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Catalytic supercritical water gasification of plastics with supported RuO₂: a potential solution to hydrocarbons-water pollution problem

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KEYWORDS: supercritical water gasification, plastics pollution, ruthenium catalysis, methane

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 (CPGP). Detailed catalytic mechanisms of RuO₂ 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, 60 min. All four plastics gave very high carbon gasification efficiencies (CGE) and hydrogen gasification efficiencies (HGE). Methane as the highest gas component, with a yield of up to 37 mol kg⁻¹_{LDPE} using the 20 wt% RuO₂ 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.

Keywords: supercritical water gasification, plastics pollution, ruthenium catalysis, methane

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1.0 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 [1-2]. This presents the possibility of applying SCWT to 'dry' feedstocks such as plastics wastes [3-6]. 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 [1, 7]. 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 Figure 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 piece of plastic materials are common on the internet. In addition, the young of bigger sea animals are often found trapped, deformed and strangled by plastics as they grow.

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.



Figure 1: An image of plastic-polluted section of sea

Research into the use of heterogeneous catalysts in SCWG has grown in recent years [8-9]. 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 [3, 8-11]. Among the ruthenium-based catalyst, the most reported have been Ru/C [12-14], Ru/TiO₂ [10, 15] and Ru/Al₂O₃ [16-17]. 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, RuO₂ 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 [11] showed that the gasification of bio-oil to methane-rich gas was influenced by reaction temperature, residence time and the wt% of RuO₂ on gamma-alumina. Working within the temperature range of 400 °C – 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% RuO₂. Byrd et al. [16] 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 [3] carried out some research with pure RuO₂ 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/RuO₂] 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 RuO₂ to promote methane formation in supercritical water conditions was significant for all sample types [3]; however the contributions of other process parameters during RuO₂ catalysis were not investigated. In addition, these authors used very high loadings of pure RuO₂ and long reaction times which would increase process costs.

In this present work, a parametric study of supported RuO₂ catalysis during the SCWG of common polyolefin plastics has been carried out at 450 °C for 60 min reaction time. As mention earlier, literature shows that the optimum temperature for carbon conversion and methane formation lies from 450 – 500 °C [3, 11]. 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 methane-rich gas.

2.0 Experimental Section

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. These

plastics are the most commonly used and often constitute a large proportion of waste plastics [18] 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 RuO₂/γ-Al₂O₃ catalysts had nominal RuO₂ loadings of 5 wt%, 10 wt% and 20 wt%, while the nickel-ruthenium bimetallic catalyst contained 5 wt% RuO₂ and 15 wt% NiO on γ-Al₂O₃. In addition, 20 wt% and 40 wt% NiO/γ-Al₂O₃ 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 RuO₂/γ-Al₂O₃ catalysts have been published earlier [11, 17]. All catalyst have similar BET surface areas of ≈ 8 m²/g, pore volumes of ≈ 0.023 cm³/g, pore adsorption diameters of ≈12.5 nm, 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 g – 2.0 g) of a particular catalyst was weighed into the 75 ml Hastelloy batch reactor, with a maximum working pressure of 45 MPa [19], 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 reactor was sealed and heated at an average rate of 21 °C min⁻¹ to 450 °C and held at this temperature for 60 min. Depending on the water loading and catalyst loading, autogenic reaction pressure ranged from 10 – 38 MPa. At the end of the reaction, the reactor was quickly withdrawn and rapidly cooled with compressed air to reach 50 °C after only 5 min. On cooling, the reactor gas pressure was noted prior to gas sampling for GC analysis.

2.2.1. Gas analysis

The product gas sampled at room temperature was analysed using a system of gas chromatographs [20]. The analysis results were obtained in volume % and converted to moles or mass using the ideal gas equation and Henry's law. The yields of the gas components are expressed in mol kg⁻¹ of plastic feed. In addition, the gas yields were used to compute the carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HGE) as follows;

$$CGE, wt\% = \frac{\sum(\text{Mass of carbon in gas products (g)}) \times 100}{\text{Mass of carbon in the feedstock (g)}}$$

$$HGE, wt\% = \frac{\sum(\text{Mass of hydrogen in gas products (g)}) \times 100}{\text{Mass of hydrogen in the feedstock (g)}}$$

2.2.2. Solid analysis

The solid and liquid residuals left in the reactor after discharging the gas products, were separated by vacuum filtra-

tion. The solid residues (where application was reacted catalyst and char) left on the filter paper was dried in an oven at 105 °C for 2 h. The dried residue was homogenized prior to further analyses. Char formation on recovered catalysts residues were determined via temperature-programmed oxidation (TPO) using a Stanton-Redcroft thermogravimetric analyser (TGA) interfaced with a Nicolet Magna IR-560 FT-IR. Furthermore, for the 20 wt% RuO₂/γ-Al₂O₃ catalyst; the fresh catalyst, the used non-calcined catalyst (as recovered and dried) and the used calcined catalyst were all analysed by X-ray diffraction (XRD) (Bruker D8) with Cu K_α radiation for the presence of crystalline phases. Moreover, the same catalyst samples were characterised using Jeol JSM-6610LV Scanning Electron Microscope coupled to an Oxford Instruments INCA X-max80 EDX system (SEM-EDX). The detailed description and use of these instruments have been published earlier [19]

3.0 Results and Discussion

3.1. Influence RuO₂: γ-Al₂O₃ weight ratio

The influence of the wt% of RuO₂ supported on the alumina on the gasification of polyolefin plastics was investigated with 2.0 g LDPE as feedstock and 1.0 g each of 5 wt%, 10 wt% and 20 wt% of RuO₂, respectively supported on γ-Al₂O₃. The tests were conducted at 450 °C for 60 min. The results of these tests are presented in Figure 2, along with the test conducted in the absence of the catalyst. Figure 2a shows clearly that yields of the gas components changed dramatically between the non-catalytic and catalytic tests as well as among the catalytic tests. In the non-catalytic tests, C₂-C₄ hydrocarbon gases dominated the gas products as a result of thermal pyrolysis of the plastic [4-5, 20-21]. Similar yields of hydrocarbon gases are obtained from conventional pyrolysis of LDPE [22]. With the 5 wt% RuO₂ loading, the yields of hydrogen, methane and CO₂ increased much more than that of the C₂-C₄ gases, with methane slightly higher than hydrogen and carbon dioxide, indicating some catalytic activity.

Further, in the presence of the 10 wt% RuO₂ catalyst, the yield of C₂-C₄ gases decreased further but so did the yield of hydrogen, whereas the yields of methane and CO₂ increased considerably compared to the 5 wt% catalyst. However, this time, there was a larger increase in methane compared to CO₂. The trend of the yields of gas components with the 20 wt% RuO₂ catalyst was similar to that of the 10 wt% catalyst. In this case however, there was much more reduction in the yields of hydrogen and C₂-C₄ gases, while the yields of CO₂ and especially methane showed dramatic increases. The decrease in hydrogen yield and increase in methane with increasing RuO₂ loading suggests the consumption of the former to produce the latter. Also, the increase in the yield of CO₂ shows that its formation must be link to the formation of hydrogen, possibly via the WGS of CO. In the absence of the catalyst, 0.11 mol kg⁻¹ of CO was found in the gas product, however no CO was found in the gas products in which RuO₂ was used at all. In addition, the dramatic decrease in the yield C₂-C₄ hydro-

carbons may also indicate their conversion to methane possibly via C-C bond hydrogenolysis.

