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Contents

EMPHASIZING SOME CHARACTERISTICS OF NATURAL SALTED WATERS' AREAS, USED FOR PUBLIC HEALTH IMPROVEMENT

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Abstract

In recent years, more and more data has become available about the benefits of green in and around cities. Vegetation helps people to recover faster from illness; this reduces costs of healthcare and improves the patients' quality of life. In highly urbanized locations, the design of green elements requires special attention. Our paper presents a multidisciplinary study of areas located near the old salt mines and their use by entering in the spa and leisure circuit. Specific components were monitored, like the salted waters quality in lakes and/or springs and the identification of different plant species adapted to high salinity of the soil and able to enrich a green zone. In recent years, the continuous degradation of environmental quality due to factors such as air pollution, noise, chemical compounds, the pandemic state due to COVID-19 and disappearance of natural areas, in combination with lifestyle changes led to the emergence of a growing number of diseases such as different forms of diabetes, cardiovascular and nervous system disorders and cancer.

Key words: natural salted waters areas, health improvement

1. Introduction

The mineral waters are those in which the content in fixed solid substances is over 1g/Kg or those which differ from the common water by the presence of rare substances, by the gases content or by temperature, over 20°C. The mineral waters have the characteristic that they regenerate through the infiltration of the surface waters in the depth and mineralization.

The assessment of a water as mineral is done by enhanced accuracy in ascertaining its physical, chemical and microbiological properties and more over through obviousness of some scientifically demonstrated curative effects.

In accordance to bibliographical data are considered therapeutic waters exclusively only those of natural origin whose mineralization processes took place

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*Corresponding author: email address: ene.nicoleta27@yahoo.com in an underground aquifer system or in a natural saline lacustrine ecosystem, protected against pollution risks and containing some specific chemical substance in distinct concentrations.

Using high performance lab instruments in physico-chemical, microbiological, geochemical and pharmacological analyses, the type of such mineral waters can be identified and determined.

Subsequently the waters can be collected from the depth of surface lakes using adequate methods, equipment and technologies. By setting up protective measures, in conformity whit the geographical region, the mineral water sources can be appropriately set up as swimming pools, spaces recreation and sport spaces.

In nature water constitutes the existence fundamental element, with which are connected all the elements that characterize an environment.

Depending of the habitats' nature, natural water sources can be classified in two major categories: surface waters and underground waters.

The Romanian mineral waters have a great hydro-chemical variety which can be classified in three major predominant types: salty, sulphureous-sulphate and with dissolved carbon dioxide gas, among them occur some secondary hydro-chemical characteristics such as a content in iron, arsenic, potassium, calcium, manganese, chlorine, type. etc., depending on the natural local rocks leeched. There are since quite a few years different studies all around the world concerning a potential connection between the properties of a green zone and their use as therapeutic landscapes [2-5]. For example, even since 2015, Mireia Gascon et al. have published a review about "Mental Health Benefits of Long-Term Exposure to Residential Green and Blue Spaces" [4]. According to their conclusions "Given the increase in mental health problems and the current rapid urbanization worldwide, the results of this systematic review should be taken into account in future urban planning". In additional we can indicate the study conducted by Margarita Triguero-Mas and her research team [3] that are presenting the relationship between the natural outdoor environments (NOE) including both surrounding greenness and green and/or blue spaces, and a better mental health, mostly observed at males, younger people and low-medium educated. Their studies were carried out in: Barcelona (Spain), Stoke-on-Trent (United Kingdom), Doetinchem (Netherlands)and Kaunas (Lithuania).

But we can find this kind of researches carried out also very recently, in 2021 and 2022 [1, 6-10]. As an example, we can select the study published in 2021 by F. Gomez et al [8] concerning "Green zones, bioclimatic studies and human comfort in the future development of urban planning", whereas their researches were conducted in Valencia (Spain) "taken as a prototype of the Mediterranean city". Their study has begun from the analysis of the climatological situation of the city and it was continued based on "the performance of several internationally well-known “comfort indices”. Their conclusion was similar with that one taken at the European level [9] and it refers to the current importance of the green zones, while “urban living limits access to nature and can increase exposure to certain environmental hazards, such as air and noise pollution”.

The task of our studies was represented by the characterization of some areas situated near the natural salted lakes and /or springs, in order to capitalize on them as resorts for recreation, which can be seen as real new “green zones”.

2. Experimental

Following some empiric, local observations upon the qualities of the natural salted waters in the treatment of different maladies, a set of physical, hydrological, chemical and microbiological analyses was established, in order to emphasize the properties which can be useful for the development of different “green zones”. Moreover, the authors had selected some areas situated in the neighborhood of the old (perhaps already closed) salt mines from Romania.

The analytical determinations were realized during different locations and seasons, in order to check the weather’s influence upon the properties of these natural salted water sources and to improve their use for the public health use.

Some elements (for ex. iron total concentrations) were determined by A Perkin Elmer FAAS, while other ones by Elan DRC-e inductively coupled plasma spectrometer ICP-MS.

Iron dosing has been achieved by atomic absorption spectrophotometry in the flame at the wavelength 248,3 nm. The calibration curves were between 0,5-3,0 mg/L for iron.

The next steps required for our issues were represented by the selection of some dendrological species, by checking their adaptability to salted areas.

Dendrological species are woody ornamental species which, unlike forestry species, have exclusively decorative function. They come from the spontaneous flora of Romania, the flora of other countries with similar climatic conditions and from the breeding of some Romanian species or hybridization. A cultivar is a plant or group of plants selected for ornamental or biological characteristics, different from the basic species from which they are coming and that can be maintained by vegetative propagation.

3. Results and discussions

Chemical characterization

The results concerning the chemical composition of some different natural salted springs are presented in the Tables and Figures 1, 2 and 3.

Table 1.

