

SUPERCRITICAL WATER GASIFICATION AS A TREATMENT FOR LABORATORY ORGANIC WASTES

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ABSTRACT

The thermodynamics of supercritical water gasification (SCWG) was studied in order to determine its potential for treatment of laboratory liquid organic wastes. A thermodynamic model based on the minimization of Gibbs energy was developed in Aspen Plus software that simulated the SCWG of liquid lab organic wastes on an ash free basis. The feed stream contained a mixture of aliphatic (hexane), oxygenated (acetone, ethyl acetate, ethyl ether, isopropyl alcohol and methanol), aromatic (toluene and xylene) and chlorinated hydrocarbons (chloroform and dichloromethane). The model showed that at a pressure of 25 MPa, low organic material concentration of 5–10% in the feed and temperatures over 600°C, SCWG resulted in hydrogen rich syngas with a trace amount of HCl in the liquid effluent. High conversion rates were obtained for oxygenated hydrocarbons having destruction and removal efficiency (DRE) greater than 99.99% with the rest of the compounds having a 100% DRE. The composition of the gaseous stream was found to be such that the gas could be released safely to the atmosphere or be stored at high pressure. The study established a proof of concept that there is potential for laboratories to use this method to deal with organic lab wastes with the SCWG process effluent that is environmentally friendly.

Keywords: Gasification; Gibbs energy; Laboratory organic wastes; Supercritical water.

1.0 INTRODUCTION

Various institutions such as hospitals, universities, schools and industrial sites are host to laboratories that perform a wide range of tasks that deal with chemical and biological experimentation. These laboratories can be defined as areas where relatively small quantities of chemicals and other substances are used for the purposes of teaching, research, diagnostic purposes or for any other purpose on a non-production basis (EPA, 2017). These laboratories use a wide variety of chemicals and as such generate a wide range of different chemical wastes, some of which pose hazards to the environment or to human health and safety. As such, to discourage the inappropriate disposal or accumulation of such wastes and to help facilitate the eventual removal of the said wastes, certain protocols are normally set in place. These protocols outline how lab wastes can be categorized, stored and disposed of in a responsible, safe and legal manner. Once the wastes are safely collected and categorized, the disposal process can begin which varies depending on the type of waste being dealt with (Council 1995). For

this study, the area of concern is on liquid waste streams with high organic content. Such waste streams fall under the category of chemical waste. Some examples of such chemical wastes include but are not limited to chlorinated solvents, aliphatic hydrocarbons, aromatics hydrocarbons, alcohols, glycols, ethers, esters, ketones, aldehydes, amines and amides. Temporary storage of waste is normally done in or near the laboratory. Safety considerations are the primary concerns during storage, therefore, safety protocols dictate that it should be ensured that wastes are classified and stored in separate containers. Wastes are labelled in containers that should be compatible with their contents. There are various regulations that indicate the allowed stored quantities and duration (Fedyeva & Vostrikov 2012; Guo *et al* 2010).

A few methods of waste disposal are currently available. Disposal through the sewer system is appropriate in some cases but it is generally becoming unacceptable in most places (Gasparovic *et al* 2011). Similarly, the landfill disposal is also becoming a concern due to environmental impacts (Waddell, 2015). The most commonly accepted method of disposal of lab wastes is incineration. For incineration to be effective, the waste should contain at least 60% combustible material and a moisture content that does not exceed 30%. Under such circumstances, pre-treatment is often required to reduce the moisture content of the waste before it can proceed to incineration process (Kratky & Jirout, 2015). Incineration is the preferred method of waste disposal due to several reasons. The most important being that it gives the waste generators the best assurance in terms of long term safety from liability as compared to other forms of disposal. Due to the thermal treatment, the associated hazards and volume of the waste are reduced, thus, allowing the residue of the treatment to be disposed of in landfills in a safe and legal manner. However, emissions from waste incineration cannot be eliminated which may emit many hazardous gases such as carbon dioxide, carbon monoxide, sulphur oxide, nitrous oxide, methane, dioxins, fluorinated, perfluorinated hydrocarbons and fine particles are also often present in emissions (Solcov *et al* 2014). Despite the fact that strict regulations and restrictions are in place to monitor and control these emissions, the concerns about the potential hazards and risks associated with such a process are still very much alive.

