Coal Wastes Gasification with in-situ Reduction of Toxic Metals Emissions as an Environmental Control Measure

Duncan A. Mwakipesile
Mbeya University of Science and Technology (MUST)
P. O. BOX 131, MBeya
Mobile phone: 0767851837
E-mail:dmwakipesile63@gmail.com

ABSTRACT
This paper addresses issues of coal wastes to recover energy through gasification and isolate the vapors of toxic metals such as lead, arsenic, selenium, chromium, antimony, nickel and cadmium from their release to the atmosphere. Coal wastes samples from Kiwira Coal Mine were used in Laboratory-scale Fluidized Bed Gasifier to investigate process parameters and sorbent to assess efficiency of the coal wastes gasification process and determine the operating conditions for Syngas production for reduction of toxic metals emissions as an environmental control measure. A clay-like (kaolinite) sorbent material from Matema - Kyela was mixed with coal waste and introduced into the Gasifier. The experimental test rig demonstrated reduction over 90% of toxic emissions. Gasification temperature of 850°C, minimum fluidization velocity of 1.2m/s and equivalent ratio of 0.4 with 1:4 sorbent-to-coal waste ratio produce optimum exiting gas compositions in the range of 18-20 vol% and 13-16 vol% for CO and H₂ respectively. In the study, CO content was high followed by H₂ and CH₄ thus making eco-friendly and effective utilization of coal wastes to produce clean fuel gas that can be used in chemical industries and to fire various types of industrial equipment that previously fired on expensive natural gas or oil.

Keywords: Coal Wastes, Gasification, Toxic metal emissions and Fluidized Bed Gasifier
1.0 INTRODUCTION

Coal is an extremely valuable resource for energy production worldwide with vast untapped potential. For example, in 2001 global coal production was 50% up from the production of twenty years before, and continues to rise (WEC 2010). However, during mining and cleaning processes of the coal, rejects and leftovers of the coal as coal wastes are accumulated and piles in many coal plants. The Coal wastes contain toxic trace metals which have negative impact to the environment that limit the utilization of these wastes as source of energy. The trend shows that continue burning same quantities for more years to come, a broad range of exhaust constituents of toxic emissions is predicted to go well beyond environmental regulations (Weiner et al., 2005). In many coal plants in developing countries, such as Tanzania, coal wastes accumulated mostly between 1953 and 2000. The piles look like hills or small mountains that are dark and barren. Coal waste piles leach lead, arsenic, selenium, chromium, antimony, nickel and cadmium pollution into waterways and cause negative impact to neighboring stream animal (Mwakipesile, DA, Mkumbwa, MM, Mtui, PL & Mkilaha, ISN 2012). These piles sometimes even catch fire, releasing toxic pollution into the air. Burning coal wastes does not make the wastes to go away. If 100 tons of coal wastes are burned, 85 tons will remain as coal wastes ash. Toxic metals cannot be destroyed by burning them.

With the fact that coal is abundantly available worldwide as major source of energy, little effort has been put to coal wastes that contains toxic metals. Kiwira coal-waste samples from Tanzania indicate that concentrations of these metals are higher than International Atomic Energy Agency (IAEA) average values, constituting significant integrated risk. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metals have been used by humans for thousands of years. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries including Tanzania, though emissions have declined in most developed countries over the last 100 years (Hazrat et al. 2019; Valkovic, 1983). Many studies which address environmental issues from coal wastes burning as source of energy reveal that gasification with in-situ reduction of toxic metals appears to be one of the remediation technologies (Duncan et al., 2012).
1.2 Gasification
Syngas as a mixture of hydrogen, carbon dioxide and small amount of methane composition depends on a number of things including the type of feedstock, type of gasifier, oxidant, and gasification temperature and pressure (Lloyd 2000; Mehdi 2011). Therefore, unique gasification process model in predetermined gasifier for unique type of coal is required. Studies by (Winaams et al., 1993) demonstrated that chemical structure of coal affects the gasification process. Low rank coals, such as coal wastes produce relatively high levels of light gases which favors gasification process. Most of these gases contain mainly of oxides (CO and CO$_2$) and light hydrocarbons that start to come out at low temperatures of 470 to 770 K (Yu et al., 2008). Also, studies demonstrated that the relatively weak bonds of oxygen in the coal promote depolymerization reaction of the coal macromolecule (Winans et al., 1993). The reactivity of these low rank coals at low temperature is certainly accelerated by relatively large amounts of oxygen-containing functional groups of carboxyl and hydroxyl.

