

Process Modelling of Chemical Looping Combustion of Paper, Plastics, Paper/Plastic Blend Waste, and Coal

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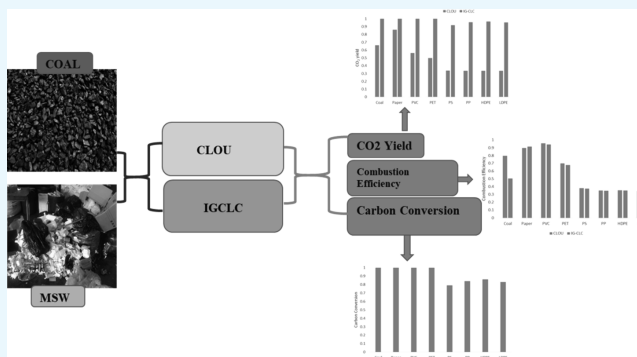


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ABSTRACT: Chemical looping combustion (CLC) is a novel carbon capture and storage technology that can be used in the proper disposal of municipal solid waste when used as a solid fuel. In this study, the results of the CLC of paper, plastics, and paper/plastic blends were compared with CLC of South African coal using Chemcad software. The simulation was done for two different CLC processes, namely, chemical looping oxygen uncoupling (CLOU) and in situ gasification CLC (IG-CLC). The results demonstrated that coal at 66% had a lower CO₂ yield than paper (86%) but a higher yield than all the plastic samples in CLOU (3356%) and an equal CO₂ yield in paper and all plastic samples in IG-CLC. Furthermore, coal had a lower CO₂ gas yield than all the optimum blends (72–85%) for CLOU and an equal yield with the entire paper/plastic blend in IG-CLC. On combustion efficiency, coal has a lower combustion efficiency at 80% than paper and polyvinyl chloride (PVC) at 90 and 96%, respectively, but a higher efficiency than other plastic samples that are between 30 and 70% in CLOU while in IG-CLC, it had a lower efficiency than paper, PVC, and polyethylene terephthalate and higher efficiency than high-density polyethylene, low-density polyethylene, polypropylene, and polystyrene. For paper/plastic blends, coal has higher combustion efficiency than all the paper/plastic blends in both CLOU and IG-CLC processes except for the paper/PVC where the combustion efficiency was higher than coal.



HIGHLIGHT

- CLOU and IG-CLC of coal, paper, plastics, and paper/plastic blend were simulated using Chemcad.
- Coal had a lower CO₂ yield than paper and paper/plastic blends but a higher CO₂ yield than all the plastic samples in CLOU.
- Coal had a similar CO₂ yield with paper, plastics, and paper/plastic blends in IG-CLC.
- The energy load from the CLOU of coal was higher than all the plastics.

The energy load for coal was lower than that of some plastics (PP, PS, LDPE, and HDPE) in IG-CLC.

INTRODUCTION

The increase in the volume of municipal solid waste (MSW) generation is a threat to the ecosystem, which has led to extensive research on ways to solve the issue of processing waste stream.¹ As the world population and economic and industrial developments increase, there would not be enough landfills to meet the population demand while energy demand will outweigh supply.^{2,3} MSW consists of plastics, paper, textiles, food wastes, garden wastes, wood, metal, and glass⁴ with about 26% of the MSW generated globally containing

paper according to the Environmental Protection Agency (EPA) as shown in Figure 1.⁵ Improper management of waste can lead to the spread of pathogens, water contamination, and soil and air pollution.^{6–9} An effective waste management system must be environmentally sustainable, viable, and generally acceptable.¹⁰ Waste to energy is one possible solution in managing MSW disposal due to its ability to generate energy while also reducing the volume of MSW.^{11–13} Reducing the emissions generated from improper management of waste by capturing the CO₂ would help in further meeting the Paris Agreement Pledge made at the 2015 Climate Change Conference.¹⁴

Carbon capture and storage (CCS) technology is an innovative technology used in reducing CO₂ emissions into the atmosphere. This involves capturing CO₂ from large stationary sources, such as fossil-fuelled power plants, cement,

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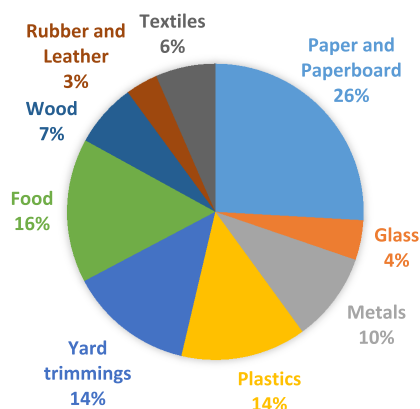


Figure 1. Amount of MSW generated globally (2015)⁵ adapted with permission from www.epa.gov (accessed 19th Sept 2019).

and steel industry, transporting of CO₂ into storage sites, and injecting into underground storage.¹⁵ Chemical looping combustion (CLC) is a type of CCS technology that has a low carbon capture cost. The cost and energy consumed in separating CO₂ from other flue gas make it a better option from other CCS technology as it is cheaper and has a higher efficiency.^{16,17} This is because during CLC, direct contact between air and fuel is circumvented, and the separation process of CO₂ and N₂ from the flue gas can be bypassed.¹⁸ CLC can be used for solid, liquid, and gaseous fuel and can also undergo significant scale-up.^{19,20} Instead of the direct contact between air and fuel, an oxygen carrier (OC) (metal/metal oxide) is introduced, which is alternately oxidized and reduced.¹⁸ For an effective heat and mass transfer between the gas–solid contacts in CLC, the interconnected fluidized bed is chosen as the best design for the reactors.²¹ The layout of a CLC process is depicted in Figure 2.

