



Process modeling of chemical looping combustion (CLC) of municipal solid waste

Z. T. Yaqub¹ · B. O. Oboirien¹ · A. T. Akintola¹

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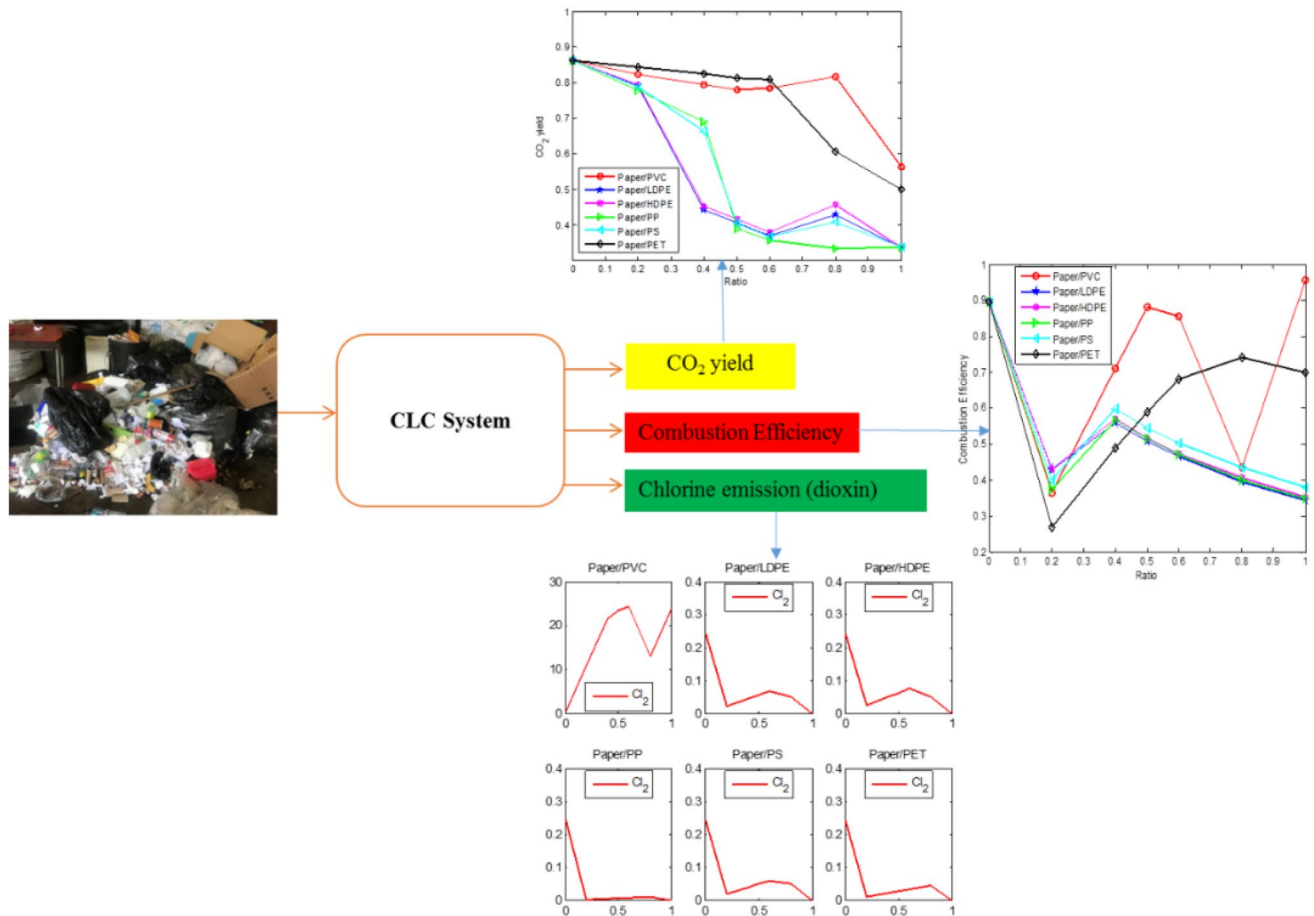
Abstract

Chemical Looping Combustion (CLC) of MSW could serve as a potential treatment method for the disposal of MSW and the recovery of energy because it can inhibit dioxins and furans formation that is associated with the traditional treatment (incineration). This study evaluated the chemical looping combustion of MSW composition (Paper + Plastics) at different ratios using Chemcad[®] process simulation software. The process simulation was done for two different CLC processes namely Chemical Looping Oxygen Uncoupling (CLOU) and In-situ Gasification CLC (IG-CLC). Plastic samples used include polyvinyl chloride (PVC), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polystyrene (PS) and polypropylene (PP). The results showed a promising CO₂ yield (higher degree of CO₂ capture) with the IG-CLC process having a higher CO₂ yield (90–100%) than the CLOU process (30–80%) for the individual paper and plastic sample and the paper/plastic blends. For the combustion efficiency, the CLOU process was marginally higher than the IG-CLC process for all the plastics and the paper and while the IG-CLC process had higher combustion efficiency (30–75%) for the blends than the CLOU process (25–70%). Chlorine formation was used to measure the amount of dioxin formed; less chlorine means less dioxin formation. The results showed that the amount of chlorine formed decreases when paper and plastics were blended for all the different plastics except in PVC which increased for both CLOU and IG-CLC processes.

✉ B. O. Oboirien
boboerien@uj.ac.za

¹ Department of Chemical Engineering Technology,
University of Johannesburg, Johannesburg, South Africa

Graphic abstract



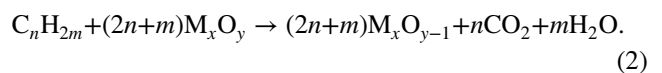
Keywords Municipal solid waste · Chemical looping combustion · Chemcad · Dioxin · Plastics

Introduction

Proper disposal of solid waste is quite a challenge especially in developing countries like South Africa. According to the Department of Environmental Affairs in South Africa, about 42 million tonnes of Municipal Solid Waste (MSW) was generated in 2017 and only 11% of it was recycled [1]. South Africa is the 14th largest emitter of greenhouse gases with about 8.98 metric tonnes of CO₂ emission per capita recorded in 2014 [2]. This is due to the country's dependence on coal for energy generation.

One way to reduce the amount of greenhouse gas in the atmosphere by capturing CO₂ which is usually emitted from fossil fuels and the incineration of MSW. Carbon Capture and Storage (CCS) is a type of technology that has the ability to capture up to 90% of the CO₂ emitted from power plants and other industrial plants from the combustion of fossil fuels and MSW [3]

Chemical looping combustion (CLC) is a type of CCS that makes use of oxygen carrier materials in an oxidation–reduction cycle [4]. Two reactors (fuel reactor (FR) and air reactor (AR)) are connected by solid transportation lines. The oxygen carrier is transported between the reactors and intermittently supplies oxygen [4]. In the AR, the oxygen carrier particles are oxidized by oxygen from the air (Eq. 1). The oxidized oxygen carrier is then transferred to the FR. The FR is fluidized with either steam or CO₂. If the fuel is a gas, the reactor can be fluidized with the fuel itself. The gaseous fuel reacts with the oxygen in the oxidized oxygen carrier (Eq. 2):



The reduced metal oxide in the FR is returned to the AR to be oxidized by air. CLC technology has an advantage of inherent CO_2 separation, cascaded utilization of energy, and low NO_x [5]. The layout of the CLC process is illustrated in Fig. 1.

CLC for solid fuels can be categorized depending on whether the fuel directly or indirectly reacts with the oxygen carrier. The first approach is to carry out solid gasification in a gasifier and the syngas produced is then introduced into the CLC system. This is referred to as Syngas-CLC Process [6, 7]. The second approach is when the solid fuel is introduced directly to the CLC fuel reactor (solid fueled-CLC). The solid fueled-CLC is further classified into two: in-situ Gasification Chemical Looping combustion (IG-CLC) and Chemical Looping Oxygen Uncoupled (CLOU) [8].