Figure 2b shows the trends in the CGE and HGE values during the SCWG of LDPE with different RuO₂ loading. In the absence of the catalyst, CGE and HGE were 33 wt% and 45 wt% respectively. Results show that these values continued to increase with increasing RuO₂ wt% loading, so that at 20 wt% loading CGE reached 95 wt% indicating very high LDPE-carbon conversion in just 1 h. Interestingly too, the HGE was more than 100 wt%, which suggest that hydrogen must have been contributed by the only other source of hydrogen in the reaction system – water. The participation of water during SCWG has been well confirmed [1-3, 7]. Hence, apart from hydrogen atoms, the formation of CO and CO₂ from a zero-oxygen LDPE confirmed that water participated in these reactions.

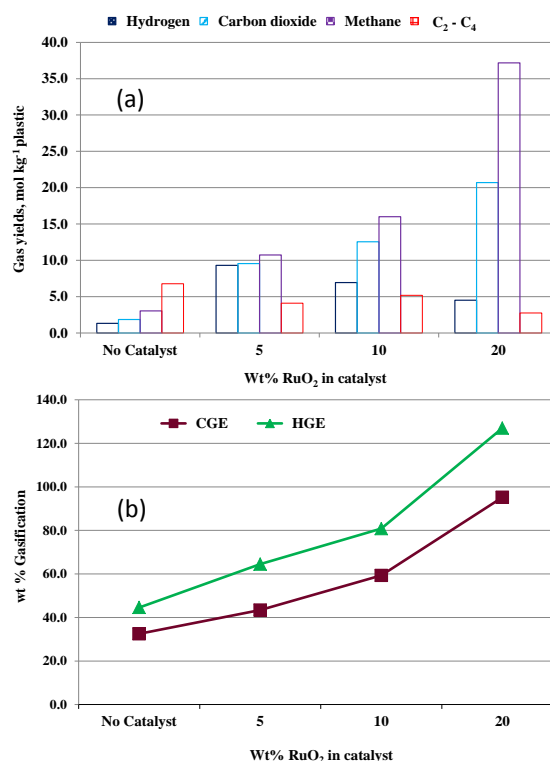


Figure 2: Influence of RuO₂: γ-Al₂O₃ weight ratio on the SCWG of LDPE at 450 °C, 60 min; (a) yields of gas components; (b) gasification efficiencies

Detailed analyses of the oil products from LDPE have not been carried out in this work but GC/FID tests showed that they contained mostly straight-chain alkanes (Supplementary Information ES1). Moreover, photographs of the dichloromethane extracts of the aqueous residuals obtained from the catalytic SCWG of LDPE have been presented in the Supplementary Information (ES2). This has been provided as evidence in support of the progressive gasification/removal/clean-up of LDPE from water with increasing RuO₂ loading.

Table 1: Gas yields (vol.%), with % standard deviations from the SCWG of different polyolefin plastics at 450 °C, 60 min

| Gas components | LDPE | | | HDPE | | | PP | | | PS | | |
|---------------------------------------|---------------------|------|------|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| | Gas yields (Vol. %) | | % SD | Gas yields (Vol. %) | | % SD | Gas yields (Vol. %) | | % SD | Gas yields (Vol. %) | | % SD |
| Hydrogen | 7.65 | 7.45 | 1.84 | 10.5 | 10.1 | 3.01 | 6.74 | 6.75 | 0.04 | 6.24 | 5.94 | 3.52 |
| CO | - | - | | - | - | | - | - | | - | - | |
| CO ₂ | 27.8 | 27.1 | 1.89 | 29.5 | 29.3 | 0.42 | 28.4 | 28.4 | 0.04 | 40.1 | 40.9 | 1.35 |
| Methane | 59.9 | 61.0 | 1.23 | 55.1 | 54.9 | 0.27 | 58.1 | 58.1 | 0.06 | 53.4 | 52.8 | 0.85 |
| Ethene | - | - | | - | - | | - | - | | - | - | |
| Ethane | 2.19 | 2.13 | 1.72 | 2.85 | 3.02 | 4.21 | 3.16 | 3.16 | 0.03 | 0.18 | 0.19 | 3.82 |
| Propene | - | - | | - | - | | - | - | | - | - | |
| Propane | 1.78 | 1.73 | 2.04 | 0.94 | 0.95 | 0.43 | 3.18 | 3.12 | 1.50 | 0.04 | 0.04 | 0.00 |
| Butenes | - | - | | - | - | | - | - | | - | - | |
| Butane | 0.68 | 0.65 | 2.42 | 1.08 | 1.06 | 1.62 | 0.45 | 0.45 | 0.00 | - | - | |
| ∑C ₂ -C ₄ gases | 4.64 | 4.52 | 1.95 | 4.97 | 5.13 | 2.56 | 6.79 | 6.73 | 0.69 | 0.22 | 0.23 | 3.14 |

3.2. Catalytic SCWG of different polyolefin plastics

Since the 20 wt% was found to be the most effective in the preceding section, it was used to investigate the SCWG of other commonly used polyolefin plastics including HDPE, PP and PS. The reactions were carried out with 2.0 g of each plastic and 1.0 g of 20 wt% RuO₂/γ-Al₂O₃ catalyst. Each test, including that with LDPE, was repeated twice and the results of the gas analysis displayed in Table 1. The volume % of each gas component for each plastic sample was very similar, with % standard deviations all below 5%, indicating the excellent repeatability of the experiments and the consistent activity of the catalyst towards the different plastic feedstocks.

The average volume % of the gas components were used in calculating the gas yields and gasification efficiencies, which are shown in Figure 3 and Figure 4, respectively. Methane was the dominant gas component for all the plastic samples, followed by CO₂, hydrogen and C₂-C₄ gases in that order as shown in Figure 3. These results suggest that the catalytic mechanism of the ruthenium-based catalyst was somewhat identical for all the plastics. It is important to note that PS produced the lowest yields of C₂-C₄ hydrocarbon gases, which agrees with the poor gas yields often associated with the pyrolysis of PS [23-25]. Both LDPE and HDPE gave similar C₂-C₄ yields, whereas PP produced the highest yields of these hydrocarbon gases. Compared with the polyethylene plastics, the C₂-C₄ yields from PP could be associated to the longer carbon chain length of the propylene monomer, which could be more prone to severe thermal pyrolysis than PE.

