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Supercritical Water Oxidation of 3-Methylpyridine with Propylene Glycol

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The destruction of 3-methylpyridine by supercritical water oxidation (SCWO) using propylene glycol (PG) and isopropyl alcohol (IPA) as co-fuels in a plug flow reactor was carried out. Hydrogen peroxide was the oxygen source. All the experiments were carried out at 25 MPa and a range of temperatures from 425-525 ºC. The residence times range from 6 s to 14 s. Results were presented in terms of total organic carbon (TOC) as a function of time with various process parameters. The findings support the positive effect that propylene glycol has on the destruction of 3-methylpyridine, where TOC removal is ≥ 97.5% at 525 ºC and 14 s. The maximum TOC removal efficiency is 93% at 425 ºC, 14 s, and the [propylene glycol]/[3-methylpyridine]$_o$ ratio of 3. The removal efficiency of nitrogen in the presence of propylene glycol reaches 89% at 525 ºC and 10 s. The oxidant ratio also has a positive effect on the removal of TOC in the three systems. Addition of propylene glycol causes a significant development in the ratio at 425 ºC, more so than when isopropyl alcohol was added. This is due to two hydroxyl groups in propylene glycol oxidation that enhance the reaction by generating various free radicals.

Keywords: Supercritical water oxidation, 3-Methylpyridine, Propylene glycol, Isopropyl alcohol, Total organic carbon.

INTRODUCTION

Supercritical water oxidation (SCWO) is a commonly used method of mineralizing a wide range of organic hazardous wastes to water and carbon dioxide. The physical and chemical properties of water change significantly above its critical temperature of 374 ºC and pressure of 22.1 MPa. Due to significantly weakened hydrogen bonds, water becomes an excellent solvent for organic compounds and gases, forming a one-phase supercritical solution with enhanced heat and mass transfer properties. Consequently, the reaction of organics with oxygen in supercritical water (SCW) is characterized by a very short residence time [1,2].

SCWO technology is regarded as highly advantageous compared to incineration (the usual process for the destruction of non-recyclable hazardous wastes). The incineration process takes place between 900 ºC and 1100 ºC. This leads to several disadvantages including toxic gas emissions (NO_x, SO_x, metal vapors, furans and dioxins) and fly ash. Additionally, the need to reduce water content makes incineration energy-intensive and inefficient, especially if the organic substance concentration is less than 30%. Incineration also produces significant solid residues or ashes that are sent to landfills. SCWO is clean, environmentally friendly technology with no toxic emissions and little solid residue production. This makes SCWO a competitive technology for the destruction of non-recyclable mixed organic wastes. However, SCWO technology has some disadvantages that have manifested on a worldwide commercial scale. The main obstacles that face SCWO development are corrosion and plugging [3,4].

Nitrogen-containing hydrocarbons are one of the essential classes of hazardous waste and found in the effluents of various sources of hazardous wastes such as medical, pharmaceutical, municipal and petrochemical wastes. Nitrogen-containing organics are particularly challenging due to the formation of biorefractory intermediates like ammonia. Ammonia is difficult to destroy and is detrimental to the environment and human health. Literature contains several examples where hydrothermal oxidation has been used to destroy models of chemical substances, such as aniline, ammonia, 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) and dimethyl formamide (DMF) [5-7]. In addition, various examples using SCWO technology to destroy the various types of wastes such as sludge of domestic waste, molasses wastewater, leachate of the landfill and the fly ash of incineration [8,9].