Analytical determinations of some natural mineralized springs from the resort Someseni, during summer

Sample No.	Characteristics	Spring No.	Spring No.	Spring No.	Spring No.
	Characteristics	**1**	**2**	**14**	**15**
1	Conductivity (ys/cm)	2257	2530	1995	2310
2	pH	7.75	7.99	7.66	7.67
3	Chlorides (mg/L)	606	737	490	587
4	Na (mg/L)	494	614	370	565
5	K (mg/L)	6.6	4.7	9.0	5.6
6	Fe (mg/L)	0.13	0.07	0.12	0.10
7	Mn (mg/L)	0.015	0.022	Under 0.01	Under 0.01

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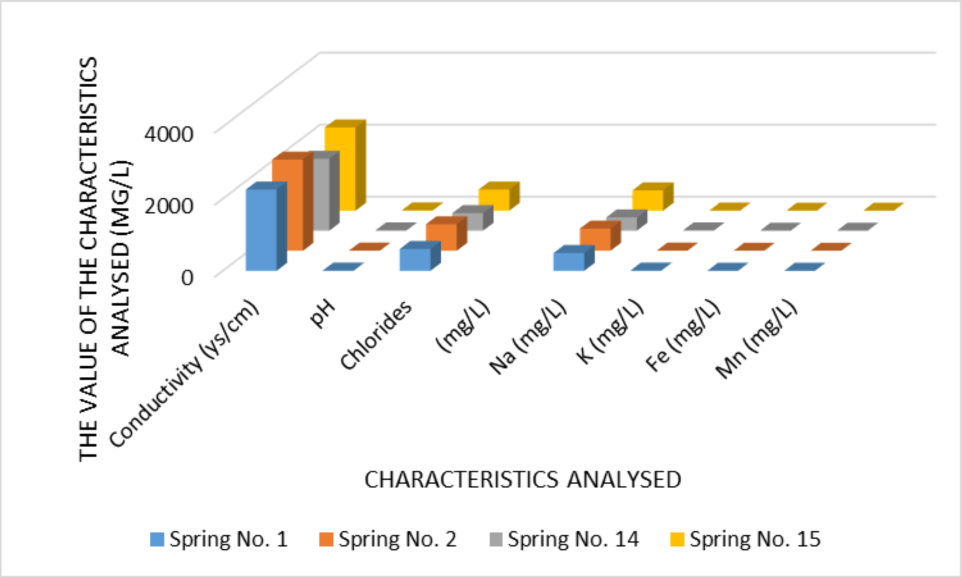

Fig. 1. Analytical determination of some natural mineralized springs from the resort Someseni, during summer

Table 2.

Analytical determinations of some natural mineralized springs from the area Pata-Rat, during spring

Sample No.	Characteristics	Spring No.	Spring No.	Spring No.	Spring No.
	Characteristics	**1**	**2**	**3**	**4**
1	Conductivity (ys/cm)	211	265	313	5.6
2	pH	7.23	7.20	7.12	8.86
3	Chlorides (g/L)	197.2	126.6	118.7	1.60
4	Na (g/L)	145.8	143.2	86.5	2.0
5	K (mg/L)	31.8	42.5	45.0	49.2
6	Fe (mg/L)	1.2	1.6	1.55	0.27
7	Mn (mg/L)	0.85	1.0	0.97	0.037

Table 3.

Analytical determinations of some natural mineralized springs from the area Pata- Rat, during summer

Sample No.	Characteristics	Spring No.	Spring No.	Spring No.
	Characteristics	**1**	**2**	**5**
1	Conductivity (ys/cm)	315	305	304
2	pH	7.49	7.70	7.48
3	Chlorides (g/L)	157.4	161.6	150.0
4	Na (g/L)	118.8	88.0	71.3
5	K (mg/L)	36.0	35.7	35.5
6	Fe (mg/L)	1.62	1.33	1.47
7	Mn (mg/L)	0.94	0.88	0.85

Selection of plant species

Our analysis had as a result the selection of some specific activities which must be realized in the future, in order to realize new green locations situated on the salted areas, such as:

- Studies on the general aspects of using dendrological species on saline soils (observations on woody vegetation of the area, research methods and techniques)
- Development of an experimental model for testing some dendrological species on saline areas (purchase of dendrological seedlings, testing the dynamics of growth and development under laboratory conditions, changes in leaf surface area, root volume and content of mineral elements of plants)
- Checking the experimental results regarding the resistance of selected species in saline environment, in order to create new green zones in the neighbourhood of the intensely developed urban areas.

Unfortunatelly this kind of reserach have to wait for better times, because of the situation due to the pandemic state with Covid-19 and to the war that is rulling near our country, which are involving other requested actions and expenses.

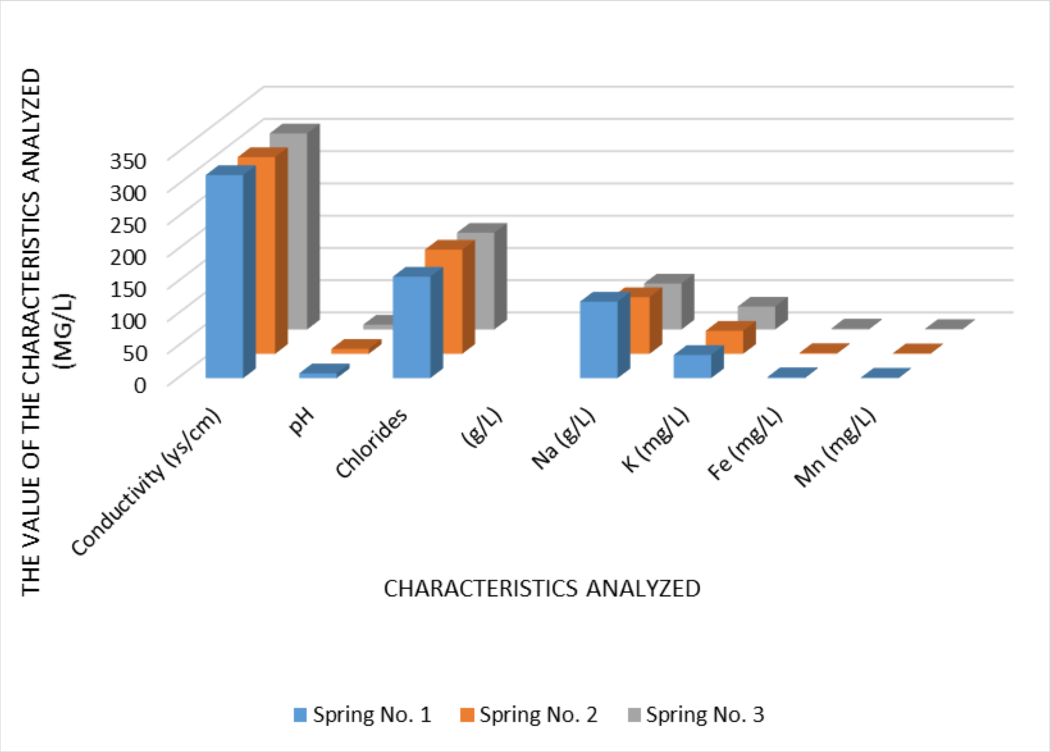

Fig. 3. Analytical determination of some natural mineralized springs from the area Pata- Rat during summer