For clarity, the CGE and HGE values obtained from the SCWG of the different plastics have been presented separately in Figure 4a and Figure 4b, respectively. Figure 4a shows that CGE values for all plastic samples were greater than 93 wt%, with PP reaching 99 wt%, possibly due to

more contributions from C₂-C₄ gases compared to other plastics as mentioned earlier.

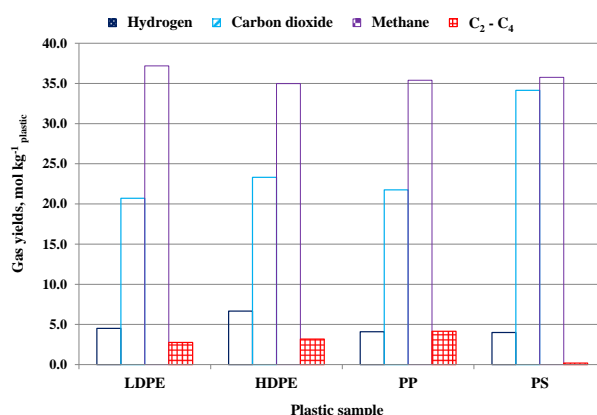


Figure 3: Gas component yields from catalytic SCWG of different polyolefin plastics at 450 °C, 60 min

Figure 4a also shows that more of feed carbons in LDPE, HDPE and PP ended up in methane compared to carbon dioxide, whereas PS gave nearly equal carbon distributions in the two main gases. This may be attributed to the molecular structural difference of PS compared to the other plastics. PS contains an aromatic ring from each styrene monomer of molecular formula C₈H₈. Hence, PS is much more carbon dense (empirical formula, CH) than the three aliphatic-based plastics (empirical formula CH₂) and this may have influenced its reaction. Indeed, PS is known to degrade during thermal pyrolysis into a cocktail of aromatic compounds including benzene, ethylbenzene, styrene, polycyclic aromatic hydrocarbons and diphenylalkanes with little hydrocarbon gases and hydrogen [23-24, 26]. Hence, the reaction of RuO₂ with aromatic rings could be different from aliphatic chains. In addition, Figure 4b shows that the HGE values exceeded 100 wt% for the aliphatic plastics,

whereas it was over 200 wt% for PS which confirmed that water contributed about half of the hydrogen atoms to the gas products, especially in methane gas formation from PS [3]. Indeed, for all four plastics, the methane product accounted for more than 75% of the gaseous hydrogen atoms, indicating effective methanation or other methane-formation mechanisms.

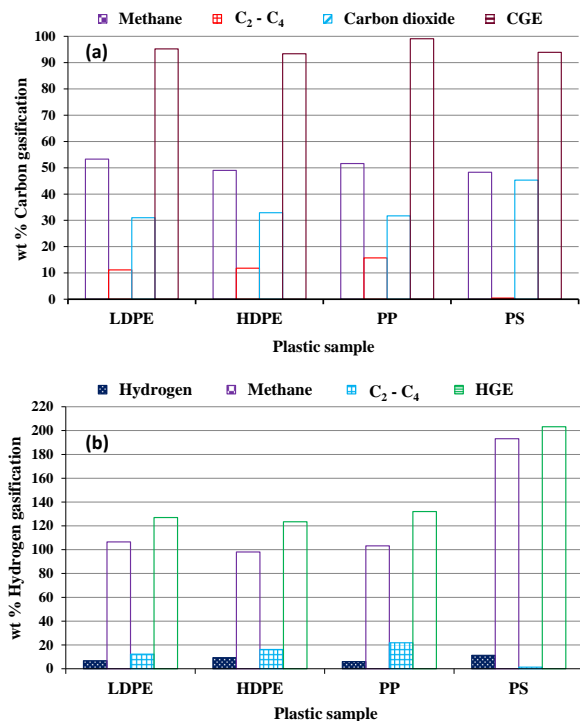


Figure 4: Gasification efficiencies from catalytic SCWG of the polyolefin plastics at 450 °C, 60 min (a) CGE (b) HGE

3.3. Influence of H₂O/C_{LDPE} molar ratios

To confirm the participation of water, tests were conducted with various H₂O/C_{LDPE} molar ratios 0, 1.94, 3.88 and 7.76. These corresponded to 0 mL, 5 mL, 10 mL and 20 mL of water addition, in the presence of the 20 wt% RuO₂/γ-Al₂O₃ catalyst as shown in Figure 5. These values also corresponded to water densities ($\rho = \text{mass of water loaded in g/reactor volume in cm}^3$) of 0, 0.067, 0.133 and 0.267 g cm⁻³, respectively). The trend of gas yields from Figure 5a is that gas production increased with increasing water molar ratios in the system. Without water, 0.54 mol kg⁻¹ of CO was produced, whereas no CO was found in reactions involving water, suggesting the occurrence of CO shift reaction in the presence of water. The formation of CO₂ in the absence of water was an interesting result because of the absence of the afore-mentioned WGS. Therefore, CO₂ formation in the absence of water would involve complete carbon oxidation by the RuO₂ and could have resulted from the poor mass transfer processes occurring in the absence of water. One of the advantages of supercritical water medium is the complete dissolution of organic materials and gases in a single-fluid phase devoid of mass transfer limitations [1]. Although pyrolysis of the plastic occurred [27]; without efficient stirring or mixing the gas-solid and gas-

liquid reaction processes occurring in the absence of water would become limited. Therefore, feed carbon atoms directly accessible to the RuO₂ in catalyst could undergo complete oxidation to CO₂.

The reactions conducted with increasing molar ratios of water show consistent increase in gas yields. Corroboratively, Figure 5b shows that CGE and HGE also increased with increased water loading. Indeed, the HGE already exceeded 100% when the H₂O/C_{LDPE} molar ratio was 3.88. Doubling the H₂O/C_{LDPE} molar ratio to 7.76 caused the HGE to increase to 127 wt%, confirming the participation of water as a hydrogen donor. Methane yield accounted for more than 90% of the reported HGE in the presence of water. Hence, this work shows that the presence of water is required as a reactant for the conversion of LDPE to a methane-rich gas product, giving up to 95 wt% carbon conversion to gas. Okajima et al. [28] investigated the SCWG of polyethylene and polyene (residue derived from dechlorination of PVC) to hydrogen at 700 °C in the presence of 20 wt% nickel and alkali catalysts and reported that about half of the hydrogen in the gas product originated from water via water-gas shift reaction (WGS) of CO.

