldehyde (4-CBA). These studies suggested that TPA synthesis is sensitive to changes in hydrothermal oxidation conditions, particularly reaction temperature, oxidant concentration and types of catalysts used. A summary of previous studies on hydrothermal oxidation of *p*-xylene is presented in Table 1.

This research examines the effects of hydrothermal reaction conditions involving reaction temperature (sub- and supercritical water, 250-400 °C), oxidant concentrations, manganese bromide catalyst loadings and water loadings during *p*-xylene conversion and yield to the TPA. The reaction temperature is expected to influence the *p*-xylene conversion reaction significantly. Changes in reaction temperature directly affect the dielectric constant of water responsible for the dissolution of organics in high-temperature water. Moreover, a higher reaction temperature accelerates the degradation of hydrogen peroxide to form hydroxyl free radicals and increases the overall oxidation reaction rate. Therefore, investigations were conducted in conditions encompassing the sub- and supercritical water range.

Table 1
Previous studies on TPA synthesis from p-xylene *under subcritical and supercritical water conditions*

Conditions	Oxidant	Catalyst	Findings	Ref.
Subcritical water, 333 °C	O_2	$MnBr_2$	Yield, 64%	Holiday et al., (1998)
Subcritical & Supercritical water, 240-400 °C & 220-300 bar	H_2O_2	No Catalyst	Conversion: SubCW ~ 89.02% SCW ~ over 99%	Kim et al., (2002)
Subcritical water, 300 °C	H_2O_2	$MnBr_2$	Yield, 49±8%	Dunn and Savage (2002)
Subcritical water, 300°C	O_2	$MnBr_2$	Yield >80 %	Dunn and Savage (2005)
Subcritical water, 300 °C	O_2	$MnBr_2$	Yield > 70 % Selectivity, 90%	Osada & Savage (2009b)
Subcritical water, 300 °C	O_2	$MnBr_2$	Yield > 80 % Selectivity > 90%	Osada & Savage (2009a)
Subcritical water, 330 °C		$Cu/Co/NH_4/Br$	Yield, 70.5%	Perez et. al. (2011)

METHODOLOGY

Materials

p-xylene 8.1M (reagent grade, 99%), TPA powder (>98%) hydrogen peroxide solution 9.7M (H_2O_2, 30% wt./wt.) and manganese (II) bromide catalyst ($MnBr_2$) 0.014M were purchased from Merck Sdn. Bhd. Organic solvents dimethyl sulfoxide (DMSO) and dichloromethane (DCM) were obtained from Chemolab Supplies Sdn Bhd. Both solvents are reagent grade (>99.9%). All hydrothermal oxidation experiments were conducted using deionised water as a reaction medium. The experiments were accomplished using a 10mL micro-bomb reactor fashioned from Swagelok's high pressure-high temperature tubing and fittings. An electrical tube furnace was used to provide heat to the reactor.

Experimental

P-xylene catalytic hydrothermal oxidation experiments were conducted in a 10mL micro-bomb batch reactor. The reactor was assembled using a ½ inch Swagelok stainless steel tubing and end caps (Figure 1). At first, reactants *p*-xylene and H_2O_2 and $MnBr_2$ catalyst were carefully charged into the micro-bomb reactor. Next, deionised water was added according to the amount specified in Table 2. Then, the reactor end cap was properly tightened using a wrench to ensure leak-free experiments. Heating is provided by a programmable tube furnace whereby heating rate and temperature are controlled using a proportional integral derivative (PID) controller. Prior to the introduction of the reactor, the furnace temperature was set to the required reaction temperature at 250 °C, 300 °C, 350 °C and 400 °C. The reaction temperature was controlled within $\underline{+}$5°C, and reaction time was taken immediately after the reactor was placed and secured. For all experiments, the reaction time was set at 60 min. At the end of the reaction, the micro-bomb reactor was quickly withdrawn from the furnace and quenched in cold water to room temperature. Subsequently, the micro-bomb reactor was carefully opened to avoid sudden release of residual pressure and losses of liquid sample. The reactor was not equipped with a gas collection port, and, therefore, gas products were not recovered.

The liquid sample was transferred to a sample vial, and the reactor was rinsed with 5.0 mL of DMSO solvent to remove any remaining products. Gas chromatography-mass spectrometer (GC-MS), Fourier transforms infrared spectroscopy (FTIR), and high-performance liquid chromatography (HPLC) was used to analyse the liquid products. An experimental error was estimated from four experiments conducted under identical conditions (H_2O_2 1.5mL, $MnBr_2$ 2mL, deionised water 1.5mL, 300 °C and 60 min). It was found that the standard deviation for this experiment was 5 for the TPA yield and the standard experimental error percentage was ±4%.