2.0 OBJECTIVE OF THE STUDY
The objective of this work focuses on the reduction of toxic trace metals emissions during gasification and eco-friendly effective utilization of coal wastes to produce clean fuel gas (syngas) that can be used in chemical industries and to fire various types of industrial equipment with reduced toxic metals

3.0 METHOD AND METHODOLOGY

3.1 Gasification Process
Studies show that, rate of coal particle decomposition is a function of temperature, composition of gaseous environment, the size and temperature of the particle (Kunii & Levenspeil 2005). However, in fluidized bed gasification, together with the above-mentioned variables, the gasification is also a dependent on operating parameters such as gasification temperature, fluidization velocity and equivalent ratio. Hence analysis of these operating parameters for optimum yield of the product gas composition in Air Blown Fluidized Bed Coal Wastes Gasifier using FLUENT and MALT simulators was
performed, followed by experimental tests. Inside the gasifier, drying, devolatilization, combustion and reduction chemical reactions take place. During the gasification process, the heat that has been produced by combustion process is absorbed by drying, devolatilization and reduction processes to combustible gases. As the gasifier operates at relatively high temperature, where most devolatilized products do not survive, then modeling of gasification reactions were simplified by considering only the principal reactions that take place with carbon, carbon monoxide, carbon dioxide, hydrogen, steam, and methane as follows:

**Combustion:**

\[ C + O_2 \rightarrow CO_2 \] (R1)

\[ H_2 + 0.5O_2 \rightarrow H_2 \] (R2)

**Gasification reactions:**

Water-gas-reaction

\[ C + H_2O \rightarrow H_2 + CO \] (R3)

Boudouard reaction

\[ CO + CO_2 \rightarrow 2CO \] (R4)

Water-Shift conversion

\[ CO + H_2O \rightarrow H_2 + CO_2 \] (R5)

Methanation

\[ C + 2H_2 \rightarrow CH_4 \] (R6)

In this work, value of equivalent ratio (Φ), which is the ratio between product of flow rate of air supply and run duration to the product of mass input of fuel and air –fuel ratio, was maintained between 0.2 and 0.4 as an excessive low value of Φ, results in incomplete gasification, more char formation and low heating value of the product gas. But if Φ is very high value, then complete combustion occurs that produces more
undesirable gas (carbon-dioxide). While Silica sand was applied as inert material for heat carrier during fluidized bed gasification process.

3.2 Modelling Technique

Coal waste gasification simulation model divided into kinetic and equilibrium models. Kinetic model was used to simulate the reaction conditions and to design the gasifier and operating parameters for optimum product gas yield. Equilibrium model predicts end reaction product distribution under assumptions that process is isothermal and steady state and the residence time for reactants was sufficiently high to reach chemical equilibrium.

3.3 Computational Models

Models of thermo-chemical processes were described by transport phenomena of fluid flow, heat and mass and chemical reactions. Eulerian-Eulerian model (Wang & Liu, 2010) which is based on averaged equations of motions that treat fluid and solid phases as interpenetrating continuum was applied through Computational Fluid Dynamics (CFD) in FLUENT software to simulate the process parameters, in which constitutive relations of fluid-particle interaction forces, such as buoyancy and drag forces were considered. Conservation laws of mass, momentum energy and species were applied, in which:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = S_\rho \\
\frac{\partial (\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla P + \nabla \cdot (\mu \nabla \vec{v}) + S_v \\
\frac{\partial (\rho H)}{\partial t} + \nabla \cdot (\rho \vec{v} H) = \nabla \cdot (\lambda \nabla T) + S_H \\
\frac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot (\rho \vec{v} Y_i) = \nabla \cdot (D \nabla (\rho Y_i)) + S_{Y_i} + R_f
\]

So the material and energy balances including heat and mass transfers and reactions have been modeled by considering that thermal energy produced by exothermic reactions is transformed into chemical energy of combustible gas species according to the reactions (R1) to (R6). Gidaspow and Syamlal-O’Brien laws used to predict the incipient fluidization conditions, such that the bed particles are in a state of suspension.
due to balance between drag and body forces and the gas-sold exchange coefficient are defined as:

\[ K_{sg} = \frac{3\varepsilon_s\varepsilon_g\rho_g}{4U_{ts}^2d_s} \left[ \frac{Re_s}{U_{ts}} \right] [U_s - U_g] \]