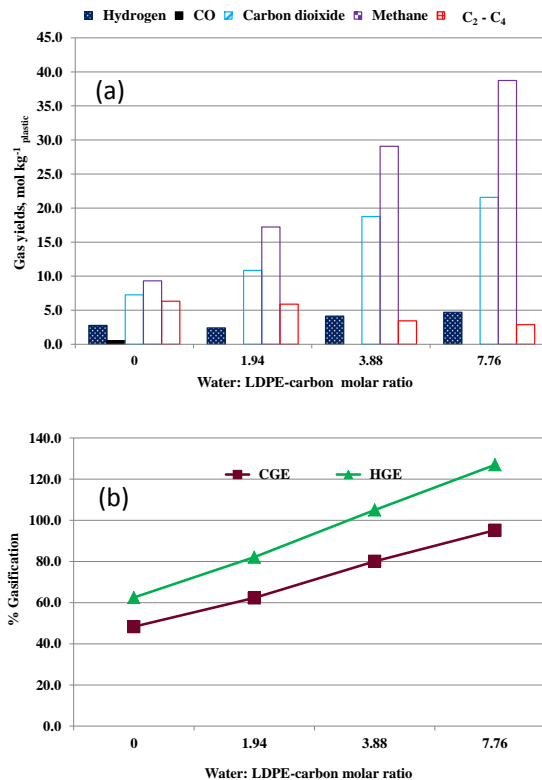


Figure 5: Influence of H₂O/C_{LDPE} molar ratios on the catalytic SCWG of LDPE at 450 °C, 60 min; (a) yields of gas components ; (b) gasification efficiencies (CGE & HGE)

3.4. Effect of C_{LDPE}/RuO₂ molar ratios (mol C_{LDPE}/mol RuO₂)

LDPE was used again to investigate the influence of C_{LDPE}/RuO₂ molar ratios on the SCWG of polyolefin plastics. In this case, 2.0 g of LDPE was reacted with different amounts of the 20 wt% RuO₂/γ-Al₂O₃ catalyst (i.e. 0.5 g,

1.0 g, 1.5 g and 2.0 g) to give C_{LDPE}/RuO_2 molar ratios of 190, 95, 65 and 48, respectively. The results of these tests are presented in Figure 6, which shows an increasing trend as the amount of the loaded 20 wt% $RuO_2/\gamma-Al_2O_3$ catalyst increased.

In Figure 6a, there is a dramatic jump in the yields of methane and CO_2 between molar ratios 190 and 95. The figure also shows much less dramatic increases in the yields of the two gases when the molar ratios decreased successively. It can be seen that the yields of CO_2 increased from 18.1 mol kg^{-1} at C_{LDPE}/RuO_2 molar ratio of 190 to 23.1 mol kg^{-1} at a C_{LDPE}/RuO_2 molar ratio of 48. Meanwhile, methane yield increased under the same conditions from 22.2 mol kg^{-1} to 43.4 mol kg^{-1} , which is nearly a double increase. In contrast, the yields of hydrogen and C_2-C_4 gases consistently decreased as the moles of RuO_2 in the system increased, showing their continued conversion or utilization to produce methane. Hence, the trend in the yields of the gas components indicate that the reactions responsible for CO_2 formation were almost complete even at low molar fractions of RuO_2 , whereas the reactions involving methane production was favoured with higher molar fractions of RuO_2 in the system.

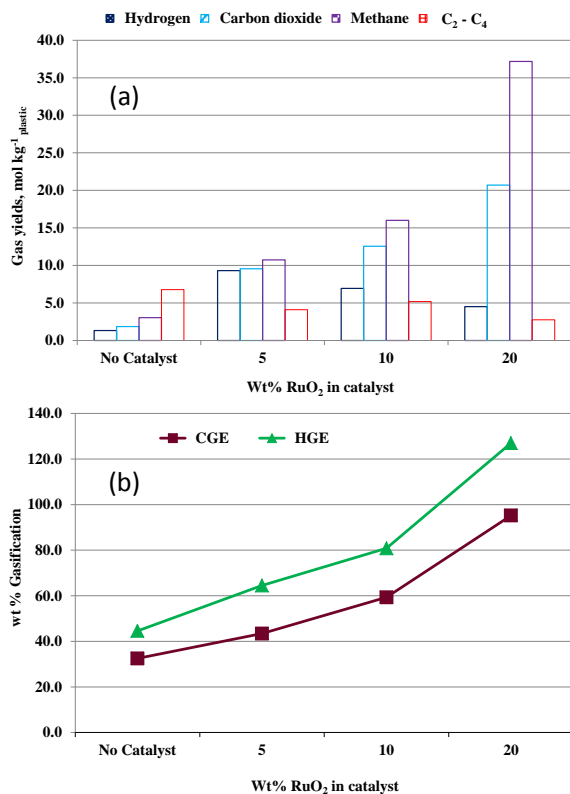


Figure 6: Effect of C_{LDPE}/RuO_2 molar ratios on the SCWG of LDPE at 450 °C, 60 min (a) yields of gas components; (b) gasification efficiencies (CGE & HGE)

Additionally, Figure 6b shows consistent increases in the CGE and HGE values with decreased C_{LDPE}/RuO_2 molar ratios. Although, CGE reached 100% at C_{LDPE}/RuO_2 molar ratio of 48, there is need to consider the incremental catalyst costs against marginal increases in gasification efficiencies and methane yields. In this work, the results sug-

gest that there might not be need to use higher RuO_2 loadings that would give C_{LDPE}/RuO_2 below 95. Also interesting was the disparity between the results from using 0.5 g of 20wt% $RuO_2/\gamma-Al_2O_3$ catalyst gave better CGE, HGE, methane, CO_2 and total gas yields when compared to gas products from using 1.0 g of 10 wt% $RuO_2/\gamma-Al_2O_3$ catalyst (Figure 1). Hence, even though both amounts of catalysts contained the same nominal molar equivalents of RuO_2 , the dispersion and concentration of the oxide on the alumina support must have influenced its catalyst activity. So that the lower mass, higher concentrated catalyst was effective than the dispersed, low concentrated one. This may also suggest that specific stoichiometric ratios were required for the initial reaction between the RuO_2 and the feed carbon atoms.

3.5. Analysis of used catalysts

In a previous publication, the stability of the catalysts were investigated and it was found that the 20 wt% $RuO_2/\gamma-Al_2O_3$ catalyst was stable when re-calcined at 750 °C for 2 h and reused three times during the SCWG of bio-oil [11]. Hence, this work has not considered catalyst stability in detailed. Briefly, $RuO_2/\gamma-Al_2O_3$ catalyst was calcined and reused for SCWG of LDPE. The gas yields obtained were 5.73 mol kg^{-1} hydrogen, 23.6 mol kg^{-1} CO_2 , 36.3 mol kg^{-1} methane and 3.36 mol kg^{-1} C_2-C_4 hydrocarbon gases. In addition, the GCE was 93.6 wt% and HE was 123.1 wt%.

These results indicate that the 20 wt% catalyst was mostly stable after the first re-calcination and reuse. Moreover, Osada and co-workers [29-30] have demonstrated that ruthenium-based catalysts are stable in hydrothermal conditions after regeneration but may require slightly longer residence time to perform at the same level as the fresh catalyst. In addition, other authors [31-32] have reported that sulphur-poisoning was a major cause of deactivation of ruthenium catalyst; hence this was not expected in this work as the feedstock used contained no sulphur.

