PREDICTIVE MODEL FOR FUELS FROM HYDROTHERMAL LIQUEFACTION OF MUNICIPAL SOLID WASTE

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ABSTRACT: Effective management of the environmental impact of municipal solid waste (MSW) is a global issue linked to urbanization and a rapid increase in the global population. Although MSW has been evaluated as possible feedstock for biofuels/energy production, prediction of possible fuel yields is difficult due to large variances in composition between different locations. Furthermore, although hydrothermal liquefaction (HTL) is well known for the conversion of wet waste to fuels and energy, yields and composition of products is not only dependent on operating conditions, but also the characteristics of the feedstock. In this paper, we present a simple additivity model based on compositional analysis of the feedstock to predict HTL production yields and characteristics from MSW. Garden waste, food waste, paper sludge, waste plastics, rubber and textiles were used as model individual components to represent MSW. Xylan, α-cellulose, lignin, protein, starch and fat was used as model components to represent typical biomass. An additivity model was derived, based on the characteristics of each individual component of MSW to predict fuel and energy yields from a typical landfill site. Plastics, rubber and textiles were poorly converted, but did not significantly influence HTL conversion of garden waste, food waste and paper pulp in a synthetic MSW mixture. The model showed a good fit for predicting bio-oil and biochar yields of a municipal solid waste mixtures based on compositional analysis of individual components of the mixture. Both the bio-oil and biochar models could be validated with published data. This work holds promise for developing a detailed predictive model that could be applied to any mixture containing any combination of organic components with a known compositional analysis. Prediction of HTL-based fuel/energy potential from a known site could significantly improve business case scenarios and fast track commercialization of waste-to-energy technologies.

Keywords: Municipal solid waste, landfill, hydrothermal liquefaction.

1 INTRODUCTION

Reduction in greenhouse gas (GHG) emissions to meet governmental targets is of critical importance to all countries dependent on fossil resources for primary energy needs. In this context, biofuels have gained a vital role in reducing emissions from fuels. The controversy surrounding 1st and 2nd generation biofuels in terms of food security and land use change has highlighted the need to look for alternative source of carbon for biofuels production. While municipal solid waste (MSW) is an abundant resource, its complex nature and high water content limits its use in current biofuels production processes.

Hydrothermal liquefaction (HTL), a thermochemical conversion process that can convert wet waste into bio-crude oil, biochar, gas and an aqueous product, is not sensitive to feedstock variability in terms of water content, free fatty acid (FFA) content and pH.

HTL would thus be well suited to convert wet MSW to fuels and chemicals. Commercialisation of HTL technology have however been limited due to uncertainty in predicting product yield and quality from laboratory or pilot scale data. Confidence in predicted yields could significantly lower the financial risk of commercialisation and pave the road for utilising this technology for biofuels and bio-based chemicals and materials production.

There are three approaches to predicting product yield and quality of real feedstock mixtures from individual components. The additive approach is the simplest and easiest to apply to a wide spectrum of feedstock. This approach is based on the assumption that the biochemical components of a complex feedstock behave individually during HTL of a mixture and therefore HTL yields of mixture can be predicted based on the biochemical composition of the feedstock [1]. The second approach is also based on additive behaviour of individual components, but acknowledges that there are positive and negative synergistic effects between the individual components that can lead to higher or lower than expected product yields [2]. The third approach is based on reaction pathways and associated kinetic parameters.

Biller and Ross [1] developed an additive model for HTL of microalgae feedstock using albumin, soya protein, sunflower oil, asparagine, glucose and starch as model compounds. The linear model (Eq. 1) was reported on a dry and ash free (daf) basis as:

$$Y_{oil} = 0.8X_L + 0.18X_P + 0.06X_C \qquad (1)$$

Where Y_{oil} is the bio-crude oil yield (wt. %) and X_L, X_P and X_C were the biochemical compositions of lipids (wt. %), proteins and total carbohydrates in the feedstock respectively, and the constants in the equation were derived from the yields of individual model compounds.