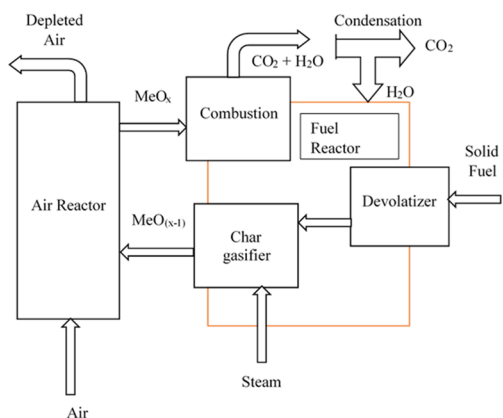
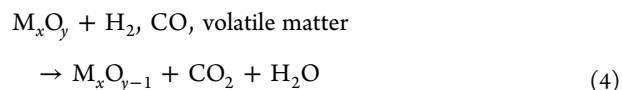
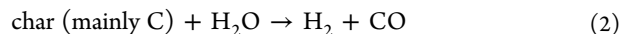
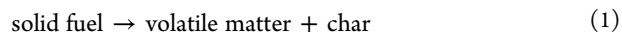


Figure 2. Schematic diagram of a CLC process adapted in part from ref 22.

In CLC, the solid fuel comes in contact with the oxygen carrier, and devolatilization (eq 1) takes place within a few seconds to generate char. After devolatilization, gasification and oxidation with the oxygen carrier take place simultaneously. The solid fuel is gasified with steam and/or CO₂ (eqs 2 and 3). The gasification product and the volatile matter then undergo combustion through the reduction of the oxidized oxygen carrier (eq 4). Steam from the flue gas is condensed, and an almost pure CO₂ is obtained. The reduced oxygen

carrier is later transferred to the air reactor for reoxidation by air (eq 5) before being reused.



Different solid fuels have been tested with CLC. Abad et al.²³ proposed a model that can compare the performance of oxygen carriers in different solid fuels based on their kinetic parameters. This model helps in predicting CO₂ capture efficiency and oxygen demand and is also useful in testing new oxygen carriers. Pérez-Astray et al.²⁴ compared the chemical looping oxygen uncoupling (CLOU) and in situ gasification CLC (IG-CLC) of the biomass process tar formation and NO_x reduction. It was observed that an insignificant amount of tar was noticed in the CLOU process. Both processes have a NO concentration below the NO_x limit for the CLOU process. On the other hand, a higher concentration was noticed for IG-CLC. Wang et al.²⁵ performed separated gasification CLC of a coal experiment to achieve an autothermal operation. The autothermal operation was achieved when the temperature in the reactor is higher than the outer surface of the test. It was however noted that the temperature difference must not be too large to avoid excess oxygen flow and an un-ideal autothermal operation.

Pérez-Vega et al.²⁶ improved the efficiency of a CLC reactor by adding ring-type internals to the fuel reactor. This was tested with bituminous coal as a solid fuel and complete combustion of the fuel was noticed with less oxygen demand. The CLOU and IG-CLC processes were also compared based on the reactivity of CuO as an oxygen carrier using coal as a solid fuel.²⁷ The result showed a lower CO₂ capture efficiency, and a lower carbon conversion rate was noticed in the IG-CLC when compared to the CLOU. A cost-effective oxygen carrier such as a bauxite cement-bonded Fe-based oxygen carrier was tested by Liu et al. in the CLC of coal.²⁸ The oxygen carrier showed high reactivity and regeneration capability after the 100-cycle experiment.

The effect of different solid wastes as solid fuel has also been tested in CLC experiments. Bi et al.²⁹ experimented to show the effect of a modified oxygen carrier (OC) on chlorine absorption in PVC and kitchen waste with Fe₂O₃ in CaSO₄ as an oxygen carrier. The experiment showed an increase in the reaction rate when CaSO₄ was added and also, the OC was found to absorb the chlorine after the reduction stage.²⁹ The highly reactive polyethylene (PE) from MSW was used to test the reduction capacity of CuO by using a simultaneous differential scanning calorimeter and 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 and that the reduction process can take place at a temperature as low as 500 °C.³⁰

Chen et al.³¹ used the CLC process to check the adsorption property of copper- and iron-based OCs on cadmium present in MSW. In this experiment, synthetic MSW, which contains

different waste samples with a large amount of cadmium, was used in a fixed bed reactor. After 2 min of the reduction process, it was noticed that 90% of the cadmium in the MSW was distributed in the OC and can then be detached gradually in the chemical looping gasification process.³¹ Ma et al.³² conducted a study on the performance of iron ore and a CaO adsorbent as an OC in IG-CLC of plastic waste. A 98% combustion efficiency was obtained, and the result showed that the addition of the adsorbent helps reduce the formation of dioxins without altering the properties of the OC.³² To the best of our knowledge, there has not been any study that compares chemical looping combustion of paper and plastic contents of MSW and coal.

The objective of this study is to compare the use of municipal solid waste and coal as solid fuel in CLC for both CLOU and IG-CLC processes by predicting their performances using Chemcad software. The municipal solid waste included paper, different types of plastics, and blends of the different plastics and paper. The energy and CO₂ yield from both CLOU and IG-CLC processes of paper, the different types of plastics, and paper/plastic blends were compared.