The method of accumulating liquid organic waste in laboratories for the purpose of disposal is burdensome and is a potential workplace hazard (Waddell, 2015). As such, there is room for improvement in the status quo and research into much more suitable and environmentally friendly alternative processes and technologies to deal with such wastes are underway. One such technology, which seems to hold promise in this regard, is the process of supercritical water gasification. Many studies done on the topic of supercritical water gasification focus mainly on using it as a means for production of syngas, using moisture rich organic feed such as wet biomass for power generation or waste treatment (Acelas *et al* 2014; Bircan *et al* 2012; Byrd *et al* 2008).

The objective of the current research study was to develop a model that simulated the supercritical water gasification process that could represent the liquid organic wastes of laboratories and to determine the products of the SCWG process and whether the reactor effluent could be safely disposed to the environment.

Supercritical Water Gasification

Supercritical water gasification, which makes use of the special properties of water at its supercritical temperature and pressure ($T > 374$ °C and $P > 22.1$ MPa), has the ability to convert feedstock with high moisture content into hydrogen rich syngas, without requiring an additional step of pre-treatment of drying the feedstock. It was also noted

that the process produces little to no char as compared to other traditional gasification processes (Modell, 1977; Chuntanapum & Matsumura, 2010; Susanti *et al.*, 2014). The supercritical water as a single component fulfils multiple functions in its role as a solvent, reactant and catalyst. These unique thermo-physical properties of water at its supercritical state can be used to break down organic compounds. The mass transfer resistance in supercritical water becomes insignificant due to the fluid's high solubility and diffusivity of gases and organic material. The low dielectric constant of water provides high solvating power for organic compounds. The result is that supercritical water acts as a single phase, non-polar gas with high density but with properties similar to that of organics with low polarity. Add to that the increased concentration of both hydrogen and hydroxide ions due to a higher degree of disassociation at supercritical conditions; the power of the hydrolysis reaction increases as a result. Therefore, while hydrocarbons and gases such as CO₂, N₂ and O₂ are highly soluble, inorganic salts remain practically insoluble in supercritical water. This further enhances the oxidation kinetics of the organic species due to the absence of mass transfer limitations under such unique conditions and properties. This is exactly what makes supercritical water compatible and applicable to a wide array of diversified feeds (Youssef, 2011). These properties allow supercritical water to act as a solvent, reactant and catalyst at the same time and create a medium for reaction that is very conducive to the destruction of organic material.

Other advantages include the easy capture and storage of gaseous products utilizing the high pressure reactor conditions. CO₂ can also be separated easily from the gaseous product due to its high solubility in water at high pressure (Guo *et al.*, 2010). The selectivity of the process can also be altered by changing the process and reaction conditions. While all these factors give SCWG an edge compared to conventional forms of treatment, taking into account the non-polar behaviour of the fluid reduces the solubility of salts in the water, which lead to salts depositing on the reactor walls alongside plugging problems (Fedyeva & Vostrikov, 2012).

Thermodynamic Analysis

Thermodynamic analysis is a very useful tool to obtain realistic information about the composition of the system when it reaches equilibrium (Withaget *et al.* 2012). The influence of various parameters such as temperature and pressure on the system can be studied independently of the reactor or gasifier design. Each of these parameters can be studied independently in the reactor. Stoichiometric and non-stoichiometric approaches are widely used in the thermodynamics of the equilibrium reactions. The stoichiometric approach is based on the reaction equilibria and their equilibrium state. The contributions on each individual reaction to the system and conversion for each reaction need to be known beforehand (Castello & Fiori, 2011). A non-stoichiometric method is another approach used to analyse the reaction system (Tushar *et al.*, 2015). In this approach, no reaction stoichiometry need to be defined, only the species in the reaction input and the expected product. The product that enables the system to reach the minimum Gibbs free energy is evaluated and when the minimum Gibbs energy is reached, the energy of reaction will equal zero. The change in Gibbs energy with respect to the extent of the reaction (ξ) is shown in Equation (1):

$$\Delta_r G = \partial G / \partial \xi \quad (1)$$

If the Gibbs energy of reaction is not zero, then there must be a point of lower Gibbs energy. Thermodynamic models found good predicting for carbon dioxide, hydrogen and methane in biomass gasification of agreement with experimental data (Withag *et al.*, 2012; Tushar *et al.*, 2015). Supercritical water gasification of wet biomass is reported in the temperature range of 500 to 700 °C and pressures from 23 – 48 MPa. The temperature found to have a significant effect on the yield of product. On the contrary, a change in pressure did not show any significant contribution to the reaction system yield. On other study on the biomass supercritical water gasification syngas and methane yields are increased with lowering the water contents in the feed (Fiori *et al.* 2012) and high biomass concentration in the feed correspond with lower production of hydrogen (Louw *et al.* 2014).