The model was validated with experimental yields of *Chlorella*, *Nannochloropsis*, *Porphyridium* and *Spirulina*. The model could relatively accurately predict the bio-crude oil yield for *Chlorella* and *Nannochloropsis*, but could not predict the yield obtained from *Porphyridium* and *Spirulina*. The model did however confirm some relation between individual component yields and the yields obtained from the complex feedstock.

Teri *et al.* [3] improved on the model of Biller and Ross [1] by incorporating interaction terms in the model.

The paper evaluated 6 model biochemical components of algal biomass (albumin, soy protein, corn starch, sunflower oil, castor oil and cellulose) in single, binary and tertiary HTL experiments. The binary results showed positive and negative interactions, especially in the presence of protein, but the tertiary results conformed to the simple additive model. The conclusion was that binary interaction of individual components cancelled each other out during HTL of tertiary mixtures. The model (Eq. 2) showed good prediction of tertiary mixture yields.

$$Y_{oil} = 0.95X_L + 0.33X_P + 0.06X_C + dX_LX_C + eX_LX_P + fX_CX_P \qquad (2)$$

Constants a, e and f where obtained from regression of binary experimental data.

Leow *et al.* [4] also developed a model for prediction HTL bio-crude oil yield from microalgae. The study differed from previous work by introducing a Fatty Acid (FA)-based model (Eq. 3) for predicting bio-crude oil and aqueous phase yields. A related model could also be applied to accurately predict the quality of the bio-crude oil in terms of parameters such as elemental composition (CHNO), higher heating value (HHV) and energy recovery (ER). The FA-based model could better predict oil yield than an additive model (Eq. 4)

$$Y_{oil} = FAs + (\text{defatted component yields})*(100-FAs) \qquad (3)$$

Where FAs is the dry wt. % FA of the feedstock.

$$Y_{oil} = 0.97X_L + 0.42X_P + 0.17X_C \qquad (4)$$

The developed models were validated against experimental yields of *Nannohloropsis oculata* as well as data from previous publications. The disadvantage of this model is that data for yields from defatted feedstock is required to use the model.

Li et al. [5] used 24 algae samples of *Chlorella*, *Scenedesmus*, *Chlorogloeopsis* and *Spirulina* (12 raw samples and 12 defatted samples) to develop a multiphase model (Eq. 5 – 8) that can be used to predict HTL yields for bio-crude, biochar gas and the aqueous product as well as some properties of the oil, char and aqueous phase. The study showed that lipid content is most significant for bio-crude yield, aqueous yield is affected by protein and ash content and the gas and biochar yields are significantly affected by the carbohydrate content of the feedstock. Ash was added as an additional component of the model to account for inorganic in the feed distributing to both the aqueous and the biochar phase.

$$Y_{oil} = 0.85X_L + 0.56X_P + 0.22X_C \qquad (5)$$
$$Y_{aq} = 0.25X_P + 0.86X_A \qquad (6)$$
$$Y_{gas} = 0.07X_P + 0.46X_C \qquad (7)$$
$$Y_{char} = 0.41X_C + 0.18X_A \qquad (8)$$

Where Y_{aq}, Y_{gas} and Y_{char} is the aqueous phase, gas phase and char product yield (wt. %) respectively. X_A is the ash content of the feed.

Déniel *et al.* [6] was the first to report an additive model for predicting HTL yields from food processing residues. Model components used were glucose, guaiacol, microcrystalline cellulose, alkali lignin, glutamic acid and linoleic acid. Quadratic correlations (Eq. 9 and 10) with interaction parameters were used to predict oil and gas yields and a linear correlation (Eq. 11) was used to predict biochar yield. The model for the aqueous phase was determine by difference (Eq. 12).

