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# Catalytic supercritical water gasification of plastics with supported RuO<sub>2</sub>: A potential solution to hydrocarbons–water pollution problem

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## ABSTRACT

Here we report on a potential catalytic process for efficient clean-up of plastic pollution in waters, such as the Great Pacific Garbage Patch (GPGP). Detailed catalytic mechanisms of RuO<sub>2</sub> during supercritical water gasification of common polyolefin plastics including low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PP) have been investigated in a batch reactor at 450 °C for 60 min. All four plastics gave very high carbon gasification efficiencies (CGE) and hydrogen gasification efficiencies (HGE). Methane was the highest gas component, with a yield of up to 37 mol kg<sup>-1</sup> LDPE using the 20 wt% RuO<sub>2</sub> catalyst. Evaluation of the gas yields, CGE and HGE revealed that the conversion of PS involved thermal degradation, steam reforming and methanation; whereas hydrogenolysis was a possible additional mechanism during the conversion of aliphatic plastics. The process has the benefits of producing a clean-pressurized methane-rich fuel gas as well as cleaning up hydrocarbons-polluted waters.

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## 1. Introduction

Supercritical water technologies (SCWT) are suitable for the processing of feedstock with high moisture contents into useful products. However, they can also be applied to 'dry' feedstocks because during supercritical water processes, water acts as medium as well as a reactant (Savage, 1999; Kruse, 2008). This presents the possibility of applying SCWT to 'dry' feedstocks such as plastics wastes (Park and Tomiyasu, 2003; Su et al., 2004; Tan et al., 2014; Goto, 2010). Supercritical water is completely miscible with common gases. It also has the ability to solubilize organic compounds, including those that are insoluble in ambient water due to its special properties, particularly the decreased dielectric constant and density (Savage, 1999; Kruse and Vogel, 2008). Among the SCWT, supercritical water gasification (SCWG) is suitable for converting

organic feedstocks to valuable simple gases such as hydrogen and methane. The simplicity of post-processing or utilization of the pressurized gas products makes SCWG an attractive technology.

In particular, SCWG can be applied to unusual hydrocarbons–water mixtures arising from serious environmental pollution for example, the Great Pacific Garbage Patch (GPGP). An example image of a plastic-polluted section of a river is shown in Fig. 1. The GPGP represents a dire plastic pollution problem that requires immediate solution due to the reported deleterious effects on marine life including fatalities mainly due to plastic ingestion and smothering. Images of dead seabirds with their guts laden with pieces of plastic materials are common on the internet. In addition, the young of bigger sea animals are often found entrapped, deformed and strangled by plastics as they grow.

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**Fig. 1 – An image of plastic-polluted section of sea.**

The clean-up of hydrocarbons-polluted waters and possible conversion of the harvested hydrocarbon/water mixtures requires innovative technologies. Therefore, with SCWG technology, plastics/water and oil/water mixtures can be reacted together under supercritical water conditions to produce fuel gases including synthetic natural gas (SNG). In comparison, the conversion of hydrocarbon/water mixtures to fuel and energy via conventional technologies such as incineration, pyrolysis and gasification would require water removal to technologically acceptable levels.

Research into the use of heterogeneous catalysts in SCWG has grown in recent years (Savage, 2000; Elliott, 2008). Ruthenium-based catalysts have been found to be very effective in the conversion of carbonaceous materials, with high carbon gasification efficiencies in moderate-temperature hydrothermal media (Park and Tomiyasu, 2003; Savage, 2000; Elliott, 2008; Vogel et al., 2007; Onwudili and Williams, 2016). Among the ruthenium-based catalyst, the most reported have been Ru/C (Duan and Savage, 2011; Stucki et al., 2009; Haiduc et al., 2009), Ru/TiO<sub>2</sub> (Vogel et al., 2007; Chakinala et al., 2010) and Ru/Al<sub>2</sub>O<sub>3</sub> (Byrd et al., 2007; Onwudili and Williams, 2013). Sometimes it is not clear from literature if the ruthenium had been used in the reduced form or as the oxide. However, the experience of the authors in this area has shown that ruthenium (IV) oxide, RuO<sub>2</sub> is very active in the gasification of both biomass-derived products (e.g., bio-oil) and hydrocarbon-derived products (e.g., plastics) in supercritical water.