The SEM micrographs in Figure 7 present the details of the surfaces of the fresh, used non-calcined and used calcined 20 wt% $RuO_2/\gamma-Al_2O_3$ catalyst. The figure shows that the morphology of the used calcined catalyst (Figure 7c) did not differ considerably from that of the fresh catalyst (Figure 7a), indicating the potential of catalyst regeneration by calcination in air.

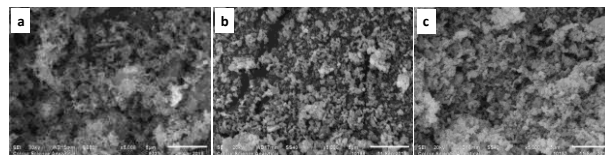


Figure 7: SEM micrographs of (a) fresh 20 wt% $RuO_2/\gamma-Al_2O_3$; (b) used non-calcined 20 wt% $RuO_2/\gamma-Al_2O_3$; (c) used calcined 20 wt% $RuO_2/\gamma-Al_2O_3$

However, Figure 7b, which is the micrograph of the used non-calcined catalyst, shows obvious morphological changes compared to Figures 7a and 7c. These changes could possibly due to segregation or transformation of the constituent metal oxides. In addition, the SEM micrographs

of the 5 wt% and 10 wt% RuO₂/γ-Al₂O₃ catalysts are presented in the Supplementary Information (ES3). EDX analyses showed the presence of carbon in the used non-calcined catalysts. This was confirmed from TPO studies, which however showed that char formation in the presence of the 20 wt% RuO₂/γ-Al₂O₃ catalyst was very small (≈ 0.06-0.2 g).

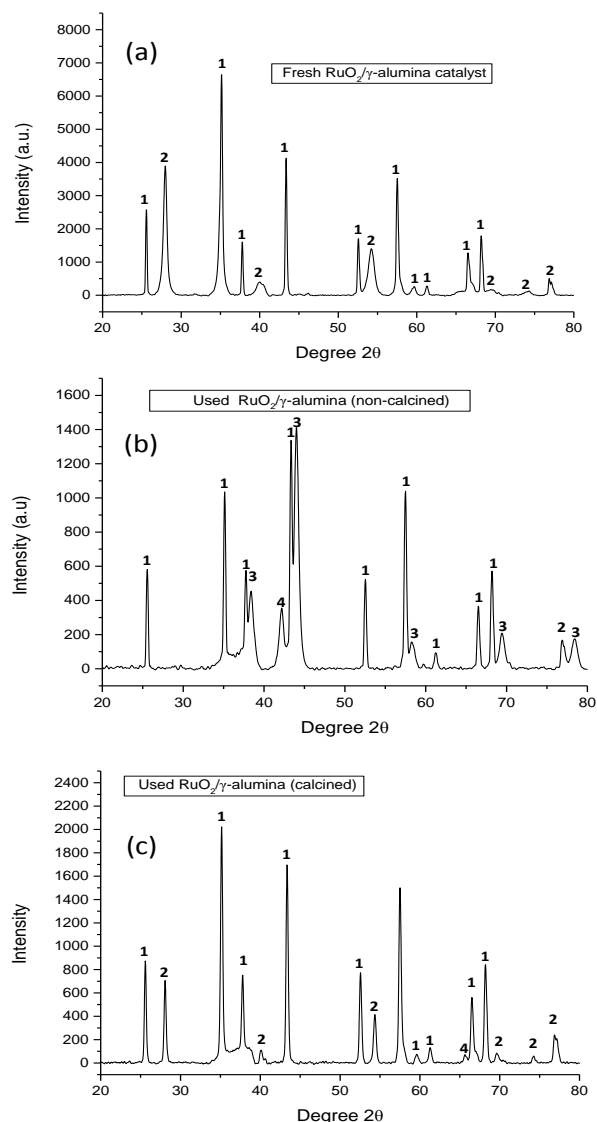


Figure 8: XRD patterns of; (a) fresh 20 wt% RuO₂/γ-Al₂O₃; (b) used non-calcined 20 wt% RuO₂/γ-Al₂O₃; (c) used calcined 20 wt% RuO₂/γ-Al₂O₃; Labels; 1- γ-Al₂O₃; 2- RuO₂; 3- Metallic Ru; 4- SiO₂

More importantly, Figure 8 shows the XRD patterns of the fresh, used non-calcined and used calcined 20 wt% catalyst from the SCWG involving LDPE. Using pure LDPE for this study ensured that the feedstock did not contribute ash to the catalyst residue. Figure 8a shows that the fresh catalyst only contained phases of RuO₂ and γ-Al₂O₃. Figure 8b, for the used non-calcined catalyst contained ruthenium metal and γ-Al₂O₃. Finally, Figure 8c, which shows the used calcined catalyst contained RuO₂ and γ-Al₂O₃. These

XRD plots show that the RuO₂ must be involved in a re-ox-type reaction with the plastic feedstock, in which case, it got reduced to Ru metal. Literature has shown the metallic ruthenium is an excellent catalyst for the methanation of CO₂ and CO [33-34]. Hence, the analysis of the used catalysts in this work has provided new insights into the catalytic reaction mechanisms, which are discussed below.

3.6. Plausible reaction mechanisms of RuO₂

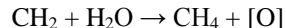
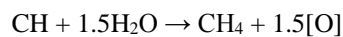
In this section, the possible reaction mechanisms involved in the formation of gas products from the polyolefin plastics in the presence of RuO₂/γ-Al₂O₃ catalyst have been proposed. Two results from this present study demonstrate unequivocally that water participated in the conversion of the polyolefin plastics; (1) the production of CO₂ from non-oxygen hydrocarbon feedstocks during the non-catalytic tests; (b) the HGE values greater than 100% obtained from some catalytic tests. Water acts as a reactant in steam reforming and particularly in WGS during SCWG [3, 11]. However, gas yields from PS on one hand and those of the aliphatic plastics (LDPE, HDPE and PP) on the other hand were sufficiently different to warrant further investigation. In addition to experiments above, 2.0 g of PS was reacted using 10 mL of water loading ($\rho = 0.133 \text{ g cm}^{-3}$) in the presence of 20 wt% RuO₂/γ-Al₂O₃ catalyst. The results obtained are presented in Table 2 along with those of LDPE with similar water loading, for ease of comparison.

