

Catalytic Supercritical Water Gasification of Refuse Derived Fuel for High Energy Content Fuel Gas

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Abstract Refuse derived fuel (RDF) was processed using hydrothermal gasification at high temperature to obtain a high energy content fuel gas. Supercritical water gasification of RDF was conducted at a temperature of 500 °C and 29 MPa pressure and also in the presence of a solid RuO₂/γ-Al₂O₃ catalyst. The effect of residence time (0, 30 and 60 min) and different ruthenium loadings (5, 10, 20 wt.% RuO₂/γ-Al₂O₃) were investigated. Up to 93% carbon gasification efficiency was achieved in the presence of 20 wt.% RuO₂/γ-Al₂O₃ catalyst. The fuel gas with the highest energy value of 22.5 MJ Nm⁻³ was produced with the 5 wt.% RuO₂/γ-Al₂O₃ catalyst after 30 min. reaction time. The results were compared with the use of NaOH as a homogeneous catalyst. When NaOH was used, the maximum gross calorific value of the product gas was 32.4 MJ Nm⁻³ at 60 min. reaction time as a result of CO₂ fixation. High yields of H₂ and CH₄ were obtained in the presence of both the NaOH and RuO₂/γ-Al₂O₃ catalysts.

Keywords: Waste; RDF; Supercritical; Gasification; Hydrogen; Catalyst

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1. Introduction

The treatment and disposal of municipal solid waste (MSW) creates major environmental and economic issues [1]. The annual worldwide generation of MSW has been projected to be 2.2 billion tonnes by 2025, according to World Bank predictions [2]. Refuse derived fuel (RDF) is a fuel produced from processing of municipal solid waste, by using mechanical treatment methods to remove materials such as glass and metals to obtain a combustible fraction. RDF can be a very complex mixture of materials, but is mainly composed of paper, plastics, textile material etc. [3]. Normally, the calorific value of a typical MSW sample is around 9 MJ kg^{-1} , while this amount increases in RDF to around 18 MJ kg^{-1} with around 75 wt% of volatile matter contained in the RDF.

The thermal processing of RDF has been investigated by pyrolysis or gasification to produce energy or fuels [3,4]. For example, pyrolysis of RDF was performed over a temperature range of $400 - 700 \text{ }^\circ\text{C}$ [3]. The gas product was mainly composed of CO_2 , CO , H_2 , CH_4 , C_2H_6 and C_3H_8 . The pyrolysis oil was reported to be chemically very complex, containing a wide range of oxygenated, aromatic and aliphatic compounds. The steam gasification of RDF in a fixed bed reactor was researched by Dalai et. al., [5]. The optimum gasification temperature was determined as $725 \text{ }^\circ\text{C}$, as the optimum selectivity for H_2 and CO was obtained at this temperature. Also, they reported that the hydrogen and carbon ratio of raw RDF highly influences the selectivity of CO and H_2 , as higher ratios resulted in higher amounts of CO and H_2 . The two-stage pyrolysis/gasification of RDF with a Ni/SiO_2 catalyst has been investigated using a two stage reactor system [6]. While 50 wt.% of RDF was gasified when a bed of sand was used, the gas yield increased to 70 wt.% with the Ni/SiO_2 catalyst. The gas

compositions were also highly affected by the catalyst, as around 24 vol.% H₂ was produced without any catalyst, increasing up to 58 vol.% in the presence of Ni/SiO₂ catalyst.

However, there are few reports investigating the hydrothermal treatment of RDF to produce energy and/or fuels. It is interesting to understand the products from hydrothermal processing of RDF since it is obviously derived from municipal solid waste which can have high moisture contents. By using a more heterogeneous material as RDF for hydrothermal processing, the results obtained could inform the range of products which could be produced from wet municipal solid waste. We have previously shown that hydrothermal gasification of RDF with NaOH additive over a temperature range of 300 – 375°C, produces a H₂-rich gas also containing CO and CO₂ and smaller amounts of C₁-C₄ hydrocarbons. The NaOH catalyzed the gasification reactions by fixing CO₂ as carbonate salts [7]. However, the NaOH is difficult to recover for re-use which would involve additional process costs. In previous work, it has been shown that solid ruthenium catalysts can produce hydrogen-rich and/or methane-rich gases, with high conversion efficiency from the hydrothermal processing of a range of hydrocarbons including biomass based feedstocks [8-10] and plastics [11]. RDF is mainly composed of biomass materials and plastics, therefore it is of interest to investigate the use of Ru-based solid RuO₂/γ-Al₂O₃, catalyst for the supercritical water gasification of RDF at 500 °C and pressure 29 MPa. The results are compared with the supercritical water gasification of RDF in the presence of NaOH at the same supercritical conditions.

2. Experimental

Materials

Refuse derived fuel (RDF) produced from municipal solid waste (MSW) from a UK municipal waste treatment plant was used in the experiments in the hydrothermal treatment of RDF. The original sample was in pellet form with dimensions of 40 mm of length and 20 mm of diameter. The RDF was obtained as pellets (40 mm long x 20 mm diameter), but were shredded and ground to obtain a stock homogenous mixture of ~ 2 kg with particle sizes between 0.25 mm and 1.0 mm. The 2 kg stock was coned and quartered to obtain as representative sample as possible. The elemental analysis of the RDF sample was 44.5 wt% carbon, 5.8 wt% hydrogen, 49.0 wt% oxygen, 0.69 wt% nitrogen and 0.03 wt% sulphur. Proximate analysis of the RDF showed 7.3 wt.% moisture content, 15.0 wt.% ash content, 67.5 wt.% volatile content and 10.2 wt.% fixed carbon. The gross calorific value of the RDF sample was determined as 22 MJ/kg, and net calorific value was 21 MJ/kg.

Ruthenium oxide-gamma alumina ($\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$) catalyst containing 5 wt.%, 10 wt.% and 20 wt.% of the RuO_2 was supplied by Catal International Ltd., UK. However, the actual ruthenium metal content of the catalysts determined by atomic absorption spectrometry was 4.05 wt.%, 7.48 wt.% and 15.1 wt.% instead of the declared, 5, 10 and 20 wt.%. The catalysts were in the form of 1 mm pellets but were pulverized and sieved to a particle size of less than 125 μm before use. XRD analysis confirmed that the ruthenium was present as ruthenium (IV) oxide (RuO_2) (Figure 1). The properties of the catalysts have been characterised before [8], but in summary, the surface areas were, 8.54, 8.06, 7.97 $\text{m}^2 \text{g}^{-1}$ and pore volumes were 0.027, 0.023 and 0.025 $\text{cm}^3 \text{g}^{-1}$ for the 5, 10 and 20 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts respectively. Sodium hydroxide (pellets), methanol and dichloromethane (DCM) were purchased from Sigma-Aldrich, UK.