$$\begin{aligned} Y_{oil} = {} & 0.05X_S + 0.95X_L + 0.18X_SX_P + 0.79X_SX_{lig} \\ & + 0.45X_SX_L + 0.23X_PX_{lig} + 0.44X_PX_L \\ & - 0.3X_{lig}X_L \qquad (9) \end{aligned}$$
$$Y_{char} = 0.33X_S + 0.64X_{lig} \qquad (10)$$
$$\begin{aligned} Y_{gas} = {} & 0.1X_S + 0.05X_P + 0.04X_{lig} + 0.32X_SX_P \\ & + 0.16X_SX_{lig} - 0.03X_SX_L + 0.16X_PX_{lig} \\ & - 0.02X_PX_L + 0.01X_{lig}X_L \qquad (11) \end{aligned}$$
$$\begin{aligned} Y_{aq} = {} & 0.48X_S + 0.05X_P + 0.68X_{lig} + + 0.95X_L \\ & + 0.5X_SX_P + 0.94X_SX_{lig} + 0.42X_SX_L \\ & + 0.39X_PX_{lig} + 0.42X_PX_L - 0.28X_{lig}X_L \qquad (12) \end{aligned}$$

Where X_S is the wt. % cellulose and hemicellulose sugars and X_{lig} the wt. % lignin in the feed. The model was validated with HTL yields for two model mixtures as well as blackcurrent pomace, raspberry achenes, brewer's spent grain and grape mace. It was concluded from this study that the inclusion of lignin as model compounds greatly improved the predictive capacity of the model for HTL product yields from lignocellulose feedstock.

Aierzhati *et al.* [7] developed a complex non-linear model that incorporated reaction temperature and reaction time in an effort to incorporate the effect of HTL conditions on bio-crude oil yield into the model (Eq. 13).

$$\begin{aligned} Y_{oil} = {} & 1.61X_L - 0.558X_P - 0.00625T_r^2 + 0.00565X_P^2 \\ & + 0.00324T_RT_r + 0.0108X_LX_C - 0.00273X_LT_R \\ & - 0.00465X_LT_r - 0.0077242X_CT_R \qquad (13) \end{aligned}$$

Where T_R and T_r is reaction temperature (°C) and reaction time (min.) respectively. Good correlation was obtained for this model compared to experimental data as well as published data.

Lu *et al.* [2] investigated the interaction effects between model compounds used in developing predictive models for HTL. Soybean oil, soy protein, cellulose, xylose and lignin were used as model compounds in single, binary, tertiary, quaternary and quinary mixtures. Models were developed that could relatively accurately predict bio-crude oil yield, elemental composition (CHNO) and higher heating value based only on feedstock biochemical composition. The models could more accurately predict the quality of the bio-crude oil than the yield.

There are thus many models developed to predict product yields and quality from HTL experiments. Surprisingly, even though some are more complex than others, most models are able to predict yields to within 10% of the experimental data, even if the same model is applied to the data of other researchers. All models are somewhat empirical in nature and make use of the behaviour of individual components during HTL to predict the yield of a complex feedstock.

In this work, we present a similar empirical model for the prediction of HTL product yields from municipal solid waste, based purely on the biochemical composition of the elements of municipal solid waste. To our knowledge, this is the first study that presents a usable model to estimate HTL-based fuel yields from landfill sites based only on the biochemical composition of the feedstock. This can be a very powerful tool to assist in narrowing down the accuracy of business case scenarios and play a vital role in fast tracking HTL technology for municipal solid waste and pollution reduction.

2 MATERIALS AND METHODS

2.1 Model compounds and chemicals

Xylan, α-cellulose, starch, sunflower oil, soya protein and lignin were used as model biochemical compounds.

Pure starch and α-cellulose were purchased from Sigma-Aldrich chemical company. Pure sunflower oil and soya protein were purchased from a local pharmacy as performance enhancement products. Sodium lignin was procured from a Kraft pulping mill (28°45'92" E and 28°53'38.76" E) in South Africa. The lignin was dried at 60 °C overnight to a moisture content of less than 10% and stored in air tight containers until used. Xylan was extracted from sugarcane bagasse that was sourced from the Sugar Mill Research Institute (29°52.3' S and 30°58.72 E) in South Africa. The bagasse was sun-dried to a moisture content of less than 10 wt. % and then milled to +1.77 mm using a hammer mill. The dried and milled bagasse was stored in air tight containers until used. Fibre analysis were done on the bagasse according to the methods of Sluiter *et al.* [8] and Wolfrum *et al.* [9].