RESULTS AND DISCUSSION

Comparing CO₂ Yield for CLOU and IG-CLC of Coal with Paper, Plastics, and Paper/Plastic Blend. A coal sample was simulated in the CLOU and IG-CLC processes and was compared with the best conditions of paper, different plastics, and paper/plastic blends to see which gives a similar energy load. In the CLOU process, the CO₂ yield of coal was lower than the paper but higher than all different plastic samples (PVC, PET, PP, PS, LDPE, and HDPE). This was because of the amount of char and carbon-containing products produced during the devolatilization process. It was noticed that the sample with the highest amount of carbon and carbon-containing products during devolatilization has the highest CO₂ yield. However, in the IG-CLC process, the coal CO₂ yield was the same for paper and some plastics, namely, PVC and PET but higher than that of PP, PS, LDPE, and HDPE. This is illustrated in Figure 3. The CO₂ yield from the IG-CLC

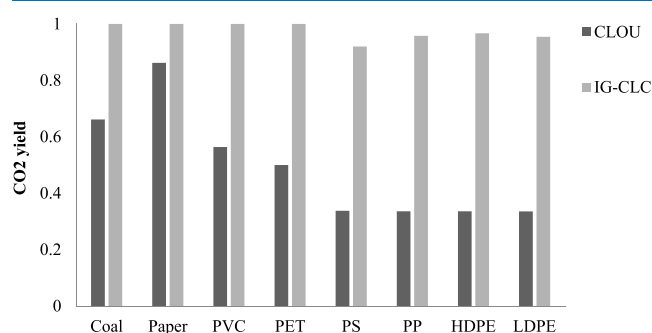


Figure 3. Comparison of CO₂ yield of coal with paper and plastics.

process is higher than that from CLOU because of the gasification process present in IG-CLC.^{33,34} The energy output from the CLOU of coal was higher than all the plastics samples (PVC, PET, PP, PS, LDPE, and HDPE). However, in the IG-CLC process, the energy output for coal was lower than that of some plastics (PP, PS, LDPE, and HDPE) and higher than that of PVC, PET, and paper, and this is illustrated in Figure 4. A large difference was noticed between the energy output of CLOU and IG-CLC of coal, which was not the case for the

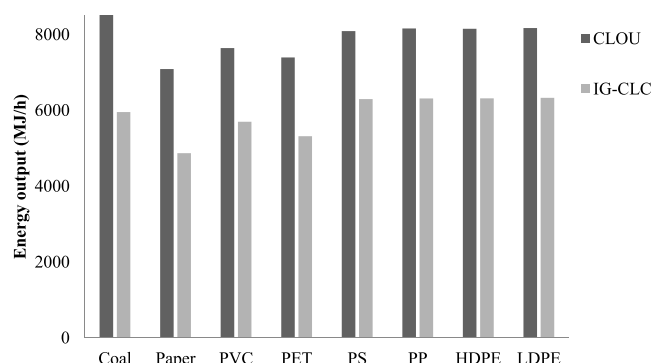


Figure 4. Comparison of energy load of coal with paper and plastics (CLOU and IG-CLC).

paper and plastic samples. This is due to the slower gasification rate of char from coal in the IG-CLC due to its lower volatile content when compared to the paper and plastic samples. It was inferred from the energy analysis on the CLC of biomass sawdust done by Kevat and Banerjee³⁵ that the complete combustion, which is determined from the char gasification step, is proportional to the energy output. The statement above is supposed to infer that coal should have the lowest energy output in the IG-CLC as it has the lowest volatile content. However, this was not the case as paper, PVC, and PET had a lower energy output. This could be due to other factors, which affect the rate-determining step such as the amount of carbon present in the sample.

A comparative analysis of chemical looping combustion of coal and paper/plastic blends at different optimum blend ratios was carried out. It should be noted that the simulation was carried out at different paper/plastic ratios of 0.2, 0.4, 0.6, and 0.8; the optimum blend ratio was obtained for the CO₂ yield, carbon conversion, and the combustion efficiency and was presented in the comparison with coal. The results showed that the optimum CO₂ yield of each of the paper/plastic blend, which was at ratio 0.2, was higher than the CO₂ yield of coal for the CLOU process, and this is presented in Figure 5. This is due to a large amount of volatiles present in the waste sample, which is more than that of coal. For the IG-CLC, the CO₂ yield was the same for all the blends, and this was also the same with that of coal as presented in Figure 6. This is because the steam gasification process supported the oxygen carrier in producing more CO₂, thereby increasing the CO₂ yield. It was

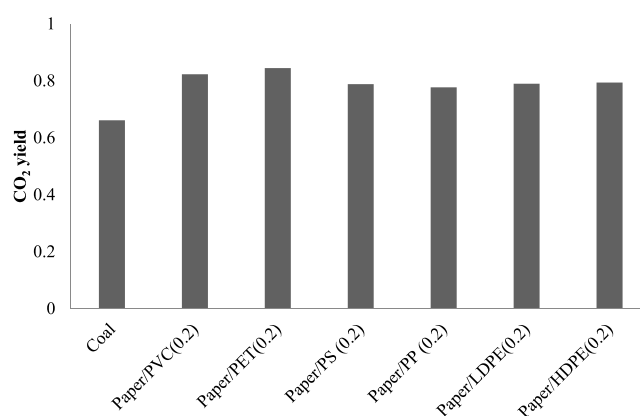


Figure 5. Comparison of CO₂ yield of coal with different optimum paper/plastic blends (CLOU).