Several studies have been carried out on CLC of solid fuels such as biomass (pine, sawdust, and wood chips), petroleum coke and coal with these fuels reacting directly or indirectly with the oxygen carries [9–11]. Wang et al. [12] investigated the direct chemical looping combustion (IG-CLC) of pine sawdust using different synthetic iron oxygen carriers. Of all the synthetic oxygen carriers tested, CuFe_2O_4 was found to have the highest reactivity. In addition, Thunman et al. [9] investigated the use of a natural oxygen carrier (ilmenite) in the direct chemical looping combustion of Swedish wood chips char, and different coal samples. They reported that the rate of conversion of the wood chip was faster than Mexican petroleum coke, Indonesia coal, and Colombian coal, but lower than the German lignite.

Perez-vega et al. [13] enhanced the productivity of a CLC reactor by adding ring-type internals to the fuel reactor in both CLOU and IG-CLC processes using coal as the solid fuel. Complete combustion of the fuel was noticed with less oxygen demand. The result also showed the IG-CLC process had a lower CO_2 capture efficiency and a lower carbon conversion rate than the CLOU process.

In other studies, syngas generated from biomass gasification was combusted in a Syngas-CLC system [14] and tar

reforming in the CLC system [15]. In both cases, the syngas and the tar were produced from woody biomass. Fan et al. [16] studied the performance of a syngas CLC combined with cooling, heating, and power production using coal as the fuel. The thermodynamic evaluation of the process showed a reduction potential in the use of coal to produce energy.

Few publications have reported on the CLC of MSW, most of which focused on a single component of MSW and ideal oxygen carriers to be used. Bi et al. [17] investigated the effect of modified oxygen carriers on chlorine absorption in PVC and kitchen waste. Fe_2O_3 in CaSO_4 was used as the oxygen carrier. The experiment showed an increase in reaction rate when CaSO_4 was added, also, the oxygen carrier absorbed the chlorine after the reduction stage [17]. Lv et al. [18] assessed the conversion of MSW to synthetic natural gas (SNG) through gasification and dual chemical looping process; chemical looping air separation (CLAS) and water–gas–shift and calcium looping with CO_2 adsorption (WGS-CaL). The WGS-CaL was found to be an efficient method for SNG production and CO_2 capturing. The highly reactive polyethylene (PE) from MSW was used to test the reduction capacity of CuO through a simultaneous differential scanning calorimeter and a TGA. The solid and gaseous products were characterized and results showed that highly volatile PE is suitable as solid fuel in the chemical looping process, while the reduction process can take place at a temperature as low as 500°C [19]. Yaqub and Oboirien [20] had compared the CLC of coal with different waste components and observed that coal had a larger CO_2 yield than all the waste components except for paper waste in CLOU but a similar CO_2 yield with the waste components in IG-CLC when ilmenite was used as an oxygen carrier. Ma et al. [21] conducted a study on the performance of Iron ore and a CaO adsorbent as an oxygen carrier in IG-CLC of plastic waste. A 98% combustion efficiency was observed and the result showed that the addition of the adsorbent helps to reduce the formation of dioxins without altering the properties of the oxygen carrier [21].

This study evaluated the combustion efficiency, CO_2 yield (higher degree of CO_2 capture) in CLC of MSW composition of (Plastics + Paper) using a Chemcad process simulator. This paper was able to determine the optimum blend ratio of plastics/paper that is required for the CLC of MSW to meet an equivalent energy load with the lowest CO_2 emission scenario. In addition, two different CLC processes (CLOU and IG-CLC) of plastics and paper blends were compared based on their CO_2 yield and combustion efficiency. Most CLC of MSW published research focus on only IG-CLC and modified oxygen carriers that can reduce the emission of Cl_2 with none comparing IG-CLC and CLOU. In addition, modeling the CLC process for converting waste to energy had also not been analyzed.

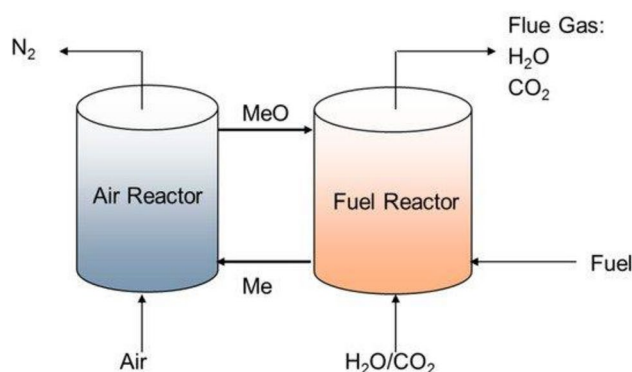


Fig. 1 Layout of a CLC process [6]

Methodology

Waste sample characterization

The waste samples examined in this process include paper and different plastic wastes (polyvinyl chloride (PVC), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS) and polyethylene terephthalate (PET)). The ultimate and proximate analysis of the samples is presented in Tables 1 and 2. The higher heating value (HHV) of the samples was calculated using the Modified Dulong equation (Eq. 3) for MSW as a function of ultimate analysis [22]:

$$\text{HHV} = -1.46 + 0.361C + 1.05H - 0.160N + 1.24S - 0.0658O \left(\frac{\text{MJ}}{\text{kg}} \right). \quad (3)$$

Modeling of the process

Chemcad software was used to predict the performance of this process by inputting in the elemental analysis, heating value, and other process conditions such as temperature, pressure, moisture content, and flow rate into the process model. A process flow diagram was developed based on the chemical looping combustion of other solid fuels from the literature [23–25]. The flowsheet of the two different chemical looping combustion process is depicted in Figs. 2 and 3. The model is based on Gibbs free energy minimization and Redlich–Kwong–Soave (RKS) cubic equation of state, while the Boston–Mathias Alpha function (BM) was used to approximate the physical properties. The model was chosen because it is suitable for non-polar or mildly polar mixtures. The Gibbs free energy minimization would help in achieving thermodynamic equilibrium and finding the equilibrium composition of the mixtures after specifying the stoichiometric number of moles of the reaction.

The feed samples were defined as non-conventional combustion solid and were input using the result of the ultimate analysis. The following assumptions were considered in the simulation: (a) the reaction is at steady state, kinetic free, isothermal, and at equilibrium; (b) all elements take part in the chemical reaction; (c) the char contains only carbon; (d) the volatile matter produced during devolatilization consists of CO, CO₂, H₂, N₂, S, and HCl; (e) the ratio of CO to CO₂ in the devolatilization reaction is unitary; (f) the initial moisture content of the waste samples is 30%; (g) the initial feed rate of 100 kg/h was used; and (h) the oxygen carrier ilmenite (FeTiO₃) is modeled on Chemcad as FeO and TiO₂. Ilmenite has being investi-

gated to be an attractive and less costly oxygen carrier for CLC and hence chosen for the simulation [26]. Different unit operations were considered for the chemical looping combustion process. For the CLOU: drying, devolatilization, combustion, metal oxide oxidation, and reduction

Table 2 Proximate analysis result (^{db})

Sample	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon (%)
Paper	3	76	12	9
PVC	0	69	14	17
HDPE	4	88	6	2
LDPE	3	92	4	1
PP	3	96	0	1
PS	7	93	0	0
PET	1	87	1	11

db dry basis

Table 1 Elemental composition of samples (^{db})

Element	C	H	O	N	S	Cl	HHV** (MJ/kg)	References
Paper	45.6	6.0	47.8	0.3	0.2	0.3	18.39	[22]
PVC	40.6	5.0	0.6	0.1	0.2	53.5	18.64	[22]
HDPE	83.7	14.1	1.9	0.2	0.1	0.0	45.61	[23–26]*
LDPE	85.5	14.3	0.1	0.0	0.1	0.0	44.54	[25, 26]*
PP	85.0	13.9	1.0	0.1	0.01	0.0	46.00	[27]
PS	90.4	8.6	0.9	0.0	0.1	0.0	39.52	[27]
PET	62.3	4.4	33.1	0.1	0.1	0.0	23.09	[27]

db dry basis

*The percentage of each element was gotten from the average of the different values from literature