Table 2
Range of experimental reaction parameters studied

Reaction parameters	Range	Units
Temperature	250–400	°C
p-xylene	0.1	mL
Water	1.5–2.5	mL
$MnBr_2$	1.5–2.5	mL
H_2O_2	0.5–2.0	mL

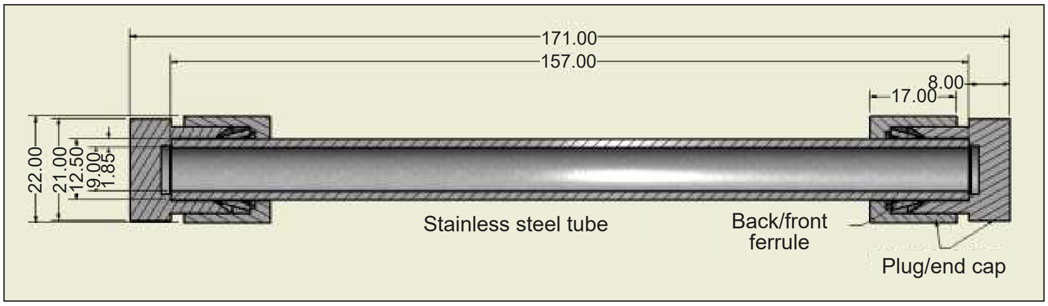

Figure 1. Construction of the hydrothermal micro-bomb reactor

Analysis

The liquid sample was analysed using a Perkin Elmer Spectrum One FTIR to identify the functional groups present in the mixture. All spectra were generated using 4 cm^{-1} and 4 scans spectral resolution at a wavelength range of 4000 to 515 cm^{-1}.

The desired TPA product was analysed by a Perkin Elmer reverse phase-high performance liquid chromatography (RP-HPLC). A mixture of acetonitrile (5%) and a diluted buffer solution of sodium acetate/acetic acid (95%) was used as the mobile phase, and the flow was adjusted to 0.7 mL/min. Standards and liquid product samples were manually injected at 6 µL, and separation was accomplished within 15 min run time using a LichroCART column maintained at ambient temperature. The peak of the TPA was detected at 254 nm wavelength using a UV detector. The TPA product concentration in the sample was determined from a calibration curve plotted using the peak area for the TPA standard solutions prepared at five different concentrations (Figure 2).

The liquid by-products obtained from the experiments were identified using a Varian 450 gas chromatography/Varian 240 mass spectrometry (GC/MS). Prior to injection, the liquid sample was diluted with DCM solvent. The GC-MS was fitted with a BP5MS column (30m, 0.25mm diameter and 0.25µm film thickness). The initial column temperature was set at 60 °C (held for 0.5 min). The temperature was then ramped to a final temperature of 180 °C at 5 °C min^{-1} and held for 0.5 min. The temperature of the injector was kept at 200 °C. Chromatogram acquisition was made in full scan mode between 50–500 m/z. Helium was used as carrier gas at 1 mL/min flowrate. The reaction by-products were identified by matching their mass spectra to the NIST mass spectrum library.

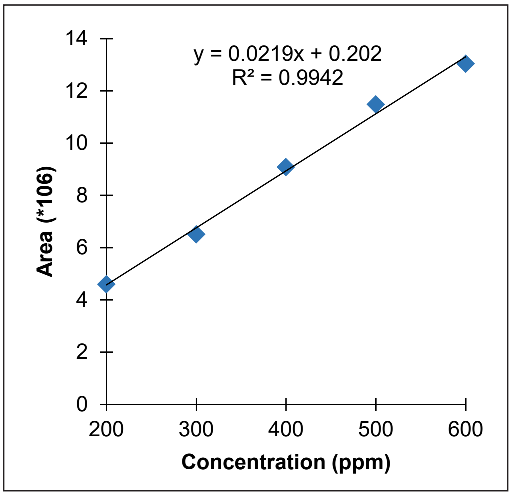

Figure 2. HPLC calibration curve for TPA product quantification prepared using TPA standard solutions

RESULTS AND DISCUSSION

Effect of Reaction Temperature

The effect of reaction temperature was investigated at a fixed catalyst loading of 2.0 mL, deionised water of 2.5 mL and hydrogen peroxide of 1.5 mL. The temperature varied between subcritical (250 °C–350 °C) and supercritical (400 °C). As shown in Figure 3, the TPA yield increases in the subcritical water region, with a maximum TPA yield of 94.6% obtained at 350 °C. As the reaction temperature approaches near-critical water condition (T_c 374 °C), the increase in *p*-xylene conversion to TPA was likely assisted by the availability of reactive oxygen species derived from hydrogen peroxide degradation. It was widely accepted that higher reactivity and yield observed in hydrogen peroxide assisted oxidation reaction system was closely related to the presence of OH and HO_2 free radicals (Croiset et al., 1997; Jiang et al., 2020). These short-lived radicals were responsible for activating the cracking of C-C and C=C bonds through a series of oxidation reactions leading to the TPA formation. In addition, higher reaction temperature also decreases the water dielectric constant (Chaudhary et al., 2021), which leads to a higher dissolution of non-polar compounds such as *p*-xylene in a high-temperature water medium.

Although the formation of the TPA was favoured in the subcritical water region, the yield was decreased under supercritical water temperature of 400 °C. Dunn & Savage (2002 & 2003) reported that the TPA was unstable hydrothermally at above 300 °C and was likely degraded to other by-products such as benzoic acid through decarboxylation reaction. Similar to the trend observed in this work, Kim et al. (2002) observed a maximum TPA yield at a subcritical water condition of 300 °C during *p*-xylene oxidation investigation in sub- and supercritical water conditions.