Paper, garden waste, food waste and plastic, textile and rubber waste were used as representative components of municipal solid waste (MSW). Paper and plastic waste was procured from the campus recycling initiative of the Potchefstroom campus of the North-West University (NWU), South Africa. Paper waste contained cardboard, newspaper, office paper and magazines. Plastic waste contained polyethylene terephthalate, high and low density polyethylene, polyvinyl chloride and polypropylene. The garden waste was collected form the campus garden services and contained leaves, twigs and grass typical of domestic garden waste. Food waste was collected from the campus cafeteria and contained meat, oil, starch and vegetable residues. Textile waste was obtained from old clothing can contained polyester, cotton, wool, linen and nylon. Rubber waste was sourced from old bicycle tyres and contained SB rubber and nylon.

The food and garden waste was dried overnight at 60°C to a moisture content of less than 10 wt.%, chopped and mashed by hand and then stored in air tight containers until used. The paper waste was mixed with an equal amount of waste (by weight) to produce a paper sludge. Feedstock was characterised using proximate analysis and higher heating value (HHV). Food, garden waste and the paper sludge was analysed for fat, protein and total carbohydrate content by ARC-Irene laboratories (Pretoria), n SANAS accredited laboratory.

2.2 Hydrothermal liquefaction (HTL)

Only single component HTL experiments were performed. Single components (either biochemical components or MSW element components) were mixed in equal amount of water (by weight) in reactor sleeve that was place inside a 950 mL SS316 autoclave equipped with heating jackets and temperature controllers. After the reactor sleeve was loaded, the reactor flanges were tightened and the reactor was pressured to 0.5 MPa using high purity nitrogen (N2) to check for leaks. The system was then purged three times with N_2. Once all oxygen had been removed, the reactor was pressurised to an initial pressure of 1 MPa. The heating jacketed were attached and the reactor system was heated to 300 °C at a heating rate of approx. 2.5 °C/min. The residence time for all experiments were kept constant at 20 minutes. After the reaction was completed, the reactor was allowed to cool down to room temperature by convection. The gas product was safely vented and the reactor sleeve was removed and carefully weighed to calculate the total gas product yield. The content of the reactor sleeve was quantitatively transferred to a Büchner filter system were the biochar and liquid products were separated. The biochar was consecutively washed with hexane and acetone to remove all non-polar and polar oils from the char. The oil products were recovered by evaporation of the solvents in a rotary evaporator. The biochar and oil products were dried overnight at 60 °C and the dry weights were recorded to calculate product yields. All yield (g/kg) were calculated as g dry ash free (daf) product per kg feedstock (daf) used.

2.3 Analysis

SANS 5925, SANS 50 and SANS 131 standard methods were used to determine the volatile content, moisture content and ash content of the feedstock, biochar and bio-crude oil samples respectively. Fixed Carbon was determined by difference.

Purity of the extracted xylan was done by hydrolysis of the solid extracted product at 121 °C for 30 min. in 4% (w/w) sulphuric acid solution in water. Analysis of the hydrolysate was done using high performance liquid chromatography (HPLC). An Agilent 1200 instrument equipped with an autosampler, Biorad Aminex HPX-87P column and a refractive index (RI) detector. A 5 mM sulphuric acid solution as used as mobile phase. The analytical procedure followed to quantify the xylose sugars formed was according to the NREL LAP method of Sluiter *et al.* [8].

HHVs of the feedstock, biochars and bio-crude oil products were determined using an IKA C5003 bomb calorimeter.

3 RESULTS AND DISCUSSION

3.1 Model biochemical components

The six model biochemical component mixtures were converted through hydrothermal liquefaction at 260 °C and 300 °C and the bio-crude oil, biochar and gas yields obtained is given in Figure 1. The yields are given on a dry ash free (d.a.f) basis as wt.% of the feed. The mixture contained 20 wt. % cellulose, 10 wt. % xylan, 20 wt. % protein, 10 wt. % fat, 20 wt. % starch and 20 wt. % lignin. The proximate analysis of the model biochemical components used is given in Table I.