Table 2: Yields of gas components (mol kg⁻¹), CGE and HGE of LDPE and PS at 450 °C, 60 min, using a water density of 0.133 g cm⁻³

| Gas components /parameters | LDPE | PS |
|---------------------------------------|-------|-------|
| Hydrogen | 4.14 | 3.35 |
| CO | - | - |
| CO ₂ | 18.8 | 24.5 |
| Methane | 29.1 | 20.8 |
| Ethene | - | - |
| Ethane | 1.58 | 0.13 |
| Propene | - | - |
| Propane | 1.26 | 0.03 |
| Butenes | 0.07 | - |
| Butane | 0.54 | - |
| ∑C ₂ -C ₄ gases | 3.44 | 0.15 |
| CGE | 82.7 | 59.4 |
| HGE | 107.8 | 118.4 |

Hence, the water/feedstock loading corresponded to H₂O/C_{PS} of 3.61 and H₂O/C_{LDPE} of 3.88, respectively. The results in Table 2 show that the CGE for PS under this condition was only 59.4 wt%, yet the HGE was 118 wt%, which is higher than the HGE from LDPE, even though the latter gave a much higher CGE (82.7 wt%). Considering these results, it is clear that water has contributed more to

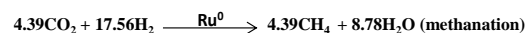
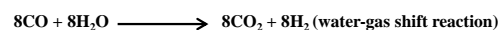
the gas products from PS than those from LDPE. Hypothetically, the reaction between water and PS (CH) on one hand, and water and LDPE (CH₂) on the other, to yield one mole of methane could be written as;



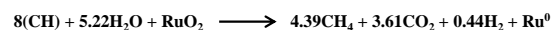
These simplified reactions suggest that more moles of water were needed during the SCWG of PS compared to LDPE. Furthermore, the symbolic oxygen atom [O] would likely end up as CO₂, and may explain why the [CH₄/CO₂] molar ratio in the product gas from PS (0.85) is far less than that from LDPE (1.6), as shown in Table 2.

In general therefore, the yields and compositions of gas products in this work suggest that the catalytic mechanisms involved in the gasification of the polyolefin plastics in the presence of RuO₂/γ-Al₂O₃ would include steam reforming, WGSR and methanation [3, 11, 28-29]. A combination of these mechanisms would likely yield nearly a 1:1 molar ratio of methane and CO₂. For instance, the large presence of water as medium would shift the equilibrium of the WGSR in favour of hydrogen and CO₂ production, while methanation would depend on the reaction conditions and equilibrium yields of hydrogen and CO₂ from the WGSR. These individual reactions have been carefully combined in the schemes proposed below to closely match the molar stoichiometries of the actual yields of the main gas components from LDPE and PS i.e. hydrogen, methane and CO₂ in Figure 3. As earlier mentioned, the formation of C₂-C₄ hydrocarbons must be via pyrolysis and obviously their yields from PS were low as expected. So the nearly equimolar yields of methane and CO₂ from PS could be explained from these reactions, especially WGSR and methanation according to the following reactions;

Scheme 1: Polystyrene



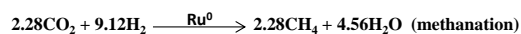
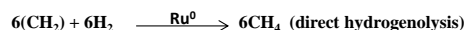
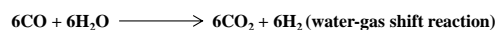
Overall



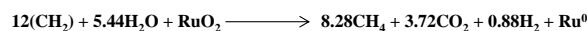
In contrast, the yields of methane, in the presence of RuO₂/γ-Al₂O₃ catalysts, were obviously much higher than CO₂ from the aliphatic polymers (LDPE, HDPE and PP). It is also important to note that these plastics are often converted to high yields of hydrocarbons (gas and oil) during pyrolysis. Moreover, Figure 2a, shows clearly that the conversion of LDPE to methane increased in relation to RuO₂/γ-Al₂O₃ weight ratio in the catalysts. Figure 2a also shows that the yields of C₂-C₄ gases decreased as wt% of RuO₂ increased. Therefore, the yields of gases from LDPE, and certainly the other aliphatic plastics, could not be fully explained by the same mechanisms suggested for PS. In particular, the much higher yields of methane compared to CO₂ indicates the possibility of additional mechanism to pyrolysis, steam reforming and methanation. This mechanism must have enhanced methane formation beyond what

could be achieved by methanation of CO₂ (or even CO) alone. Using the details of this work, it is very probable that hydrogenolysis of C-C bonds in ≥C₂ hydrocarbon compounds occurred either in the gas or liquid phase to yield more methane. The presence of only alkane gases (no alkenes) from the catalytic tests with RuO₂ in this present study may provide subsisting evidence of hydrogenolysis. Hydrogenolysis of hydrocarbon C-C bonds would require less hydrogen gas consumption than methanation of CO₂. Based on the yields of products, therefore the following reaction scheme has been proposed for the SCWG of aliphatic polyolefin plastics e.g PE;

Scheme 2: Aliphatic polyolefin plastics



Overall



Again, the stoichiometries of the overall equation have been adjusted to match the molar ratios of the components in the gas products from the tests involving the 20 wt% RuO₂/γ-Al₂O₃ catalyst. In addition, the much higher HGE obtained from the conversion of PS compared to LDPE would confirm that the aromatic ring in PS was more inclined to redox steam reforming (partial oxidation) to CO by RuO₂ than its conversion to pyrolytic gases. PS is known to produce very little hydrocarbon gases and a wide range of aromatic compounds during pyrolysis [5]. On the contrary, the aliphatic polymers would undergo initial pyrolysis to produce both gaseous and liquid hydrocarbons of various carbon chain lengths, which could then be partially oxidized to CO and also would be more prone to hydrogenolysis of C-C bonds to produce methane. The combination of these mechanisms agrees with the HGE values obtained in this work, which showed that PS produced 1.6 times more hydrogen in the gas phase than LDPE. Considering that the molecular structure of PS contained fewer hydrogen atoms than LDPE; most certainly, these additional hydrogen atoms came from water [1, 17]. Therefore, the additional hydrogenolysis mechanism for the aliphatic plastics would justify the higher water/feedstock molar ratio in Scheme 1 compared to Scheme 2.

3.7. Test with other catalyst systems

Nickel-based catalysts are often seen as cheaper alternatives to more expensive noble metal-based catalyst. In the section, 20 wt% NiO/γ-Al₂O₃ and 40 wt% NiO/γ-Al₂O₃ catalysts prepared by impregnation method have been used in the SCWG of LDPE alone. In addition, a bimetallic catalyst comprising of 15 wt% NiO and 5 wt% RuO₂ on γ-Al₂O₃ (20 wt% metal oxides) has been tested on the four plastic samples.

Figure 9a shows the results of the gas products, CGE and HGE from the SCWG of LDPE with the supported 20 wt%

and 40 wt% NiO catalysts, along with the result from the non-catalytic test. In general, it appears that the nickel catalysts mainly influenced the pyrolysis of LDPE, producing high yields of C₂-C₄ hydrocarbon gases, which increased with the wt% of NiO loading. CGE were 43.6 wt% and 66.3 wt%, respectively in relation to increased NiO loading, in which case C₂-C₄ gases accounted for more than 80% in both cases. For HGE, the 20 wt% NiO gave a value of 66.7 wt%, while the 40 wt% catalyst gave 97.1 wt%. Similar to the contributions to CGE, C₂-C₄ gases accounted for 71.7 wt% and 77.5 wt% of the HGE values with respect to NiO loading in the catalysts. These results show that the main catalytic role of the nickel oxide catalyst was to provide incremental yields of the same range of fuel gases similar to those obtained from the non-catalytic test. Reforming of hydrocarbon in supercritical water with nickel-based catalysts requires temperatures of up to 750 °C as reported in literature [28]. The oil products from the tests with NiO were similar to those from the non-catalytic test (albeit lighter) as shown in the photographs presented in the Supplementary Information (ES4).