**The HHV of the sample was gotten from the average of the different ultimate analysis from literature

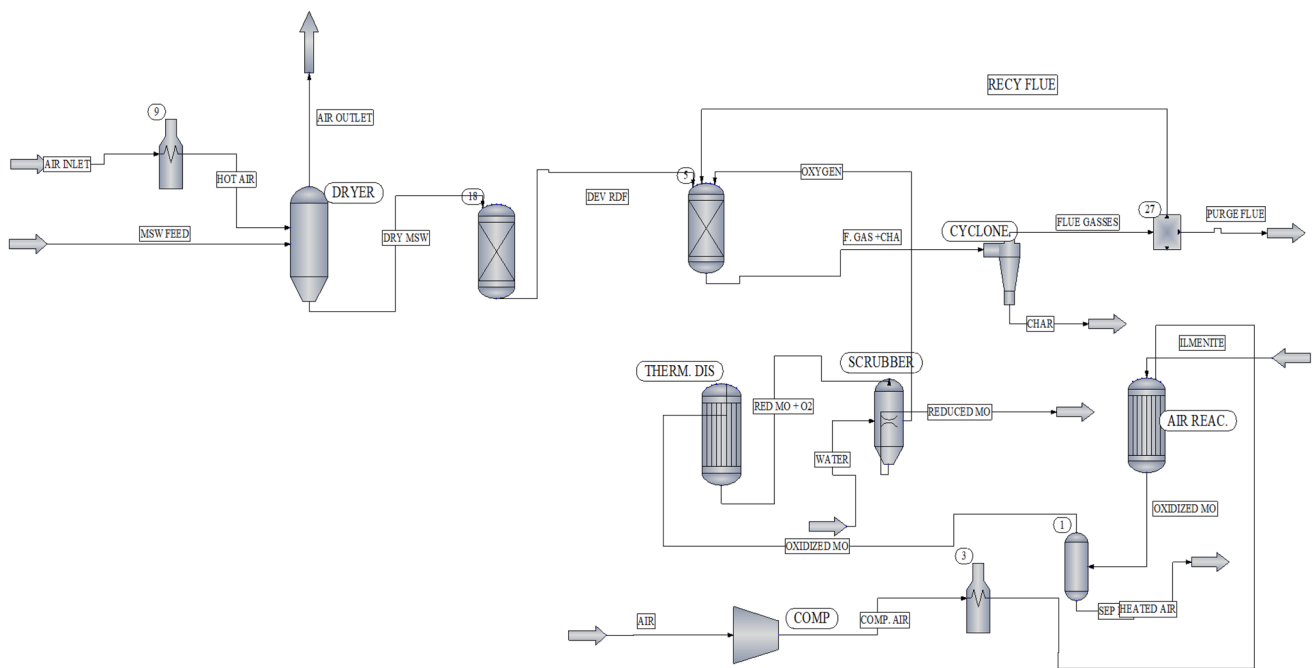


Fig. 2 Process flow diagram of the CLOU System of MSW

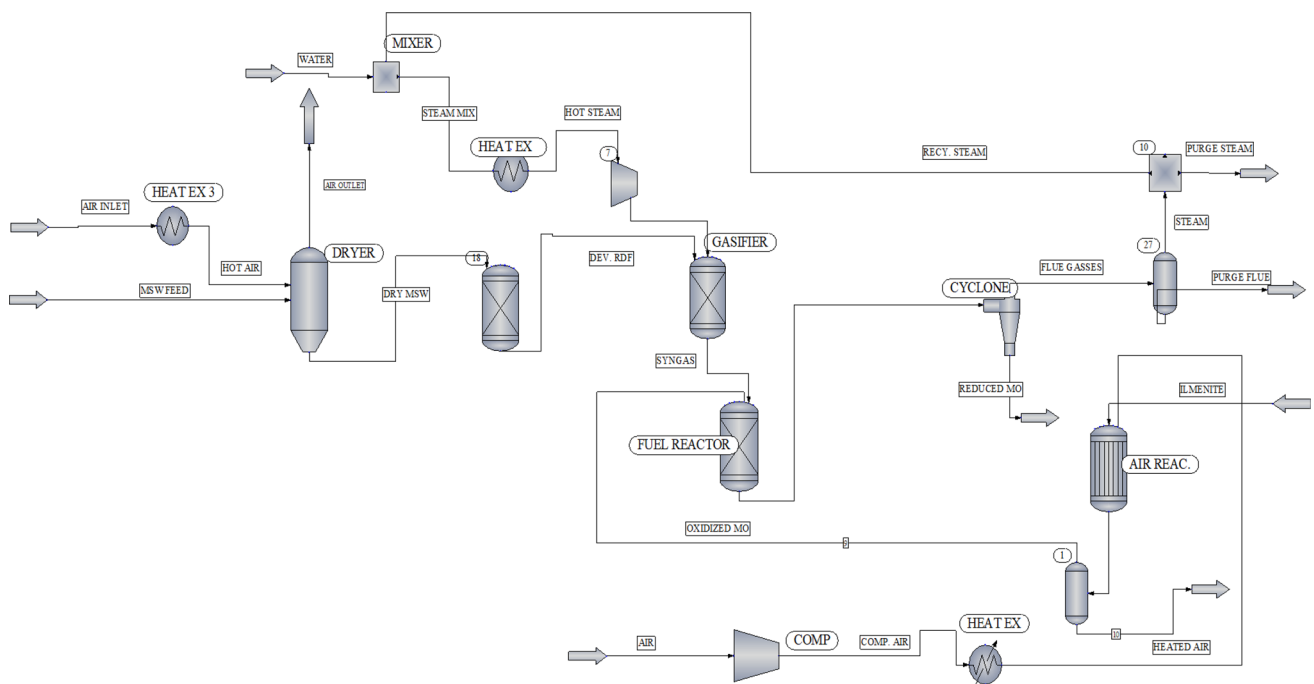


Fig. 3 Process flow diagram for IG-CLC of MSW

process was used. For IG-CLC, drying, devolatilization, gasification, combustion, and metal oxidation process were considered.

Unit operations and parameters

Different unit operation was considered for the chemical looping combustion process and the operating parameters used are indicated in Table 3. All the reactions presented

Table 3 Operating parameters for simulation

	Operating parameters
Feed flow rate (kg/h)	100
Fuel reactor temperature (°C)	800–1000
Air reactor temperature (°C)	935
Steam flow rate (kg/h)	200
Pressure (bar)	1
Air flow rate (kg/h)	251
Metal oxide flow rate (kg/h)	1798

in the simulation were based on similar CLC processes of different solid fuels from [11, 27], and the review of the process by Adanez et al. [28] For the CLOU: drying, devolatilization, combustion, metal oxide oxidation, and reduction process was used. For IG-CLC, drying, devolatilization, gasification, combustion, and metal oxidation process were considered.

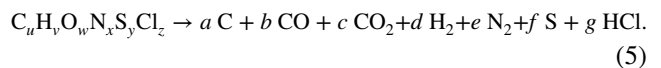
Air reactor

For this simulation, ilmenite (FeTiO_3) was used as the metal oxide for IG-CLC and CLOU process. Although, ilmenite is not a suitable oxygen carrier to be used for CLOU due to its low oxygen transport capacity as concluded by Ryden et al. [29]. Part of the steam which is a by-product from the combustion process is recycled as a fluidization agent which helps in increasing the oxygen concentration produced. As mentioned previously, ilmenite is a low-cost iron–titanium mineral that is cheap and readily available. It has also been tested for various gaseous and solid fuels and found to be highly reactive due to the Fe_2O_3 that forms a layer around the TiO_2 core. The structure was suggested to enhance the oxygen transport capacity of the ilmenite [30]. Although, ilmenite is found to have a different composition in its reduced and oxidized form. However, the most reduced form which will be used in this simulation is FeTiO_3 which was modeled on Chemcad as FeO and TiO_2 and the most oxidized form is Fe_2TiO_5 which was modeled as Fe_2O_3 and TiO_2 [26]. The TiO_2 is assumed to be inert; hence, only the Iron oxide is taking place in the reaction. A stoichiometric reactor (RSTOIC) was used for the oxidation process and the air was introduced into it. The amount of air entering the reactor is modeled in terms of O_2 and N_2 and the nitrogen is assumed to be inert. Hence, only oxygen takes part in the reaction. The reaction taking place in the air reactor is stated in Eq. 4. The Fe_2O_3 reacts with the volatile matter produced during the devolatilization of the MSW to produce the flue gas which is mostly CO_2 and steam:



Devolatilization

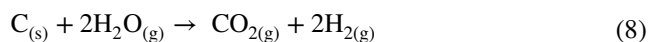
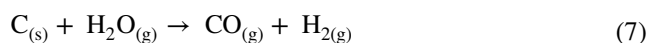
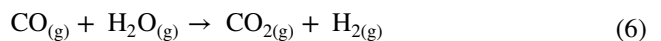
Devolatilization reaction which is sometimes referred to as decomposition or pyrolysis is one of the main steps in the combustion reaction. The reaction takes place in the fuel reactor. The non-conventional feed sample is being broken down into a conventional element at a specified temperature (Eq. 5). A stoichiometric reactor (RSTOIC) was used to denote that on CHEMCAD where the char and volatile matters were specified and the stoichiometric mole balance was also specified. For each paper and plastic blend ratio, the limiting reactant was specified. This was determined by finding the number of moles of each sample in the blend and picking the smaller one as the limiting reactant:



Gasification

The gasification step only occurs in the IG-CLC process. A multi-phase equilibrium reactor (EREA) based on fractional conversion was used to simulate the gasification process. The process was gasified by fresh and recycled steam introduced into the reactor. The decomposed feed sample is also fed into the reactor. In the equilibrium reactor, the different reactions taking place will be specified and their stoichiometric number of moles and fractional conversion would also be specified. The gasification zone is completely isothermal and the sulfur, chlorine, and nitrogen compounds are not considered. The following equations are specified in the gasification process:

Water shift reaction

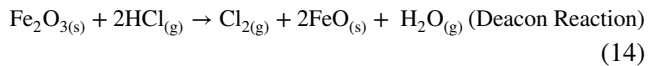
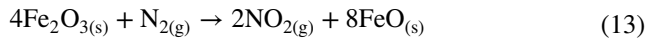
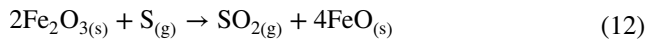
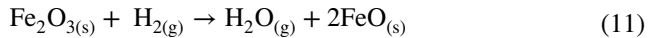
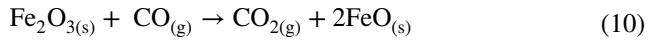
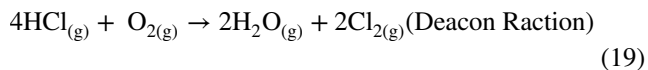


Boudouard reaction



Combustion reaction

This is a reaction between the fuel and an oxidant to produce gaseous products. Different reactions occur for the combustion of both the IG-CLC process (Eqs. 10, 11, 12, 13 and 14) and the CLOU process (Eqs. 15, 16, 17, 18, 19, 20 and 21). Part of the CO_2 and H_2O produced in the flue gas from the CLOU process was also recycled back into the fuel reactor as a fluidizing agent:

IG-CLC combustion reaction**CLOU combustion reaction****Decomposition reaction**

The decomposition reaction occurs in the CLOU process. A stoichiometric reactor (RSTOIC) was used to model the reaction (Eq. 22):

**Data evaluation****Gas yield (η)**

This is used to quantify the conversion of gas in the simulation. η_{CO_2} is the fraction of CO_2 in the outgoing gas divided by the fraction of all the carbon containing gas in the outgoing gas from the fuel reactor. If the yield of CO_2 is 1, it means there was a total conversion of the fuel to CO_2 . In the simulation, there were enough oxygen carriers to react with the solid fuel, hence, it was predicted that no methane was formed in the flue gas. The formula for finding the CO_2 yield is (Eq. 23):

$$\eta_{\text{CO}_2} = \frac{\chi_{\text{CO}_2}}{\chi_{\text{CO}_2} + \chi_{\text{CO}}} \quad (23)$$

χ_i is the mole fraction of component i in the outgoing gases.

Combustion efficiency

Combustion Efficiency (φ_{comb} , FR) in the fuel reactor is the amount of fuel oxidized to form the products of complete [31]. This can be calculated by summing up the molar flow of the gaseous product in the flue gas and integrating with the oxygen demand of the waste as stated in the following equation following the same assumption by [21, 31]:

$$\varphi_{\text{comb, FR}} = \frac{(\text{FCO}_{\text{out}} + \text{FH}_2\text{O}_{\text{out}} + 2\text{FCO}_{2, \text{out}}) - (\text{FCO}_{\text{in}} + \text{FH}_2\text{O}_{\text{in}} + 2\text{FCO}_{2, \text{in}})}{\dot{n}_{\text{o, w}}} \quad (24)$$

$\dot{n}_{\text{o, w}}$ is the oxygen demand molar rate of the waste sample. This can be calculated using the following equation [21]:

$$\dot{n}_{\text{o, w}} = \dot{m}_w \left(\frac{2\beta_c}{M_c} + \frac{2\beta_s}{M_s} + \frac{\beta_H}{2M_H} - \frac{\beta_o}{M_o} - \frac{\beta_{\text{cl}}}{2M_{\text{cl}}} \right). \quad (25)$$

Result**Comparing CO_2 yield of the CLOU and IG-CLC process for paper, plastics and paper/plastic blends**

The gas yield (CO_2 yield) for paper, plastics, and the different paper and plastics mixtures for CLOU and IG-CLC processes are presented in Figs. 4, 5 and 6, respectively, at a temperature of 1000 °C. Higher CO_2 yield was obtained for paper (86% and 100%) than plastics (30–60% and 90–96%) and this was observed for CLOU and IG-CLC, respectively. This indicates a better CO_2 yield was obtained in IG-CLC than CLOU, thus, it presents a better opportunity for CO_2 capture in IG-CLC because of the high CO_2 yield (concentration). The CO_2 yield from the IG-CLC process is higher than that from CLOU because of the gasification process present in IG-CLC [32, 33] which increases the amount of volatiles and gasification product formed. The trend noticed among the CO_2 yield of the waste samples for the CLOU is due to the amount of char produced after devolatilization. The waste sample with the lowest amount of char (paper) was able to produce more CO_2 than CO. This is because the gaseous oxygen produced from the oxygen carrier is limited and led to incomplete combustion. It should also be noted that the CO_2 which was used to fluidize the fuel reactor favors the production of CO. Hence, more CO will be produced in the CLOU process. This is due to the oxygen carrier used which has a low oxygen transport capacity and not very suitable for the CLOU process [29].

Fig. 4 Comparing the CO₂ yield of paper and plastics (CLOU and IG-CLC)

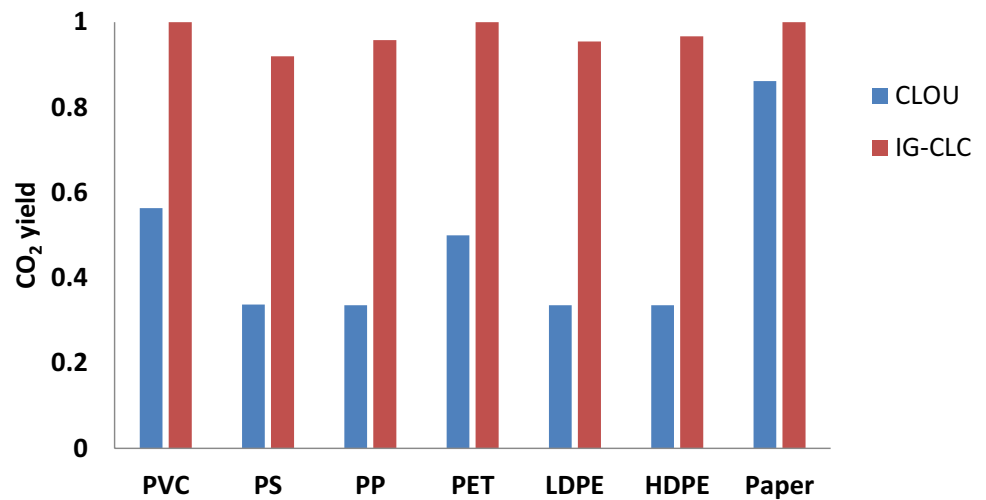
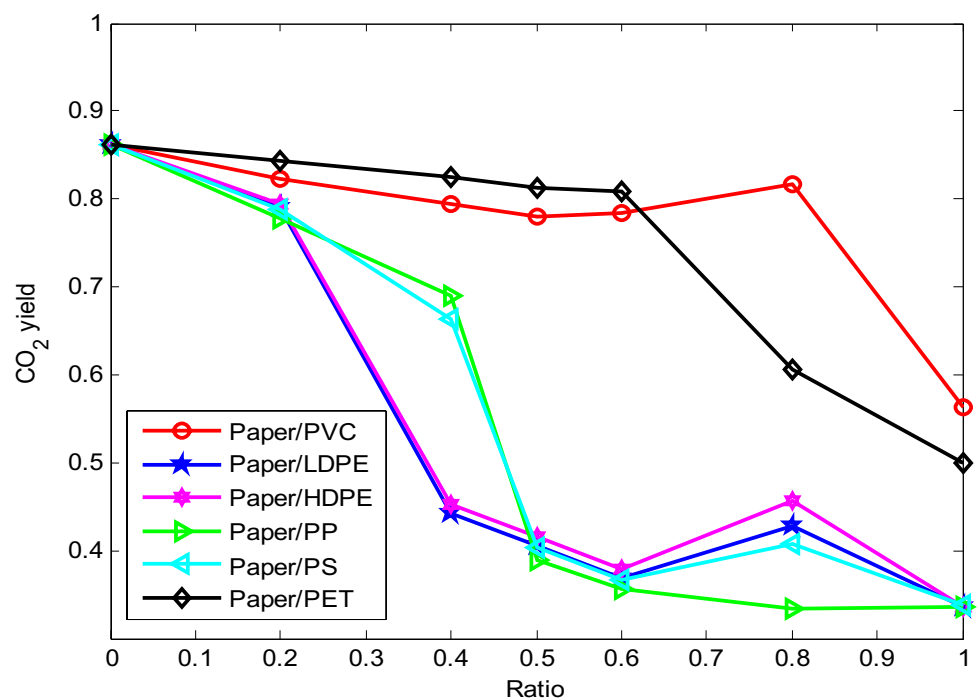