3-Methylpyridine (3MP) is the model of a heterocyclic, aromatic nitrogen-containing hazardous hydrocarbon selected for this study and considered an important compound in several industries [10,11]. This work investigates the degradation of 3-methylpyridine for several reasons, one being that there are a limited number of studies on the degradation of 3-methylpyridine. Therefore, treatment of degradation of 3-methylpyridine by SCWO will contribute to the knowledge of it, as well as provide novel kinetics data on the behaviour of this compound in different conditions. The majority of the existing studies on the degradation of 3-methylpyridine do not achieve complete removal of 3-methylpyridine. For example, wastewater containing 3-methylpyridine was degraded by the ozonation as a pre-treatment to reduce the cost of biological treatment. This study shows that the removal efficiency of 3-methylpyridine is 75% at 80 min [10]. In another study, 3-methylpyridine treated with activated carbon (coconut shell fibers). When the pH solution increases from 2 to 4, the removal efficiency of 3-methylpyridine was also enhanced. Moreover, when the temperature increased from 10 ºC to 40 ºC, the removal efficiency also increased as well. The optimum maximum removal efficiency was > 90% at 30 h and 25 ºC [11]. However, two units of treatment need to be applied to avoid the harmful effects of 3-methylpyridine on the environment and public health.

Despite its importance as an industrial compound, if 3-methylpyridine is present in effluents, it can cause significant environmental problems. Ominously, the slow decomposition of 3-methylpyridine generates ammonia, which also affects the environmental ecosystems. Simultaneously, 3-methylpyridine decomposition generates other compounds such as nitrite and nitrate, can cause diseases, such as cancer, methemoglobinemia, enlargement of thyroid gland and diabetes mellitus, when present in high concentration [12,13].

Propylene glycol (PG) is used as a co-fuel in this study since it contains two hydroxyl groups. Most of the SCWO researchers choose monohydric alcohols as co-fuels. Ploeger *et al.* [14] increased the conversion of ammonia by using ethanol, Oe *et al.* [15] reported the effect of methanol on the conversion of ammonia, while Al-Duri *et al.* [16] studied the influence of isopropyl alcohol (IPA) on SCWO of 1,8-diazobicyclo[5.4.0]-undec-7-ene) and its intermediate compounds. In these works, monohydric alcohols were the main co-fuel used in SCWO. Thus, considering about the facts, propylene glycol is used as co-fuel in this work in order to study the effect of dihydric alcohol on the treatment of organic hazardous wastes under supercritical conditions. Using isopropyl alcohol (IPA) as a co-fuel will allow the comparison of the effects of different co-fuels on total organic carbon (TOC) and nitrogen removal.

EXPERIMENTAL

All the chemicals *viz.* 3-methylpyridine (3MP), propylene glycol (PG, ≥ 99.5%), isopropyl alcohol (IPA, ≥ 99.5%), hydrogen peroxide (≥ 30% aqueous solution) were purchased from Sigma-Aldrich, UK.

Experimental procedure: Fig. 1 shows the SCWO process diagram was built at the University of Birmingham. Oxidant and organics were pumped through two high performance liquid chromatography (HPLC) pumps (Jasco/PU-2086) to 25 MPa and preheated through coiled-pipe heaters to the reaction temperature, before they were mixed at a cross union and entered the plug-flow reactor. The reactor was a 3.175 mm nominal size stainless steel (SS-316/316L, 1.397 mm inner diameter) pipe having 9 m in length, so the reactor volume was 13.795 mL. The reactor exit stream was cooled in a heat exchanger then depressurized *via* a manual back pressure regulator (BP66, GO) before separation into gas and liquid streams. Liquid products were taken for TOC analysis. In addition, co-fuel was premixed with 3-methylpyridine, before it was fed into the SCWO system at the desired amount and concentration. Temperatures of the input and output reactor were measured by thermocouples.