The thermodynamic equilibrium model to determine the equilibrium product compositions in the SCWG, with a wide variety of model feedstock compounds is well addressed in the literature (Magdeldin *et al.*, 2016; Louw *et al.*, 2014). The results of these models vary slightly but there are general trends that are in agreement and can be extracted from all these studies. (1) An increase in temperature resulted in an increase in the yield of hydrogen and a decrease in the yield of methane. (2) An increase in the water to biomass feed ratio resulted in an increase in the yield of hydrogen and a decrease in the yield of methane. (3) Increasing the pressure of the system above that of the critical pressure of water did not have any significant effect on the gaseous yields.

The thermodynamic properties of a chemical can be calculated using a properly selected property method. The equation-of-state (EOS) method that can be applied to all phases, while activity co-efficient method is preferred in predicting the properties of polar components. EOS method is recommended when considering high-pressure and high temperature process such as supercritical water conditions (Withag *et al.* 2012). Aspen Plus software hosts a wide range of property methods including the activity coefficient and equation of state methods. For SCWG, an EOS is a more suitable method owing to the high pressure under which the process operates. Fiori *et al.* (2012) used a Peng-Robinson (PR) equation of state to model the SCWG process and to perform thermodynamic equilibrium calculations. Withag *et al.* (2012) did a comprehensive review to ascertain which EOS would be most suitable for SCWG. The study noted that while the property method Ideal (based on the ideal gas law) was simple and easy to use, it had difficulties when calculating vapour-liquid equilibrium. This property method also does not consider intermolecular interactions or the volume of the molecules. The study noted that while the Peng-Robinson (PR) and the Redlich-Kwong (RK) methods did account for intermolecular interactions and the volume of the molecules, they were not very accurate when it came to predicting the fluid behaviour at high pressures. The study noted that these EOS were useful to predict the thermodynamic properties of a pure components but not that accurate for mixture. As such, the study advised to use a mixing rule to better predict the thermodynamic properties of polar mixtures. A mixing rule adds onto the EOS and helps to better predict such thermodynamic properties. The study concluded that a good property method for such chemical processes at supercritical conditions was the Soave Redlich-Kwong method with the modified Huron-Vidal mixing rule (SRK-MHV2).

The results of a study by Tushar *et al.* (2015) show that the pressure only had a slight and rather insignificant effect on the equilibrium gas yield. This can be attributed to the thermodynamic model that was used. The fluid package or Equation of State that was used was “IDEAL” on Aspen Plus. In this fluid package, the equilibrium and phase calculations are done mainly using the ideal gas law. The authors used this fluid

package for the sake of simplicity. It is possible that using such a method does not accurately predict the kinetics and effects of pressure at the supercritical phase. Therefore, the model under-predicts the product gas yield at different pressures. The reason for this claim is that Withag *et al.* (2012) used a similar thermodynamic model as that of Tushar *et al.* (2015). The main difference between the two models was that of which fluid package or EOS which was used. Withag *et al.* (2012) used the EOS of RKS-BM (Redlich-Kwong-Soave with Boston Mathias mixing rule). This predicted the effect of pressure on the SCWG process much more accurately. The ideal EOS does not work accurately at supercritical conditions, as it does not consider the intermolecular interactions and the volume of the molecules themselves. However, the RKS-BM EOS accounts for both of these factors and therefore, is much more accurate. It can be inferred from this that the use of the proper EOS is very important when developing a model that operates at supercritical conditions.

The reason that a non-stoichiometric method was chosen for this study is mainly the fact that the influence of various parameters on the system can be studied without the need to consider the reactor or gasifier design. The method of modelling shows good agreement with experimental studies. The choice of property method or EOS is an important aspect to ensure good accuracy of result. The conclusion reached from the review of established literature and studies is that a cubic form of EOS such as the ones based on Peng-Robinson and Redlich-Kwong-Soave are much more accurate than a simple one based on the Ideal Gas Laws.