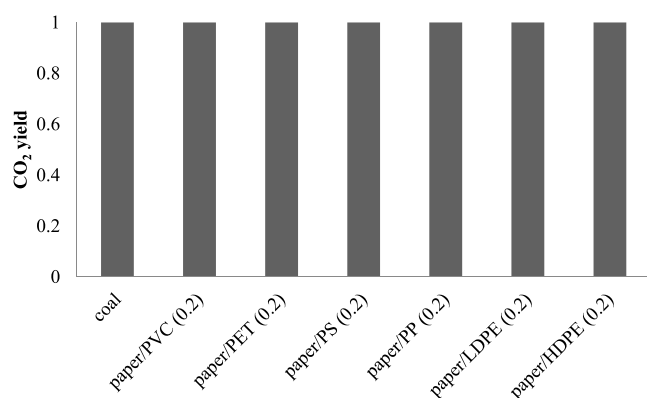


Figure 6. Comparison of CO₂ yield of coal with optimum paper/plastic blends (IG-CLC).

observed that the paper/plastic blend ratio with the highest CO₂ yield (ratio 0.2 in this case) had the lowest energy output. This is because more energy is needed to produce CO₂ than CO. For this reason, the energy output for coal is higher than that of the optimum paper/plastic blend ratio (0.2) as presented in Figure 7. It should also be noted that the

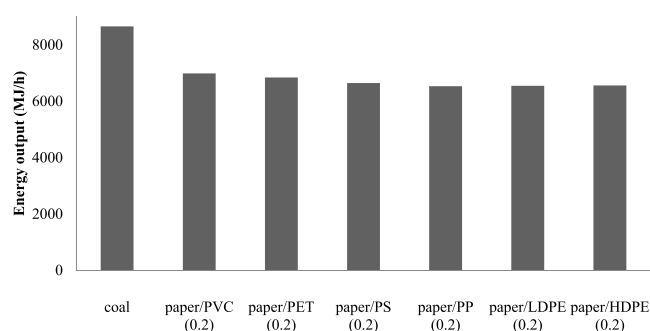


Figure 7. Comparison of the energy load of the optimum paper/plastic blend with coal (CLOU).

optimum paper/plastic blend also followed the same trend as the blend with the highest CO₂ yield (paper/PET) had the lowest energy output. However, for IG-CLC, because all the blends had the same CO₂ yield, it was difficult to pick the optimum blend ratio. For easy comparison, the same blend ratio (0.2) was chosen with that of CLOU as shown in Figure 8. Since the CO₂ yield of all the blends was the same, the amount of char that reacted was used to explain the trend since

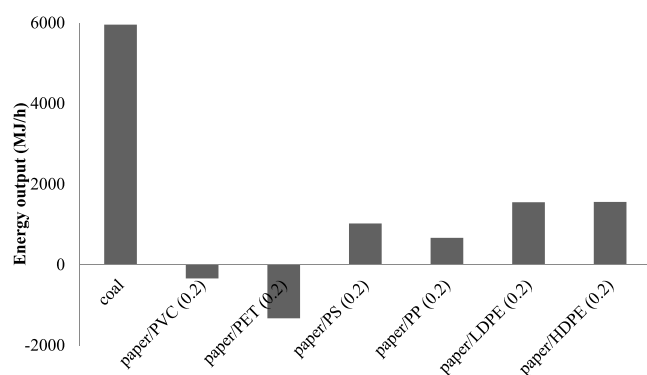


Figure 8. Comparison of the energy load of the optimum paper/plastic blend with coal (IG-CLC).

the amount of char reacted was found to be directly proportional to the CO₂ yield. It was noticed that the solid fuel sample with the highest amount of char reacted had the highest energy output. In essence, if the steam flow rate used in gasification was reduced or the oxygen carrier flow rate was reduced, the solid fuel with the highest char would have the lowest CO₂ yield as there would not be enough oxygen for complete combustion.

Comparing Carbon Conversion for CLOU and IG-CLC of Coal Paper, Plastics, and Paper/Plastic Blend. The carbon conversion is enhanced by the gasification rate of the solid fuel, which is determined by the direct contact between the fuel and the oxygen carrier.³⁶ It was also observed that the amount of carbon present in the solid fuel sample affects the carbon conversion.^{32,37} A comparison of the carbon conversion of coal with the different solid wastes showed that coal had a similar carbon conversion with all the waste samples as presented in Figure 9. The carbon conversion for the CLOU

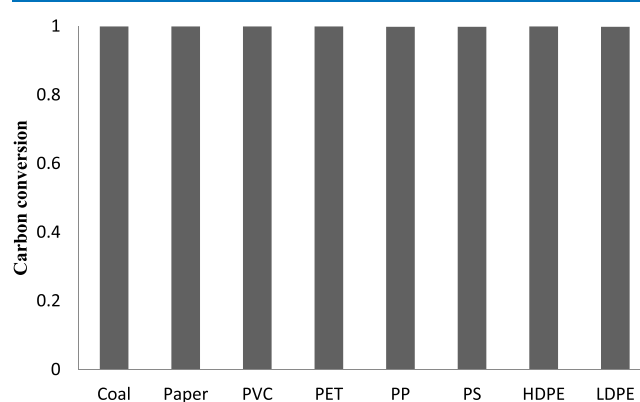


Figure 9. Comparing carbon conversion of coal, paper, and different plastics.

and IG-CLC was the same in this case. This is because the same amount of oxygen carrier was used for both processes to ensure an effective comparison. In an ideal case, the OC/fuel ratio of CLOU is usually higher than that of IG-CLC due to its low oxygen transport capability.²⁷ The carbon conversion was approximately 100% for all the samples. This is because all the carbon present in the sample was devolatilized, and all the carbon char reacted to produce CO₂ and CO.

In comparison with the optimum blended paper/plastic sample, coal had a better carbon conversion than all the paper/plastic blends as seen in Figure 10. This is because not all the carbon atom present in the paper/plastic blend was converted to carbon char in the devolatilization reactor as a limiting reactant was specified. It was observed that the blend with the highest amount of char that reacted had the highest carbon conversion. This is due to the better contact between the char and the oxygen carrier as explained previously.^{36,37} The highest carbon conversion for each paper/plastic blend was at a ratio of 0.5 for paper/PVC, 0.8 for paper/PET and paper/PP, and 0.6 for paper/PS, paper/LDPE, and paper/HDPE.