Table I: Proximate analysis of model biochemical components (wt. %)

	Moisture	Ash	Volatile Matter	Fixed Carbon	HHV (MJ/kg)
Cellulose	6.5	-	86.2	7.3	27.8
Xylan	-	-	100	-	3.8
Protein	5.2	5.3	84.1	5.4	29.0
Fat	-	-	100	-	39.7
Starch	11.8	0.3	86.4	1.5	19.9
Lignin	6.3	12.8	56.3	24.6	18.4

Only approx. 60% of the cellulose feedstock was recovered in the bio-crude oil, char and gas products.

The crystalline nature of cellulose results in slower degradation than hemicellulose. Sakaki *et al.* [10]

reported complete conversion of cellulose only at 295 °C, and thus under our reaction conditions it is conceivable that the initial sugar degradation products were dehydrated to water soluble levoglucosan, furfurals and glucoaldehydes and phenols [11, 12] resulting in low overall conversion to oil, char and gas. The relatively high biochar yield obtained from cellulose can probably be attributed to the dehydration, fragmentation and condensation of monomeric sugars [13].

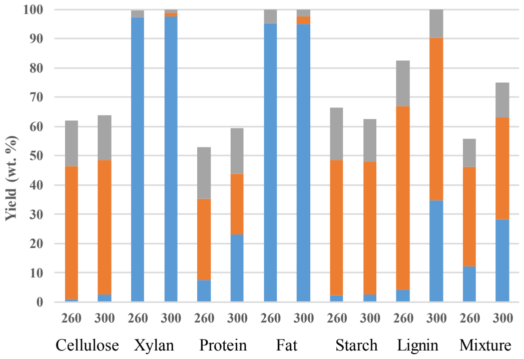

Figure 1: Hydrothermal liquefaction yields for different components. Product yield (wt. %): 🟦, Bio-crude oil; 🟧, Biochar; ⬜, Gas

In contrast to the results from most studies [14, 15], xylan primarily decomposed to form bio-oil in this study.

This result cannot be readily explained. Pínkowska *et al.* [15] showed that an increase in temperature will favour bio-crude oil formation above water soluble molecules, but low bio-oil yields (4 wt. %) were obtained. Yang *et al.* [14] reported that hemicellulose mostly decomposes to form solid products (biochar). All studies investigating the HTL decomposition of individual components of lignocellulose for model development purposes has used xylose as representative component for hemicellulose, with the study by Yang et al (2018) being the exception. All studies have also used low solids to water ratios, with 2 wt.% being the lowest and 17% being the highest. In this study, a solid to water loading of 50% was used, which would result in less water being available causing more dehydration products to form. The xylan model biochemical compound used in this study was extracted from sugarcane bagasse and consisted of 99.8 wt. % xylan and 0.2 wt. % arabinan.

Early and rapid degradation of xylan to pentose sugars and acetic acid together with relatively low water availability could have resulted in the preferential formation of furfural and aldehyde derivatives that are more soluble in the organic bio-crude phase than the water phase. Sandquist *et al.* [16] also reported that higher HTL temperatures favours the formation of organic soluble components as opposed to aqueous soluble chemicals.

Bio-crude and biochar yields from protein obtained in this study were similar to other reports [14]. Higher bio-crude yields were observed at 300 °C than 260 °C with higher bio-crude yields obtained at the higher temperature. Bio-crude from protein is formed through hydrolysis of the peptide bonds and subsequent decarboxylation and deamination of the amino acids to intermediate products that, under severe conditions, will re-polymerise to phenols indoles and pyrroles.

As expected, the sunflower oil produced mostly bio-crude oil with a small amount of char observed at 300 °C due to repolymerisation of radicals to more stable products. High biochar yields were observed for starch in this study. Reduced bio-crude yields in favour of biochar from starch under ionic HTL conditions has previously been reported. [17]. The authors also showed that the lower oil yields at more severe reaction conditions resulted in a higher quality oil being produced. In our study, we could confirm a high HHV value of the bio-crude (34.5 MJ/kg) obtained from starch liquefaction compared to the relatively low HHV of the biochar product that was formed (21 MJ/kg).