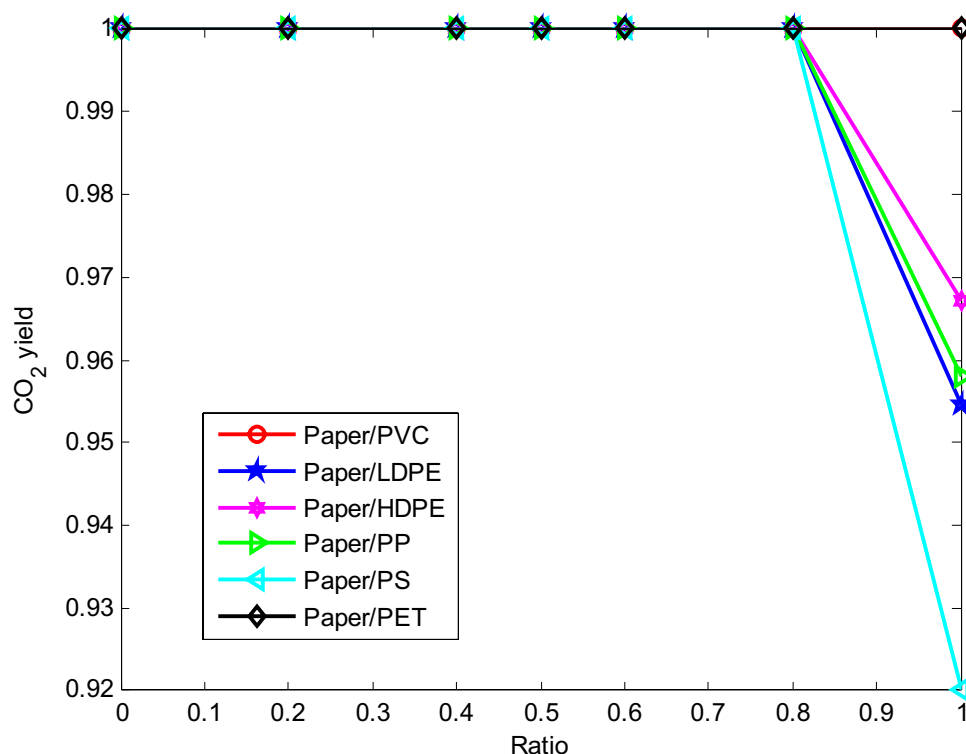
Fig. 5 Effect of different ratios on CO₂ yield of the different plastic/paper blends at 1000 °C CLOU



Similar results were observed when paper and plastics were blended as a mixture. A higher CO₂ yield was obtained in the IG-CLC process than the CLOU process for all the different paper and plastics ratios. The CO₂ yield of IG-CLC was between 90 and 100% and that of CLOU was between 35 and 85%. For the IG-CLC process, the CO₂ yield was constant at 100% for all the different paper/plastic mixture from a ratio of 0.2–0.8. This is because of the rapid gasification step, which is the limiting step in the reactions, more so, the high content of volatile within the sample favored the rapid reaction, however, it was different in CLOU. For the CLOU process, paper/PET mixture and paper/PVC gave the highest CO₂ yield. Paper/PET ratios at 0.2–0.6 resulted in a

CO₂ yield of 80–85%, however, the CO₂ yield decreased to 60% when the ratio was increased to 0.8. This is due to the change in the limiting reactant between the paper and PET samples within the reactor. The stoichiometric reactor which was used to model the devolatilization process produced char based on the stoichiometric coefficient of the reactant and product and the paper/plastic blend ratio specified. It was observed that the paper/plastic blend with the lowest amount of char that was input into the combustion reactor in the CLOU produced the highest CO₂ yield. This was due to the limited amount of O₂ produced from the decomposition of the oxygen carrier which is needed to produce CO₂ instead of CO. Hence, a higher amount of char could only produce

Fig. 6 Effect of different ratios on CO₂ generation of the different plastic/paper blends at 1000 °C IG-CLC

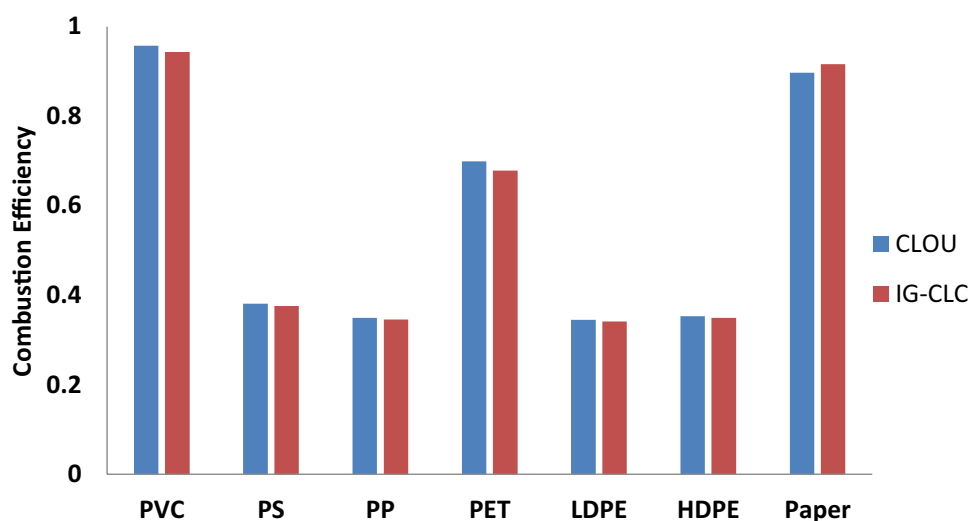


more CO instead of CO₂. For the paper/PVC mixture, the CO₂ yield was highest at ratio 0.2 at 83% and reduces until it gets to a blend ratio of 0.5 when it starts to increase till ratio 0.8 at 82% when the limiting reactant was changed to paper. The other paper/plastics mixtures (paper/PS, paper/PP, paper/LDPE, paper/HDPE) had a CO₂ yield of 35–80%. As explained earlier, the limiting reactant and the amount of char produced were calculated based on the stoichiometric coefficient of the reactant, product, and the paper/plastic blend ratio specified in the devolatilization reactor.