Experimental reactor system

The reactor was 75 ml internal volume, constructed of stainless steel and was purchased from Parr Instruments Co. USA. Details of the system have been provided previously [12]. A schematic diagram of the supercritical water gasification system is shown in Fig. 2. For the supercritical water gasification experiments, approximately 1.0 g of RDF sample was added to the 75 ml reactor. For each experiment, the liquid volume in the reactor was no more than 15 ml and the amount of catalyst (5 wt%, 10 wt%, 20 wt% RuO₂/γ-Al₂O₃ and NaOH) was 0.5 g. The reactor was sealed and flushed through with N₂, and heated at 12 °C min⁻¹ to 500 °C. Since the reactor was sealed, auto-generation of pressure at the 500 °C temperature related to the added liquid was obtained at ~ 29 MPa. Once the water/RDF/catalyst sample reached 500 °C, the reactor was removed from the furnace and rapidly cooled to ambient temperature (experiments assigned as 0 min. reaction time). For investigation of the influence of reaction time, the reactor was held at 500 °C for an additional 30 or 60 mins.

After the cooling, the gaseous effluent was collected with the help of a gas-tight plastic syringe and analysed using gas chromatography. After gas sample collection, the reactors were opened and the contents filtered to produce a liquid and solid product. The solid residue collected after filtration was dried at 105°C to determine its mass. The reactor was rinsed with a known amount of DCM for any remaining organic compounds, and the solution was kept in a separate container.

Analysis of Reaction Products

The product gases were quickly analyzed offline using two Varian 3380 gas chromatographs (GC), one for permanent gases and a separate one for hydrocarbons, using a methodology

described previously [13]. Briefly, the procedure involved H₂, CO, O₂ and N₂ analysis on a molecular sieve column and CO₂ with a HayeSep 80–100 mesh column and thermal and thermal conductivity detection. Hydrocarbons (C₁–C₄) were analysed with a HayeSep 80–100 mesh column and flame ionization detection. The conversion to gas products was evaluated as “Carbon Gasification Efficiency (CGE)” which was defined with the formula shown in the following Equation.

$$CGE, \% = \frac{\text{Amount of carbon in gas phase [g]}}{\text{Amount of carbon in RDF [g]}} \times 100 \quad \text{Equation 1}$$

The gross calorific values of the product gases were calculated based on equation 2

$$HHV = \sum_{i=1}^n X_i \cdot HHV_i \quad \text{Equation 2}$$

Where i...n = each combustible gas in the product mixture

Where, X_i is the volume fraction of each gas in the product mixture [vol/vol%] and HHV_i is the calorific value of each gas in the product mixture [MJ Nm⁻³] (values were taken from [14]).

The product liquid after reaction was analysed for total organic carbon (TOC) and inorganic carbon (IC) using a Hach-Lange IL550 TOC-CN and two NDIR detectors at 800 °C to determine a carbon balance for the experiments as described before [13].

3. Results and Discussion

Supercritical water gasification of RDF with Ru-based catalyst

The supercritical water gasification of RDF was carried out at 500 °C, and the effect of reaction time, the presence of catalyst and different catalyst loadings were studied. For this purpose, 5,

10, 20 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ and NaOH catalysts were investigated at reactor residence time variations of 0, 30 and 60 min.

Fig. 3 shows the carbon gasification efficiency in relation to the Ru catalyst loading and reaction time and compared to the addition of NaOH. Experiments conducted in the absence of any catalyst produced a carbon conversion to the gas phase of ~40%. The hydrothermal gasification of RDF in the presence of $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst led to conversion of the organic compounds in the waste into a fuel gas. The addition of NaOH gave lower carbon gasification efficiency. This might be due to the CO_2 fixation ability of NaOH, resulting in sodium salt production, which yielded less CO_2 in the gas phase. Fig. 3 shows that the maximum carbon conversion of carbon in the RDF to product gas was ~93% after 60 min. reaction time in the presence of 20 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst. The gasification rate was affected by the reaction time and the catalyst loading. The lowest carbon conversion with ruthenium catalyst was observed at 5 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ and zero minute reaction time, as 52% of the carbon in RDF was detected in the gas phase. With NaOH, 75% of the carbon in RDF was converted to the gas phase at 60 min. reaction time.

Fig. 4 shows the influence of reaction time from 0 min. to 60 min. in relation to the Ru loading on the catalyst for 3(a), the 5 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$, 3(b), the 10 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ and for 3(c) the 20 wt.% $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst. The main gases produced (mol of gas produced per kg RDF), were CO_2 , H_2 , and CH_4 . In the absence of any catalyst, the gas composition after the supercritical water gasification of RDF resulted in low amounts of gas production for example at 0 min. reaction time, the yield of gas was 3.3 mol H_2 , 1.5 mol CH_4 , 0.5 mol CO , 8.1 mol CO_2 and 1.7 mol hydrocarbon gases (C_{2-4}) per kg of RDF. However, in the presence of the $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst the yield of the individual gases was influenced by the Ru-catalyst loading and the reaction time. Fig. 4 shows that the increase in the loading of RuO_2 in

the catalyst produced an increase in the individual gas yields, especially for CO₂. The compositions of all the gas components increased when the reaction time was extended from 0 to 30 min. except for CO. However, a small reduction was observed when the reaction time was 60 min. Almost 11 mol H₂ and 6.5 mol CH₄ per kg RDF was produced at 30 min. and these amounts stayed fairly stable when the reaction time was increased to 60 min. Fig. 4 shows that the highest H₂ yields were observed at 30 min. reaction time with 10 wt.% and 20 wt.% RuO₂ loadings producing 12.4 mol and 13.1 mol H₂ per kg RDF, respectively. When the reaction time was further extended to 60 min., the H₂ yield decreased while CH₄ and CO₂ yields were increased.

For better comparison of the catalyst loadings, the gas compositions at 60 min. reaction time after hydrothermal gasification of RDF are shown in Fig. 5. Since gases with highest heating values were obtained after 60 min. reaction time, the comparisons between the catalyst loadings were made at this reaction time. The higher catalyst loading yielded more CO₂, H₂ and CH₄. The composition of hydrocarbon gases (C₂-C₄) and CO decreased with the increasing RuO₂ wt% in the catalysts. Fig. 3 also shows that the carbon gasification efficiencies were also increased with the increasing catalyst loading, as 88.2%, 89.3% and 92.8% of the carbon initially fed was detected in the gas phase after the hydrothermal gasification with 5 wt%, 10 wt% and 20 wt% RuO₂/γ-Al₂O₃ catalysts, respectively at 60 min. reaction time.