Where \( U_{ts} \) = terminal velocity for solid phase
\( U_s \) = Velocity for solid phase
\( U_g \) = Velocity for gaseous phase

### 3.3.1 Computational of Energy Flows

In gas-solid fluidized beds, the energy dissipated in the system is a net energy that may be determined as a difference between energy entering in the fluidized bed, energy leaving the fluidized bed by gas phase and energy gained by solid phase:

\[ \Delta E = E_i - E_o - E_T \] \hspace{1cm} (5)

Where \( E_i \) is the energy entering in the fluidized bed, \( E_o \) is the energy leaving the fluidized bed by gas phase and \( E_T \) is the energy gained by solid phase.

\[ E_i = \frac{\pi}{4} D^2 H g U_g (\varepsilon_g \rho_g + \varepsilon_s \rho_s) \] \hspace{1cm} (6)

In eqn. (6), \( D \) is diameter of the bed; \( H \) is expanded bed height and \( U_g \) is the superficial velocity of gas.

In this system the species transport equation is given by:

\[ \frac{\partial C}{\partial t} + \frac{\partial (U_iC)}{\partial x_i} = \frac{\partial}{\partial x_i} \left[ D_i \frac{\partial C}{\partial x_i} \right] + S \] \hspace{1cm} (7)

Where \( C \) is the concentration of the chemical species \( D \) is the diffusive coefficient and \( S \) is the source term.

The domain is modelled in 3D cylindrical case with the following assumptions: There are two main phases in the bed, emulsion and bubbles; the bubbles are considered free of particles; two phase theory is only applied at \( z = 0 \). Consequently, the flow velocity
of the suspension is assumed to be the same as that of minimum fluidization velocity at
the base of the gasifier such that any excess flow inters the bubbling phase; pyrolysis
occurs just in the feeding zone of the gasifier; Consequently, the pyrolyzed gas
concentration can be used as the boundary conditions (at z=0) in the calculus. A good
solid mixing and a larger sand particles flux compared to char particles flux implies
isothermal conditions in the bed (any heat excess is absorbed by sand which is then
cooled by air); No second-order terms of the transport equations are considered.

Global reaction for the gasification process was raised from cola waste chemical
composition and amount of air for the reaction as:

\[ x_1(3.05C + 5.83H + 2.29O + 0.24N) + x_2(O_2 + 3.76N_2) + aH_2O + bH_2O \rightarrow \]
\[ x_7(12CO + 4H_2 + 3CH_4 + x_3H_2O + x_4CO_2 + x_5N_2) + x_6C \]

\[ \text{... (R7)} \]

In this global reaction, (a) is the water content in coal wastes and the air (b) is the air
obtained from ultimate analysis of the fuel. The mass flow of air \( \dot{m}_a \) for the fluidization
may be determined from the following expression:

\[ \dot{m}_a = 3600(U_f - A\rho_f) + 0.648b \text{... (8)} \]

The coefficient of reaction for air in the gasification is calculated by:

\[ x_2 = \frac{\dot{m}_a}{4.76MW_a} \]

For each element, molar balances were calculated and the global reaction for the
gasification coefficients and elemental formulae were obtained as:

\[ xC = 46.51\%; xH = 6.36\%; xO = 43.66\%; xN = 2.04\%; xS = 1.43\% \]

\[ C_{m,H_n,O_x,N_y,S_z} \]

\[ m = \frac{46.51}{12} = 3.8758; \quad n = \frac{6.36}{1} = 6.3; \quad x = \frac{43.66}{16} = 2.7287; \quad y = \frac{2.04}{14} = 0.1457 \]

\[ :z = \frac{1.43}{32} = 0.0447 \]

Normalizing by carbon, m,
The elemental formula is:

$$\text{CH}_{1.6409}\text{O}_{0.7040}\text{N}_{0.0376}\text{S}_{0.01153}$$

Pyrolysis of the coal wastes

$$\text{Coal} \rightarrow \text{Char} + \text{gases}$$

$$\text{CH}_{1.6409}\text{O}_{0.7040}\text{N}_{0.0376}\text{S}_{0.01153} \rightarrow \alpha_1C + \alpha_2\text{CO} + \alpha_3\text{CO}_2 + \alpha_4\text{CH}_4 + \alpha_5\text{H}_2 + \alpha_6\text{H}_2\text{O} + \alpha_7\text{NH}_3 + \alpha_8\text{H}_2\text{S}$$