4. Conclusions

In recent years, the continuous degradation of environmental quality due to factors such as air pollution, noise, chemical compounds and disappearance of natural areas, in combination with lifestyle changes led to the emergence of a growing number of diseases such as different forms of diabetes, cardiovascular and nervous system diseases and disorders and cancer. Vegetation helps people to recover faster from illness; this reduces costs of healthcare and improves the patients' quality of life. A positive correlation exists between the amount of green in a person's living environment and that person's sense of safety.

Our issues were to verify the chemical characteristics of some natural mineralized springs and lakes from Romania, to find the proper plant species adapted to saline soils and to establish if some special security measures are requested.

ACKNOWLEDGEMENTS

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LANDFILLING OF PLASTIC WASTE AND RELATED TOXICITY IMPACTS ON FRESHWATER AND MARINE ECOSYSTEMS AND HUMANS

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Abstract

Landfilling municipal solid waste (MSW) is a common practice globally. This study evaluated the freshwater and marine ecotoxicity and human toxicity impacts associated with the landfilling of various plastic types, including waste electrical and electronic equipment (WEEE) related plastic waste, to determine research investment priorities. The key findings are that all plastic waste landfilling negatively impacts human health and should not be encouraged. However, exploring alternative end-of-life treatments should prioritize polystyrene (PS), WEEE plastic waste and polyethylene (PE) as they have the highest impact potentials overall compared to other plastic types. Hotspot analysis is critical in the manufacture of plastics to determine the sources of pollutants that impact the toxicity profile of end-of-life treatments used in plastic waste management.

Keywords: freshwater ecotoxicity, human toxicity, landfilling, life cycle assessment, plastic waste

1. Introduction

Landfills are facilities used to dispose of non-hazardous or treated hazardous waste. Municipal solid waste landfilling is commonly practised globally at various scales, as indicated in Figure 1 [1]. In 2016, plastic waste accounted for 12% of MSW [1]. In 2019, approximately 49% of plastic waste was landfilled, 19% incinerated, 22% indiscriminately dumped as litter and 9% recycled [2]. However, landfilling has also been regarded as problematic, as it is environmentally unsustainable and represents a linear approach to managing plastic waste [2- 4].

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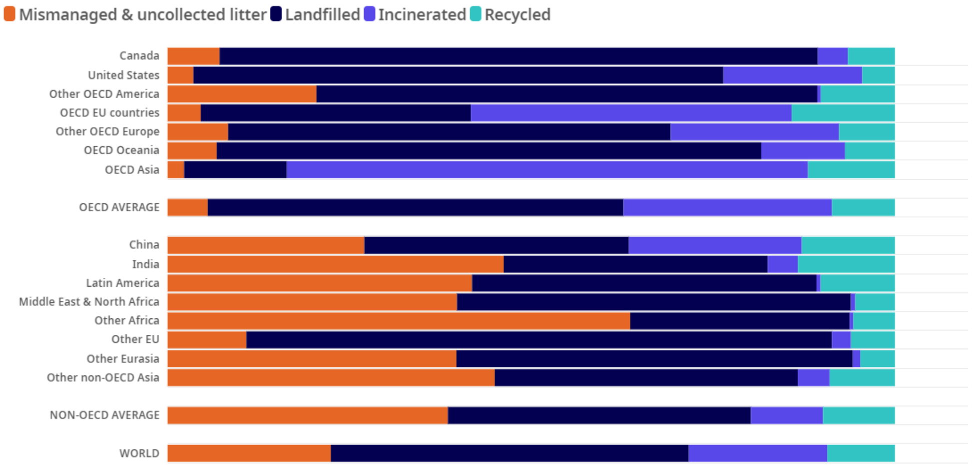

Source: OECD Global Plastics Outlook Database

Fig. 1. Global plastic waste management profile adopted from [1]

The advent of landfilling seemed to have brought to a halt environmentally unfriendly practices that included burning, ocean, and open-pit dumping. However, it became apparent that landfilling was also associated with adverse environmental consequences [5]. These included environmental degradation during the construction phase, asphyxiation of plants from landfill gas, spontaneous fires at the landfill site due to flammable methane gas, and soil and groundwater contamination from leachate. Such fires could also pose a health hazard, and if there is plastic waste, this could lead to the formation of dioxins and furans [6-8].

Numerous authors have documented the effects of plastic waste in landfills, but limited studies are available that compare toxicity impacts between the various commonly used plastic types. The objective of this study was to assess the impacts of landfilling various plastic types; namely polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), and plastic associated with waste electrical and electronic equipment (WEEE) to determine research investment priorities. WEEE waste contains various plastics including the following approximate proportions 30% acrylonitrile butadiene styrene (ABS), 25% high impact polystyrene (HIPS), 8% PP, 10% polycarbonate (PC), 9% PC and ABS combination. Twenty-five per cent of WEEE plastic is reportedly flame-retardant [9]. Figure 2 shows a breakdown of plastics converted per type in South Africa in 2012. Polyethylene accounted for 43.5%, followed by PP at 27.8%, PVC at 10.5%, PET at 10.4% and other plastics at 7.8%.