Similar gas compositions have been reported for the supercritical water gasification of biomass and plastic wastes with ruthenium as catalysts [11,15]. For instance, low concentrations of biomass model compounds including glucose and cellulose and industrial biomass samples such as paper sludge and sewage sludge were gasified by Yamamura et al. [15] in supercritical water at 500 °C with a Ru catalyst and produced H₂, CH₄, and CO₂ as major products in the gas phase. Also it was reported that complete gasification of cellulose

and glucose was observed, with the Ru-based catalyst [15]. Park et al. [11] used a RuO₂ catalyst for the supercritical water gasification of polyethylene, polypropylene, polystyrene and polyethylene terephthalate plastics at 450 °C and ~44 MPa. Gasification efficiencies for the plastics in terms of carbon conversion were between 97-100% and CH₄, CO₂ and H₂ were the main gases produced. Methane yields were high at ~67% for the polyethylene and polypropylene, but lower at ~54% and 37% for the polystyrene and polyethylene terephthalate respectively. Increased CO₂ (51%) was produced for the oxygen containing polyethylene terephthalate.

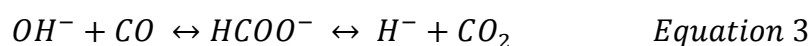
Under supercritical water gasification conditions, bonds between the carbon atoms would break and formation of short-chain products and intermediates would occur. From these intermediates and short-chain organic compounds, gasification reactions become favourable [8]. Therefore, it could be suggested that the RuO₂/γ-Al₂O₃ catalyst was able to increase the carbon-carbon bond cleavage and gasification efficiency. According to Sato et. al., [16] mainly CH₄, CO₂ and H₂ were obtained in the gas phase after the hydrothermal gasification of alkylphenols at 400°C. They stated that the Ru/γ-alumina as catalyst gave the highest gasification efficiency, compared to the other catalysts investigated which were Ru, Rh or Pd on carbon and Pt or Pd on γ-alumina.

The gas compositions in terms of volume percent were also calculated and the results of hydrothermal gasification of the RDF with 5, 10 and 20 wt% RuO₂/γ-Al₂O₃ are shown in Fig. 6(a), 6(b) and 6(c) respectively. The results show that CO₂ was the main component in the product gas phase, followed by H₂, and CH₄. In the case of all the catalyst loadings, the CO₂ contribution to the gas composition decreased with the increasing reaction time, for example CO₂ was 56.2 vol.% after zero min. reaction time, and decreased to 39.7 vol% after 60 min. reaction time, in the presence of the 5 wt.% RuO₂ catalyst. When no catalyst was present,

around 22 vol.% of H₂ and 10 vol.% of CH₄ was produced, while with the addition of the RuO₂/γ-Al₂O₃ catalyst, H₂ was in the range of 29 – 33 vol.%.

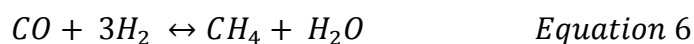
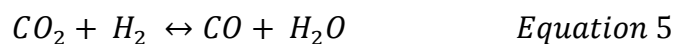
Byrd et al. [9] conducted hydrothermal gasification experiments with biomass model compound in the form of glucose over a temperature range of 700 – 800°C and a pressure of 25 MPa. When Ru/Al₂O₃ was used as catalyst, almost 12 mol of H₂ was produced from 1 mol glucose, which is the maximum theoretical amount that can be produced. They suggested that the glucose underwent dehydrogenation on the catalyst surface to give intermediate species, before the rupture of C-C bonds and/or C-O bonds. The breakage of C-C bonds yielded CO and H₂, and with the help of the water-gas shift reaction, formation of CO₂ and H₂ was observed. In this work, carbon monoxide composition was in the range of 0.4 – 2 vol.%, which agreed with the work of Byrd et al. [9], suggesting that the water-gas shift reaction occurred during the supercritical water gasification of RDF resulting in higher yields of H₂ [9,17].

At supercritical conditions, water dissociates into its ions and this self-dissociation is increased with the presence of metals [18]. The high H₂ yields obtained suggested that the water gas shift reaction could be initiated with the interaction of CO with OH⁻, which was formed from water as described in the work of Byrd et. al. [9]. With the self-dissociation of water on the metal surface, OH⁻ ions were formed and reacted with CO, producing formate ion. Then the formate ion decomposed into hydride anion and CO₂. And by electron transfer, hydride anion reacted with water to form H₂ and OH⁻. They suggested the following reactions;



However, the high yield of H₂ and domination of the water-gas shift reaction might be due to high temperature in which typical experiments are carried out (700 – 800 °C). In this work, hydrothermal gasification of RDF was carried out at 500 °C. Also in the literature, there

are reports indicating that methanation reactions become dominant in the presence of ruthenium catalyst. The mechanisms have been reported to involve the following; first hydrogenation of CO₂ to CO and then to CH₄ as in Equations 5 and 6 [19,20].



According to the reactions shown in Equations 5 and 6, the concentrations of H₂ and CO₂ are important for the selectivity of CH₄. At the supercritical point, water becomes a reactant, as well as a solvent and a catalyst. In this work, it was likely that water became a reactant and due to the presence of a large amount of water, the selectivity of the reactions was determined by the partial pressure of water, producing mainly CO₂ and H₂ via the water-gas shift reaction pathway.

Supercritical water gasification of RDF with NaOH additive

The supercritical water gasification of RDF in the presence of NaOH was investigated in relation to different reaction times to compare with the gasification with RuO₂/γ-Al₂O₃ catalyst. The carbon gas efficiency and the gas composition after hydrothermal gasification of RDF in the presence of NaOH are shown in Fig. 7. The presence of NaOH increased the carbon gasification efficiency, from 40.7% in the absence of any catalyst, and increased to 57.5% with NaOH. With the increasing reaction time, carbon gasification efficiency reached 75% at 60 min. reaction time. The analysis of the gas compositions in relation to reaction time with the RDF are also shown in Fig. 7 and were influenced by the addition of NaOH. When no NaOH was present, carbon dioxide was the main gas component at 53.1 vol.%, and decreased to a range of 16 – 23 vol.% with the addition of NaOH. This was due to the effect of NaOH to

promote the capture of CO₂ and consumption of CO. For all reaction times, the concentration of CO was zero, which supports the suggested process. At 500 °C, after 60 min. of reaction time, hydrothermal gasification of RDF yielded 36.9 vol.% H₂, 23.2 vol.% CH₄, 20.6 vol.% CO₂ and 19.3 vol.% hydrocarbon gases (C₂₋₄).