Molar elemental balance:

$$C - \text{balance: } 1 = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$$
$$\text{H - balance: } 1.6409 = 4\alpha_4 + 2\alpha_5 + 2\alpha_6 + 3\alpha_7 + 2\alpha_8$$

$$O - \text{balance: } 0.7040 = \alpha_2 + 2\alpha_3 + \alpha_6$$

$$N - \text{balance: } 0.0376 = \alpha_7 \text{and } S - \text{balance: } 0.01153 = \alpha_8$$

Experimental species distribution:

$$\frac{\text{CO}}{\text{CO}_2} = \frac{2.5}{2.8}; \text{CO} = 0.8929\text{CO}_2; \alpha_2 = 0.8929\alpha_2$$

$$\frac{\text{CH}_4}{\text{CO}_2} = \frac{5.92}{2.8}; \text{CH}_4 = 2.11428\text{CO}_2; \alpha_4 = 2.11428\alpha_4$$

$$\frac{\text{H}_2}{\text{CO}_2} = \frac{8.5}{2.8}; \text{H}_2 = 3.0357\text{CO}_2; \alpha_5 = 3.0357\alpha_3, 0.71 = 1.8929\alpha_5 + \alpha_4 + 0\alpha_6: 0.86574$$
$$= 6.0714\alpha_3 + 4\alpha_4 + 2\alpha_6$$
0.7040 = 2.8929\alpha_3 + 0\alpha_4 + \alpha_6. In matrix form:

\[
\begin{bmatrix}
1.8929 & 1 & 0 \\
6.0714 & 4 & 2 \\
2.8929 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\alpha_3 \\
\alpha_4 \\
\alpha_6
\end{bmatrix}
= 
\begin{bmatrix}
0.71 \\
0.86574 \\
0.7040
\end{bmatrix}
\]

Solving:

\[\alpha_1 = 0.29 \text{ (Fix carbon from proximate analysis)} \hspace{1em}, \hspace{1em} \alpha_2 = 0.15820, \alpha_3 = 0.17718 \hspace{1em}, \hspace{1em} \alpha_4 = 0.37462, \alpha_5 = 0.53781, \alpha_6 = 0.1914, \alpha_7 = 0.0376 \hspace{1em} \text{and} \hspace{1em} \alpha_8 = 0.01157\]

\[CH_{1.6469}O_{0.7040}N_{0.0376}S_{0.01153} \rightarrow 0.29C + 0.15820CO + 0.17718CO_2 + 0.37462CH_4 + 0.53781H_2 + 0.1914H_2O + 0.0376NH_3 + 0.01157H_2S\]

.......................................................... (R8)

Based on the stoichiometric balance, the coal wastes mass flow is:

\[m_{cw} = 3.6x_1 + 0.648a\] .......................................................... (9)

The total amount of solid residue resulting from the gasification process, as 20% of carbon not converted [2], and added to the ash content, we have:

\[m_r = 0.22m_{cw}\] Therefore, \[m_g = m_{cw} + m_a - m_r.\] Table 1 shows the determined mass flows.

<table>
<thead>
<tr>
<th>Table 1: Mass flows of the coal wastes gasification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td><strong>Value</strong></td>
</tr>
<tr>
<td><strong>Source:</strong></td>
</tr>
</tbody>
</table>

The equivalence ratio (\(\Phi\)) was used for adjustment of the operating conditions. Its value is defined as:

\[\Phi = \frac{\text{flow rate of air supply} \times \text{run duration}}{\text{mass input of fuel} \times (A:F) \text{ for } \theta = 1}\]

The Air/fuel ratio was determined by dividing the mass of air required to the mass of fuel for air-coal real relation from:

\[(R_{A/C})_R = \frac{m_A}{1.292m_{cw}}\] .......................................................... (10)
For the established model, an equivalence ratio (Φ) of 0.40 was obtained.