Comparison of the Combustion Efficiency for CLOU and IG-CLC of Coal, Paper, Plastics, and Paper/Plastic Blend. The combustion efficiency in a CLC process depends on the char conversion in the fuel reactor and the reactivity of the oxygen carrier with the gasification products and the volatile content.³⁸ A comparison of the combustion efficiency of coal with that of paper and the different plastics showed that

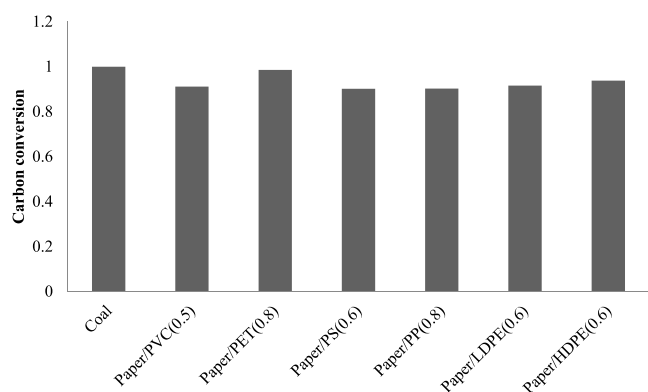


Figure 10. Comparing coal with the optimum blend for carbon conversion (CLOU and IG-CLC).

paper and PVC have higher combustion efficiencies than coal (80%), while the other types of plastics (PET, PP, PS, LDPE, and HDPE) had a lower efficiency in the CLOU process. Meanwhile, in the IG-CLC process, paper, PVC, and PET had higher combustion efficiencies than coal (50%) as seen in Figure 11. The trend observed in the sample is due to the high

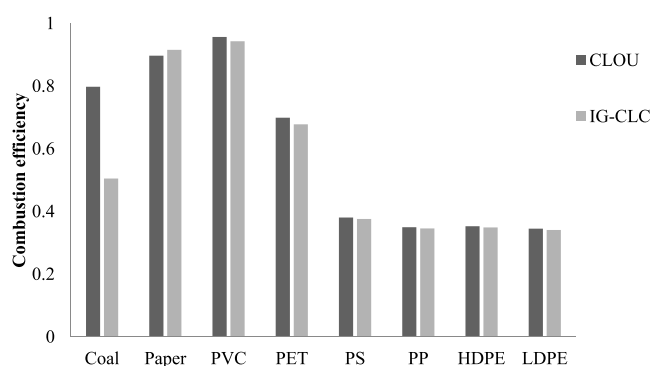


Figure 11. Combustion efficiency of coal with that of paper and the different plastics.

oxygen demand gotten from the samples with high volatile content. The chemical looping combustion experiment performed by Lyngfelt and Linderholm³⁹ observed that high-volatile solid fuels tend to have high oxygen demand, and this was also observed with the different waste samples analyzed. The high oxygen demand was also observed to cause a reduction in combustion efficiency.⁴⁰ This is because higher oxygen demand gives poorer contact between the volatiles and the oxygen carrier, which leads to reduced combustion efficiency.³⁸ The higher combustion efficiency observed in CLOU compared to IG-CLC was due to the improved gasification rate of reaction between the volatile matters and the oxygen produced from the decomposition of the metal oxides.^{38,41} The high gasification rate is attributed to the part of the CO₂ from the flue gas, which is recirculated into the fuel reactor.⁴² The combustion efficiency of coal could be increased by using a higher reactivity of OC such as natural hematite,⁴³ hematite and copper ore blend,⁴⁴ and hematite and manganese blend.⁴⁵ The higher volatile content of the solid waste compared to the coal sample could also make it a suitable feed for blending with coal to achieve a better CLC process. It should also be noted that the high alkaline earth content present in the ash of the solid waste could serve as a source of

catalysts during the gasification process and enhance the gasification rate, which can increase the combustion efficiency of the coal when blended with the waste sample.^{46,47}

A large amount of chlorine present in PVC was expected to reduce the combustion efficiency of PVC due to the formation of HCl and subsequent formation of Cl₂ from the deacon reaction (eqs 7, 16, and 21), which can lead to corrosion formation. However, the indirect contact of the solid fuel with the O₂ greatly reduced the formation of Cl₂, and the use of ilmenite as the oxygen carrier was also found to generate the minimum amount of Cl₂ when compared with other oxygen carriers.⁴⁸ Hence, the formation of alkali metal chloride, which causes corrosion, will be greatly reduced.

A comparison of the combustion efficiency of coal and the optimum paper/plastic blends for the different plastics showed that paper/PVC at an optimum blend ratio of 0.5 was the only paper plastic blend that had a higher combustion efficiency than coal. The other optimum paper/plastic blend had lower combustion efficiency than coal for the CLOU process. Meanwhile, for the IG-CLC process, all the optimum paper/plastic blends had higher combustion efficiency than coal, and this is illustrated in Figure 12. The reason for the higher

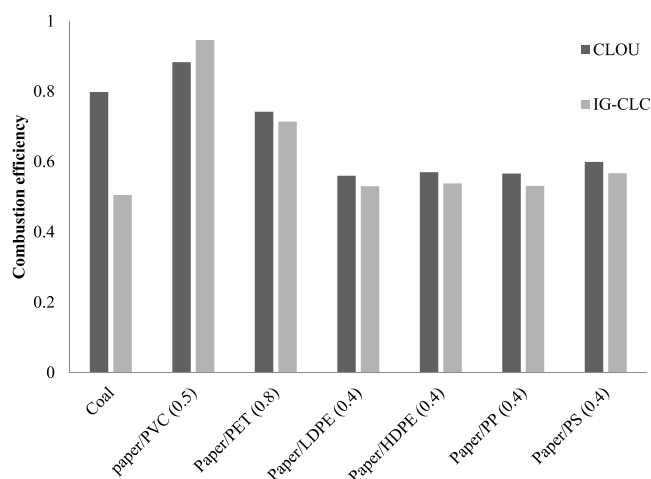


Figure 12. Comparison of the combustion efficiency of coal with the optimum blends of paper/plastic.

combustion efficiency of the optimum paper /plastic blends in IG-CLC is that there is a lower oxygen demand for combustion of the paper/plastic at optimum blend ratios than in coal, and this results in an increase in a higher combustion efficiency as explained earlier.⁴⁹ Another factor that affected the trends between the optimum paper/plastic blends was the unreacted char present in the reactor. The optimum paper/PVC and paper/PET blends had a very little unreacted char compared to that of the other blends. A large amount of unreacted char led to a decrease in combustion efficiency.