A previous investigation [21] suggested that the role of NaOH might be through reaction of the sodium in the water phase, forming intermediates such as hydroxylated ketones, aldehydes and acids that can subsequently be easily gasified [21]. Decarbonylation of the hydroxylated compounds would produce carboxylic acids such as formic and acetic acid in the form of sodium salts due to the presence of NaOH. The results of the TOC analyses and the distribution of carbon are shown in Table 1. The increase in the amount of the inorganic carbon in the liquid effluent might be due to sodium salt formation, as after the hydrothermal gasification, they would be dissolved in the aqueous phase. For example, sodium formates could react with water to yield sodium bicarbonate and H₂ as shown in Equation 7 [22,23].

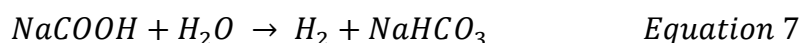


Table 1 shows that the carbon gasification efficiency in the presence of NaOH, was 57.7% at 0 min. reaction time and increased to 75% at 60 min. reaction time. By comparison with the RuO₂/γ-Al₂O₃ catalyst, the RDF carbon gasification efficiency was 64.3% at 0 min. reaction time and increased to 92.8% at 60 min. reaction time. The composition of gases also changed in relation to the change of the catalyst type as presented in Fig. 8. While H₂ and CH₄ were the main gas components for the supercritical water gasification of the RDF with NaOH, CO₂ and H₂ were the main gases with the Ru catalysts. Also, addition of NaOH increased the hydrocarbon gas (C₂₋₄) concentration.

Fig. 9 shows the calculated calorific values for the product gases. With NaOH, a gas mixture with a higher calorific value was obtained which were in a range of 27.5 – 32.5 MJ

Nm^{-3} . The average gross calorific value of natural gas is around 38 MJNm^{-3} , compared to this value; the gas produced with the addition of NaOH, particularly at the longer reaction times, was comparable. This was because the gas contained less CO_2 and much higher hydrocarbon gases (C_{2-4}) in the product gas (Fig. 8). At 60 min. reaction time, $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts produce gas mixtures having calorific value in a range of $18 - 22.5 \text{ MJNm}^{-3}$. However, the carbon gasification efficiencies were higher with the Ru catalysts.

The results have shown that RDF can be successfully gasified in supercritical water to generate a hydrogen-rich syngas with a maximum gross calorific value of 32.5 MJ Nm^{-3} with NaOH and 22.5 MJ Nm^{-3} with the $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst; the higher calorific value with NaOH due to the capture of the CO_2 in the product gas. RDF is a fuel product derived from the processing of municipal solid waste with a moisture content in this work of 7.3 wt.%. However, municipal solid waste will have moisture contents which are much higher, for example, in the UK ~ 40 wt.% [24], the US between 20-30 wt.% and for developing countries as high as 60-75 wt.% [25]. Therefore, the results presented here indicate that for wet municipal solid waste hydrothermal processing could have potential to produce a high calorific value gas.

4. Conclusions

RDF was processed using supercritical water gasification at $500 \text{ }^\circ\text{C}$ temperature and ~ 29 MPa pressure with the aim to obtain a fuel gas with high calorific value. High yields of H_2 were obtained in the presence of both the NaOH and $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts, as both promoted the water-gas shift reaction. Also due to the CO_2 fixation ability of NaOH and higher yields of H_2 , the energy value of the product gas had much higher heating value compared to the gas

produced in the presence of RuO₂ catalyst. Therefore, a fuel gas with a maximum energy value of 22.5 MJ Nm⁻³ in the presence of 5 wt.% RuO₂/γ-Al₂O₃ catalyst and 30 min. reaction time was produced, but a fuel gas with an energy value of 32.4 MJ Nm⁻³ was produced in the presence of NaOH and 60 min. reaction time. Almost 93 % of the carbon in the RDF was converted to gaseous products after supercritical water gasification, in the presence of 20 wt.% RuO₂/γ-Al₂O₃ catalyst. However, there was a high CO₂ concentration in the gas, which reduced the calorific value of the gas mixture.

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References

- [1]. Tammemagi, H.Y.: The waste crisis: landfills, incinerators, and the search for a sustainable future. Oxford University Press (1999).
- [2]. Hoornweg, D., Bhada-Tata P.: What a waste: a global review of solid waste management. Urban Development Series Knowledge Papers. 2012. The World Bank, Washington DC (2012)
- [3]. Buah, W.K., Cunliffe, A.M., Williams P.T.: Characterization of products from the pyrolysis of municipal solid waste. *Proc. Saf. Environ.* 85(5) 450-457 (2007).
- [4]. Cozzani, V., Nicoletta, C., Petarca, L., Rovatti, M., Tognotti L.: A fundamental study on conventional pyrolysis of a refuse-derived fuel. *Ind. Eng. Chem. Res.* 34(6) 2006-2020 (1995).
- [5]. Dalai, A.K., Batta, N., Eswaramoorthi, I., Schoenau, G.J.: Gasification of refuse derived fuel in a fixed bed reactor for syngas production. *Waste Manag.* 29(1) 252-258 (2009).
- [6]. Blanco, P., Wu, C., Onwudili, J.A., Dupont, V., Williams, P.T.: Catalytic pyrolysis/gasification of refuse derived fuel for hydrogen production and tar reduction: Influence of nickel to citric acid ratio using Ni/SiO₂ catalysts. *Waste Biomass Valor.* 5(4) 625-636 (2014).
- [7]. Onwudili, J.A., Williams, P.T.: Hydrothermal catalytic gasification of municipal solid waste. *Energ. Fuel.* 21(6) 3676-3683 (2007).
- [8]. 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. *Appl. Catal. B-Environ.* 180 559-568 (2016).
- [9]. Byrd, A.J., Pant, K.K., Gupta, R.B.: Hydrogen production from glucose using Ru/Al₂O₃ catalyst in supercritical water. *Ind. Eng. Chem. Res.* 46(11) 3574-3579 (2007).
- [10]. Vogel F., Waldner M.H., Rouff, A.A. Rabe, S.: Synthetic natural gas from biomass by catalytic conversion in supercritical water. *Green Chem.* 9 616–619 (2007).
- [11]. Park K.C., Tomiyasu, H.: Gasification reaction of organic compounds catalysed by RuO₂ in supercritical water. *Chem. Comm.* 6 694 – 695 (2003)
- [12]. Yildirim, E., Onwudili, J.A., Williams, P.T.: Recovery of carbon fibres and production of high quality fuel gas from the chemical recycling of carbon fibre reinforced plastic wastes.: *J. Supercrit. Fluid.* 92 107-114 (2014).
- [13]. Onwudili J.A., Williams, P.T.: Enhanced methane and hydrogen yields from catalytic supercritical water gasification of pine wood sawdust via pre-processing in subcritical water. *RSC Adv.* 3 12432-12442 (2013).
- [14]. Seader, J., Siirola, J.J., Barnicki, S.D.: *Perry's Chemical Engineers Handbook*, McGraw-Hill (1997).
- [15]. Yamamura, T., Mori, T., Park, K.C., Fujii, Y., Tomiyasu, H.: Ruthenium(IV) dioxide-catalyzed reductive gasification of intractable biomass including cellulose, heterocyclic compounds, and sludge in supercritical water. *J. Supercrit. Fluid.* 51(1) 43-49 (2009).