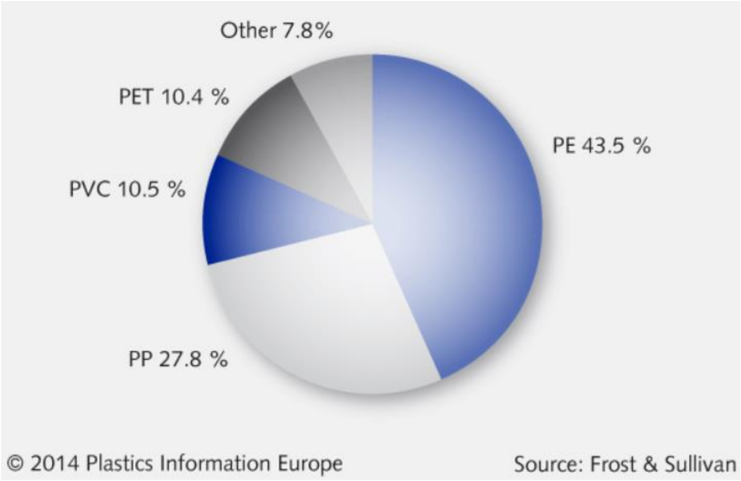

Fig. 2. Percentage of plastics converted by type in 2012 adapted from [10]

Literature Review

Landfills are typified by landfill gas and leachate. Landfill gas is formed from the anaerobic decomposition of organic matter into methane and carbon dioxide. Leachate formation occurs when run-off, rain or irrigation water, seeps through landfilled waste while simultaneously resulting in the dissolution of soluble compounds [11-13]. Figure 3, illustrates waste management at a landfill site [14-16].

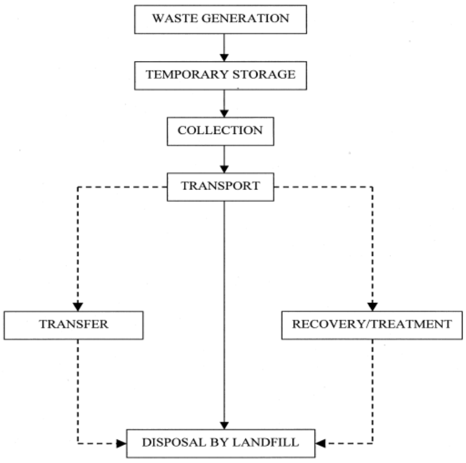

Fig. 3. Simplified illustration of waste management using landfilling adapted from [17]

The leachate quantity generated depends on the following; water availability, climate, characteristics of the waste, landfill plane, and soil type at the site while leachate quality is dependent on waste composition, co-deposition with other wastes and the treatment procedures used at the landfill site to treat the leachate [11-13,18, 19]. Table 1 shows a typical leachate composition [17].

Table 1

Chemical composition of landfill leachate [17]

Parameter	**Concentration range (mg/l)**	**Parameter**	**Concentration range (mg/l)**
Alkalinity ($CaCO_3$)	0-20 850	Ammonia	0-1 250
Aluminium	0.5-85	Nitrate	0-9.8
Antimony	0-3.19	Nitrite	0-1.46
Arsenic	0-70.2	Nitrogen (Organic)	0-1 000
Barium	0-12.5	Nitrogen (Kjeldahl)	3 320
Beryllium	0-0.36	Nickel	0-7.5
BOD_5*	0-195 000	Phenol	0.17-6.6
Boron	0.413	Phosphorous (Total)	0-234
Cadmium	0-1.16	Phosphate	0.01-154
Calcium	5-4 080	pH	1.5-9.5
Chloride	11 375	Potassium	0.16-3 370
Chromium	0-22.5	Selenium	0-1.85
Chemical Oxygen Demand	0-89 520	Silver	0-1.96
Conductivity	480-72 500	Sodium	0-8 000
Copper	0-9.9	Thallium	0-0.32
Cyanide	0-6	Tin	0-0.16
Fluoride	0.1-1.3	Total Dissolved Solids	584-55 000
Hardness ($CaCO_3$)	0.1-225 000	Total Suspended Solids	140 900
Iron	0-42 000	Total Volatile Acids	335 000
Lead	0-14.2	Total Organic Carbon	0-19 000
Magnesium	115 600	Turbidity	40-500
Manganese	0.05-1 400	Sulphate	0-1 850
Mercury	0-3	Zinc	0-1 000

Leachates contain organic compounds such as aromatics and aliphatics and heavy metals including arsenic, cadmium and chromium [20] and plastic waste landfilling results in an increased load of these pollutants. Upon closure of a landfill site, soil contamination reportedly progresses for decades [21-23]. This creates a health hazard for communities residing close to the sites.

Landfills have various classes, that depend on the design and the waste handling regime employed at the site, the availability of engineering controls that prevent the accumulation of gas, and the seepage of leachate underground. Typically, an HDPE liner and clay or bentonite are employed as liners at the landfill bottom. Monitoring controls are also available onsite [24]. Figure 4 illustrates a basic view of a sanitary landfill.

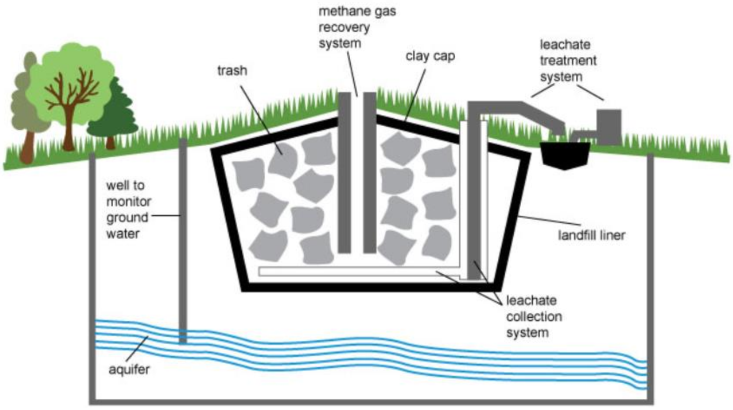

Fig. 4. Modern/sanitary landfill adapted from [25]

Figure 5 shows the unit processes used during leachate treatment [26].

Reference [24] found that from a total of 31 landfills evaluated in Sub-Saharan Africa, 80% were in classes 0 and 1, indicating poor waste management in this region, while 10% were in class 3. The authors concluded that corrective measures/engineering controls would need to be implemented to upgrade these landfills and make them more environmentally sustainable, while those under class 0 should be closed. On a global scale, 70% of waste is managed through landfilling as follows; 33% in open dumps, 3.7% in controlled landfill sites, 8% in sanitary landfills, and 25.2% in unspecified landfills. High-to-upper-middle-income countries employ controlled landfills, while in low-income countries, open dumps are common, and they dump around 93% of their waste compared to 2% for high-income countries.