CONCLUSIONS

The result obtained from the comparison of MSW and coal in CLC using Chemcad process simulation software showed the following:

- Coal had a lower CO₂ yield than paper but a higher yield than PVC, PET, LDPE, HDPE, PP, and PS in CLOU and an equal CO₂ yield with the paper and all the plastic samples in IG-CLC.

Table 1. Elemental Composition of Samples on a Dry Basis

element	C	H	O	N	S	Cl	HHV (MJ/Kg) ^b	ref
paper	45.62	6.01	47.78	0.34	0.22	0.28	18.39	51
PVC	40.59	5.00	0.59	0.08	0.20	53.53	18.64	51
HDPE	83.70	14.09	1.90	0.20	0.11	0.00	45.61	52–55a
LDPE	85.51	14.30	0.10	0.00	0.10	0.00	44.54	54,55a
PP	85.02	13.93	0.960	0.08	0.01	0.00	46.00	56
PS	90.37	8.64	0.9	0.00	0.09	0.00	39.52	56
PET	62.30	4.43	33.13	0.09	0.05	0.00	23.09	56
South African coal	78.40	4.46	1.84	1.03	14.27	0.00	17.37	

^aThe percentage of each element was gotten from the average of the different values from the literature. ^bThe HHV of the sample was gotten from the average of the different ultimate analyses from the literature.

- Also, coal has a lower CO₂ yield than all the optimum blends for CLOU and an equal yield with the entire paper/plastic blend in IG-CLC.
- The carbon conversion of coal is 100% since all the carbon reacted, which is similar to that of all the paper and the different plastics
- However, not all the carbon present in the paper/plastic blend reacted since a limiting reactant was specified, and the excess reactant based on the number of moles was unreacted.
- Coal has a lower combustion efficiency than paper and PVC but a higher efficiency with the other plastic samples in CLOU while in IG-CLC, it had a lower efficiency than paper, PVC, and PET and higher efficiency than HDPE, LDPE, PP, and PS.
- In the case of the paper/plastic blends, coal has higher combustion efficiency than all the paper/plastic blends in both CLOU and IG-CLC processes except for that of paper/PVC where the combustion efficiency was higher than coal.
- A higher combustion efficiency can be achieved by using a more reactive oxygen carrier, blending with highly volatile solid fuels, using a secondary fuel reactor, and recirculating unburnt char into the fuel reactor.^{26,47}
- The energy load from the CLOU and IG-CLC of coal was higher than all the plastic samples (PVC, PET, PP, PS, LDPE, and HDPE).
- The CO₂ yield is inversely proportional to the energy output. Hence, samples with higher CO₂ yield have lower energy output.

The simulation has demonstrated that using MSW has a solid fuel in CLC and has an equal (IG-CLC) and better (CLOU) CO₂ capture efficiency and combustion efficiency than coal.

METHODOLOGY

Waste Sample Characterization. The MSW 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 was gotten from the literature and is stated in Tables 1 and 2. The coal characterization was conducted in the laboratory. The higher heating value (HHV) of the samples was calculated using the modified Dulong equation (eq 6) for MSW as a function of ultimate analysis.⁵⁰

Table 2. Proximate Analysis Result (db^a)

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
coal	2.1	22.7	37.5	37.7

^adb = Dry basis

$$\text{HHV} = -1.46 + 0.361\text{C} + 1.05\text{H} - 0.160\text{N} + 1.24\text{S} - 0.0658\text{O} \left(\frac{\text{MJ}}{\text{kg}} \right) \quad (6)$$

Chemcad software was used to predict the performance of this process by inputting the elemental analysis and heating value of the samples and to process conditions like temperature, pressure, moisture content, and flow rate into the process model. A process flow diagram was developed based on the chemical looping combustion description from the literature.^{57–59} The flow sheet of the two different chemical looping combustion processes of MSW is depicted in Figures 13 and 14. The feed samples were defined as a nonconventional combustion solid and were input using 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. (h) The metal oxide ilmenite (FeTiO₃) is modeled separately on Chemcad as FeO and TiO₂.

Unit Operations and Parameters. Different unit operations were considered for the chemical looping combustion process, and the operating parameters used are indicated in Table 3. For the CLOU, drying, devolatilization, combustion, metal oxide oxidation, and reduction processes were used. For IG-CLC, drying, devolatilization, gasification, combustion, and metal oxidation processes were considered.