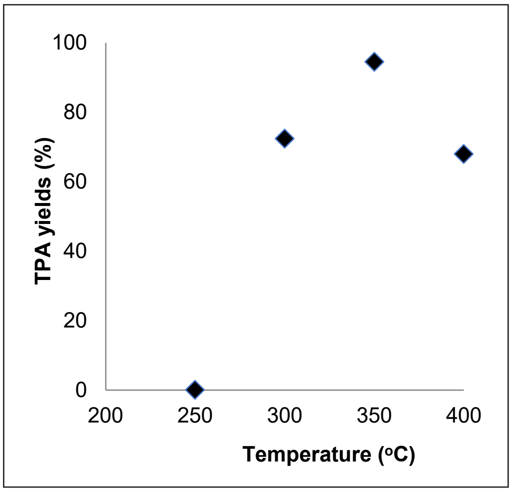

Figure 3. Effect of temperature on TPA yield. Reaction conditions: $MnBr_2$ catalyst loading 2.0 mL, water loading 2.5 mL, hydrogen peroxide loading 1.5 mL and 60 min reaction time.

Effect of Catalyst Loading

Figure 4 shows two distinctive trends for the TPA yields obtained at different $MnBr_2$ catalyst loadings and reaction temperatures. Firstly, the TPA yield obtained was maximum in sub- and supercritical water conditions using 2.0 mL MnBr2 catalyst loading. Secondly, the trend showed an increase in the TPA yield with increasing temperature under the subcritical water region, reaching a maximum of 350 °C. It is followed by a decrease in yields at the supercritical water temperature of 400 °C for all catalyst loadings investigated, mimicking the trend observed in Figure 3. An optimum condition was observed at 2.0 mL $MnBr_2$ catalyst loading and 350 °C reaction temperature.

During hydrothermal oxidation, *p*-xylene was transformed through a series of oxidation reactions starting with the production of *p*-tolualdehyde. It is then further oxidised to *p*-toluic acid and 4-carboxybenzaldehyde before being converted to the TPA. This pathway is limited by forming an oxidation-resistant *p*-toluic acid intermediate, which can be

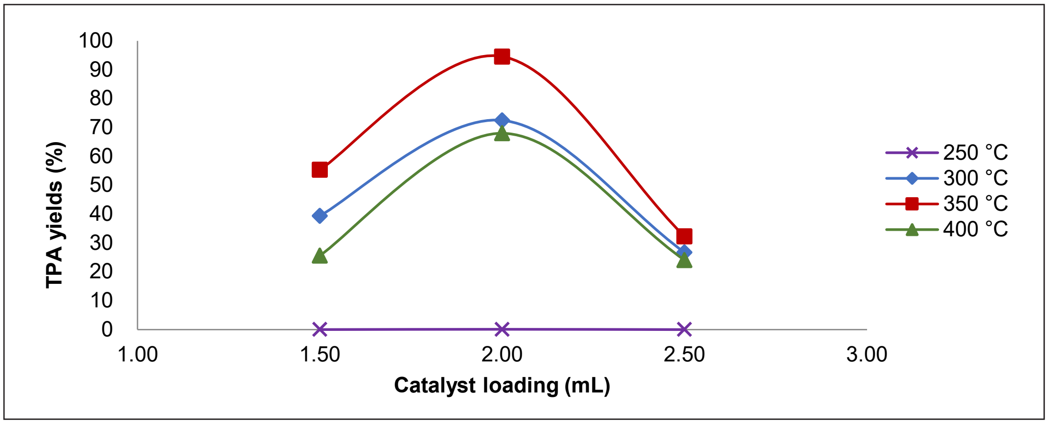

Figure 4. Effect of $MnBr_2$ catalyst loadings on TPA yields at different reaction temperatures. Water and hydrogen peroxide loadings were fixed at 2.5 mL and 1.5 mL, respectively. Reaction time 60 min.

overcome using catalysts such as $MnBr_2$. In the presence of a bromine initiator, the oxidation rate was enhanced, increasing the TPA yield (Holiday et al., 1998; Tomás et al., 2013). The trend observed in Figure 4 is similar to the works of Li and Li (2008), which found that an optimum condition for the TPA formation existed during catalytic hydrothermal oxidation of the *p*-xylene. The authors found that increasing the catalyst loading beyond the optimum condition will negatively affect the TPA yield. Dibromide radicals were formed in excess at high catalyst concentration during fast chain reactions leading to undesired benzylic bromides. This reaction reduces the concentration of the catalytic sites needed for the oxidation reactions.

Effect of an Oxidant Loading

The effect of hydrogen peroxide oxidant loadings was assessed at different reaction temperatures, as illustrated in Figure 5. The TPA yield obtained at the lower end of the reaction temperature investigated (250 °C) was below 1%, indicating *p*-xylene resistance to hydrothermal oxidation at low temperature. It is consistent with the previous results presented in Figures 3 and 4. By contrast, the TPA yields increase at a higher hydrothermal temperature of 350 °C and oxidant loading of 1.5 mL. The increase in *p*-xylene oxidation reactivity coincides with the degradation of hydrogen peroxide occurring at between 280–300 °C, which releases the OH and HO_2 radicals. It is thought that these radicals had a role in activating and increasing the reactivity of the reaction system. After the initial free radical activated reactions stage, the higher oxygen concentration was likely available in the hydrothermal system, allowing *p*-xylene and its subsequent intermediates to be oxidised to the TPA.