- [16]. Sato, T., Osada, M., Watanabe, M., Shirai, M., Arai, K.: Gasification of alkylphenols with supported noble metal catalysts in supercritical water. *Ind. Eng. Chem. Res.* 42(19) 4277-4282 (2003).
- [17]. 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. *Energ. Fuel.* 18(2) 327-333 (2004).
- [18]. Kruse, A., Dinjus, E.: Hot compressed water as reaction medium and reactant: Properties and synthesis reactions. *J. Supercrit. Fluid.*, 39(3) 362-380 (2007).
- [19]. Karn, F.S., Shultz, J.F., Anderson, R.B.: Hydrogenation of carbon monoxide and carbon dioxide on supported ruthenium catalysts at moderate pressures. *Ind. Eng. Chem. Prod. DD.* 4(4) 265-269 (1965).
- [20]. Lunde, P.J., Kester, F.L.: Rates of methane formation from carbon dioxide and hydrogen over a ruthenium catalyst. *J. Catal.* 30(3) 423-429 (1973).
- [21]. Onwudili, J.A., Williams, P.T.: Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass. *Int. J. Hydrogen Energ.* 34(14) 5645-5656 (2009).
- [22]. Sinađ, A., Kruse, A., Rathert, J.: Influence of the heating rate and the type of catalyst on the formation of key intermediates and on the generation of gases during hydrolysis of glucose in supercritical water in a batch reactor. *Ind. Eng. Chem. Res.* 43(2) 502-508 (2004).
- [23]. Onsager, O.T., Brownrigg, M.S.A., Lødeng, R.: Hydrogen production from water and CO via alkali metal formate salts. *Int. J. Hydrogen Energ.* 21(10) 883-885 (1996).
- [24] Williams P.T., *Waste Treatment & Disposal*, 2nd Edition, Wiley & Sons, Publishers, London, 2005
- [25] El-Fadel M., bou-Zeid E., Chahine W., Alayli, B. Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content. *Waste Manag.*, 22, 269-282, 2002

Figure Captions

Fig. 1. X-ray diffraction pattern of the unused 5 wt.% RuO₂/γ-Al₂O₃ catalyst.

Fig. 2. Schematic diagram of the supercritical water gasification reactor system

Fig. 3. Carbon gasification efficiencies in relation to reaction time and catalysts

Fig. 4. Gas compositions obtained from the supercritical water gasification of RDF at 500 °C in relation to different reaction times with (a) 5 wt.% RuO₂/γ-Al₂O₃ (b) 10 wt.% RuO₂/γ-Al₂O₃ (c) 20 wt.% RuO₂/γ-Al₂O₃

Fig. 5. Gas compositions obtained for the supercritical water gasification of RDF at 500 °C and 60 min. reaction time with 5 wt.%, 10 wt.% and 20 wt.% RuO₂/γ-Al₂O₃

Fig. 6. Product gas composition (Vol.%) produced from the supercritical water gasification of RDF at 500 °C with 5 wt.%, 10 wt.% and 20 wt.% RuO₂/γ-Al₂O₃

Fig. 7. Product gas composition (Vol.%) and carbon gasification efficiency produced from the supercritical water gasification of RDF at 500 °C with NaOH in relation to reaction time

Fig. 8. Product gas composition (Vol.%) and carbon gasification efficiency for the supercritical water gasification of RDF at 500 °C and 60 min. reaction time in relation to different catalysts and catalyst loadings.

Fig. 9. Gross calorific values of the gas products in relation wto temperature and catalyst loading/type