Comparing combustion efficiency of the CLOU and IG-CLC process of paper, plastics and paper/plastic blends

The combustion efficiency of paper and all the different plastic samples was analyzed for both IG-CLC and CLOU process as seen in Fig. 7. For the individual samples (only plastics and only paper), the combustion efficiency for the CLOU process is higher than that of the IG-CLC process. The difference in combustion efficiency between the two

Fig. 7 Combustion efficiency of paper and different plastics (CLOU and IG-CLC)



processes is similar to what was observed in the comparison of biomass combustion with the two processes by Mendiara et al. [32]. This is due to the high volatile content in the fuel sample and the high reactivity of the waste sample char [34]. Although, the presence of steam gasification in IG-CLC is supposed to increase the gasification rate and thereby increase the combustion efficiency. However, steam generation consumes a lot of energy which reduces the efficiency of the process [31]. However, in CLOU, there is no steam generation and part of the CO_2 produced is recirculated into the fuel reactor to serve as a fluidization agent which increases the gasification rate and thereby increases the combustion efficiency. For the IG-CLC process, PVC has the highest combustion efficiency at 94%, then paper with 92%. LDPE, HDPE, and PP have an efficiency of 35% and PS with 38% combustion efficiency. For the CLOU, PVC also has the highest combustion efficiency at 96% and paper at 90%. LDPE, HDPE, and PP have combustion efficiency similar to that of IG-CLC at 35% and PS at 38%. This difference in combustion efficiency between the samples is due to differences in the volatile matter in the fuel sample [34]. The solid fuels with high volatile content tend to have a higher oxygen demand which causes a poor contact between

the volatiles and the oxygen carrier and leads to a reduced efficiency [35]. The oxygen demand of the waste samples is presented in Table 4.

The combustion efficiency of the paper/plastic blends (ratio 0.2–0.8) is presented in Figs. 8 and 9 for CLOU and IG-CLC, respectively. For the IG-CLC process, paper/PVC and paper/PET have the same trend. An increase in the blend ratio from 0.2 to 0.6 leads to an increase in combustion efficiency. However, when the blend ratio was increased from 0.6 to 0.8 the combustion efficiency of paper/PVC reduced while it increased in paper/PET. For the other paper/plastics blends namely paper/LDPE, paper/HDPE, paper/PP, and paper/PS the combustion efficiency increased from when the blend ratio was increased from 0.2 to 0.4 and then decreased (combustion efficiency) as a blend ratio of 0.4. Similar results were obtained for the CLOU process. The trend in the combustion efficiency of the paper/plastic blend could be attributed to two factors; the oxygen demand and the amount of char that reacted during the gasification process. It was noticed that the oxygen demand increased as the amount of plastic in the blend increases which could be attributed to a larger amount of volatile matter present in the plastics. However, the reacted char did not follow the trend.

Table 4 Oxygen demand molar rate for the different plastic waste

Waste sample	Paper	PVC	PET	LDPE	HDPE	PP	PS
Oxygen demand molar rate	7.64	7.73	10.53	21.40	20.88	21.08	19.33

Fig. 8 Combustion efficiency against different ratios of paper/plastic blends (CLOU)

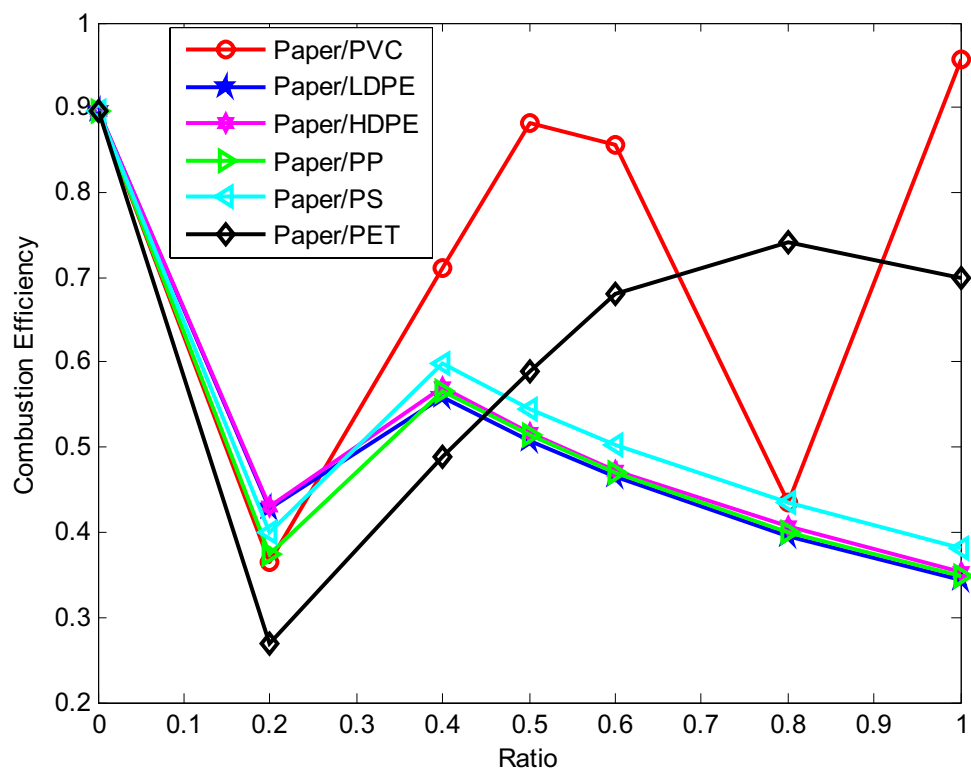
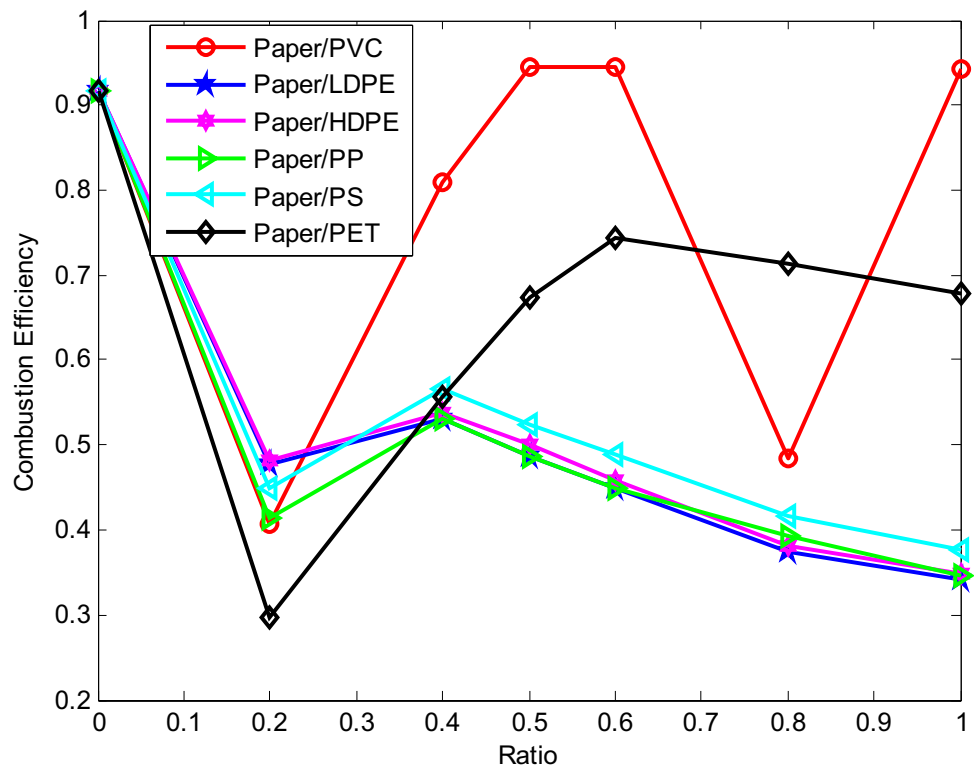


Fig. 9 Combustion efficiency against paper/plastic blends (IG-CLC)



The amount of reacted char for each paper/plastic blend was based on the limiting reactant which was specified in the Fig. 10 devolatilization reactor as explained in “Comparing CO₂ yield of the CLOU and IG-CLC process for paper, plastics and paper/plastic blends”.