Similar to the trends observed in Figure 4, Figure 5 suggests an optimum condition for the TPA yields were obtained at 350 °C and an oxidant loading of 1.5 mL. A significant

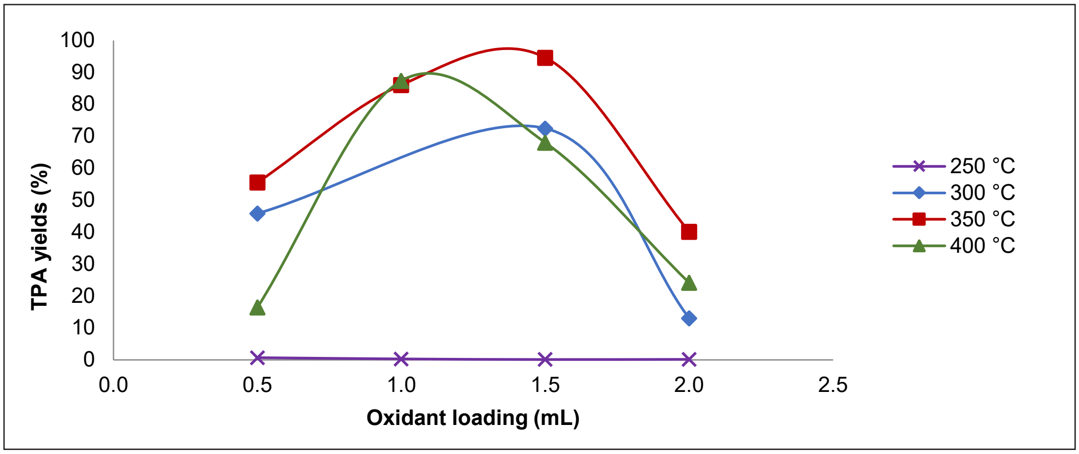

Figure 5. Effect of oxidant loadings on TPA yields at different reaction temperatures. Water and $MnBr_2$ catalyst loadings were fixed at 2.5 mL and 2.0 mL, respectively. Reaction time 60 min.

drop in the TPA yield can be observed at higher oxygen loading above the optimum condition. The trends show that the oxidative conversion of *p*-xylene requires a moderate reaction temperature of 300-350 °C due to the strong oxidant agent and the exothermic nature of the reaction. When a high reaction temperature of 400 °C was used together with a high oxidant concentration of above 1 mL, the combination may have induced multiple cleavages of *p*-xylene structure through radical intermediates leading to the transformation of *p*-xylene into unwanted liquid products and gases. In this regard, the *p*-xylene was either converted to other intermediates than the target TPA through oligomerisation reaction (Osada & Savage, 2009b) or experienced burning and coking (Dunn & Savage, 2005) when oxygen was present in excess at a high enough temperature.

Effect of Water Loading

Water loadings' effect was evaluated and conducted at the optimum temperature of 350 °C as previously determined. The water loading as a solvent was varied at 1.5 mL and 2.5 mL. As shown in Figure 6, a satisfactory TPA yield of around 94% was obtained using 2.5 mL water loading. The TPA yield was slightly reduced to 88% at lower water loading. The change in the TPA yields observed could be due to the water density effect. At higher water density, the

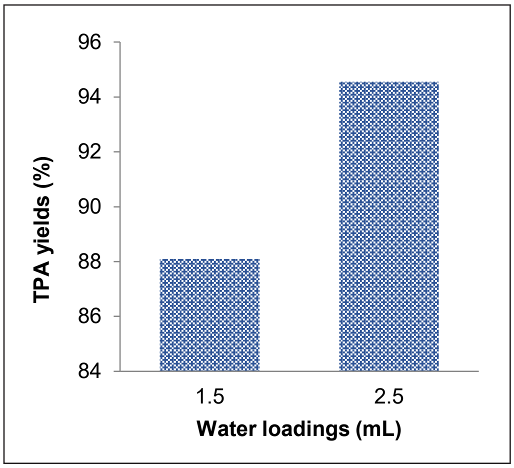

Figure 6. Effect of water loadings on TPA yields. Reaction conditions fixed at 1.5 mL hydrogen peroxide, 2.0 mL $MnBr_2$ catalyst, 350 °C and 60 min reaction time.

water solvent surrounds the reactant and thus facilitates the dispersion of the reactant for catalytic oxidation reaction to occur. The results indicate the viability of the hydrothermal medium as a replacement for AcOH solvent to produce the TPA.

p-Xylene Hydrothermal Oxidation Products Characterization

Figure 7 shows the FTIR spectra accumulated for products of *p*-xylene hydrothermal oxidation obtained at different temperatures. All spectra showed similar patterns with several identifiable peaks that characterised the *p*-xylene oxidation products at absorption bands between 1700 cm^{-1} and 1600 cm^{-1}. The appearance of the absorption band signal at 1738 cm^{-1} corresponds to the C=O stretching for carboxylic acid, while absorption bands 1740 cm^{-1}–1690 cm^{-1} match those of C=O stretching in ketones and aldehydes. The peak at 2970 cm^{-1} (between 3000 cm^{-1}–2500 cm^{-1}) corresponds to O-H stretching from carboxylic acid constituents. Other peaks ascribing to the vibrations of C-H bending (originating from benzene ring), C=C aromatic bending, and aromatic fingerprint region were detected at 3016 cm^{-1}, 1654.31 cm^{-1} and 707 cm^{-1} wavelengths, respectively. As seen in all spectra obtained, the reaction products were characterised by chemical functionalities associated with the TPA and other by-products. The spectra for the 250 °C sample showed lower peak intensities than higher temperature samples indicating a lower concentration of the respective functionalities. The low TPA confirms it yields at 250 °C reaction temperature.