Energy balance of the gasification process was expressed by:

\[ E_{\text{in}} + E_{\text{a}} = E_g + E_l \] .......................... (11)

where \( E_{\text{in}} = \frac{n_{\text{in}} LHV_{\text{in}}}{3600} \)

Since the air entering the gasifier was taken as ambient temperature (25°C), and then the fluidization-gasification air energy is zero. The energy contained in the product gas from the process was obtained by through the useful energy due to chemical energy of gaseous mixture and the sensible energy:

\[ E_g = E_u + E_s \]

in which \( E_u = \frac{n_u LHV_g}{3600} \) .......................... (12)

\[ LHV_g = 0.1263(\% CO) + 0.1079(\% H_2) + 0.358(\% CH_4) \] .......................... (13)

The sensible energy \( E_s \) of the product gas involves enthalpy of each constituent at the exit temperature (at 750°C) is calculated from:

\[ E_s = \frac{n_g \sum (y_i h_i)}{3600 \sum (y_i M_W_i)} \]

The energy losses \( E_l \) in the solid residues and to the surrounding is: \( E_l = E_r + E_w \)

The energy contained in the residues \( E_r \) is a total energy of residue carbon and ash:

\[ E_r = E_c + E_{\text{ash}} \]

Assuming 20% of residue carbon \( E_c = \frac{0.20 n_u (LHV_{\text{in}} + h_{\text{in}})}{3600} \) and the energy loss by sensible heat in the ash is: \( E_{\text{ash}} = \frac{0.8 n_u (920 + 1.67 (T_{\text{ash}} - 273))}{3600} \).

The energy flows of the coal wastes gasification are shown in table 2.

**Table 2: Calculated Energy flows of the coal wastes gasification**

<table>
<thead>
<tr>
<th>Energetic</th>
<th>( E_{\text{in}} )</th>
<th>( E_{\text{a}} )</th>
<th>( E_g )</th>
<th>( E_l )</th>
</tr>
</thead>
</table>
By applying Fick’s diffusion law, we quantify rate of energy diffusion as follows:

\[
\text{Rate of diffusion} = -D \frac{\partial c}{\partial n} A.
\]

The transport equation for specie concentration, C, is defined by:

\[
\frac{\partial \rho c}{\partial t} + \frac{\partial \rho u_j c}{\partial x_j} = \nabla \cdot \text{Source} \quad \text{(15)}
\]

The source term describes the effects of sorbent material which creates or destructs pollutant species due to chemical reactions in the system.

Boundary conditions considered were: (i) Wall flux = 0, (ii) Inlet flux is \( U_1 c - D \frac{\partial c}{\partial n} \), (iii) Inlet concentration/mass fraction = 0.46 and (iv) Outlet mass fraction of species

### 3.3.2 Kinetic Parameters

The kinetic rate parameters for reactions are given in table 3.

**Table 3:** Kinetic parameters for chemical reactions during gasification

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Rate constant</th>
<th>A (kg/m²·Pa⁻⁰.⁵)</th>
<th>E (J/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid – gas heterogeneous reactions:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_2O(\text{liq}) \rightarrow H_2O(\text{gas}) ) Drying</td>
<td>( k = A e^{\frac{-E}{RT}} )</td>
<td>5.56x10⁻²</td>
<td>8.79x10⁴</td>
</tr>
<tr>
<td>Coal ( \rightarrow ) 0.9684Tar + 0.0484O₂ + 0.0238H₂ + 0.0070CO</td>
<td>( k = A e^{\frac{-E}{RT}} )</td>
<td>5.76x10⁻⁴</td>
<td>6.63x10⁴</td>
</tr>
<tr>
<td>Reaction</td>
<td>Equation</td>
<td>Rate Constant ($k$)</td>
<td>Arrhenius Parameter ($E_a$)</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-----------</td>
<td>----------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Devolatilization</td>
<td>$Tar \rightarrow 0.7288C + 0.1914H_2O + 0.2052H_2 + 0.1429CH_4 + 0.0613CO + 0.0677CO_2$ (Tar cracking)</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$5.76 \times 10^{-2}$</td>
</tr>
<tr>
<td>$C(s) + 0.5O_2 \rightarrow CO$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$2.5 \times 10^6$</td>
<td>$1.794 \times 10^7$</td>
</tr>
<tr>
<td>Char combustion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C(s) + CO_2 \rightarrow 2CO$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$0.1732$</td>
<td>$1.125 \times 10^8$</td>
</tr>
<tr>
<td>(Bourdouard reaction: CO$_2$ gasification)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C(s) + H_2O \rightarrow CO + H_2$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$0.0782$</td>
<td>$1.15 \times 10^8$</td>
</tr>
<tr>
<td>(Gasification)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C + 2H_2 \rightarrow CH_4$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$1.180 \times 10^{-7}$</td>
<td>$1.15 \times 10^8$</td>
</tr>
<tr>
<td>(Methanation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gas phase, homogeneous reactions:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO + H_2O \leftrightarrow CO_2 + H_2$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$1.75 \times 10^4$</td>
<td>$8.40 \times 10^7$</td>
</tr>
<tr>
<td>(Water-gas- shift reaction)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO + 0.5O_2 \rightarrow CO_2$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$2.2 \times 10^{12}$</td>
<td>$1.67 \times 10^8$</td>
</tr>
<tr>
<td>(CO combustion)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$</td>
<td>$k = Ae^{E_a/kT}$</td>
<td>$4.4 \times 10^2$</td>
<td>$1.26 \times 10^4$</td>
</tr>
<tr>
<td>(CH$_4$ combustion)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Physical property for the gas and solid phase materials of the system for modeling is given in table 4. Coal wastes flow rate was treated with reference to moisture content, ash and volatile matter as per proximate analysis. A thermal decomposition was modelled giving char and gaseous species (CO, CO₂, CH₄, H₂O, H₂, H₂S etc). All combustion reactions were modelled from first order kinetic model in which the parameters were adapted with adjustment from (Armstrong, 2011) for atmospheric pressure and relatively low temperatures (800°C-950°C). Kiwira Coal wastes (Moisture 25.45wt%, VM 36wt%, FC 29.12wt%, ash 7.8wt%, C 46.46wt%, H6. 3wt%, O 43.8wt%, N 2.08wt% and S1.41wt%) with a flow rate of 0.004kg/s was used for gasifier model. As gasification temperature is a function of operating conditions, heat balance was solved from separate main steps for its accurate determination.