Lignin is difficult to degrade under hydrothermal liquefaction conditions, leading to high biochar yields and relatively low oil yields [14]. During HTL, the lignin polymer is degraded through cleavage of the ether and carbon bonds between lignin oligomers leading to the formation of both organic and water soluble phenolic derivatives. In our work, we also observed high biochar yields from lignin, but the high HHV (31.78 MJ/kg) of the biochar obtained at 300 °C compared to the lignin feedstock (18.38 MJ/kg) together with the increased bio-crude oil yield, confirmed degradation of the lignin structure and formation of a high quality deoxygenated biochar product.

A simple additive model was derived from this data to predict HTL product yields from a mixture of biochemical components using least squares regression.

The model coefficients for 260 °C and 300 °C is given in Table II. The accuracy of the fit was confirmed with a R^2-value of 0.98 and a p-value for the fit of $3.36 \cdot 10^{-5}$ at a 95% confidence level.

$$Y_i = aX_C + bX_H + cX_P + dX_L + eX_S + fX_{Lig} \quad (14)$$

Where Y_i is the bio-crude, biochar or gas yield and X_C, X_H, X_P, X_L, X_S and X_{Lig} is the weight fraction of cellulose, hemicellulose, protein, fat, starch and lignin in the mixture respectively.

Table II: Fitted coefficients for Eq. 14

	Bio-crude oil		Biochar		Gas	
	260	300	260	300	260	300
a	0.01	0.03	0.50	0.50	0.17	0.17
b	1.07	1.07	-	0.01	0.03	0.01
c	0.08	0.25	0.30	0.23	0.19	0.17
d	1.04	1.04	-	0.03	0.05	0.03
e	0.03	0.03	0.50	0.50	0.20	0.16
f	0.04	0.38	0.69	0.61	0.17	0.14

The predicted HTL product yields using Eq. 14 with the coefficients in Table II are compared to experimental mixture yields in Figure 2.

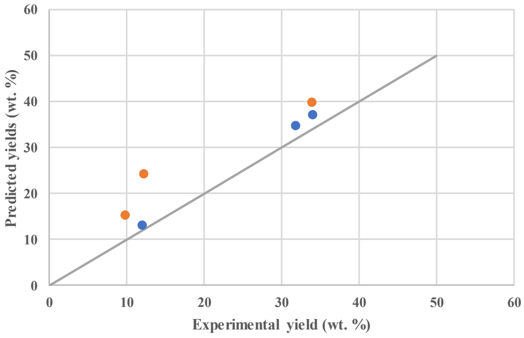

Figure 2: Predicted vs. experimental values for mixture of biochemical components. Temperature: ●, 260 °C; ●, 300 °C

The model could very accurately predict the HTL product yields from the biochemical composition of the mixture at a reaction temperature of 300 °C; with only 7.3%, 1.2% and 1.3% % difference between predicted and experimental yields for the bio-crude oil, biochar and gas yields respectively. The model could predict the gas yield exactly. These results in in agreement with literature [3] that indicated that additional model terms to account for inter-components interactions are not necessary to accurately predict model mixture yields from biochemical composition data. HTL yields at 260 °C was not as well predicted by the model. Lignin is not completely degraded at 260 ° [11, 18] and crystalline cellulose is only completely degraded at approx. 280 °C [16]. Both cellulose and lignin contributes towards bio-crude and biochar formation and if these components have not been completely degraded. Then the model would over predict both the bio-crude oil and biochar yields as seen from the results.

3.2 Model MSW elements

Compositional analysis of the food waste, garden waste and paper waste used as representative model organic MSW elements are given in Table III.

Table III: Compositional analysis (wt. %) of model MSW elements

	Food waste	Garden waste	Paper waste
Cellulose*	-	30.1	52.0
Hemicellulose8	-	22.3	18.5
Protein*	10.1	5.8	-
Fat*	73.2	4.6	-
Starch*	6.1	55.7	-
Lignin*	-	3.3	9.4
Moisture	7.6	10.9	48.0
Ash	6.3	16.4	8.4
VM[a]	84.8	62.4	38.5
FC[b]	1.3	10.3	5.1
HHV (MJ/kg)	32.2	18.8	12.69

*Wt. % d.a.f. basis
a. VM = Volatile Matter
b. FC = Fixed Carbon

Hydrothermal liquefaction was done on the 3 individual MSW elements at 280 °C, 300 °C and 320 °C and the product yields are given in Figure 3.