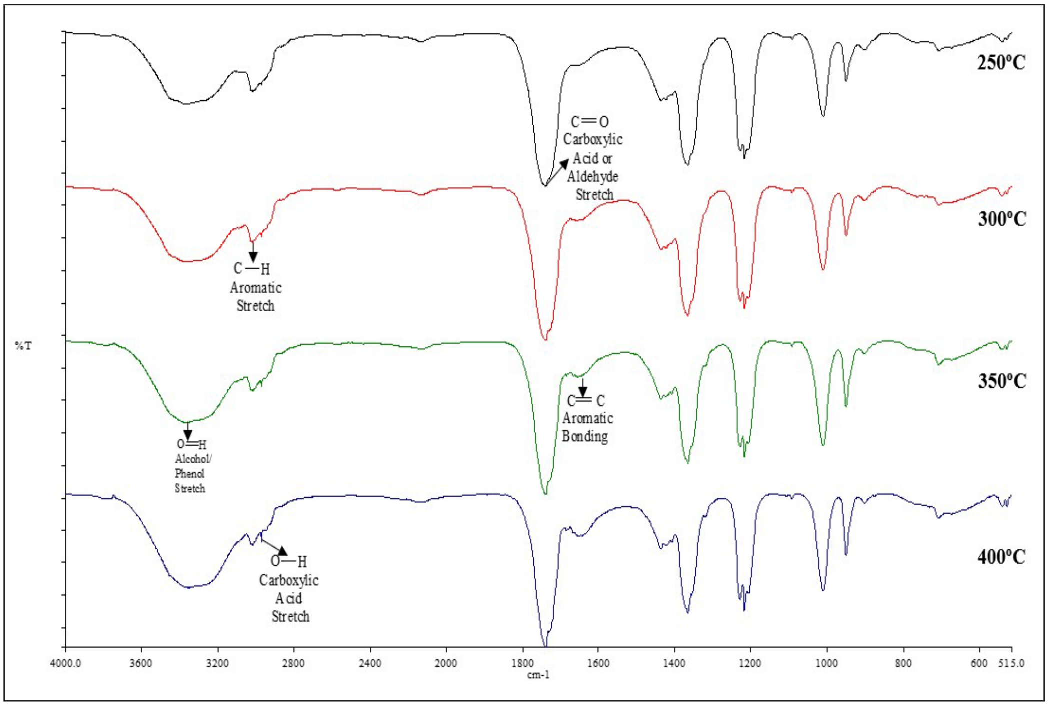

Figure 7. FTIR spectra of *p*-xylene hydrothermal oxidation products obtained between 250–400 °C.

Figures 8 to 10 show the GC-MS chromatograms for *p*-xylene hydrothermal oxidation reaction liquid products at 250-350 °C. The chromatograms tracked the evolution of reaction products (other than TPA, which HPLC analysed) as the reaction condition changed from subcritical to supercritical water temperatures. At 250 °C, *p*-tolualdehyde was the sole reaction product identified alongside the unreacted *p*-xylene indicating minimum *p*-xylene conversion had occurred at the lower end of the subcritical water temperature investigated. As the reaction temperature was raised to near-critical water conditions of 300 and 350 °C (Figures 9 and 10), a higher degree of *p*-xylene oxidation and degradation were observed. At these temperatures, the product mixture consisted of high proportions of oxygenated compounds such as *p*-tolualdehyde and 1,4-benzene dicarboxaldehyde, having a higher mass to charge ratio (m/z) than the starting *p*-xylene. Other constituents detected at lower intensities were benzene, 1,4-methylbenzyl methanol, and 1,4-hydroxymethyl benzaldehyde. The occurrence of compounds with carboxylic, hydroxyl, carbonyl and aldehyde chemical characteristics complimented the FTIR results. Their presence in the product mix suggested that the pathway for TPA synthesis using high-temperature water as a reaction medium resembles the pathway of the conventional AcOH solvent process (Tomas et al., 2013). The conventional pathway involves consecutive partial oxidation of methyl groups to form p-tolualdehyde, p-toluic acid and 4-carboxybenzaldehyde compounds as major intermediates.