Comparing dioxin emission (Cl₂) of the CLOU and IG-CLC process of paper, plastics and paper/plastic blends

The formation of dioxin was evaluated based on the deacon reaction which is a necessary step in dioxin formation. This is because dioxin comprises of 210 compounds and their thermodynamic data are not easily accessible [36]. Chlorine formation was used to measure the amount of dioxin formed; hence, less chlorine means less dioxin. Figures 11

Fig. 10 Cl₂ emission of paper and different plastics

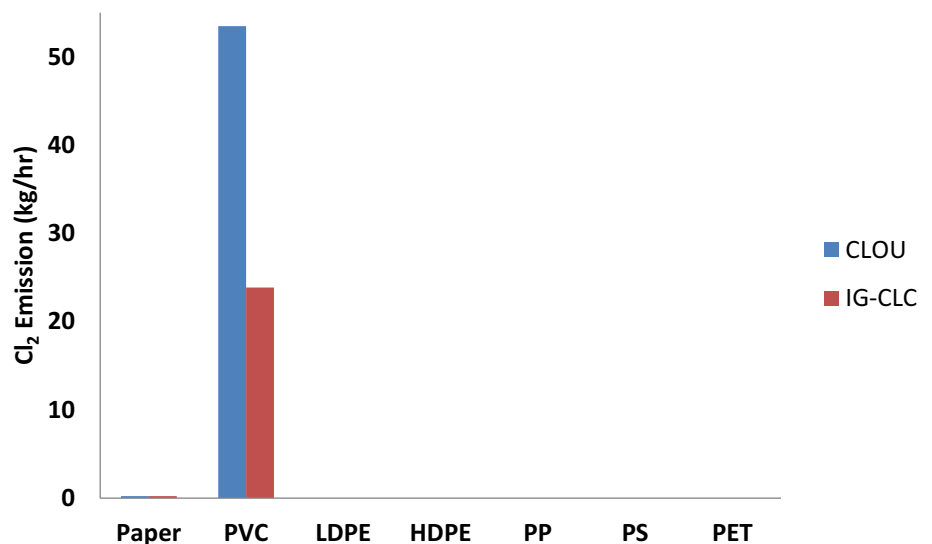


Fig. 11 Effect of different ratios on Cl_2 generation of the paper, plastics, and paper/plastic blends at 1000 °C CLOU

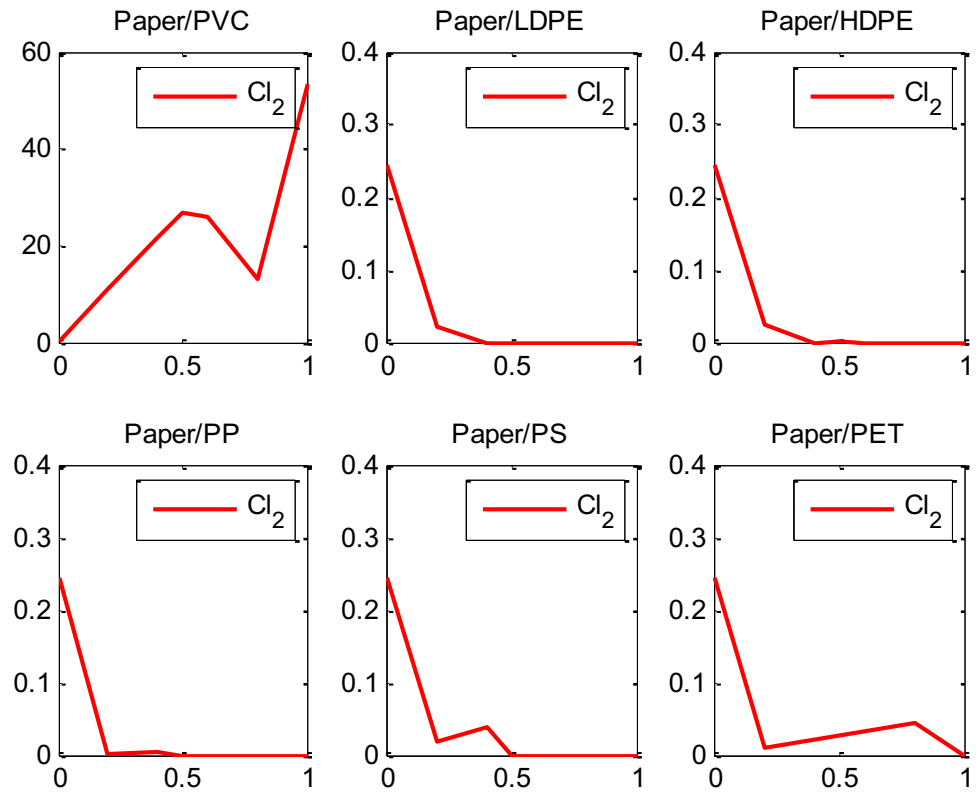
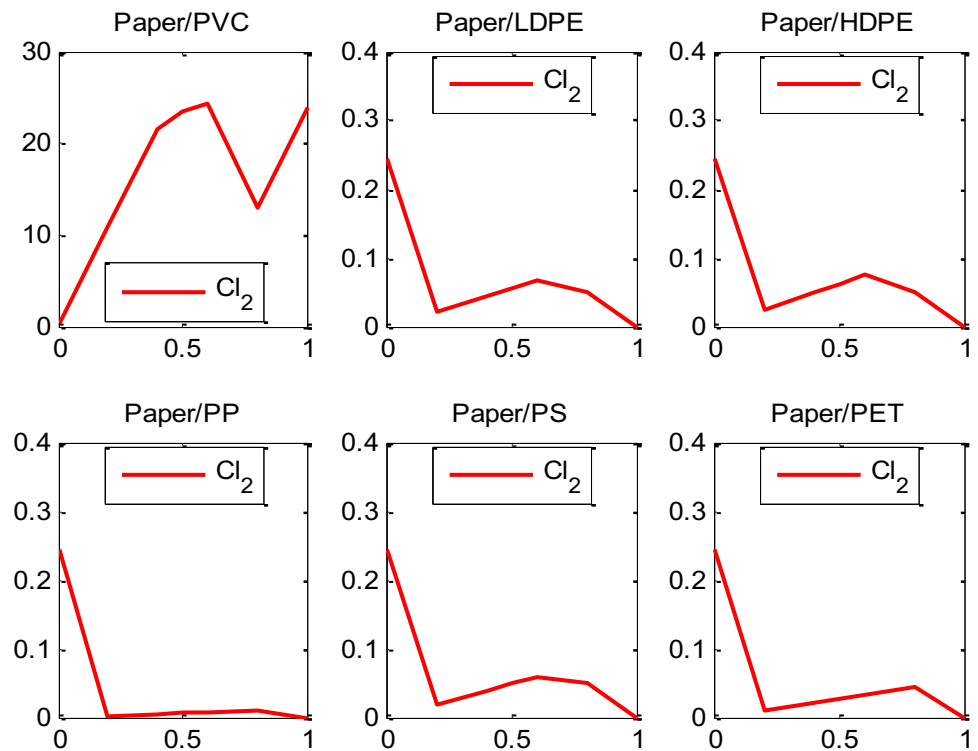


Fig. 12 Effect of different ratios on Cl_2 generation of paper, plastics and their blends at 1000 °C IG-CLC



and 12 show the amount of Cl_2 formed for paper, plastics, and blends of paper and plastics at different ratios for CLOU and IG-CLC processes. The presence of steam gasification inhibits the formation of Cl_2 which is why a smaller amount of Cl_2 emission was noticed for the IG-CLC in Fig. 10 [37, 38]. Apart from PVC, the other waste samples have little or no chlorine present in the sample, hence, no chlorine gas was formed during the reaction. The results showed that the amount of chlorine formed decreases when paper and plastics were blended for all the different plastics except in PVC which increased for both CLOU and IG-CLC processes. For the CLOU, the amount of chlorine in paper/PVC increased from 0.2 to 30 kg/h at a blend ratio of 0.5, i.e., equal amounts of paper and PVC. For the other types of plastics, the amount of chlorine reduced from 0.2 to 0 kg/h at a blend ratio of 0.5. Similar results were obtained in the IG-CLC process.

Comparing energy balance for IG-CLC and CLOU of the process for paper, plastics and paper/plastic blends

From the simulation result, it was noticed that the CLOU has a better energy load than that of IG-CLC as shown in Fig. 13. This is because higher energy is required in fluidizing the oxygen carrier and also generating the steam used in gasification in IG-CLC. This is similar to the result obtained by Sahir et al. [27] when the IG-CLC and CLOU process was compared for coal. The LDPE, HDPE, PP, and PS have the highest energy load at around 8100 MJ/h while paper has the lowest energy load at 7100 MJ/h. The energy output of the waste samples for the CLOU and IG-CLC followed the same trend. Paper, which had the highest CO_2 yield, had the lowest energy output and LDPE with the lowest CO_2 yield had the highest energy output for both CLOU and IG-CLC. This is because more energy is needed to convert to CO_2 than CO . hence, samples with higher CO_2 yield will have a lower energy output.