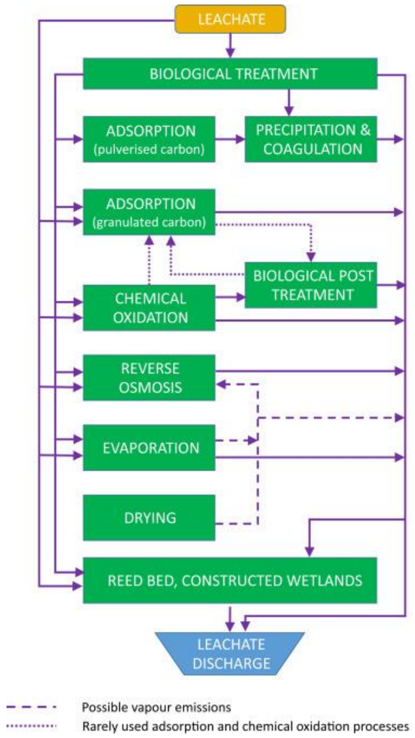

Fig. 5. Landfill leachate treatment adapted from [26]

2. Methodology

The plastic waste landfilling process was modelled using the SimaPro software and its associated databases. The ReCiPe 2016 Midpoint indicators were initially used to analyse models, followed by endpoint indicators to evaluate a single score. The functional unit in this work was the landfilling of 1 kg of plastic waste per type. The plastic types considered were polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC. After normalising the impact assessment results, the impacts of significance in plastic waste landfilling were found to be Freshwater Ecotoxicity (FE), Marine Ecotoxicity (ME), Human Carcinogenic Toxicity (HCT), and Human non-Carcinogenic Toxicity (HnCT). These impacts were then compared for the various plastic waste types.

3. Results and discussions

3.1 Freshwater Ecotoxicity (FE)

In the FE category, impact potentials were 0.183, 0.0843, 0.154, 0.181, 0.0358 and 0.715 kg 1,4-DCB for PE, PET, PP, PS, PVC, and WEEE plastic waste, respectively, as shown in Figure 6.

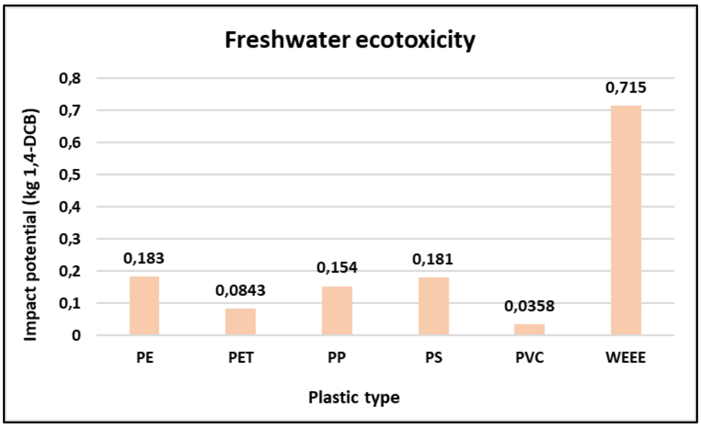

Fig. 6. Impact potentials for Freshwater ecotoxicity per plastic type

Therefore PVC<PET<PP<PE≈PS<WEEE. PE and PS landfilling had approximately the same contributions to the impact category, while WEEE had the worst environmental impact. However, the plastic type with the most negligible negative impact in this category was PVC. Aryan et al. (2019) also found PET landfilling less impactful on the environment than PE landfilling. According to [28], PET plastic waste in landfills does not cause groundwater contamination due to its stability. Figures 7 to 12 show the percentage contributions of various metals to the category.