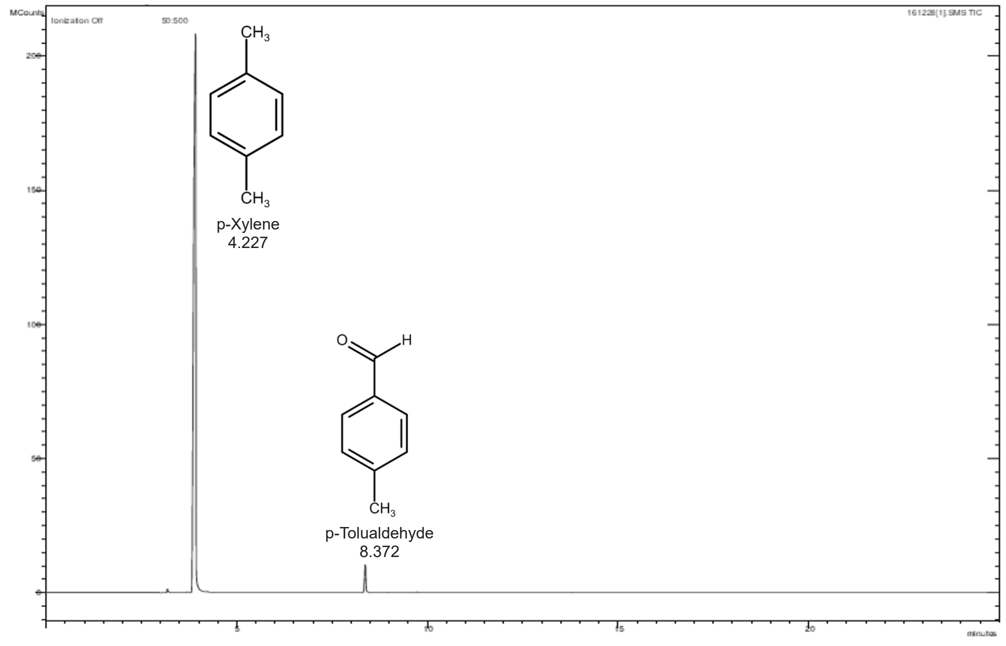

Figure 8. Products of *p*-xylene hydrothermal oxidation identified at 250 °C. Reaction conditions: $MnBr_2$ catalyst loading 2.0 mL, water loading 2.5 mL, hydrogen peroxide loading 1.5 mL and 60 min reaction time.

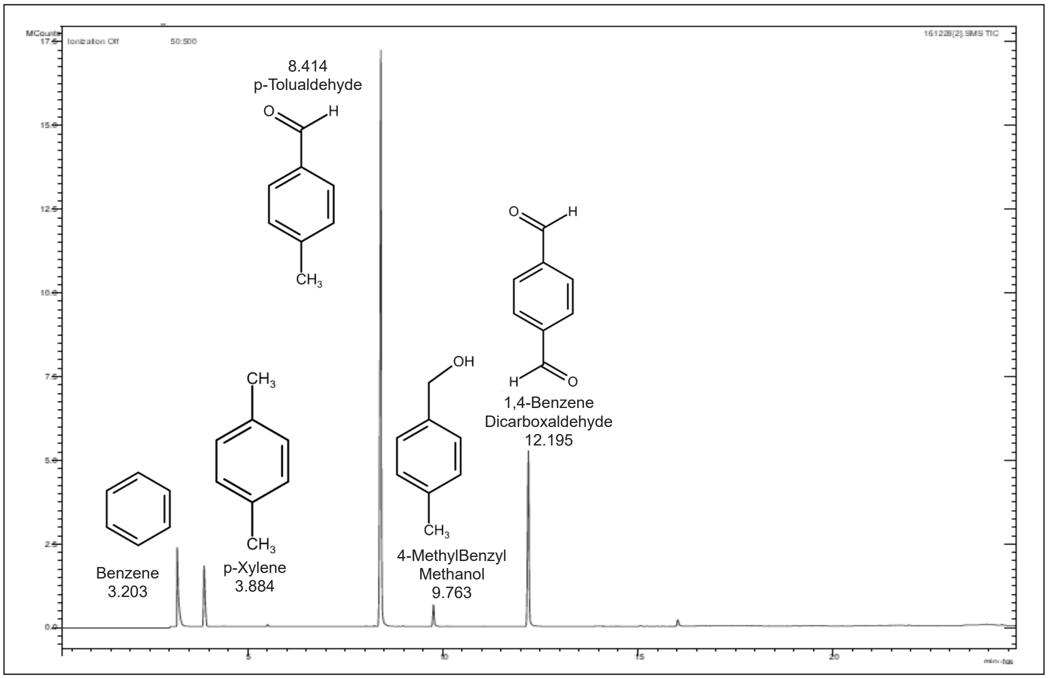

Figure 9. Products of *p*-xylene hydrothermal oxidation identified at 300 °C. Reaction conditions: $MnBr_2$ catalyst loading 2.0 mL, water loading 2.5 mL, hydrogen peroxide loading 1.5 mL and 60 min reaction time.