2.0 MATERIALS AND METHODS

2.1 Model compound selection

The model compounds were determined using a survey conducted by Nagasawa *et al.* (2011). In this survey, various types of solvent and their air-borne vapour concentrations were measured and compared to safety regulations. A total of 47 organic solvents were tested and compared to safety regulations as prescribed by the Ordinance on Prevention of Organic Solvent Poisoning. This regulation categorized organic solvents into three groups, Group 1, Group 2 and Group 3 solvents based on the danger they posed to the humans they were exposed to. Solvents in Group 1 are the most dangerous and those in Group 3 are the least dangerous. Nagasawa *et al.* (2011) only tested for the 7 Group 1 solvents and 40 Group 2 solvents prescribed in the regulation. 1909 laboratories were surveyed and the results were categorized into five groups in terms of research field. These were agriculture (AGR), biological (BIOL, excluding medicine), medicine (MED), natural science (SCI), and technology and engineering (T&E). For this study, only the Group 2 solvents were considered. The results of the survey of Group 2 solvents and that those solvents with a normalized percentage of prevalence of more than 10% were included. This narrowed down the list to 10 compounds as shown in Table 1. These compounds were used in the simulation as a representation of liquid organic lab waste. The property of the selected compounds was obtained from Aspen Plus databank.

2.2 Product species

To utilize the Gibbs free energy minimization approach, the species that are expected as the products of the process need to be defined. In the current study, only the organic compounds in the feed were included. The modelling was made based on ash/char free basis. It should also be noted that there are chlorinated hydrocarbons present in the set of chosen model compounds in Table 1.

Table 1:List of Group 2 Solvents with more than 10% prevalence.The organic compounds along with the fraction in total waste and the concentration of each respective organic species in 5, 15, 25, and 35 wt% of total organic concentration.

Total Organics Species	NormalizedPrevalence (%)	Organic Feed Concentration (wt%)			
		5	15	25	35
Chloroform	15.86	0.79	2.38	3.97	5.55
Acetone	15.67	0.78	2.35	3.92	5.48
Dichloromethane	4.44	0.22	0.67	1.11	1.56
Ethyl acetate	6.78	0.34	1.02	1.70	2.37
Ethyl ether	7.36	0.37	1.10	1.84	2.57
Hexane	8.01	0.40	1.20	2.00	2.80
Isopropyl alcohol	10.46	0.52	1.57	2.61	3.66
Methanol	18.93	0.95	2.84	4.73	6.62
Toluene	5.63	0.28	0.84	1.41	1.97
Xylene	6.86	0.34	1.03	1.71	2.40
Total	100.00	5.00	15.00	25.00	35.00

In a study of the supercritical water gasification of chicken manure by Bircan *et al.* (2012), the chlorinated species detected in the products was mainly HCl. The presence of dioxins such as polychlorinated dibenzo para dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) were also tested. PCDDs and PCDFs were not detected but some PCBs were detected. Therefore, 4,4-dichlorobiphenyl was also included as a model compound for PCBs that could be formed in the product streams. Some studies also have found the presence of ethane and ethylene in trace amount, therefore, these compounds were included as possible products as well. Under these circumstances, the most important elements and compounds that were included in the product species are water, hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, hydrogen chloride, chlorine gas, and 4,4-dichlorobiphenyl. The product species in this list are selected based on the assumption that they are the products of the decomposition of organic materials. Organic materials are rich in hydrogen, carbon and oxygen, and decompose into basic compounds of these elements. Methane, ethane, ethylene is included as they are a small chain hydrocarbons and they may form during SCWG. Longer chain hydrocarbons are not included in the list of products as they all assumed to decompose at SCWG reaction condition (Fiori *et al.*, 2012).

2.3 Modelling and simulation

The supercritical pressure of water is 22.1 MPa. The pressure that the simulation for this study was run at was set at 25 MPa. The temperature was ranged from 450 °C to 700 °C. And, the feed concentration was varied between 5% to 35% organics in feed as shown in Table 1. A thermodynamic equilibrium model, based on a non-stoichiometric approach using the minimization of Gibbs free energy was generated using Aspen Plus software. The RGIBBS reactor module employs calculations based on the Gibbs free energy minimization that can be used to model thermodynamic and chemical equilibrium at a specified temperature and pressure. Under such a set-up, the following assumptions are made:

1. The reactor was considered to be zero-dimensional.

2. The gasifier was considered to be perfectly insulated so heat losses were neglected.
3. There was perfect mixing and uniform temperature throughout the reactor.
4. Reaction rates were fast and the residence time was sufficient enough so as to allow the system to reach an equilibrium state.
5. The simulation was performed on an ash/char free basis so there was no char production in the process.