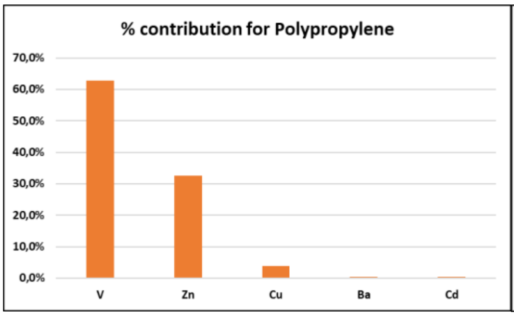

Fig. 7. PP contributions to FE

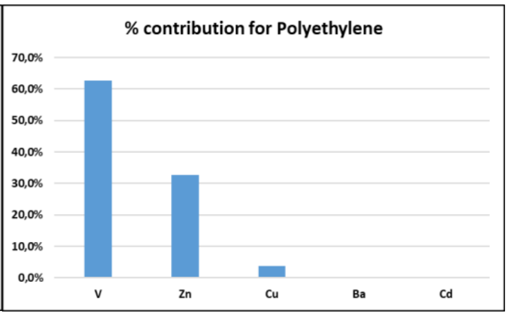

Fig. 8. PE contributions to FE

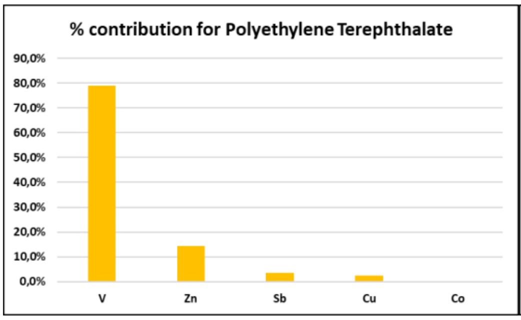

Fig. 9. PET contributions to FE

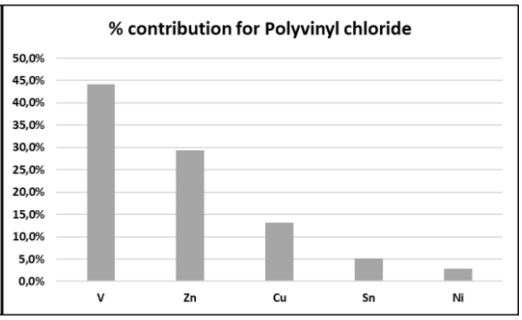

Fig. 10. PVC contributions to FE

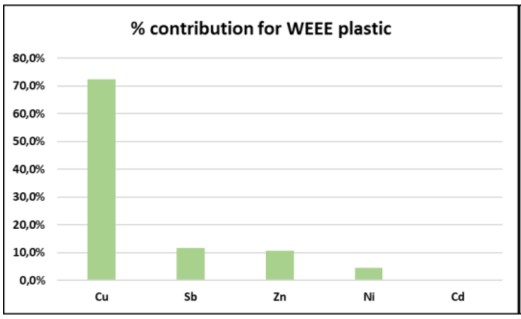

Fig. 11. WEEE contributions to FE

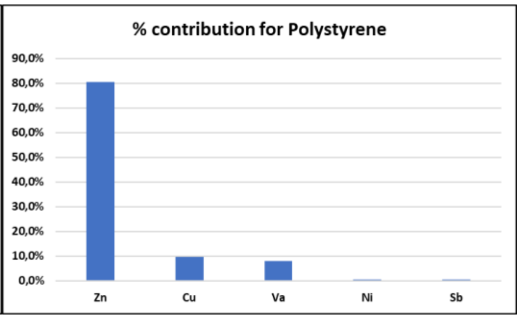

Fig. 12. PS contributions to FE

In four plastic types, namely PVC, PP, PE and PET, vanadium (V) contribution ranged between 44% to 79%. Zinc and copper release were common to all the plastic types. The highest contributions for zinc were 80.5% from PS followed by PE and PP with 32.6% each. In WEEE waste, copper accounted for 72.4%, followed by PVC at 13.2% and PS at 9.8%. Reference [9] also mentions high copper concentrations from WEEE waste which contaminate the soil and groundwater. Antimony (Sb) release was associated with PET, PS and WEEE, Ni release was from PVC, PS and WEEE waste, Cd from WEEE, PE and PP, Ba from PE and PP, Sn from PVC, and cobalt (Co) from PET albeit in small quantities. Reference [29] attributes Co and Sb from PET to the cobalt acetate used in color management and antimony trioxide used as a catalyst in the polycondensation step. Organotin compounds are used as heat stabilizers in PVC plastic, explaining the release of Sn from landfilled PVC plastic waste. PVC plastic may contain approximately 10 to 15% by weight of heavy metal additives. Heat stabilizers protect the plastic from discoloration or degradation, for example, by trapping hydrogen chloride molecules in PVC plastic during heating.

Other heavy metals also include zinc, which can be combined with barium. Calcium and zinc formulations have been commonly used for PVC, PS and PE plastics [30], [31]. Reference [32] assessed the impact of leachates from various plastic types on microalgae. The authors confirmed the presence of Co, Ni, Cu and

Zn. Plastic waste leachates are toxic to microalgae both in freshwater and seawater. Microalgae are beneficial as they help reduce the carbon footprint during photosynthesis [33]. Heavy metals tend to bioaccumulate in aquatic animals and are biomagnified. This results in their transference into the human food chain. Heavy metals also reportedly lead to developmental problems and hinder marine animals' reproductive processes [34]–[36].

4.2 Marine Ecotoxicity (ME)

In the ME category, impact potentials were 1 470, 525, 1 240, 2 220, 244, 1 510 kg 1,4-DCB for PE, PET, PP, PS, PVC, and WEEE plastic waste, respectively, as shown in Figure 13.

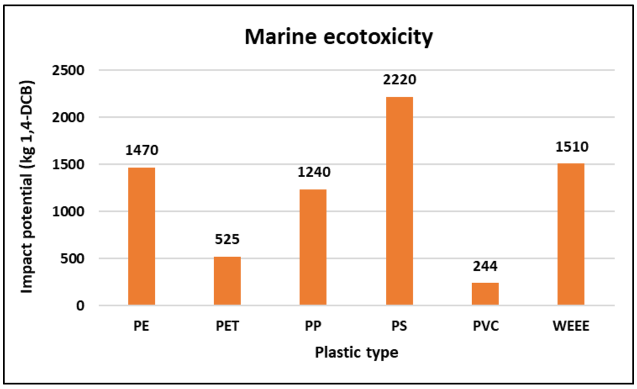

Fig. 13. Impact potentials for Marine ecotoxicity per plastic type

For this category, PVC<PET<PP<PE<WEEE<PS. Aryan et al. (2019) also found a lower impact potential for PET than PE. The metalloids causing freshwater toxicity were similar to those detected for marine ecotoxicity as shown in Figure 14. Therefore, the effects on marine life are also expected to be the same. Zinc and Vanadium were the top contributors to marine ecotoxicity for PP, PE, PET and PVC. For PS waste and WEEE waste, zinc was the main contributor, while for WEEE waste, copper and antimony also contributed, albeit to a lesser extent. Reference [37] found that landfilling of plastic waste impacted marine aquatic ecotoxicity significantly more than other impact categories, including freshwater ecotoxicity. This agrees with the results of this study, where marine ecotoxicity was more dominant, as evidenced by the impact potentials, which were several magnitudes higher than in the freshwater ecotoxicity categories. According to [38], although 35% of plastic waste is managed through open dumping in India, this end-of-life method accounts for 64% towards the marine ecotoxicity category. In Indonesia, open dumps and sanitary landfills used to manage 53% of plastic waste generated account for 88% of the marine ecotoxicity impact [38].