In a recent publication, Onwudili and Williams (2016) showed that the gasification of bio-oil to methane-rich gas was influenced by reaction temperature, residence time and the wt% of RuO<sub>2</sub> on gamma-alumina. Working within the temperature range of 400–500 °C, the authors showed that near-total conversion of heavy fraction of bio-oil was achieved at 450 °C and above, with 20 wt% RuO<sub>2</sub>. Byrd et al. (2007) reported that a similar catalyst completely converted glucose to give the theoretical yield of hydrogen gas at a much higher temperature of 750 °C. Their work showed co-production of methane and hydrogen at lower temperatures but that methane yield decreased while hydrogen yield increased with increasing temperature, which suggested promotion of methane steam-reforming at high temperatures. Park and Tomiyasu (2003) carried out some research with pure RuO<sub>2</sub> as catalyst for the gasification of different low-oxygen carbonaceous materials including plastics. They reported high gasification efficiencies at 450 °C after 120 min reaction time, while using various [Org/RuO<sub>2</sub>] molar ratios ranging from 3.44 for polyethylene

terephthalate (PET) to 15.7 for polyethylene. They found that the plastic materials produced more methane and less carbon dioxide than the biomass samples such as cellulose. Essentially, the ability of RuO<sub>2</sub> to promote methane formation in supercritical water conditions was significant for all sample types (Park and Tomiyasu, 2003); however, the contributions of other process parameters during RuO<sub>2</sub> catalysis were not investigated. In addition, these authors used very high loadings of pure RuO<sub>2</sub> and long reaction times which would increase process costs.

In this present work, a parametric study of supported RuO<sub>2</sub> catalysis during the SCWG of common polyolefin plastics has been carried out at 450 °C for 60 min reaction time. As mentioned earlier, literature shows that the optimum temperature for carbon conversion and methane formation lies from 450 to 500 °C (Park and Tomiyasu, 2003; Onwudili and Williams, 2016). The aim was to investigate the possible reaction mechanisms involved in the formation of the observed gas products, especially methane. Detailed understanding of the reaction mechanisms would facilitate the application of the catalytic SCWG process for the treatment of hydrocarbons-polluted waters, with the added advantage of producing a useful fuel gas.

## 2. Experimental

### 2.1. Materials

Virgin plastic samples including low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) were all purchased from Sigma-Aldrich in the form of pellets and used as received. The pellets were approximately 3 mm long by 2 mm OD in dimension. These plastics are the most commonly used and often constitute a large proportion of waste plastics (Aguado et al., 2008) Dichloromethane also obtained from Sigma-Aldrich was used to extract any oil products in order to recover the solid residues. The ruthenium-based catalysts were obtained from an SME industrial partner, Catal (UK) limited, based in Sheffield, UK. The RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts had nominal RuO<sub>2</sub> loadings of 5 wt%, 10 wt% and 20 wt%, while the nickel–ruthenium bimetallic catalyst contained 5 wt% RuO<sub>2</sub> and 15 wt% NiO on Al<sub>2</sub>O<sub>3</sub>. In addition, 20 wt% and 40 wt% NiO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared in-house were also tested. All the catalysts were prepared by impregnation method unto the same sample of 1 mm spheres and crushed to <125 μm before use. The characteristics of the RuO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts have been published earlier (Onwudili and Williams, 2013, 2016). All catalyst have similar BET surface areas of ≈8 m<sup>2</sup>/g, pore volumes of ≈0.023 cm<sup>3</sup>/g, pore adsorption diameters of ≈12.5 nm and pore desorption diameters of ≈15.5 nm. Hence, they differed only in the type and amount of metal oxide contents.

### 2.2. Methods

In each experiment, 2.0 g of plastic samples was used. For tests involving catalysts, a known amount (0.5–2.0 g) of a particular catalyst was weighed into the 75 mL Hastelloy batch reactor, with a maximum working pressure of 45 MPa (Onwudili, 2015), followed by a known volume of water (usually 20 mL except for tests investigating the effect of water/feedstock ratio). Thereafter, the plastic sample was added and the loaded reactor purged for 10 min with nitrogen flow to exclude air. Then, the

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