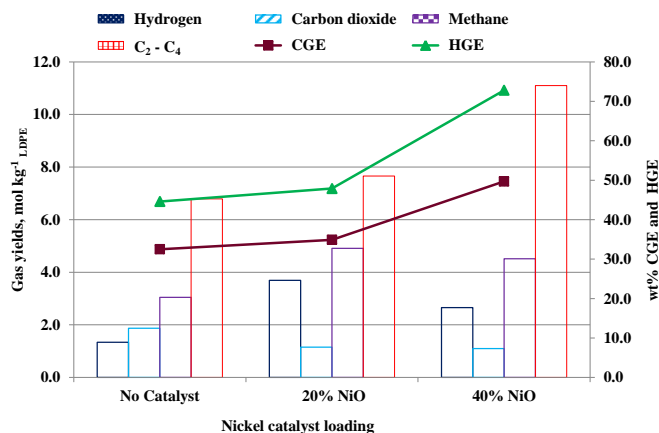


Figure 9: Gas component yields and gasification efficiencies (CGE & HGE) from the SCWG of LDPE using nickel catalysts at 450 °C, 60 min

The gas yields, CGE and HGE from the SCWG of all four plastic samples using the supported bimetallic nickel-ruthenium catalyst are presented in Figure 9b. The trends in the GCE and HE values are similar, with PS giving the lowest values and PP, the highest. There is an interesting trend between HDPE and LDPE in the yields of hydrogen, CO₂ and methane. LDPE produced more hydrogen and CO₂ than HDPE, while HDPE produced more methane than LDPE. The reason for this is not very clear however, it can be said that more methanation occurred with the HDPE leading to the consumption of hydrogen and CO₂ compared to LDPE. It is clear though that when compared to the results from using only NiO, the presence of RuO₂ improved the ability of the bimetallic catalyst to produce more hydrogen, CO₂ and methane, while reducing the yields of C₂-C₄ gases. Hence, RuO₂ was the main catalyst in this SCWG process.

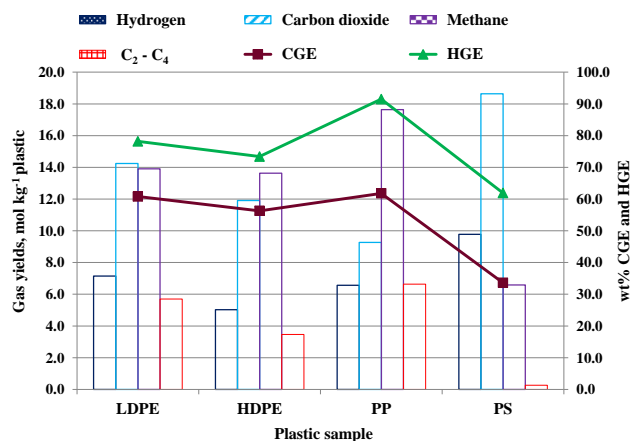


Figure 10: Gas component yields and gasification efficiencies (CGE & HGE) from the SCWG of different polyolefin plastics LDPE using bimetallic nickel-ruthenium catalyst at 450 °C, 60 min

Interestingly, apart from hydrogen, the bimetallic catalyst produced more of the other gases compared to the 5 wt% RuO₂/γ-Al₂O₃, as reported in Section 3.1 above. The yields (mol kg⁻¹) of hydrogen, CO₂, methane and C₂-C₄ gases from the RuO₂/γ-Al₂O₃ catalyst were 9.32, 9.56, 10.7 and 4.10; while the bimetallic catalyst produced 7.14, 14.2, 13.9 and 5.7 mol kg⁻¹ of the same gases, respectively. Although, this could be evidence of synergy between nickel and ruthenium in catalyzing the SCWG of plastics, the gas yields and gasification efficiencies were disappointingly less than those obtained from the 20 wt% RuO₂/γ-Al₂O₃ catalyst. These tests show that nickel was far less active than ruthenium for methane production from carbonaceous materials under supercritical water conditions. In addition, results also showed that the γ-Al₂O₃ support for these catalysts was hardly effective during the SCWG process.

4.0 Conclusions

This present study has provided some insights into the catalytic SCWG of common olefin plastics in the presence of RuO₂-based catalysts to produce methane. An attempt has been made to understand and explain the reaction mechanisms responsible for the yields of gas products during this process. Essentially, the yields of methane, hydrogen and carbon dioxide appear to be via redox steam reforming of the plastics to produce CO and hydrogen and the consequent reduction of RuO₂ to Ru metal. Subsequently, the CO reacted with water via the WGS to produce CO₂ and more hydrogen. It is likely that the steam reforming and water-gas shift reactions occurred almost simultaneously in the presence of RuO₂. The resulting CO₂ and hydrogen products reacted over Ru metal catalysis to produce methane.

However, the relative molar yields of CO₂ and methane from PS and the aliphatic plastics (LDPE, HDPE and PP) suggest that some differences in the overall reaction mechanisms. The aliphatic plastics produced PS relatively

more methane than CO₂, while PS produced nearly equimolar yields of methane and CO₂. This indicates some additional mechanism, possibly hydrogenolysis of C-C bonds. Overall, the production of CO₂ was inevitable as a consequence of the possible reaction mechanisms involved - a combination of steam reforming and WGSR of hydrocarbons for hydrogen production would always yield CO₂ co-product. The CO₂ coming this point-source process can be utilized as chemical feedstock or easily sequestered. This work demonstrates the potential of using catalytic supercritical water gasification for the treatment of hydrocarbon pollution of water. RuO₂ exhibited strong catalytic activity during the process leading to nearly complete CGE and high yields of a methane-rich gas product. Under the same conditions, nickel-based catalysts were far less effective. Overall, this process has the potentials of providing a sustainable technology for cleaning up the oceans and other water-bodies of hydrocarbons pollution