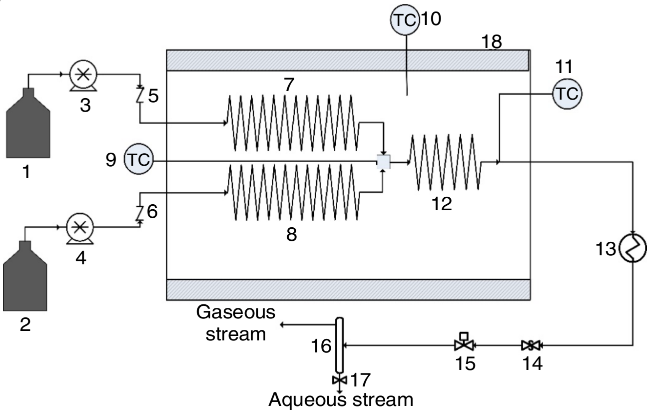

Fig. 1. Process diagram of the SCWO apparatus; 1 = Oxidant tank, 2 = Organic tank, 3,4 = HPLC pumps, 5,6 = Check valves, 7 = Pre-heater (oxidant), 8 = Pre-heater (organic), 9,10,11 = Thermocouple, 12 = Reactor, 13 = Cooler, 14 = Relief valve, 15 = Back pressure regulator, 16 = Separator phase, 17 = Valve, 18 = Furnace

Experimental conditions: Experimental conditions in which the initial concentration of 3-methylpyridine (3MP) at different temperatures was 4 mM, and the molar ratio [Co-fuel]/[3MP]$_o$ was 1, as shown in Table-1.

TABLE-1
EXPERIMENTAL CONDITIONS USED IN THIS WORK

Variable	Experimental values
Temperature (°C)	425, 450, 475, 500, 525
Oxidant ratio (nSR)	0.75, 1, 1.5, 2
Residence time (s)	6, 8, 10, 12, 14
Initial 3MP concentration (mM)	2, 4, 6, 8
[PG]/[3MP]$_o$ ratio	0.5, 1, 1.5, 2, 2.5, 3
[IPA]/[3MP]$_o$ ratio	0.5, 1, 1.5, 2, 2.5

All the experiments were conducted at 25 MPa. The main conditions in this study were 425 ºC, the [Co-fuel]/[3MP]$_o$ ratio = 1.0, the oxidant dosage was at stoichiometric ratio (nSR = 1.0), and the initial concentration of 3-methylpyridine = 4 mM. The amount of oxygen required for complete destruction was calculated depending on eqns. 1-3 as follows:

$$C_6H_7N + 7.75O_2 \longrightarrow 6CO_2 + 3.5H_2O + 0.5N_2 \quad (1)$$

$$C_3H_8O_2 + 4O_2 \longrightarrow 3CO_2 + 4H_2O \qquad (2)$$

$$C_3H_8O + 4.5O_2 \longrightarrow 3CO_2 + 4H_2O \qquad (3)$$

The stoichiometric ratio (SR) is the molar flow rate of oxygen which is delivered to achieve complete destruction of the organic substance (eqns. 1-3). In Table-1, n refers to the multiples of the SR used in the reaction, hence $n > 1$ refers to oxygen excess, $n < 1$ refers to oxygen deficiency and $n = 1$ refers to stoichiometric amounts of oxygen.

Water formed was ≥ 99%, hence the thermodynamic properties of water under supercritical conditions were applied to the relevant calculations. Due to the furnace being isothermal, it was assumed that the thermodynamic properties of water remained the same inside the reactor. Each residence time was calculated based on the total flow rate of oxidants and organics and the volume of the reactor at different supercritical conditions.

RESULTS AND DISCUSSION

Effects of system conditions : Foster Wheeler system was used to treat shipboard wastes and adapted the design by manufacturing a new reactor, using pure oxygen as an oxidant and new pumps for a high flow rate. In the Foster Wheeler system, propylene glycol was pumped in separately and premixed with the waste to enhance the oxidation conditions [17]. In current study, isopropyl alcohol and propylene glycol were applied to degrade 3-methylpyridine. It is of interest to investigate the effect of isopropyl alcohol and propylene glycol on the removal efficiency of total organic carbon (TOC) and to assess the feasibility of using dihydric alcohol to improve SCWO.