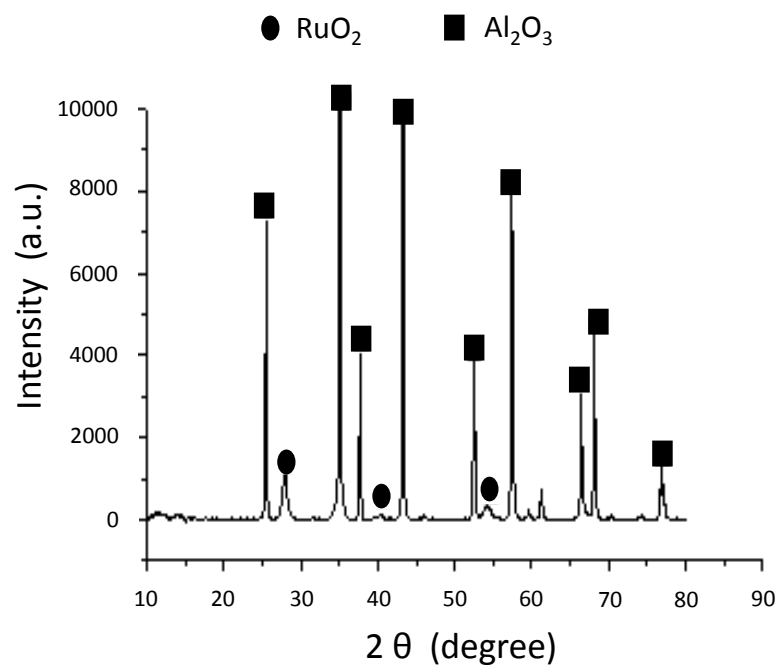


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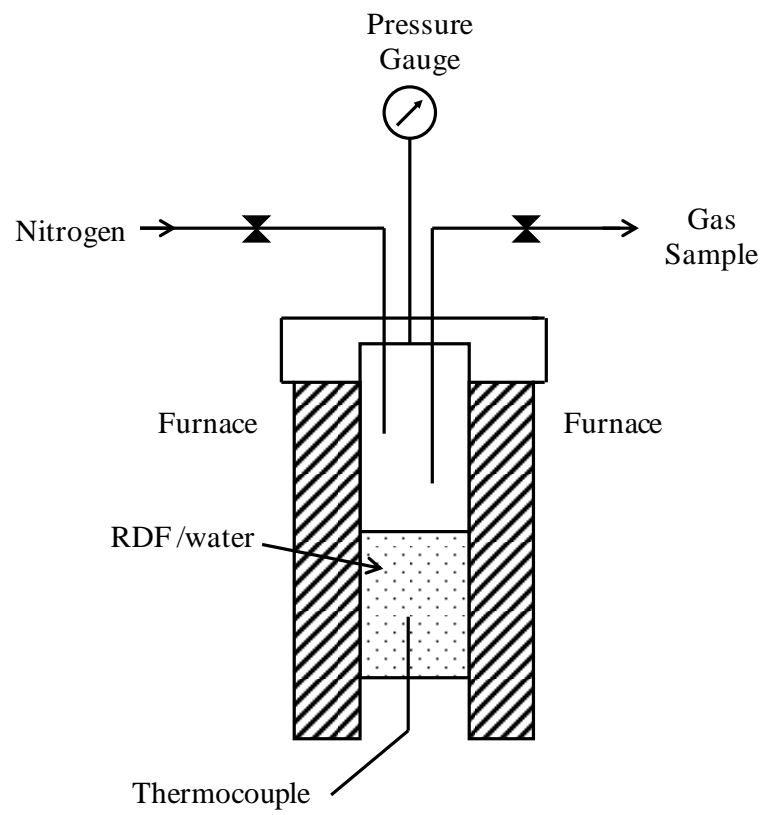


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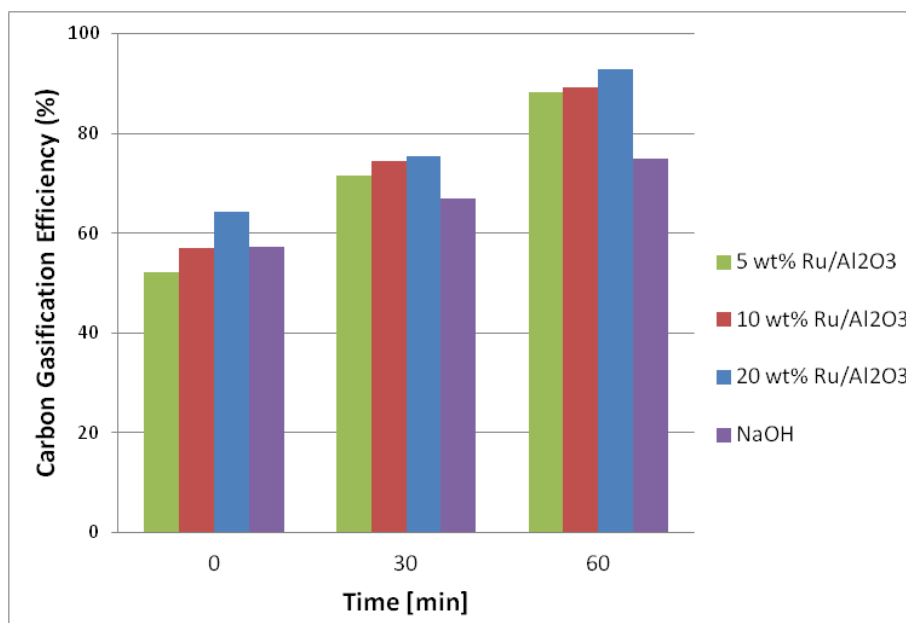


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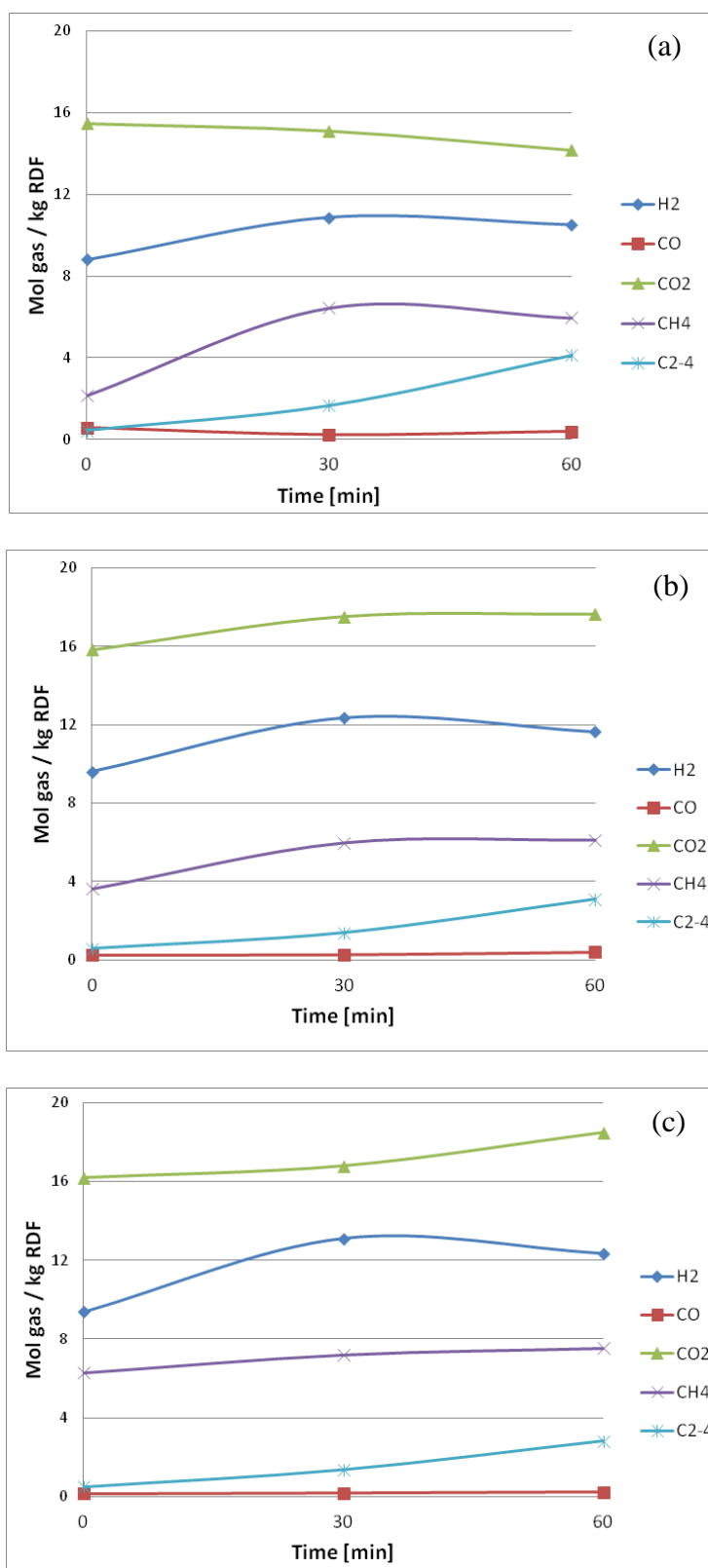