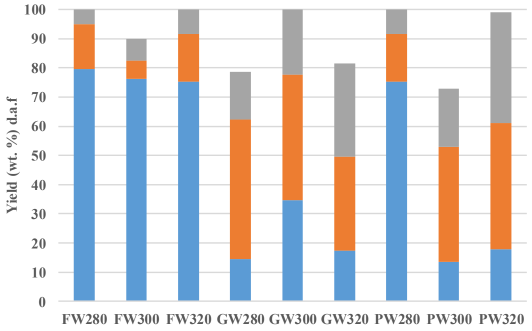

Figure 3: Effect of operating temperature on yield. Product yields: ■, Bio-crude oil; ■, Biochar; ■, Gas

Food waste, consisting mainly of fat had the highest oil yield with a decrease in oil yield observed from 80 wt. % to 75 wt. % with an increase in temperature. Garden waste produced the highest biochar yield and gas yield at all temperatures. This is consistent with the biochemical component results that showed that cellulose, hemicellulose and starch is formed through re-polymerisation of intermediate dehydration products to produce biochar. Paper sludge consists mostly of cellulose and hemicellulose and initially produced a large amount of bio-crude oil (75 wt. %) due to the degradation of the cellulose and hemicellulose components to intermediate organic soluble products and lignin fractions to organic soluble phenol derivatives. As the temperature increases, condensation and re-polymerisation of intermediate products result in an increase in biochar production and degradation of bio-crude oils result in an increase in gas production. The cellulose, hemicellulose and lignin present in the paper sludge is not as structured as that found in the garden waste, since the paper has already been processed through the Kraft pulping process and these components are thus present as separate components and not as part of a cell wall structure as in garden waste. It is thus expected that these components would behave differently during HTL as is seen in the significantly different product yield distributions. These results are in agreement with literature [4] that reported a FA-model for predicting HTL bio-crude oil yield and quality while non-FA yields could be predicted from defatted microalgae feedstock with varying biochemical composition.

Product yields for the MSW elements as well as a MSW mixture were predicted using Eq. 14 and the experimental and predicted product yields (daf) is compared in Figure 4.

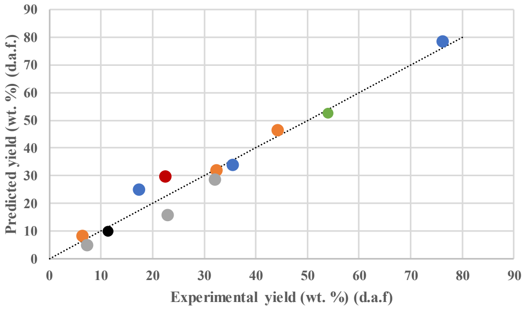

Figure 4: Predicted vs. experimental yields for MSW elements based on biochemical composition. Product

yields: ●, Bio-crude oil; ●, Biochar; ●, Gas, ●, MSW crude oil yield, ●, MSW biochar yield, ●, MSW gas yield

All HTL product yields could be accurately predicted by the biochemical component–based model with all predicted values within 5% of the experimental values. The model was further validated by prediction of the product yields of a MSW landfill mixture containing equal amounts of food waste, garden waste and paper waste as well as waste tyres, waste plastic and textile waste. The latter was done to assess if the presence of these components would significantly influence the prediction of product yields using the additive model. The experimental product yields are compared to predicted yields calculated using Eq. 14 in Table IV. The bio-crude, biochar and gas yield of the complex MSW mixture could be predicted within 7% of the experimental yields based only on the biochemical composition of the organic fraction of the elements of the MSW mixture. The results showed that the presence of non-convertible components such as tyres, textiles and plastics during HTL does not significantly influence the HTL product yields. Furthermore, the biochar yield could be predicted with the greatest accuracy in all mixtures, probably because it is the most chemical stable of the HTL product and less likely to degrade to gas or other products. The bio-crude oil was over predicted by the model. This could be due to degradation of the lipids to form heavier char fractions which cannot be accurately predicted by the model.