Effect of propylene glycol: Upon oxidation under supercritical conditions, propylene glycol generated various free radicals with powerful oxidation ability such as $HO^•$ and $HO_2^•$. These radicals attacked organic molecules and combined with the free radicals from hydrogen peroxide to increase the mineralization of organic substances to water, carbon dioxide and nitrogen. Díaz *et al*. [18] showed the oxidation of propylene glycol at 400-500 K and estimated the reaction pathways that produced free radicals under low pressure.

Effect of [co-fuel]/[3MP]$_o$ ratio: The effect of changing the [co-fuel]/[3MP]$_o$ ratio was investigated and its effect of propylene glycol on enhancing the SCWO performance was also studied. The experimental results showed a better rate of TOC removal efficiency when the concentration of co-fuel was increased. The removal of TOC was more efficient with a higher [co-fuel]/[3MP]$_o$ ratio (Fig. 2), which reflects the faster rate of reaction due to the generation of free radicals from co-fuel during the oxidation [19,20].

Under supercritical conditions, isopropyl alcohol decomposition was less than the decomposition of methanol and ethanol [21]. Consequently, both hydroxyl groups in propylene glycol contributed an higher increase in the reaction rate as compared to ethanol or methanol and results in the generation of active free radicals during the oxidation of propylene glycol. Thus, the removal efficiency enhanced from 68.5% at isopropyl alcohol ratio of 0.5% to 81.0% at the same propylene glycol ratio. Therefore, an increased propylene glycol ratio would enhanced the TOC conversion at 425 ºC, and this increase would increase the degradation of byproducts.

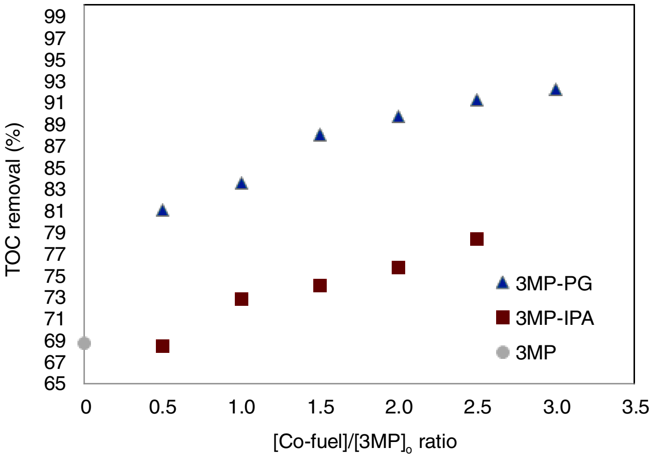

Fig. 2. Effect of various [co-fuel]/[3MP]$_o$ ratios on TOC removal % at 425 °C, SR of 1, 4 mM 3MP and 10 s

The yield of NH_4-N was low in the fuel and fuel-free systems because nitrogen was released as a gas. According to Yang *et al.* [22] N_2 and NH_3 are the main products of 3-methylpyridine during oxidation. Trace amount of NO_2^- was also present in the fuel-free, isopropyl alcohol and propylene glycol systems. The occurrence of NO_3^- in the propylene glycol system illustrates the advantage of propylene glycol, because NO_3^- is a byproduct of the oxidation of ammonia. Therefore, propylene glycol had a positive influence on the ammonia that converted to NO_3^- at 425 ºC. The effect of co-fuel ratio on nitrogen species is shown in Fig. 3. The efficiency of nitrogen removal clearly illustrates the better effects of propylene glycol and isopropyl alcohol.

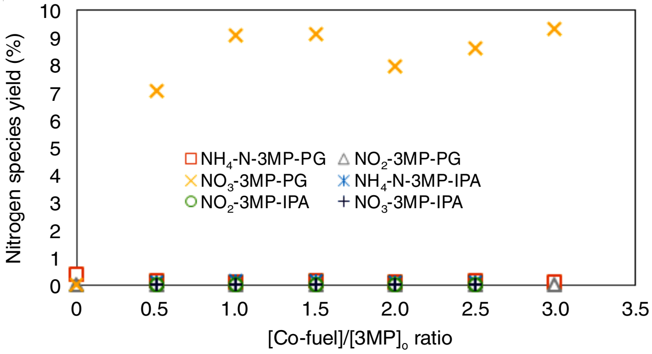

Fig. 3. Nitrogen species yield as a function of various [co-fuel]/[3MP] ratios at 425 °C, SR of 1, 4 mM 3MP and 10 s