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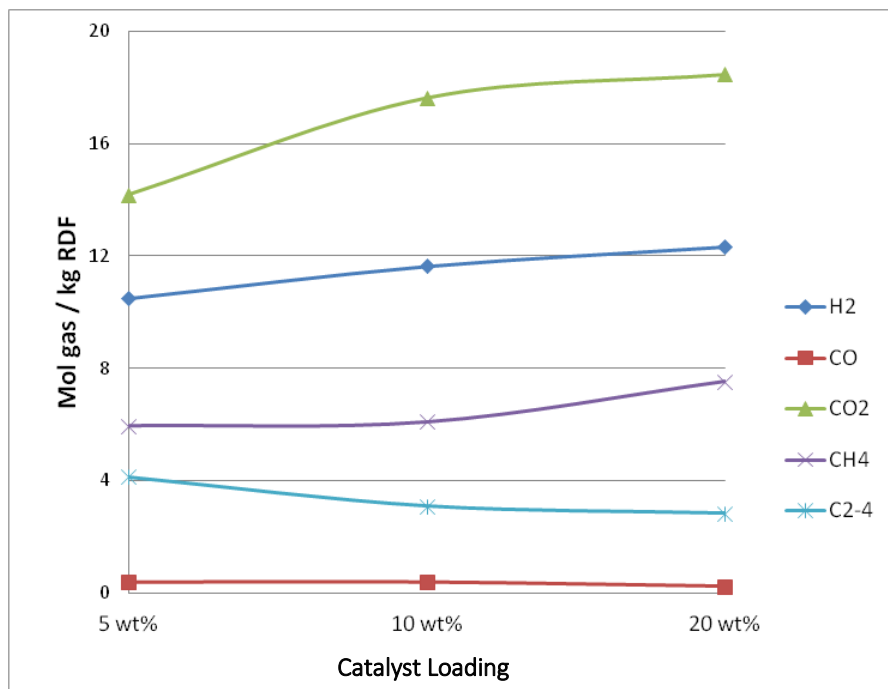


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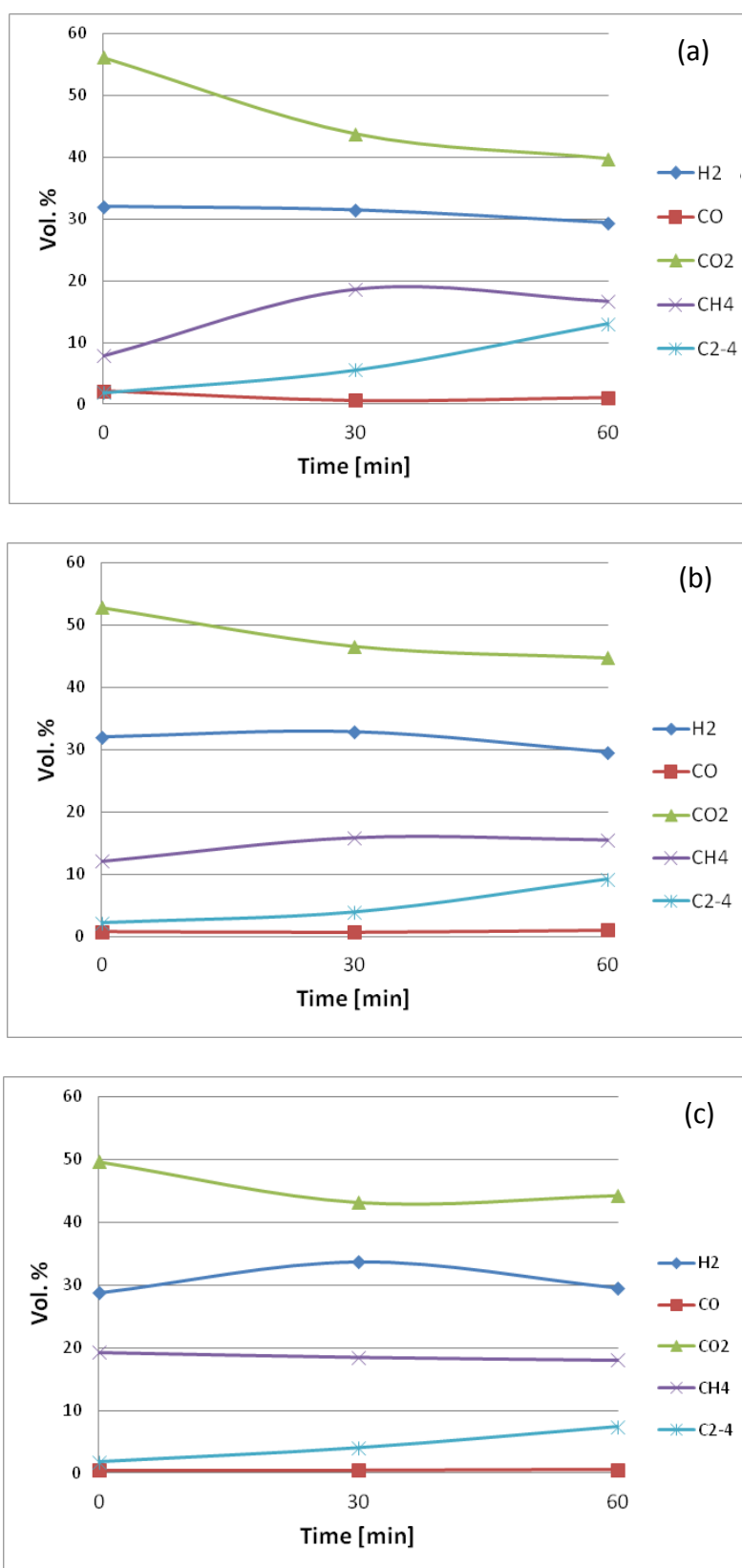


Fig. 6. Product gas composition (Vol.%) produced from the supercritical water gasification of RDF at 500°C with 5 wt.%, 10 wt.% and 20 wt.% RuO₂/γ-Al₂O₃