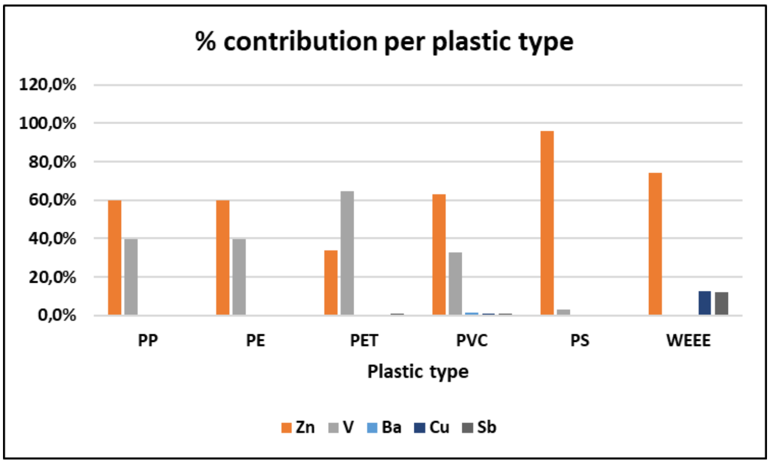

Fig. 14. Contributions to marine ecotoxicity per plastic type

4.3 Human Toxicity and Single Score results

In the Human carcinogenic toxicity category, PET<PP<PE<PS<PVC<WEEE with main pollutants from WEEE associated with arsenic (40.4%, nickel (40%) and chromium VI (19%). In the Human non-carcinogenic toxicity category, PVC<PET<PP<PE<WEEE<PS with zinc from PS contributing the highest percentage of 99% to the impact similar to the freshwater and marine ecotoxicity categories. This was followed by vanadium at 0.29% and barium at 0.23%.

Single score results were 1.13, 0.897, 0.22, 0.758, and 0.172 Pt for WEEE, PE, PET, PP, PS and PVC respectively. PS landfilling was the most impactful process on the environment, followed by landfilling. Among the three endpoint indicators, human health was the most affected by plastic waste landfilling, followed by the ecosystem and resources, respectively, as illustrated in Figure 15. Overall, PVC<PET<PP<PE<WEEE<PS. The single score results show that plastic waste landfilling adversely affects human health and should not be promoted. However, exploring alternative end-of-life treatments should prioritize PS, WEEE plastic waste and polyethylene.

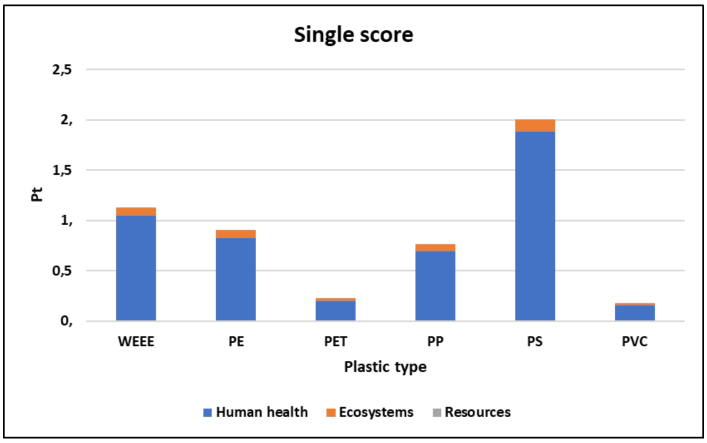

Fig. 15. Single score results

4. Conclusions

Heavy metals such as zinc, vanadium, chromium, and arsenic are released during plastic waste landfilling. These metals contaminate the soil and groundwater, adversely affecting human health and aquatic life. Hotspot analysis is critical in the manufacture of plastics to determine the sources of pollutants that impact the toxicity profile of end-of-life treatments used in plastic waste management. Furthermore, as alluded to in earlier works, the current class of plastic additives should be re-evaluated. Overall, all plastic waste leachates are toxic, with polystyrene, WEEE waste and polyethylene the most impactful and as such, they should be prioritised when evaluating alternative treatment processes. Air contamination impacts from plastic waste landfilling are lower than toxicity impacts via water emissions, thus confirming the minimal effect of landfilling on global warming and ozone depletion compared to other plastic waste treatment processes.

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THE LEGAL REGIME OF RECOVERY/RECYCLING HAZARDOUS WASTES RESULTING AT THE END OF LIFE OF BATTERIES AND ACCUMULATORS

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Abstract

Given the discussions about a transition to a climate neutral economy in the EU's, batteries, and accumulators (B/As) will play an increasingly important role in the area of zero- emission mobility and the storage of renewable energy. Unfortunately, the components of B/As are both very difficult to recover and extremely harmful to the environment. Therefore, without a legal regime statuating the use, the recycling, and the neutralizing of B/As, the impact at the environmental level may be very harmful.

Keywords: batteries, accumulators, law, recycling, hazardous wastes, environment

1. Introduction

Considering the severe consequences of climate changes, countries all over the world have begun to take more and more seriously the creation of a legislative framework to reduce and stop pollution factors, which have a serious impact on the environment and on people's health. Thus, to reduce the sources of pollution produced by vehicles that use fossil fuels, environmental policies have been adopted regulating the use of renewable energy sources, which heavily depend on B/As. As a result of European policies, Romania has transposed into the domestic legislation a series of legislative provisions regarding B/As.

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2. The context of the development of a strategic plan on batteries and accumulators

In May 2018, the European Commission presented a communication on sustainable mobility for Europe, which it called "*Europe on the move*" and which was based on principles such as safety, connectivity, and clean development. This supported the policy of the Junker Commission, known as the "*European Energy Union*", a document that aimed at fulfilling the objectives of the Paris Agreement. Thus, a special attention is given to the reduction of CO_2 emissions caused using fossil fuels and road transport in Europe with internal combustion engines, based on fossil fuels.

As an annex to the "*Europe on the move*" communication, a specific *Action Plan* was developed for the development and production of batteries, an important space being dedicated to the "*Strategic Action Plan on Batteries*".

In time, B/As have become an indispensable part of our daily life, starting from the mobile phones, PCs and reaching electric vehicles (EVs). Thus, the Action Plan regarding batteries raises the issue of the development of B/As, especially for EVs, to extend their lifespan, but also on other aspects such as battery second use and recycling, given their significant potential for recovery/recycling.

In this regard, the focus should be on the development of good, safe, and ecological batteries for a huge market which, according to estimates, could have a volume of over 400 GWh and 250 billion euros in 2025 [1].