Effect of co-fuel ratio: The effect of co-fuel ratio on the efficiency of nitrogen removal is shown in Fig. 4. Nitrogen removal efficiency was improved by an increase in the ratio of propylene glycol when compared with the isopropyl alcohol at different ratios. The improvement in the nitrogen removal corresponds with the increasing concentration of the co-fuel. For example, the nitrogen removal efficiency increased from 80% at 0.5 ratio of propylene glycol to 88% at 3 ratio of propylene glycol. Simiarly, the removal efficiency of nitrogen also improved from 77.5% with isopropyl alcohol to 80% with propylene glycol at the co-fuel ratio of 0.5.

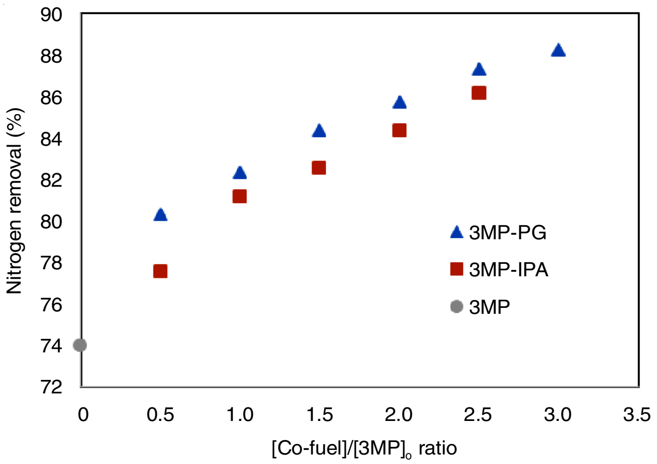

Fig. 4. Nitrogen removal % as a function of various [co-fuel]/[3MP]$_o$ ratios at 425 °C, SR of 1, 4 mM 3MP and 10 s

The concentration of propylene glycol from 0 to 12 mM was increasing and boosted the removal of nitrogen from 74% (in fuel-free system) to 88%, at a propylene glycol ratio of 3, and 10 s. An increase in the nitrogen removal efficiency demonstrated a significant factor in the role of propylene glycol ratio. Thus, the degradation of 3-methylpyridine and its byproducts at 425 ºC was an essential step in improving the performance of SCWO while using propylene glycol.

Effect of temperature: The effect of various temperatures on the degradation of 3-methylpyridine in fuel-free and co-fuel systems is displayed in Fig. 5. In fuel-free system, the effect of temperature was observed on the TOC removal efficiency. For example, at 10 s, the TOC conversion increased from 68.80% at 425 ºC to 90.70% at 525 ºC. This enhancement was a result of the increase in the rate of the reaction and an increase in the generation of free radicals at high temperature. When propylene glycol was added, the results were consistent with the results of fuel-free system. Moreover, in the presence of IPA, the efficiency of TOC removal were also consistent with the increased temperatures, but the enhancement of TOC removal in the presence of propylene glycol is remarkable. This result confirmed that propylene glycol is a competitive co-fuel with isopropyl alcohol, methanol and ethanol in SCWO.