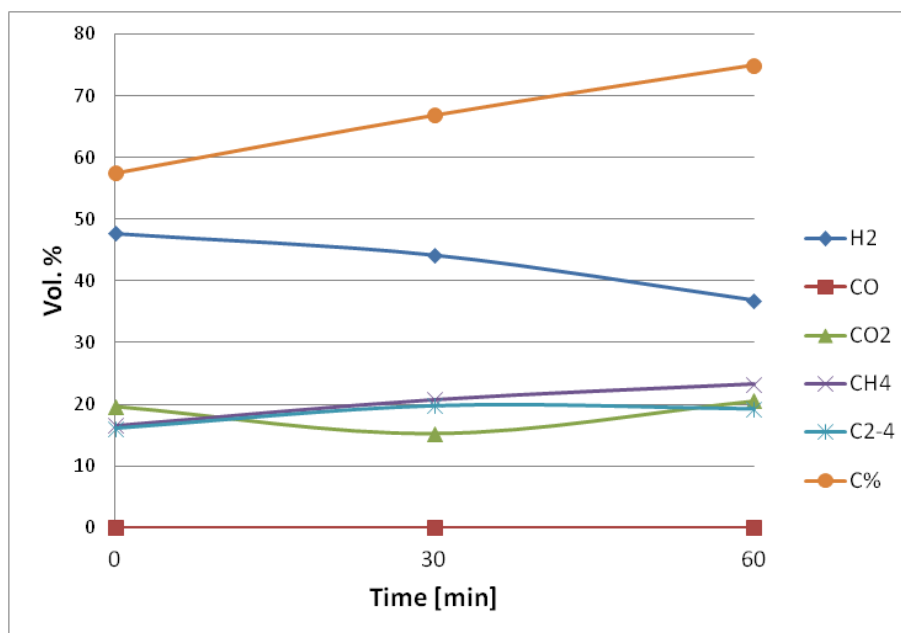


Fig. 7. Product gas composition (Vol.%) and carbon gasification efficiency for the supercritical water gasification of RDF at 500 °C with NaOH in relation to reaction time

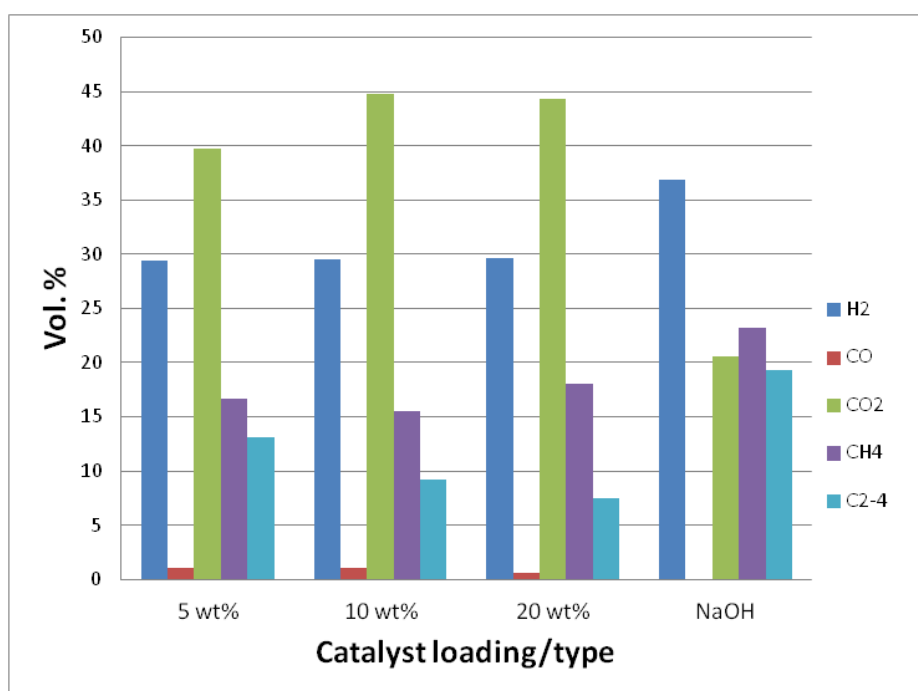


Fig. 8. Product gas composition (Vol.%) and carbon gasification efficiency for the supercritical water gasification of RDF at 500 °C and 60 min. reaction time in relation to different catalysts and catalyst loadings.

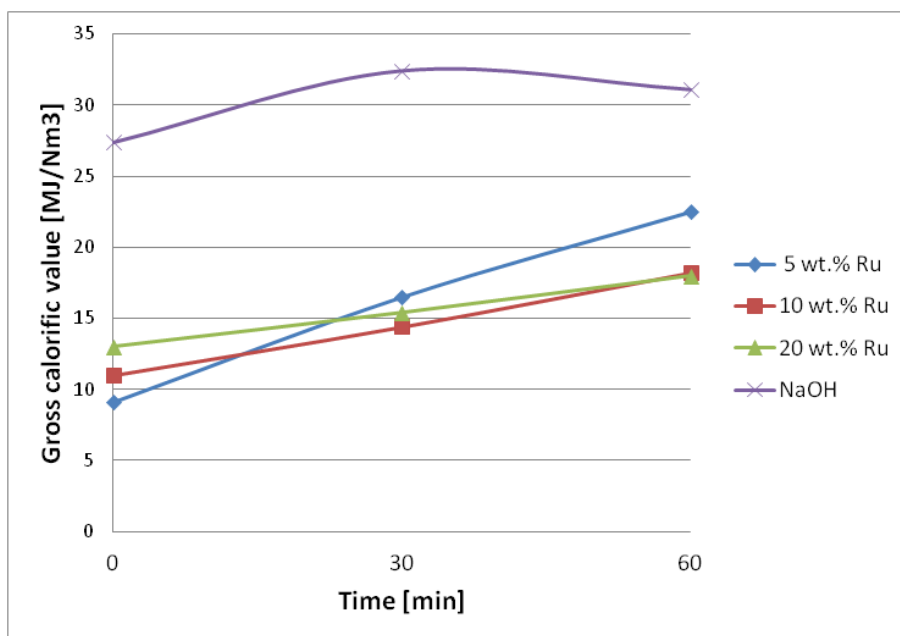


Fig. 9. Gross calorific values of the gas products in relation to temperature and catalyst loading/type

Table 1. Distribution of RDF-carbon after catalytic hydrothermal gasification

Catalyst	Time (min)	TOC (g C/g RDF _c)	IC (g C/g RDF _c)	Gas (C wt.%)	Liquid (C wt.%)	Solid (C wt.%)*
Ru 5 wt%	0	0.10	0	52.1	21.3	26.6
Ru 10 wt%		0.08	0	57.1	17.0	25.9
Ru 20 wt%		0.05	0	64.3	12.0	23.7
NaOH		0.08	0.08	57.5	18.4	24.0
Ru 5 wt%	30	0.04	0	71.5	8.1	20.4
Ru 10 wt%		0.03	0	74.4	7.7	17.9
Ru 20 wt%		0.03	0	75.5	5.6	18.9
NaOH		0.07	0.11	66.9	15.7	17.4
Ru 5 wt%	60	0.04	0	88.2	9.2	2.7
Ru 10 wt%		0.04	0	89.3	8.0	2.7
Ru 20 wt%		0.02	0	92.8	5.1	2.1
NaOH		0.07	0.09	75.0	15.1	9.9

* Calculated by difference