Peng-Robinson (PR) was selected as property equation. This property method is accurate in predicting conditions at supercritical states (Louw *et al.*, 2014; Withag *et al.*, 2012). The effluent of the reaction system is analysed in terms of its composition so as to determine whether the chemical composition of the effluent can be disposed of through the municipal drainage system. This is done through the destruction and removal efficiency (*DRE*) and organic chloride conversion (*OCC*). The requirements for an incinerator is that the destruction of hazardous waste must achieve a *DRE* greater than 99.99 percent for each principal organic hazardous constituent (POHC) (Lee *et al.*, 1986). The same standards can be applied to a gasifier as they are both being used to treat the same kind of waste. The Destruction and Removal Efficiency (*DRE*) is defined in Equation (2) and the Organic Chloride Conversion (*OCC*) is defined in Equation (3).

$$DRE (\%) = \left(\frac{W_{in} - W_{out}}{W_{in}} \right) \times 100 \quad (2)$$

Where

W_{in} = Mass flow rate of going in (kg/h)

W_{out} = Mass flow rate of going out (kg/h)

$$OCC (\%) = \left(\frac{W_{in} - W_{out}}{W_{in}} \right) \times 100 \quad (3)$$

Where

W_{in} = Mass flow rate of organic chloride going in (kg/h)

W_{out} = Mass flow rate of organic chloride going out (kg/h)

3.0 RESULTS AND DISCUSSION

3.1 Model validation

Results of the model were validated by comparing them with the results in the literature. By comparing the trend of the effect of temperature on the gaseous species between the model in this study and the model published by Tushar *et al.* (2015), it could be ascertained whether the base model was working correctly. Regardless of what organic feed is used, the trend that is seen in experimental studies is similar to the model data at different temperature in which H_2 and CO_2 yields increases and CH_4 and CO yields decreases (Bryd *et al.*, 2008; Susanti *et al.*, 2012; Nanda *et al.*, 2016). Tushar *et al.* (2015) used glucose as the feed and the results were in line with the experimental studies. Therefore, as a test run for model validation, the feed was changed to glucose. If the simulation gives results that are in good agreement with Tushar *et al.* (2015), then the base model is validated with acceptable accuracy. The feed compounds can then be changed to the ones selected as the model compounds for lab waste. It was observed that the gaseous species followed a similar trend. The model has a better correlation at higher temperatures than at lower temperatures. It should be noted that the model used by Tushar *et al.* (2015) uses ideal gas law for thermodynamic property calculations in which they tend to over-simplify a complex process such as SCWG by ignoring many of the intermolecular interactions, which occur at high pressures. This could over-

predict the results, which explains the discrepancies between the two models. Peng-Robinson property method is used in this study, which provides results that are more accurate under supercritical conditions.

The equilibrium mole fraction of the four gaseous products at different equilibrium temperatures in the range of 450 – 700 °C are presented in Table 2. The root mean square error (*RMSE*) for the four products are presented in Table 3. The %*RMSE* for CO and CO₂ were found within acceptable bounds. The %*RMSE* is higher for H₂ and CH₄. This is because the model that this is being compared with over predicts the results for hydrogen at lower temperatures and under-predicts the results for methane at higher temperatures. Nonetheless, the equilibrium data obtained from the simulation are in good agreement with established models. This base model that was used in this study and by Tushar *et al.* (2015) are one of the most commonly used models for the SCWG process. It can be concluded that the modelling approach is capable of predicting the product yield with reasonable accuracy.

Table 2: Equilibrium composition (mole fraction) of the gaseous product in the temperature range of 450 –700 °C.

Product species	Temperature (°C)					
	450	500	550	600	650	700
Hydrogen (H ₂)	0.2077	0.3291	0.4413	0.5315	0.5952	0.6330
Carbon monoxide (CO)	0.0009	0.0020	0.0039	0.0066	0.0101	0.0139
Carbon dioxide (CO ₂)	0.4473	0.4161	0.3867	0.3621	0.3435	0.3312
Methane(CH ₄)	0.3439	0.2526	0.1680	0.0996	0.0510	0.0217

Table 3: The difference (error) ΔE and the root mean squared error between the current model and that of reference Tushar *et al.* (2015).