Table 4: Physical Property for the Gas and Solid Phase Material

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>( \rho ) (kg/m³)</th>
<th>( \mu ) (kg/m·s)</th>
<th>K (W/m·K)</th>
<th>C (J/kg·K)</th>
<th>d (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Air</td>
<td>1.28</td>
<td>1.8x10⁻⁵</td>
<td>0.0257</td>
<td>994</td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>sand</td>
<td>2600</td>
<td>1.0</td>
<td>1.0</td>
<td>973</td>
<td>3.5 – 5.0</td>
</tr>
</tbody>
</table>

Source: Armstrong, L., 2011

Pressure drop and incipient velocity were calculated using Egurn equation without the turbulent term as laminar flow regime was assumed.

\[
-\Delta P = \frac{150 \mu H U (1 - \varepsilon)^2}{d_p \varepsilon z^2} = \left( \rho_p - \rho_f \right) (1 - \varepsilon) g H
\]

At incipient velocity, \( U_{mf, \varepsilon} = \varepsilon_{mf} \). Then \( U_{mf} = \frac{\left( \rho_p - \rho_f \right) g d_p^3 \varepsilon_{mf}^3}{150 \mu(1 - \varepsilon_{mf})} \)
3.4 Equipment

The laboratory scale gasifier model of 0.30 m I.D. and 1.20 m high from the bottom level of air distributor was used as shown in figure 1.

![Laboratory scale gasifier model](image)

Figure 1: Laboratory scale gasifier model

The distributor was designed to promote uniform fluidization and to prevent aggregation of solids in the bed. K-type thermocouple probes were used in monitoring the temperature along the height of the gasifier. Three gasifier zones were monitored, (bed zone, freeboard zone and at the syngas exit before the cyclone). The Test rig model is equipped with instruments monitor the process parameters - temperature, product gas composition, air flow rate and fuel flow rate. Prior to this investigation, a model gasifier was simulated with CFD-FLUENT 6.2.3 software using two-fluid Eulerian-Eulerian model and Gidaspow drag model to study these process parameters. Incipient fluidization velocity of 1.2m/s, gasification temperature of 1143 K and pressure drop of 1.2 atm was achieved. Simulation results were used for design optimization of gasifier for the low rank carboneous fuels in order to improve efficiency and reduce pollution.

3.5 Test Procedures

First the reactor bed is partly filled with fluidizing sand approximately 250 μm size. Air blower is turned on to allow air to the reactor through the plenum. Gasification process is initiated in the reactor bed by first preheated externally by supplying heat using liquefied petroleum gas (LPG) at flow rate of 0.06 l/min. After the bed temperature reaches 873 K, a mixture of coal wastes and sorbent material is introducing near bottom of the reactor feed
section using screw feeder rotating at about 16 rpm. The feeder speed is controlled to prevent blocking of the fuel in the screw feeder section. Gasification starts at about 873 K during which the LPG supply is discontinued because the exothermic reactions during coal waste gasification provides sufficient heat to sustain the process until all the fuel is gasified.