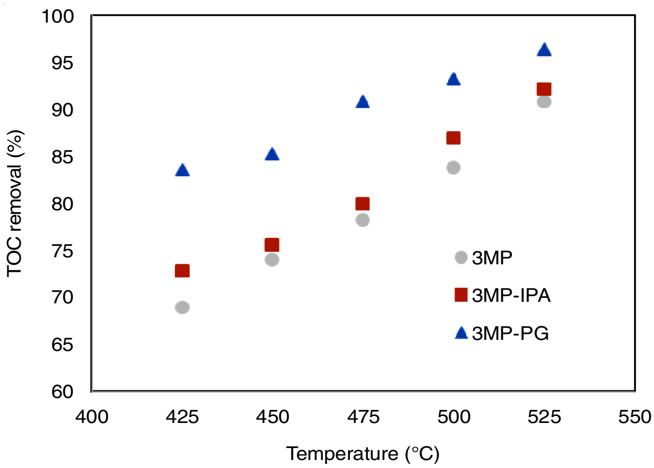

Fig. 5. Effect of operating temperature on TOC removal % at 4 mM 3MP, 4 mM PG, 4 mM IPA, 10 s and SR of 1

The effects of temperature on nitrogen species in three systems at 10 s are shown in Fig. 6. The main oxidative by-products of 3-methylpyridine are NH_4-N and NO_3^-. It was also observed that as temperature increased, so did the yield of NH_4-N, but the yield of NH_4-N in the presence of co-fuel was slightly less than the yield of NH_4-N in the absence of co-fuel. The yield of NO_3^- with propylene glycol was higher than the yield of NO_3^- in the fuel-free and the isopropyl alcohol systems at 425 ºC. The yield of NO_3^- decreased with increased temperature. Two reasons are attributed for this increase first, higher conversion of 3-methylpyridine led to an increased yield of NH_4-N, while ammonia is oxidized to NO_3^- (minor product) and N_2 (major product) [23]. The second reason is that NO_3^- and NO_2^- occurred with the increase in the oxidant ratio [24].

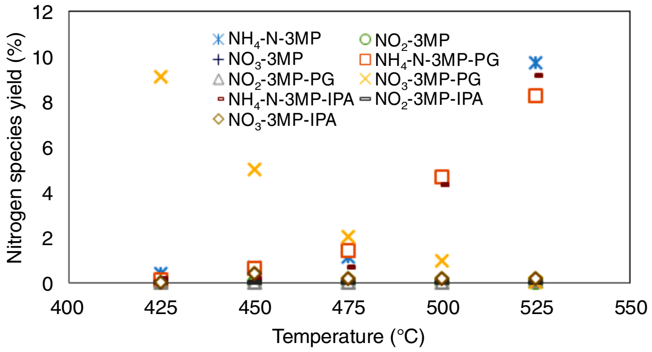

Fig. 6. Effect of operating temperature on nitrogen species at 4 mM 3MP, 4 mM PG, 4 mM IPA, 10 s and SR of 1

Effect of temperature: The effect of temperature on the nitrogen removal efficiency is displayed in Fig. 7. The influence of various temperatures and co-fuel on nitrogen removal seems to be significant. For example, the nitrogen removal efficiency improved from 74.0% at 425 ºC to 82.0% at 525 ºC in the fuel-free system. The effect of propylene glycol on the nitrogen removal was also optimistic as the removal efficiency increased from 74.0% (fuel-free system) to 82.0% at 425 ºC (3MP-PG system). In the presence of isopropyl alcohol, the nitrogen removal was also improved by increasing the temperature, but the better choice between the propylene glycol and isopropyl alcohol remained. The addition of propylene glycol confirmed its significant effect on the nitrogen removal due to the rise in reaction rate. In addition, the addition of two co-fuels helped to add heat to the reaction [21]. The maximum removal of nitrogen was 89% at 525 ºC in the presence of propylene glycol.

Effect of oxidant ratio (nSR): The effect of oxidant ratio (nSR) on the TOC removal efficiency and nitrogen species in the absence and presence of co-fuel is demonstrated in Figs. 8 and 9, respectively. Generally, the oxidant ratio has significant effect on TOC conversion and nitrogen byproducts when it is increased from 0.75 SR to 2 SR in three systems. Several studies have also illustrated the effect of the oxidant ratio on the conversion of DMF, quinoline and DBU [7,25].