Product species	Temperature (°C)						Error (E) $\sum E$	<i>RMSE</i> $\sqrt{(\sum E/n)}$	<i>RMSE (%)</i> $100\sqrt{(\sum E/n)}/\sum E$
	450	500	550	600	650	700			
Hydrogen (H ₂)	0.0180	0.0126	0.0070	0.0031	0.0010	0.0002	0.0419	0.0836	18.31
Carbon monoxide (CO)	2.1E-09	2.6E-08	1.3E-07	4.9E-07	1.5E-06	3.4E-06	5.6E-06	0.0010	15.45
Carbon dioxide (CO ₂)	0.0011	0.0008	0.0004	0.0002	5.1E-05	5.9E-06	0.0025	0.0207	5.42
Methane(CH ₄)	0.0101	0.0071	0.0039	0.0017	0.0006	0.0001	0.0235	0.0626	40.09

The overall decomposition reaction for such a feed compound in supercritical water is summarized in Equation (4). CO can subsequently undergo a water-gas-shift (WGS) reaction that may increase yield of the H₂ and CO₂ gas as shown in Equation (5). CO and CO₂ may also undergo methanation reactions to produce CH₄ as shown in Equations (6) and (7). The effect of the oxygen content in a biomass SCWG, with high carbon and low oxygen content, a gas product with a maximum theoretical hydrogen yield is produced (Louw *et al.*, 2014).



3.2 Destruction and removal efficiency (DRE)

The Complete gasification of the aliphatic, aromatic and chlorinated hydrocarbons in the feed was obtained at all the different temperatures and concentrations. The *DRE* for the oxygenated hydrocarbons (acetone, ethyl acetate, ethyl ether, isopropyl alcohol and methanol) in the feed was above 99.999% at all the simulated temperatures. This is considered to be near complete gasification of the hazardous feed material. This is in line with the results of multiple studies that have been reported at temperatures above 500 °C. (van Bennekom *et al.*, 2011; May *et al.*, 2010; Schmieder *et al.*, 2000). However, it should be noted that in this simulation, the *DRE* for oxygenated hydrocarbons decreased slightly with an increase in temperature, which is inconsistent with experimental studies. It should also be noted that the simulation results that were run with a high concentration of organics showed a trend of decreasing *DRE* with increasing organic concentration in the feed. This trend is in line with the reported results that complete gasification can be achieved even with high organic concentrations of up to 20 wt% in feed (Susanti *et al.*, 2012). However, the simulation over predicts the *DRE* at feed concentrations higher than 20%. This could be due to how the Gibbs Reactor operates in the Aspen Plus software as it assumes that equilibrium is reached after an infinite reaction time (Castello *et al.*, 2014). In reality however, this equilibrium is not always reached and this could explain why there is an over-prediction of results as compared to experimental studies.

3.3 Effect of temperature on product composition

The effect of temperature of the yields of hydrogen, carbon monoxide, carbon dioxide and methane is presented in Figure 1. Trace amounts of ethylene and ethane were also detected in the simulation results on magnitude of 10^{-6} kmol/h in the product stream. At such insignificant concentrations, they were not included in Figure 1. The temperature has a prominent effect on the hydrogen and methane yields. It can be noted from Figure 1 that with increasing temperature, the hydrogen yield increased and the methane yield decreased. The water gas shift reaction, which is endothermic, is favoured at high temperatures and the methanation reaction, which is an exothermic reaction, is favoured at relatively lower temperatures. The theory and experimental studies suggest that with increasing temperature, an increase in carbon dioxide alongside a slight increase and carbon monoxide is expected so as to compensate for the methane consumption (van Bennekom *et al.*, 2011). The small increase in CO can be observed in Figure 1. However, the model in this study shows that an increase in temperature resulted in a slight decrease in the production of carbon dioxide. Tushar *et al.* (2015) and Withag *et al.* (2012) reported similar simulation results. Nevertheless, this small inconsistency does not affect the overall accuracy of the results as the trends are still within good agreement with experimental studies (Byrd *et al.*, 2008; Castello *et al.*, 2014; van Bennekom *et al.*, 2011).