Devolatilization. This is the removal of volatiles from a solid substance; in this case, MSW solid waste. This was

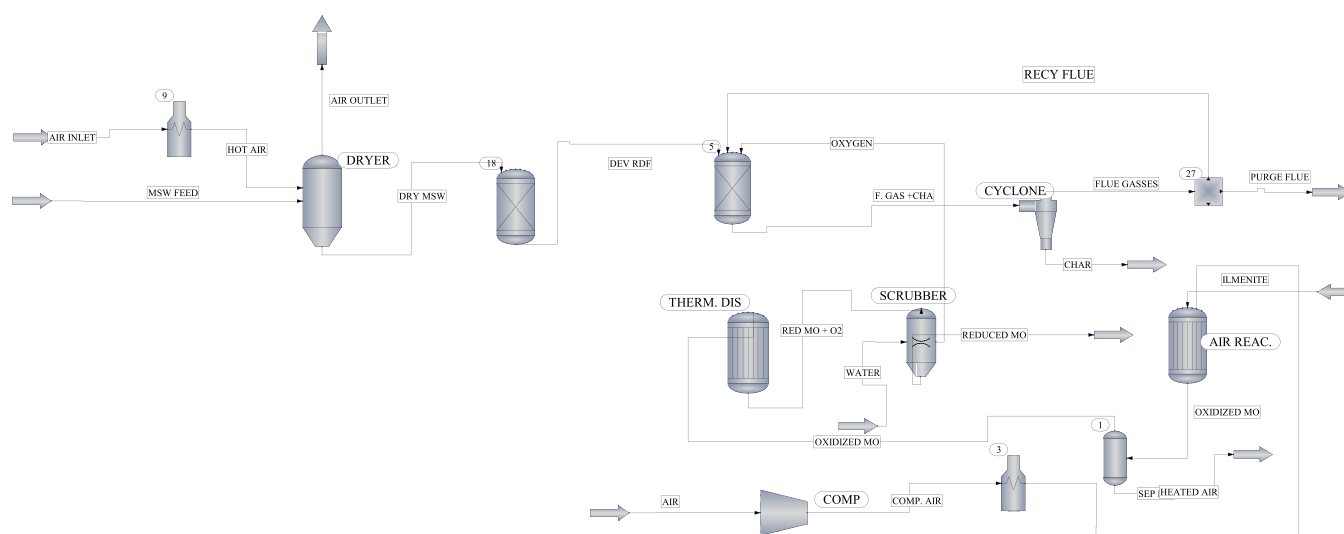


Figure 13. Process flow diagram of the CLOU system of MSW.

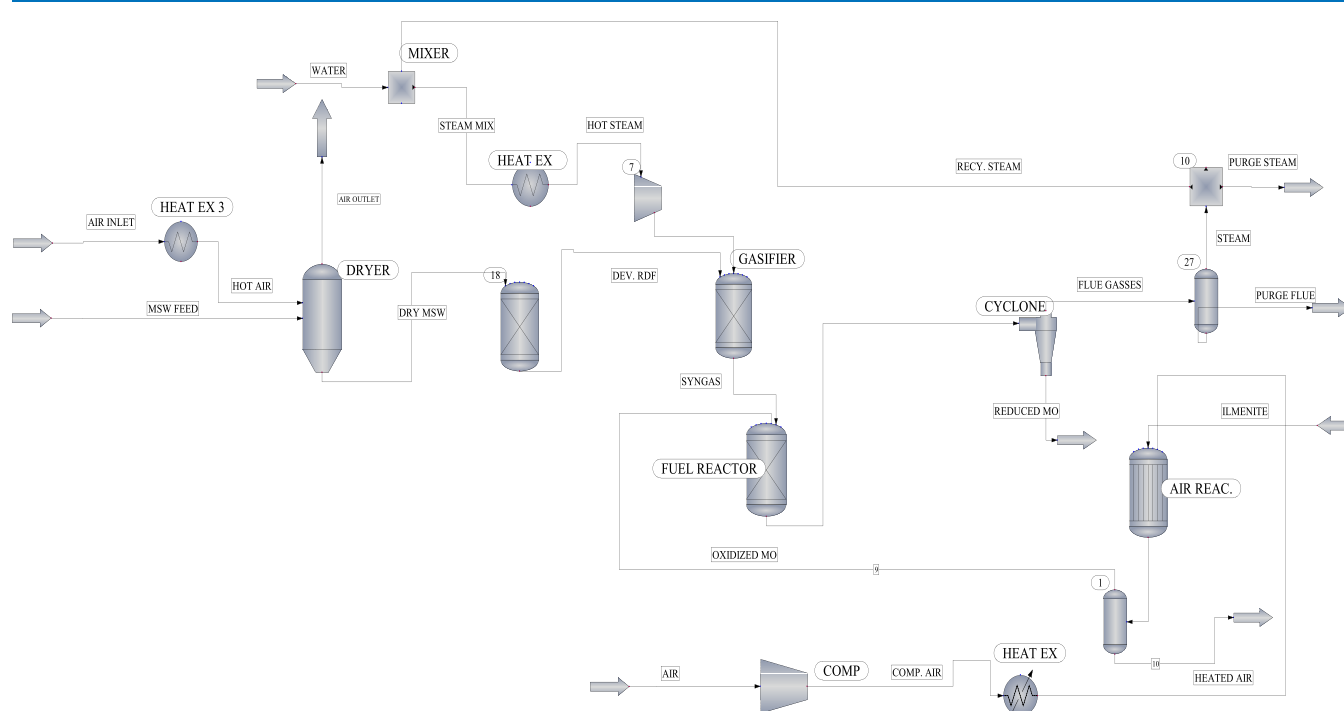
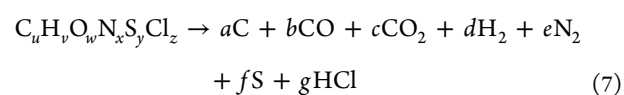


Figure 14. Process flow diagram for IG-CLC of MSW.