Comparing the paper/plastic blends at a ratio of 0.2–0.8 also shows the CLOU process having a higher energy load than that of IG-CLC as shown in Fig. 14. While the paper/PET and paper/PS show an increase in energy load as the ratio increases from 0.2 to 0.8 in IG-CLC, the other paper/plastic blends show an increase in the energy load up until 0.6 then decreases as it gets to a ratio 0.8. The optimum energy load for paper/PET, paper/PP, and paper/PS is at ratio 0.8 at a value of 5300, 5700 and 6300 MJ/h, respectively, while the optimum energy load for the paper/PVC, paper/LDPE, and paper/HDPE are at the ratio 0.5, 0.6 and 0.6 and values 5200, 5500 and 5500 MJ/h, respectively. For the CLOU process, the same trend was observed. paper/PVC, paper/LDPE, and paper/HDPE have their optimum energy load at ratio 0.6 while the other paper/plastic blends have its optimum energy load at ratio 0.8. The optimum energy load for all the different paper/plastic blends is between 7300 and 7700 MJ/h.

Discussion

The increase in the generation of MSW and the negative effect of landfilling on the environment has led to research on the different ways in managing the disposal of MSW. One of such ways was to convert waste to energy. The energy produced from this technology can be used to generate electricity and to power plants. This study focused on one of the thermal processes for converting waste to energy (CLC). A steady-state simulation was performed on waste paper and different plastic samples from MSW for the two types of CLC: IG-CLC and CLOU and compared. Among the individual MSW component, the paper had the highest CO_2 yield than all the different plastics for both IG-CLC and CLOU. An improvement in the CO_2 yield of the plastic was noticed when it was

Fig. 13 Comparing the energy load of paper and different plastics at 1000 °C

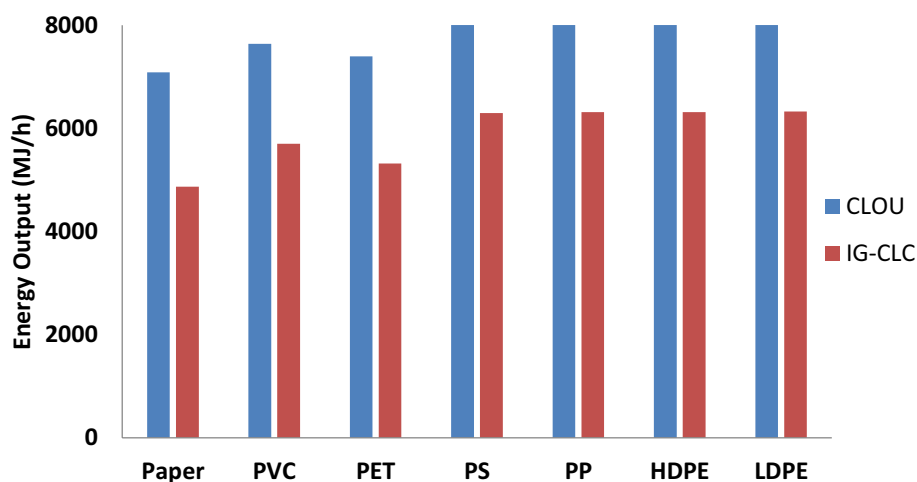
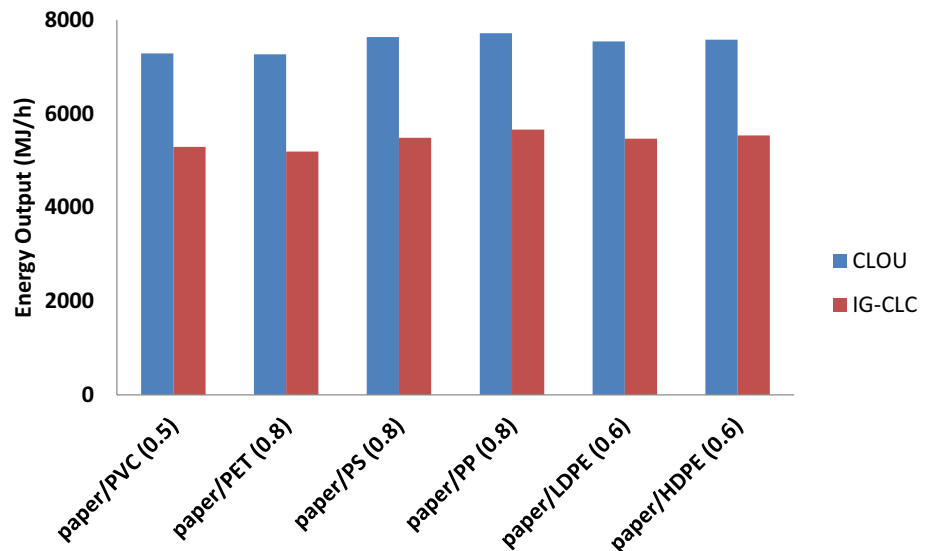


Fig. 14 Comparison of the energy load of the optimum paper/plastic blends (CLOU and IG-CLC)



blended at different ratios. This shows that blending the plastic components of MSW with waste paper can help in improving its yield.

The result also showed a higher CO₂ capture in IG-CLC than in CLOU for all the MSW samples tested. This was different from what was observed in the literature for other solid fuels (coal and biomass) [32, 39]. This could, however, be because of the different oxygen carriers used for CLOU which is found to have a better oxygen transfer capacity than ilmenite and found to be more suitable for CLOU based on its reaction mechanism [8]. Although to the best of the authors' knowledge, no reports have been conducted to study the effect of dioxin (Cl₂) on CLOU, hence difficult to compare with literature. However, the presence of steam gasification in IG-CLC which is absent in CLOU was found to diminish the emission of dioxins.

The better energy load observed in CLOU agrees with what has been tested for different solid fuels in literature. The higher energy penalty in IG-CLC is due to the steam gasification process which uses a lot of energy. This means that when a techno-economic analysis is carried out for this process, the utility cost for CLOU will be lower than that of IG-CLC which can help to achieve a reduced capital cost. This was confirmed from the economic analysis carried out by Sahir et al. on IG-CLC and CLOU of coal using the aspen economic analyzer [27].

For all the different parameters analyzed (CO₂ yield, combustion efficiency and energy load), the paper was found to have a better result when compared with the plastic samples. However, blending the plastics with paper was found to have a higher CO₂ yield, combustion efficiency and a lower energy output than the plastics.

Conclusion

A process simulation study was carried out on Paper and different plastic samples from Municipal Solid waste in a Chemical Looping Combustion process at different process conditions at a constant fuel flow rate of 100 kg/hr. Based on the steady-state simulation done in this paper, the following conclusions were drawn:

- The IG-CLC process had a higher CO₂ yield than the CLOU process for paper and plastic and also in the different paper/plastic blends (paper/PVC, paper/PET, paper/LDPE, paper/HDPE, paper/PP, and paper/PS). This presents a better opportunity for CO₂ capture in IG-CLC than CLOU because of the high CO₂ yield.
- For the combustion efficiency, the CLOU process marginally higher than the IG-CLC process for all the plastics and in the paper. A different trend was observed with the blends (paper and plastics) with the IG-CLC process having higher combustion efficiency than the CLOU process. The optimum combustion efficiency of paper/PVC, paper/PET, paper/LDPE, paper/HDPE, paper/PP, and paper/PS was at a ratio of 0.5, 0.8, 0.4, 0.4, 0.4 and 0.4, respectively, for both IG-CLC and CLOU.
- The IG-CLC process was also more advantageous in the reduction of dioxin emission, a lower amount of dioxin emission was observed in the IG-CLC process than in the CLOU process.

Recommendation

This paper has been able to estimate the combustion efficiency and the CO₂ yield from the CLC of different components of MSW. However, other factors were not considered in the scope of this work which is very important. The proximate analysis in Table 1 shows that a small amount of ash content is present in paper and PVC which might affect the efficiency of the CLC system. Future research on this study would investigate the effect of the ash content on the gas yield and ways to mitigate the effect of ash on the efficiency of the CLC of MSW. In addition, reaction kinetics was not fully analyzed in this work as it was modeled in a steady state. The detailed reaction kinetic will give a better analysis of how the reaction occurs with time and how the change in the reaction will give a better understanding of the efficiency of the process.

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