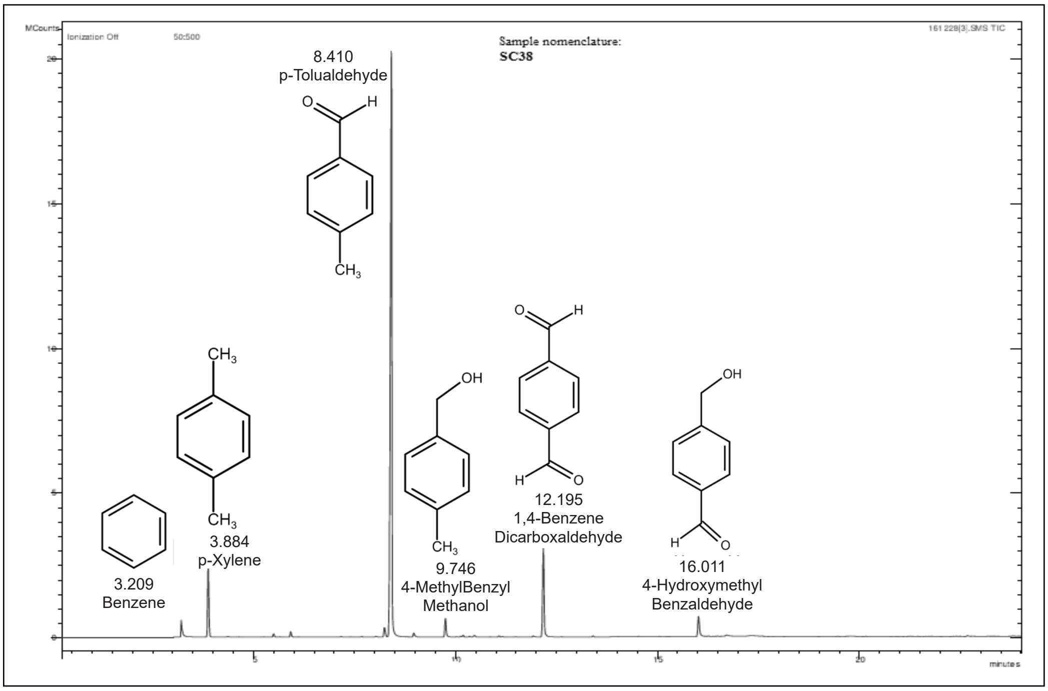

Figure 10. Products of *p*-xylene hydrothermal oxidation identified at 350 °C. Reaction conditions: $MnBr_2$ catalyst loading 2.0 mL, water loading 2.5 mL, hydrogen peroxide loading 1.5 mL and 60 min reaction time.

CONCLUSION

This study successfully evaluated the influence of hydrothermal process conditions (reaction temperature, catalyst loading, oxidant loading and water loading) on *p*-xylene conversion to TPA. The catalytic *p*-xylene conversion was promoted under subcritical water conditions with an optimum TPA yield of 94.6% obtained at 350 °C. Apparently, under catalytic subcritical water conditions, sufficient reactive oxygen species were available to initiate and support the *p*-xylene oxidation reactions leading to satisfactory yields of the TPA obtained. The results suggested the potential of the hydrothermal method as a promising alternative route for *p*-xylene oxidation to TPA as the main product. Replacing acetic acid with water as a solvent and reaction medium for the TPA synthesis has tremendous potential. Not only water is a green solvent, but hydrothermal could also present an economic TPA synthesis technology by eliminating the need for expensive acetic acid-water separation steps commonly formed during the reaction. Although the effectiveness of water as a medium for TPA synthesis was demonstrated in this work, further assessments on the diffusion of reactive species in high-temperature water and solvent cage effects which may cause the catalytic activity to drop, must be explored.

ACKNOWLEDGMENT

The authors thanked the School of Chemical Engineering, Universiti Teknologi MARA, and the Ministry of Higher Education Malaysia for FRGS research grants (600-RMI/FRGS 5/3 (25/2013).

REFERENCES

Byrappa, K., & Yoshimura, M. (2012). *Handbook of Hydrothermal Technology* (2nd Ed.). William Andrew.

Brunner, G. (2014). Reactions in hydrothermal and supercritical water. *Supercritical Fluid Science and Technology, 5,* 265-322. https://doi.org/10.1016/B978-0-444-59413-6.00005-4

Carr, A. G., Mammucari, R., & Foster, N. R. (2011). A review of subcritical water as a solvent and its utilisation for the processing of hydrophobic organic compounds. *Chemical Engineering Journal*, *172*(1), 1-17. https://doi.org/10.1016/j.cej.2011.06.007

Chaudhary, A., Dwivedi, A., & Upadhyayula, S. (2021). Supercritical fluids as green solvents. In *Handbook of Greener Synthesis of Nanomaterials and Compounds* (pp. 891-916). Elsevier. https://doi.org/10.1016/B978-0-12-821938-6.00028-1

Cocero, M. J. (2018). Supercritical water processes: Future prospects. *The Journal of Supercritical Fluids, 134*, 124-132. https://doi.org/10.1016/j.supflu.2017.11.018

Croiset, E., Rice, S. F., & Hanush, R. G. (1997). Hydrogen peroxide decomposition in supercritical water. *AIChE Journal*, *43*(9), 2343-2352. https://doi.org/10.1002/aic.690430919

Daud, A. R. M., Berrueco, C., Hellgardt, K., Millan, M., & Kandiyoti, R. (2021). Oxidative cracking of three to five-member ring polycyclic aromatic hydrocarbons in subcritical and supercritical water. *The Journal of Supercritical Fluids, 167*, Article 105050. https://doi.org/10.1016/j.supflu.2020.105050

Dunn, J. B., & Savage, P. E. (2002). Terephthalic acid synthesis in high-temperature liquid water. *Industrial & Engineering Chemistry Research*, *41*(18), 4460-4465. https://doi.org/10.1021/ie0107789

Dunn, J. B., Burns, M. L., Hunter, S. E., & Savage, P. E. (2003). Hydrothermal stability of aromatic carboxylic acids. *The Journal of Supercritical Fluids*, *27*(3), 263-274. https://doi.org/10.1016/S0896-8446(02)00241-3

Dunn, J. B., & Savage, P. E. (2005). High-temperature liquid water: A viable medium for terephthalic acid synthesis. *Environmental Science & Technology*, *39*(14), 5427-5435. https://doi.org/10.1021/es048575+

Eckert, C. A., & Chandler, K. (1998). Tuning fluid solvents for chemical reactions. *The Journal of Supercritical Fluids, 13*(1-3), 187-195. https://doi.org/10.1016/S0896-8446(98)00051-5