The present study demonstrated that TOC conversion depends on the stoichiometric ratio (SR) and it improved the TOC removal percentage at 10 s from 63.80% at 0.75 SR to 86.50% at 2 SR in the fuel-free system. This was due to the

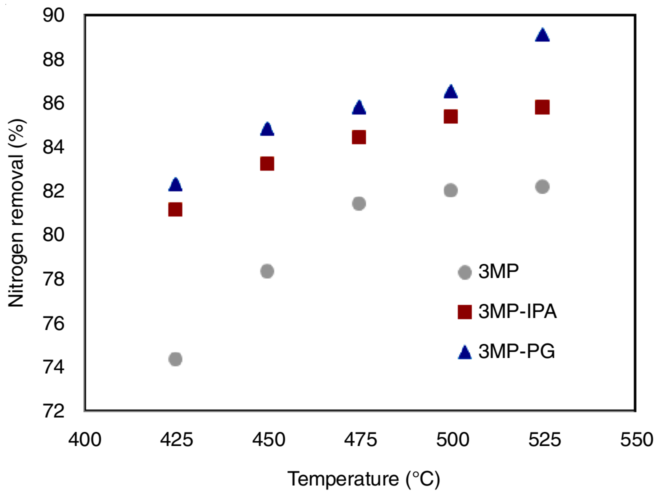

Fig. 7. Effect operating temperature on nitrogen removal % at 4 mM 3MP, 4 mM PG, 4 mM IPA, 10 s and SR of 1

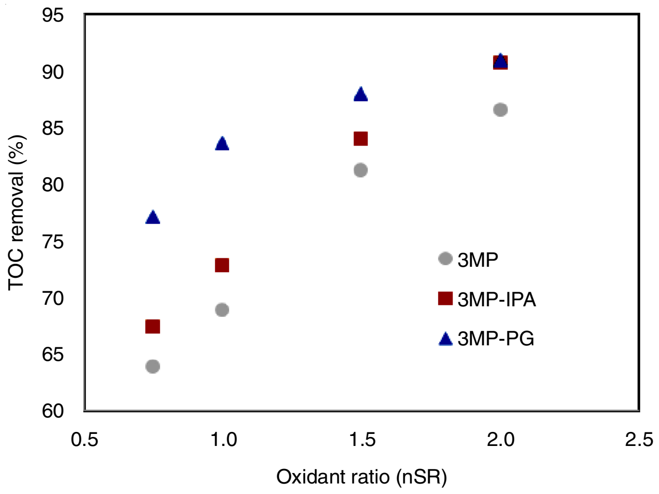

Fig. 8. Effect oxidant ratio on TOC removal % at 425 °C, 4 mM 3MP, 4 mM PG, 4 mM IPA and 10 s

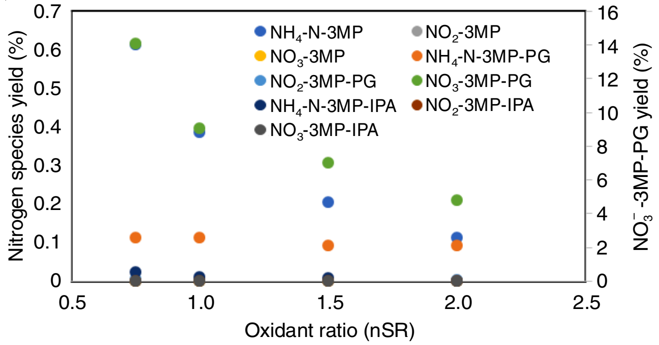

Fig. 9. Effect oxidant ratio on nitrogen species at 425 °C, 4 mM 3MP, 4 mM PG, 4 mM IPA and 10 s

generation of free radicals from oxygen reactions under SCWO conditions [25]. The oxidant ratio (1 SR) was not enough to degrade 3-methylpyridine at 425 ºC. Consequently, increasing the oxidant ratio and temperature would improve the TOC conversion.