Effect of sorbent on the retention of toxic trace elements has been examined during the gasification of coal wastes with varying ratios of coal to sorbent during gasification at constant temperature of 1123 K. The six mixture ratios were 100:0, 90:10, 80:20, 70:30, 50:50 and 25:75, respectively. Air at ambient temperature of about 25°C, was fed into the gasifier at 74.3 kg/h. The coal-sorbent mixture was fed into the gasifier by variable frequency motor at feed rates of 32-54kg/hr. The feed rates were varied to achieve a desired range of equivalence ratios. During the experiment, the pressure in the reactor was kept to be slightly lower than ambient in order to prevent any gas leakage.

The produced syngas is passed through gas sampling ports for analysis. Data such as air pressure and the bed temperature were recorded. The gasification byproduct ash was removed and analyzed for toxic metals contents for final determination of their removal efficiency. Product gas flame temperature was also measured for quality of the syngas produced.

3.6 Chemical Kinetics of Sorbent

The removal of metal vapour compounds by solid sorbent involved chemical reaction; physisorptions, chemisorptions or a combination of these processes. So, the overall process of metal vapour removal is referred to as sorption, and the material used for in-situ retaining metal vapour as soon as they are vaporized is called sorbent. The kaolinite obtained from Matema – Kyela consists of two pseudo-species; Al₂SiO₅(OH)₄ and Al₂O₃.2SiO₂. The Al₂SiO₅(OH)₄ breaks down to produce Al₂O₃.2SiO₂ and H₂O. The Al₂O₃.2SiO₂ produced would then become the active solid in the adsorption of heavy metals.

Trace metal adsorption in fluidized bed was controlled by mass transfer of the trace element between two phases of bubble and dense phases through the following global reaction: 

\[ Al_2Si_2O_5(OH)_4 + MO \rightarrow AlMSi_2O_4 + H_2O \] 

Where, M represents toxic trace metal to be adsorbed. Take example of Arsenic oxide; 

\[ Al_2Si_2O_5(OH)_4 + AsO \rightarrow AlAsSi_2O_4 + H_2O \]  

The metal conversion in the gasifier certainly was enhanced by mass transfer in and around the kaolinite particle and the chemical reaction rate, by which also, it is controlled by the amount of sorbent (kaolinite). For an optimum reduction of trace metals emissions, the temperature is
dominating the metal conversion and energy consumption, while the equivalence ratio is important for the gas throughput.

4.0 RESULTS AND DISCUSSIONS

Results in figures 2 and 3 show that the gas composition in the freeboard differs from that measured within the fluidized bed. It is observed that carbon monoxide (CO) concentration in the gasifier before freeboard is higher than that in the freeboard, while the hydrogen (H₂) concentration measured in the gasifier before freeboard is lower than the freeboard concentration. These results suggest that the water-gas-shift reaction takes place to some extent prior to the gases entering the freeboard.

Effect of equivalence ratios on product gas composition for coal wastes from Kiwira gasification is presented in Figure 4a. Results show that increase in equivalence ratio leads into increase in the concentration of CO and H₂ while CO₂ concentration decreases significantly. This is due to the Boudouard reaction: \[ C + CO₂ \leftrightarrow 2CO \], consequently, the CO₂ concentration diminishes with a corresponding increase in CO. The results agree with simulated by CFD, that as CO₂ is also the reactant of the Boudouard reaction, then any additional CO₂ with increasing temperatures promotes this reaction leading to an increase in CO, as was observed during the simulation. Therefore, while CO₂ is being produced faster with increasing temperatures it is also being consumed faster leading to the small average composition in the model as shown in Figures 2 and 3.
Figures 4-6 demonstrate the effect of gasification temperature on the produced syngas. An increase in temperature to about 1123 K brings about an increase in CO and H₂ yields. This is because of the increasing equilibrium constants by the increase in temperature, in which product gas is dependent on the gasifier temperature; so an increase in temperature causes more production of combustible gases. However, more increase in temperature say above 1123 K, more CO₂ is produced due to full combustion in the gasifier.

As observed during simulation, higher carbon monoxide (CO) concentrations were also observed during the air gasification experiments, whereas the hydrogen concentration in the syngas was lower, due to the limited of steam in the system that reduces hydrogen formation through water-gas shift reaction. The bed temperature was significantly high enough to favor the relatively higher concentration of carbon monoxide. Further increase of temperature above 850°C decreases CO and CH₄ with increase of H₂ and CO₂.