Falcon, H., Campos-Martin, J. M., Al-Zahrani, S. M., & Fierro, J. L. G. (2010). Liquid-phase oxidation of p-xylene using N-hydroxyimides. *Catalysis Communications*, *12*(1), 5-8. https://doi.org/10.1016/j.catcom.2010.07.010

Fraga-Dubreuil, J., & Poliakoff, M. (2006). Organic reactions in high-temperature and supercritical water. *Pure and Applied Chemistry, 78*(11), 1971-1982. https://doi.org/10.1351/pac200678111971

Holliday, R. L., Jong, B. Y., & Kolis, J. W. (1998). Organic synthesis in subcritical water: Oxidation of alkyl aromatics. *The Journal of Supercritical Fluids*, *12*(3), 255-260. https://doi.org/10.1016/S0896-8446(98)00084-9

Jiang, Z., Li, Y., Wang, S., Cui, C., Yang, C., & Li, J. (2020). Review on mechanisms and kinetics for supercritical water oxidation processes. *Applied Sciences, 10*(14), Article 4937. https://doi.org/10.3390/app10144937

Kim, Y. L., Kim, J. D., Lim, J. S., Lee, Y. W., & Yi, S. C. (2002). Reaction pathway and kinetics for uncatalyzed partial oxidation of p-xylene in sub-and supercritical water. *Industrial & Engineering Chemistry Research*, *41*(23), 5576-5583. https://doi.org/10.1021/ie010952t

Kruse, A., & Dinjus, E. (2007a). Hot compressed water as reaction medium and reactant: Properties and synthesis reactions. *The Journal of Supercritical Fluids*, *39*(3), 362-380. https://doi.org/10.1016/j.supflu.2006.03.016

Kruse, A., & Dinjus, E. (2007b). Hot compressed water as reaction medium and reactant: 2. Degradation reactions*. The Journal of Supercritical Fluids*, *41*(3), 361-379. https://doi.org/10.1016/j.supflu.2006.12.006

Kwak, J. W., Lee, J. S., & Lee, K. H. (2009). Co-oxidation of p-xylene and p-toluic acid to terephthalic acid in water solvent: Kinetics and additive effects. *Applied Catalysis A: General, 358*(1), 54-58. https://doi.org/10.1016/j.apcata.2009.01.037

Lee, H. L., Chiu, C. W., & Lee, T. (2021). Engineering terephthalic acid product from recycling of PET bottles waste for downstream operations. *Chemical Engineering Journal Advances*, *5*, Article 100079. https://doi.org/10.1016/j.ceja.2020.100079

Li, K. T., & Li, S. W. (2008). CoBr2-MnBr2 containing catalysts for catalytic oxidation of p-xylene to terephthalic acid. *Applied Catalysis A: General*, *340*(2), 271-277. https://doi.org/10.1016/j.apcata.2008.02.025

Li, M., Niu, F., Zuo, X., Metelski, P. D., Busch, D. H., & Subramaniam, B. (2013). A spray reactor concept for catalytic oxidation of p-xylene to produce high-purity terephthalic acid. *Chemical Engineering Science*, *104*, 93-102. https://doi.org/10.1016/j.ces.2013.09.004

Osada, M., & Savage, P. E. (2009a). Terephthalic acid synthesis at higher concentrations in high-temperature liquid water. 1. Effect of oxygen feed method. *AIChE Journal*, *55*(3), 710-716. https://doi.org/10.1002/aic.11718

Osada, M., & Savage, P. E. (2009b). Terephthalic acid synthesis at higher concentrations in high-temperature liquid water. 2. Eliminating undesired byproducts. *AIChE Journal*, *55*(6), 1530-1537. https://doi.org/10.1002/aic.11761

Pérez, E., Fraga-Dubreuil, J., García-Verdugo, E., Hamley, P. A., Thomas, M. L., Yan, C., & Poliakoff, M. (2011). Selective aerobic oxidation of para-xylene in sub-and supercritical water. Part 2. The discovery of better catalysts. *Green Chemistry, 13*(9), 2397-2407. https://doi.org/10.1039/C1GC15138J

Savage, P. E. (2009). A perspective on catalysis in sub-and supercritical water. *The Journal of Supercritical Fluids*, *47*(3), 407-414. https://doi.org/10.1016/j.supflu.2008.09.007

Tomás, R. A., Bordado, J. C., & Gomes, J. F. (2013). p-xylene oxidation to terephthalic acid: A literature review oriented toward process optimization and development. *Chemical Reviews, 113*(10), 7421-7469. https://doi.org/10.1021/cr300298j

Vakros, J. (2021). Recent advances in cobalt and related catalysts: From catalyst preparation to catalytic performance. *Catalysts*, *11*(4), Article 420. https://doi.org/10.3390/catal11040420

Walt, P. (2020). A chemical model for the Amoco “MC” oxygenation process to produce terephthalic acid. In D. W. Blackburn (Ed.), *Catalysis of Organic Reactions* (pp. 321-346). CRC Press. https://doi.org/10.1201/9781003066446

Xu, L., Chen, D., Jiang, H., & Yuan, X. (2020). Efficient oxidation of p-xylene to terephthalic acid by using N, N-dihydroxypyromellitimide in conjunction with Co-benzenetricarboxylate. *Applied Catalysis A: General*, *599*, Article 117569. https://doi.org/10.1016/j.apcata.2020.117569