Table 3. Operating Parameters for Simulation (IG-CLC and CLOU)

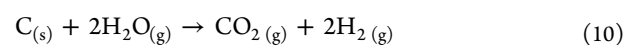
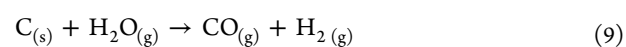
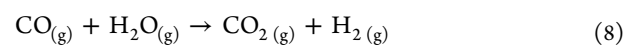
parameter	operating parameters
feed flow rate (kg/h)	100
fuel reactor temperature (°C)	800–1000
air reactor temperature (°C)	935
steam flow rate (kg/h)	200
pressure (bar)	1
air flow rate (kg/h)	251
metal oxide flow rate (kg/h)	1798

analyzed by balancing the equation of each of the solid waste sample as stated in eq 7



Gasification. This involves the conversion of organic and carbonaceous materials into carbon monoxide, hydrogen, and carbon dioxide. This is done at a high temperature with a little amount of oxygen or steam. This is indicated in eqs 8–11.

Water Shift Reaction.

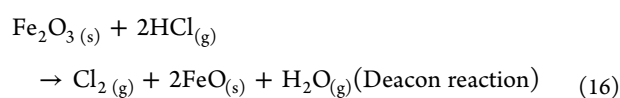
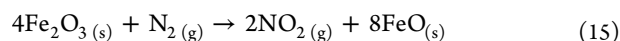
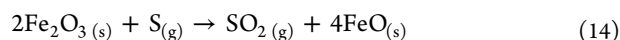
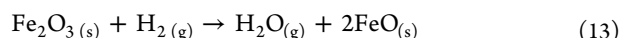
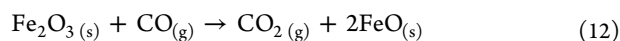


Boudouard Reaction.

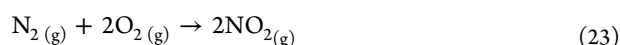
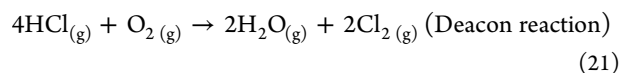
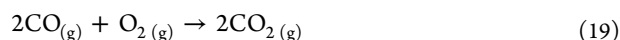


Combustion Reaction. This is a reaction between the fuel and an oxidant to produce gaseous products. Different reactions occur for the combustion of both the IG-CLC process and the CLOU process. For CLOU, the oxidant is molecular oxygen obtained from the decomposition of the OC while that of IG-CLC is the oxidized OC as seen in eqs 12–23. The decomposition reaction, which produces the oxygen used in the CLOU, is stated in eq 24.

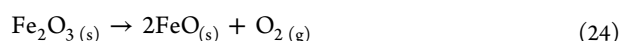
IG-CLC Combustion Reaction.



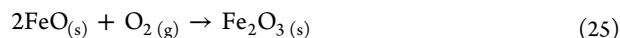
CLOU Combustion Reaction.



Decomposition Reaction.



Air Reactor. For this simulation, ilmenite (FeTiO_3) was used as the oxygen carrier. The oxygen carrier was used for both the IG-CLC and the CLOU. A stoichiometric reactor (RSTOIC) was used for the oxidation process, and air was introduced into it. In the RSTOIC, TiO_2 was assumed to be inert. The amount of air entering the reactor was 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 as seen in eq 25.



Data Evaluation. The result from the simulation was evaluated based on the CO_2 yield, carbon conversion, and combustion efficiency.

Gas Yield (η). This is used to quantify the conversion of gas in the simulation. ηCO_2 is the fraction of CO_2 in the outgoing gas divided by the fraction of other carbon-containing gas in the outgoing gas. If a CO_2 yield of 1 is gotten, then it means there was a total conversion of the fuel to CO_2 . The formula for finding the gas yield is seen in eq 26. Methane was not included in the devolatilization product since we assumed that all the carbon was converted to CO and CO_2 and was hence excluded from the calculation.

$$\eta\text{CO}_2 = \frac{\chi\text{CO}_2}{\chi\text{CO}_2 + \chi\text{C}} \quad (26)$$

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

Carbon Conversion. This is the ratio of mole C in the output gas to the mole of C in the input. It is calculated using the equation from³² eq 27.

$$\gamma_c = 12(\text{FCO}_{\text{out}} + \text{FCO}_{2,\text{out}})/(\dot{m}_w\beta_c) \quad (27)$$

$F_{i,\text{out}}$ ($i = \text{CO}$ and CO_2) is the molar flow of the gaseous product in the flue gas. $\dot{m}_w$ is the mass rate of the waste fed into the reactor, and β_c is the mass fraction of active component carbon in the waste.

Combustion Efficiency. Combustion efficiency ($\varphi_{\text{comb,FR}}$) in the fuel reactor is the amount of fuel oxidized to form the products completely.⁴² 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 eq 28 following the same assumption by^{32,42}

$$\begin{aligned} \varphi_{\text{comb,FR}} = (\text{FCO}_{\text{out}} + \text{FH}_2\text{O}_{\text{out}} + 2\text{FCO}_{2,\text{out}}) \\ - (\text{FCO}_{\text{in}} + \text{FH}_2\text{O}_{\text{in}} + 2\text{FCO}_{2,\text{in}})/\dot{n}_{\text{o,w}} \end{aligned} \quad (28)$$

$\dot{n}_{\text{o,w}}$ is the oxygen demand molar rate of the waste sample. This can be calculated using eq 29³²

$$\dot{n}_{\text{o,w}} = \dot{m}_w \left(\frac{2\beta_c}{M_c} + \frac{2\beta_s}{M_s} + \frac{\beta_H}{2M_H} - \frac{\beta_o}{M_o} - \frac{\beta_{cl}}{2M_{cl}} \right) \quad (29)$$

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Notes

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ACRONYM

CCS	carbon capture and storage
CLC	chemical looping combustion
CLOU	chemical looping oxygen uncoupling
GHG	greenhouse gas
HDPE	high-density polyethylene
IG-CLC	in situ gas chemical looping combustion
LDPE	low-density polyethylene
MSW	municipal solid waste
OC	oxygen carrier

PET	polyethylene terephthalate
PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride

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