Table IV: Comparison of experimental MSW mixture yields with predicted yields (wt. %)

	Experimental yield	Predicted yield
Bio-crude oil	22.38	29.72
Biochar	54.00	52.8
Biogas	11.28	11.28

The model was further validated by using it to predict yields from other studies, based only the chemical composition as reported on a d.a.f. basis for the different feedstock. The results for bio-crude oil, biochar and biogas are show in Figure 5, 6 and 7 respectively.

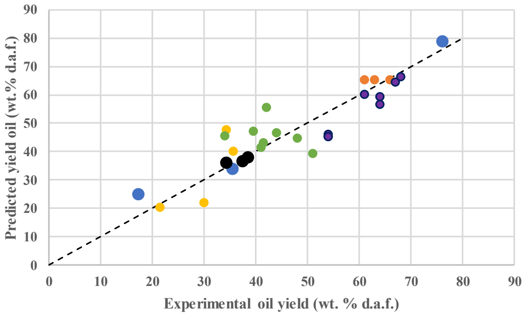

Figure 5: Validation of model for predicting literature yields. Oil yields: ●, Our data; ●, [6]; ●, [1]; ●, [13]; ●; [5]; ●, [4]

The oil yields from feedstock with a high lignocellulose content could be well predicted, but the model under predicted yield for feedstock with a very high lipid content and feedstock containing hard woods.

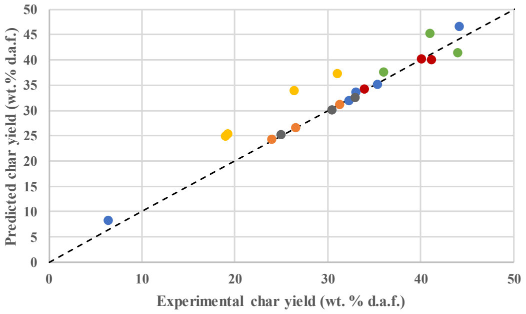

Figure 6: Validation of model for predicting literature yields. Char yields: ●, Our data; ●, [6]; ●, [19]; ●, [13]; ●, [1]; ●, [20]

Biochar yields were very well predicted and again, the model better predicted for waste feedstock [6] that have been subjected to one processing step or another to remove some oil and/or starch for food application.

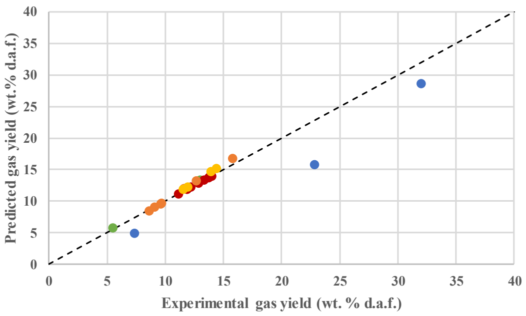

Figure 7: Validation of model for predicting literature yield. Gas yields: ●, Our data; ●, [5]; ● [6]; ● [4]; ●; [13]

Gas yield for published data was better predicted in most cases that for the feedstock used in this study.

4 CONCLUSIONS

The good predictions of HTL product yield holds excellent promise for development of HTL commercial plants from any number of feedstock, but in the context of this study, specifically for utilising MSW for biofuels and energy production. South Africa annually produces approximately 35 million tons of organic landfill waste (24% garden waste, 48% paper waste and 28% food waste) [21]. If it is assumed that the organic waste has approx. the same biochemical composition as the organic wastes used in this study, it can be estimated that 9.2 billion litre of bio-crude oil for replacement of approx. 42% of South Africa's oil imports can be produced from organic MSW through HTL. South Africa's annual coal demand is 177.2 Million tonne per annum. Using our model, we can estimate that approx. 26 million tons of GreenCoal pellets can be produced from the organic MSW through HTL to replace 11% of South Africa's low grade coal demand and lower particulate, NO_X and SO_X emissions [22]. Furthermore, if the gas product at the exit pressure is used directly for energy generation, approx. 620 GWh/a of green electricity can be generated.

The results and projections show the value of investing in clean conversion technologies to produce bio-based products that can significantly reduce greenhouse gas emissions.

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7 LOGOS