The results obtained by sampling directly from the bed clearly showed inter-bed variations in the gas composition. Figures 5 and 6 show both CO and H₂ concentration varies with gasifier height reaching a maximum near to the top of the bed. However the measured concentration of carbon dioxide (CO₂) was observed to initially drop, reach a minimum at some location within the bed, and then to rise again to levels similar to those measured immediately above the
distributor. The CO₂ gas has high partial pressure that encourages reaction of the gas with carbon by the Boudouard reaction: \( C + CO_2 \leftrightarrow 2CO \), consequently, the CO₂ decreases in favor of CO. At some point in the bed, however, due to bed density and superficial fluid velocity, the bed percolates less and tends to bubble more, forming pockets of gases that expand as they move through the bed. At this point, the gas phase equilibrium \( CO + H_2O \leftrightarrow CO_2 + H_2 \) shifts to the right and continues to do so, until the gases are ejected into the freeboard and equilibrium is attained in the splashing zone just above the bed. The effect of equivalence ratio \( \varnothing \) shows that high \( \varnothing \) increases the rate of syngas production, and low \( \varnothing \) results in the production of lower syngas yields and energy content. To attain the optimum carbon conversion efficiency when proportion of coal wastes in the mixture was increased then \( \varnothing \) was reduced to meet the minimum limit of operation temperature. Optimum value of \( \varnothing \) of 0.4 is established to achieving good syngas quality and toxic trace elements contamination of acceptable level, while the temperature is below the fusion temperature of coal ashes.

![Figure 4](image1.png)

**Figure 4:** (a) Variation of Equivalence ratio (\( \varnothing \)) with exiting gases concentrations

**Figure 4:** (b) Variation of temperature with dominating exiting gases

![Figure 5](image2.png)

**Figure 5:** (a) Variation of \( H_2 \) and \( CH_4 \) with temperature
The produced synthesis gas from coal wastes gasification reaction consists of mainly CO, H₂, small amount of CH₄ and incombustible gases of CO₂ and N₂. The percentage by volume of each gas species obtained at various equivalence ratios and mixing ratios are illustrated in Figure 6a. It may be seen that, in all cases 52-58% of the product gas composition is N₂ which in fact, dilute the syngas and hence decreases its heating value. In order to eliminate this effect of dilution that may also lead to a misinterpretation of the product gas formation, the concentration of each gas was converted into the N₂-free basis.

The effect of mixing ratio of kaolinite and coal wastes on concentration of syngas was analyzed. As the proportion of kaolinite in the fuel mixture increased, the CO increased, while CO₂ decreased (Fig.6b). The higher proportion of kaolinite in the fuel mixture seems to influence Boudouard reaction (i.e. C+CO₂ ↔ 2CO). This is because a higher proportion of kaolinite would decrease the average moisture in the fuel-mixture and therefore increasing the bed temperature favoring the forward Boudouard reaction. Upper limit of ER of 0.4 and mixing ratio of 20% were established such that the gas quality and toxic trace elements contamination are in acceptable level, while the temperature is below the fusion temperature of coal ashes. Figure 8 illustrates retention performance of kaolinite, the Al-based natural occurring solid trace metals inhibitor during coal waste gasification, in which all toxic studied trace metals were reduced by 90%.
5.0 CONCLUSIONS AND RECOMMENDATIONS

Coal wastes gasification with in-situ reduction of toxic metals emissions has been studied. The experimental test rig demonstrated reduction over 90% of toxic emissions. Gasification temperature of $850^\circ$ C, minimum fluidization velocity of 1.2m/s and equivalent ratio of 0.4
with 1:4 sorbent-to-coal waste ratio produce optimum exiting gas compositions in the range of 18-20 vol% and 13-16 vol% for CO and H₂ respectively. In the study, CO content was high followed by H₂ and CH₄. This means that, toxic metals in coal wastes were found to be effectively reduced hence make eco-friendly effective utilization of coal wastes.

This work has built upon this foundation to raise the level of understanding of toxic metal capture by sorbents to an in-depth comprehension of the mechanisms, interactions, temperature dependence, and applicability of this technology for both single-metal and multi-metal emissions for production of clean fuel gas (syngas) that can be used in chemical industries and to fire various types of industrial equipment with reduced toxic metals.
6.0 REFERENCES


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