References

- [1] Savage, P. E., Organic chemical reactions in supercritical water. *Chem. Rev.* **1999**, 99, 603–622
- [2] Kruse, A., Supercritical water gasification. *Biofuels, Bioprod. & Bioref.* **2008**, 2, 415-437
- [3] Park, K. C., Tomiyasu, H., Gasification reactions of organic compounds catalyzed by RuO₂ in supercritical water. *Chem. Comm.* **2003**, 6, 694 – 695
- [4] Su, X., Zhao, Y., Zhang, R., Bi, J., Investigation on degradation of polyethylene to oils in supercritical water. *Fuel Proc. Technol.*, **2004**, 85, 1249 – 1258
- [5] Tan, X. -C., Zhu, C. -C., Lia, Q., -K., Ma, T. -Y. Yuan, P. -Q. Cheng, Z. -M., Yuan, W. -K., Co-pyrolysis of heavy oil and low density polyethylene in the presence of supercritical water: The suppression of coke formation. *Fuel Proc. Technol.*, **2014**, 118, 49–54
- [6] Goto, M., Supercritical water process for the chemical recycling of waste plastics. *AIP Conf. Proc.* **2010**, 1251, 169-172
- [7] Kruse, A., Vogel, H., Heterogeneous catalysis in supercritical media: 2. Near-critical and supercritical water. *Chem. Eng. Technol.* **2008**, 31, 1241–1245
- [8] Savage, P. E., Heterogeneous catalysis in supercritical water. *Catalysis Today*, **2000**, 62, 167-173
- [9] Elliott, D. C., Catalytic hydrothermal gasification of biomass. *Biofuels Bioprod. & Bioref.* **2008**, 2, 254–265
- [10] Vogel, F., Waldner, M, H., Rouff, A. A., Rabe, S., Synthetic natural gas from biomass by catalytic conversion in supercritical water. *Green Chem.*, **2007**, 9, 616–619
- [11] Onwudili, J. A., Williams, P. T., Catalytic conversion of bio-oil in supercritical water: Influence of RuO₂/γ-Al₂O₃ catalysts on gasification efficiencies and bio-methane production. *App. Catal. B: Environ.* **2016**, 180, 559–568
- [12] Duan, P., Savage, P. E., Hydrothermal liquefaction of a microalga with heterogeneous catalysts. *Ind. Eng. Chem. Res.*, **2011**, 50, 52–61
- [13] Stucki, S., Vogel, F., Ludwig, C., Haiduc, A. G., Brandenberger, M., Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. *Energy Environ. Sci.*, **2009**, 2, 535
- [14] Haiduc, A. G., Brandenberger, M., Suquet, S., Vogel, F., Bernier-Latmani, R., Ludwig, C., SunChem: an integrated process for the hydrothermal production of methane from microalgae and CO₂ mitigation. *J. App. Phicol.*, **2009**, 21, 529-541
- [15] Chakinala, A. G., Brilman, D. W. F., van Swaaij, W. P. W., Kersten, S. R. A., Catalytic and Non-catalytic supercritical water gasification of microalgae and glycerol. *Ind. Eng. Chem. Res.*, **2010**, 49, 1113–1122
- [16] Byrd, A. J., Pant, K.K., Gupta, R. B., Hydrogen production from glucose using Ru/Al₂O₃ catalyst in supercritical water. *Ind. Eng. Chem. Res.*, **2007**, 46, 3574–3579
- [17] Onwudili, J. A., Williams, P. T., Hydrogen and methane selectivity during alkaline supercritical water gasification of biomass with ruthenium-alumina catalyst. *Appl. Catal. B Environ.*, **2013**, 132-133, 70–79
- [18] Aguado, J., Serrano, D. P., Escola, J. M., Fuels from waste plastics by thermal and catalytic processes: A Review. *Ind. Eng. Chem. Res.*, **2008**, 47, 7982-7992
- [19] Onwudili, J. A., Influence of reaction conditions on the composition of liquid products from two-stage catalytic hydrothermal processing of lignin. *Biores. Technol.*, **2015**, 187, 60-69
- [20] Moriya, T., Enomoto, H., Characteristics of polyethylene cracking in supercritical water compared to thermal cracking. *Polymer Degrad. Stability*, **1999**, 65, 373-386
- [21] Watanabe, M. Mochiduki, M., Sawamoto, S., Adschiri, T., Arai, K., Partial oxidation of n-hexadecane and polyethylene in supercritical water. *J. Supercritical Fluids*, **2001**, 20, 257-266
- [22] Brebu, M., Bhaskar, T., Murai, K., Muto, A., Sakata, Y., Uddin, M. A., Recycling of waste lubricant oil into chemical feedstock or fuel oil over supported iron oxide catalysts. *Fuel* **2004**, 83, 2021–2028

[23] Houshmand, D., Roozbehani, B., Badakhshan, A., Thermal and catalytic degradation of polystyrene with a novel catalyst. *Int. J. Sci. Emerging Tech.*, **2013**, 5, 234-238

[24] Achillas, D. S., Kanellopoulou, I., Megalokonomos, P., Antonakou, E., Lappas, A. A., Chemical recycling of polystyrene by pyrolysis: potential use of the liquid product for the reproduction of polymer. *Macromol. Mater. Eng.* **2007**, 292, 923-934

[25] Muhammad, C., Onwudili, J. A., Williams, P. T., Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis-catalysis reactor for fuel production. *Energy Fuels*, **2015**, 29, 2601-2609

[26] Onwudili, J. A., Williams, P. T., Degradation of brominated flame-retarded plastics (Br-ABS and Br-HIPS) in supercritical water. *J. Supercritical Fluids*, **2009**, 9, 356-368

[27] Huo, Z. B., Liu, J. K., Yao, G. D., Zeng, X., Luo, J., Jin, F. M., Efficient hydrothermal conversion of cellulose into methane over porous Ni catalyst *App. Catal. A: Gen.* **2015**, 490, 36-41

[18] Okajima, I., Shimoyama, D., Sako, T., Hydrogen production from cross-linked polyethylene with water in high temperature and pressure. *J. Chem. Eng. Japan*, 2004, 37, 1521-1527

[29] Osada, M., Sato, T., Watanabe, M., Adschiri, T., Arai, K., Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water. *Energy Fuels* **2004**, 18, 327-333

[30] Osada, M., Sato, O., Arai, K., Shirai, M., Water density effect on lignin gasification over supported noble metal catalysts in supercritical water. *Energy Fuels* **2006**, 20, 2337-2343

[31] Dreher, M. Steib, M. Nachttegaal, M., Wambach, J., Vogel, F., On-stream regeneration of a sulphur-poisoned ruthenium-carbon catalyst under hydrothermal gasification conditions. *ChemCatChem*, **2014**, 6, 626-633

[32] Guan, Q., Wei, C., Savage, P. E., Hydrothermal gasification of nannochloropsis sp. with Ru/C. *Energy Fuels*, **2012**, 26, 4575-4582

[33] Jiménez, V., Sánchez, P., Panagiotopoulou, P., Valverde, J. L., Romero A., Methanation of CO, CO₂ and selective methanation of CO, in mixtures of CO and CO₂, over ruthenium carbon nanofibers catalysts. *App. Catal. A: Gen.*, **2010**, 390, 35-44

[34] Solymosi, F., Erdöhelyi, A., Kocsi, M., Methanation of CO₂ on Supported Ru Catalysts. *J. Chern. Soc. Faraday Trans. I*, **1981**, 77, 1003-1012