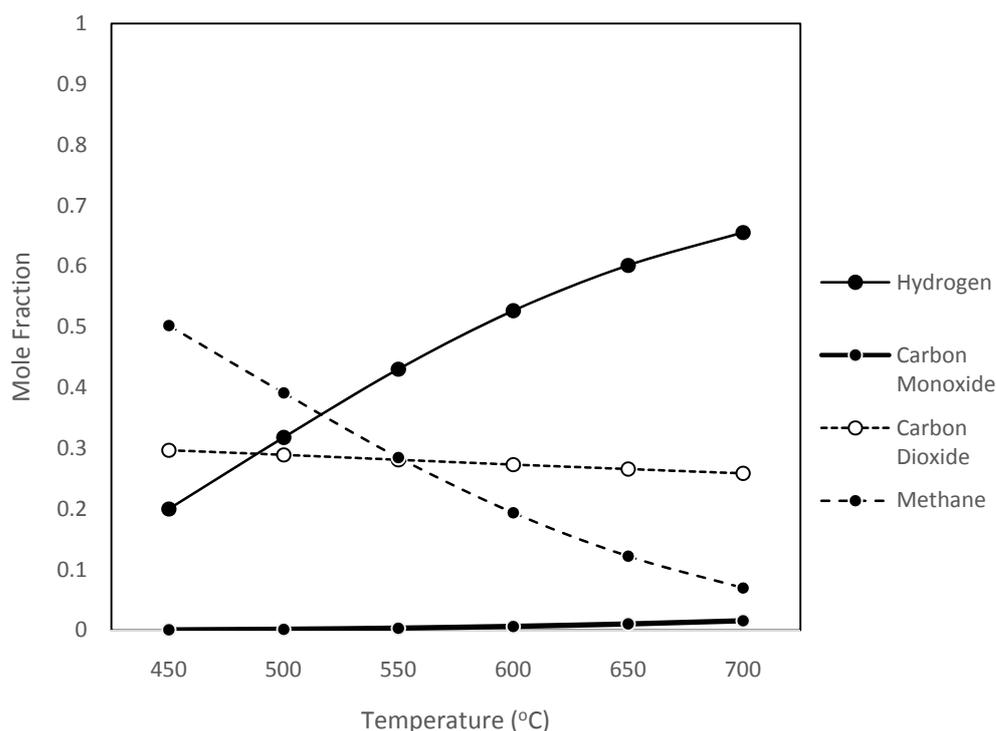


Figure 1: The effect of temperature on the product gas species (dry gas basis)

3.4 Effect of feed organic concentration

The concentration of the organic material in the feed also has a prominent effect on the hydrogen and methane yields. The water gas shift reaction, which is endothermic, is favoured at high temperatures and the methanation reaction, which is an exothermic reaction, is favoured at relatively lower temperatures. This is confirmed from Figure 2 which shows that with increasing organic concentration in the feed, the hydrogen yield decreases and the methane yield increases. Similar trends from simulations were observed in a study by Withag *et al.* (2011) and Tushar *et al.* (2015), and in experimental studies by Susanti *et al.* (2014) and Bennekorn *et al.* (2011). Trace amounts of ethylene and ethane were also detected in the product stream. The largest amounts of ethane and ethylene were detected at the 35% organic feed concentration on a magnitude of 10^{-3} and 10^{-5} kmol/h, respectively. At such insignificant concentrations, they were not included in Figure 2.

3.5 Organic chloride conversion (OCC)

The organic chloride conversion (OCC) is found to be 100%. At all temperatures above 450 °C with a 5% organic material in the feed, the PCB concentration (4,4-dichlorobiphenyl) was found to be zero. It can be inferred that at higher temperatures, the destruction of intermediate compounds, which form such PCBs, is much more thorough. The results, as shown in Table 4, also show that at feed concentrations higher than 5%, some PCBs are produced. These are in the range of 10^{-46} to 10^{-39} kmol/h. The trend is such that the higher the feed concentration, the higher the concentration of PCBs that are produced. These results are in agreement with experimental studies by Bircan *et al.* (2012) which also concluded that at higher temperatures and lower concentrations, the concentrations of PCBs produced are lower.