The propylene glycol as co-fuel had a affirmative effect on the TOC removal efficiency, which was higher when the amount of oxidant increased. For example, the TOC conversion increased from 63.8% (fuel-free system) to 77.0% (3MP-PG system) at 0.75 SR. The effect of propylene glycol and oxidant ratio on the TOC removal efficiency is shown in Fig. 8. In the presence of isopropyl alcohol, TOC removal efficiency achieved maximum at 67.0% at 0.75 SR. These results demonstrated that propylene glycol played an essential role when compared with isopropyl alcohol. Even though an increased oxidant ratio contributed to an enhancement in TOC conversion, however, the higher amount of oxygen could generate N_2O [16].

Effect of oxidant ratio: The effect of oxidant ratio on the nitrogen species is displayed in Fig. 9. The yield of nitrate/nitrite as byproducts was low. This result confirmed that nitrogen in 3-methylpyridine converted mainly to nitrogen. In the presence of propylene glycol, the yield of NO_3^- decreased from 14% at 0.75 SR to 4.7% at 2 SR, while the yield of NO_3^- was low in both a fuel-free and 3MP-IPA systems. Although the yield of NO_3^- was low, the presence of NO_3^- illustrated the oxidation of NO_2^- and/or NH_4-N due to the further degradation of 3-methylpyridine [23]. The impact of propylene glycol is significant when compared to the effect of isopropyl alcohol.

Fig. 10 demonstrates that the higher nitrogen removal efficiency depended on increased oxidant ratio. The efficiency of nitrogen removal was improved by increasing the oxidant ratio from 0.75 SR to 2 SR in the absence and presence of co-fuel. The effect of co-fuels contributed significantly to an improvement in nitrogen removal. For example, the nitrogen removal efficiency was 68.9% in the fuel-free system and 76.8% in the 3MP-PG system at 0.75 SR. In 3MP-IPA system, it was 76.0% at the same oxidant ratio. These results illustrated the positive effect of propylene glycol and isopropyl alcohol on the nitrogen removal. Several researchers have also demonstrated the similar influence of isopropyl alcohol on nitrogen removal under supercritical conditions [16,21].

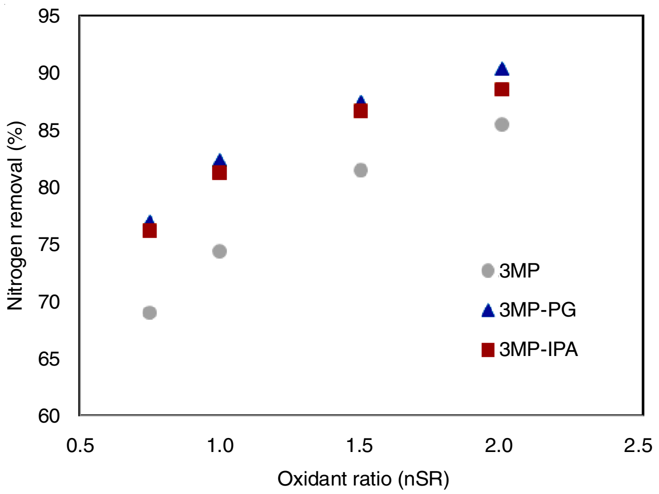

Fig. 10. Effect oxidant ratio on nitrogen removal efficiency at 425 °C, 4 mM 3MP, 4 mM PG, 4 mM IPA and 10 s

Conclusion

The destruction of 3-methylpyridine by supercritical water oxidation (SCWO) was successfully achieved using propylene glycol and isopropyl alcohol as co-fuels. In addition, TOC and nitrogen removal efficiencies were enhanced by using propylene glycol. At 425 ºC and after 10 s, TOC and nitrogen removal efficiencies were improved from 68.8% and 74.0% (in fuel-free system) to 83.5% and 82.0% (in 3MP-PG system), respectively. The enhancement of TOC removal percentage was experimentally observed at different propylene glycol ratios, temperatures and oxidation ratios.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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