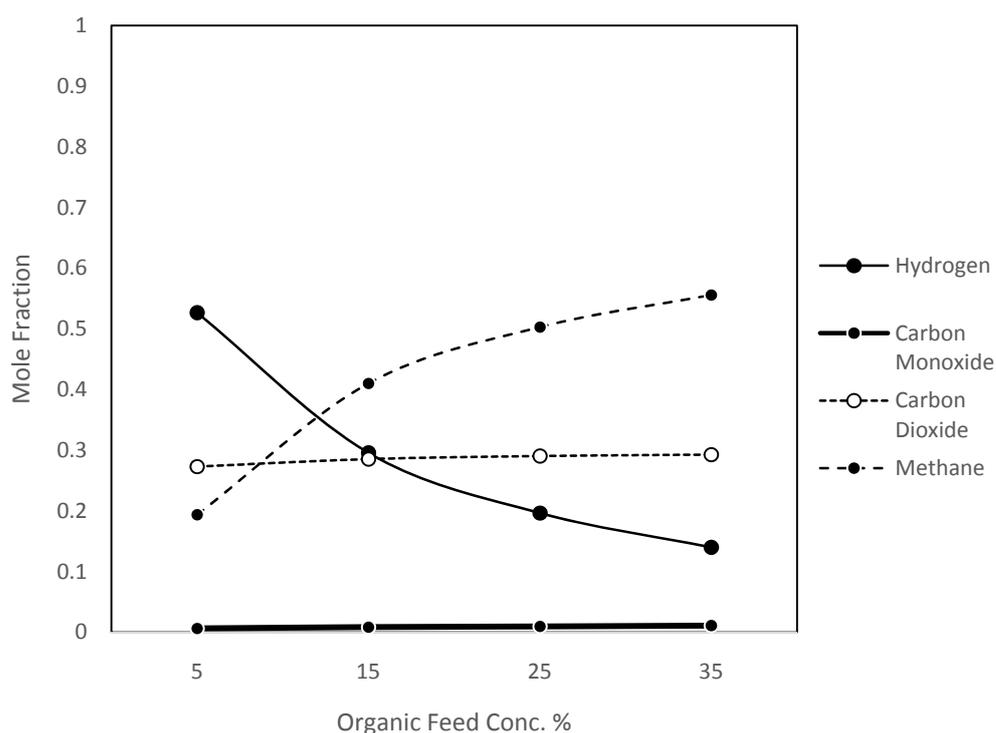


Figure 2: Effect of organic feed concentration on the product species (dry gas basis)

Table 4: The molar flow rate and mole fraction of PCBs in the product liquid stream

Organics Feed Conc. (%)	5	15	25	35
PCB (kmol/h)	0	9.15E-46	5.06E-42	3.10E-39
PCB (Mole Frac.)	0	2.1E-46	1.3E-42	9.7E-40

The results from the simulation indicate that there was a complete conversion of organic chloride at all different temperature and concentrations. Studies show that there is virtually no Cl_2 gas produced during SCWG process (Fedyeva & Vostrikov, 2011). In reality, this Cl_2 will become HCl when it comes into contact with water. The reason this simulation shows the production of Cl_2 is the fluid package that was used to simulate the process at supercritical conditions. This fluid package that gives relatively accurate results for processes operating at supercritical conditions is not so accurate when it comes to the prediction of the production of ionic species. Another fluid package is needed to accurately determine the ionic and dissociative activities of compounds such as HCl and Cl_2 in water. Unfortunately, these two fluid packages cannot operate side by side in the same model due to the limitations of the modelling software. Overall, the results are still in agreement with studies by Bircan *et al.* (2012) and Fedyeva and Vostrikov (2011).

4.0 CONCLUSIONS

High destruction and removal efficiency (*DRE*) was observed at all temperatures with low concentrations of organics in the feed in 5–10% range. A one hundred per cent organic chloride conversion (*OCC*) were obtained at all temperatures and feed concentrations. The formation of PCBs was found to be suppressed at high temperatures with low organic feed concentrations 5–10%. Within the context of the obtained results,

the proposed operating parameters to achieve a 99.99% *DRE* are at an inorganic feed concentration of 5–10% and a temperature above 600 °C. The liquid effluent was found to be water with traces of HCl, which could then be safely disposed of through the municipal drainage system. Therefore, the study established a proof of concept that supercritical water gasification (SCWG) process can be applied for the destruction and treatment of liquid lab organic wastes in order to reduce the waste toxicity and aid with disposal through the municipal drainage system.

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