Nevertheless, there is a gap between Europe and Asian countries as to the development and production of B/As. The data presented in the *Opinion of the European Economic and Social Committee on the Implementation of the Strategic Action Plan on Batteries: Building a Strategic Battery Value Chain in Europe* show the fact that around 85% of all the batteries in use at the European level come from China, Japan or Korea, while the European production represents a mere 3% of world production [1]. Thereat, an emphasize should be made on the problem of the raw materials used to produce B/As, such as nickel, lithium, manganese, and cobalt, which can be extracted in limited quantities at the EU level, despite some potential reserves. These European reserves will need to be exploited but being aware that their exploitation can lead to pollution. Furthermore, there is a particular interest at the EU level for building a competitive sector for the development and production of B/As, looking for the most viable solutions both for the identification of raw materials and for reducing the impact on the environment and on people's health.

Global demand for batteries is set to increase 14-fold by 2030 and the EU could account for 17% of that demand [2]. The increase of EVs usage will make this market a strategic one at the global level. Recycling is an important topic at EU level, so there are studies that claim that in 2035 over a fifth of lithium and nickel, and 65% of the cobalt, needed to make new batteries could come from recycling [3].

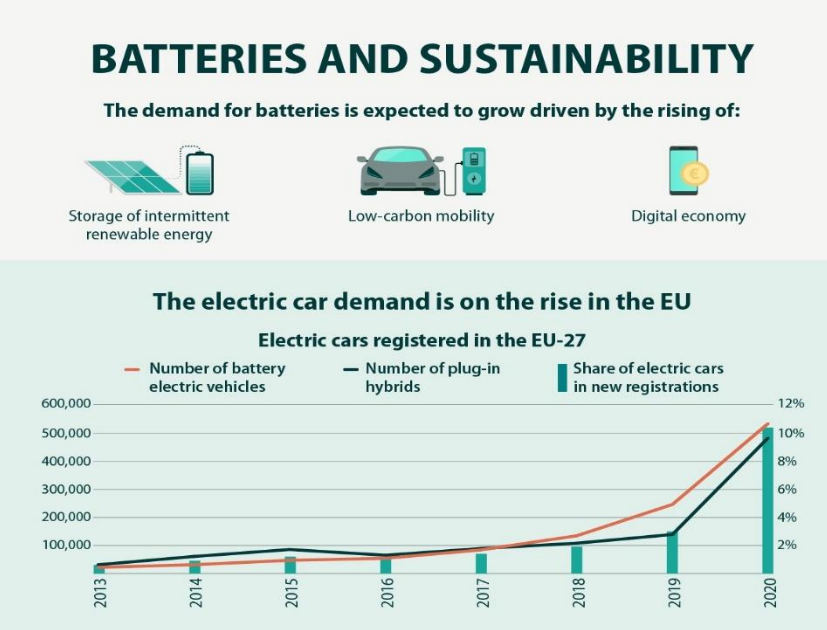

Fig. 1. Batteries and sustainability – rapid expansion of EVs

Thus, the import of B/As on the European market supported by a continuously growing demand (figure 1), the development of production at the EU level, as well as the challenges arising from the problem of their recovery/recycling, brought into discussion the legislative sector, as it is mandatory to apply control over imports, but also to regulate the situation in matter of recovery/recycling of B/As at the level of European countries. It is also important to constantly update the legislation at both European and national levels.

3. Legislative aspects regarding the regime of batteries and accumulators

Every year, several hundred thousand tons of industrial and portable B/As containing significant amounts of mercury, lead and cadmium as well as nickel, copper, zinc, manganese, and lithium are introduced on the EU market.

At the EU level, the regime of B/As is regulated by the Directive 2006/66/CE [4], which must be transposed into the national legislation of each member state. In this way, the authorities wanted to improve the environmental performance of B/As, as well as the activities of the economic operators involved in their life cycle, respectively the producers, distributors and end users, and the operators directly involved in the process of treatment and recycling of waste resulting at the end of life of B/As (figure 2).

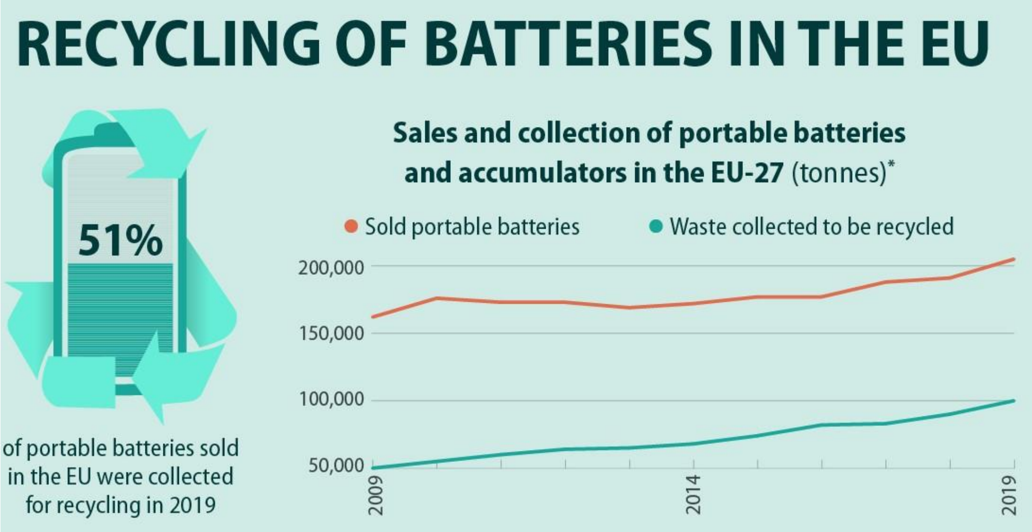

Fig. 2. Recycling batteries in the EU

The Romanian legal regime seeks to reduce environmental pollution, caused by B/As wastes, both at the level of the atmosphere (in the case of incineration), as well as at the level of the soil and water (in the case of storage or burial), by establishing in the internal legislation mandatory rules that producers, traders and users must respect, otherwise they can and should be sanctioned according to the law.

Government Decision (GD) no. 1132/2008 regarding the regime of B/As and B/As wastes, amended and supplemented by GD no. 540/2016, transposes Directive 2006/66/EC at the national level. This GD applies to all types of B/As, regardless of weight, component materials or shape, but apart from B/As used in: “a) equipment associated with the protection of Romania's essential interests, weapons, ammunition and war material, with the exception of products that are not intended for specific military purposes; b) the equipment intended to be launched into space” [5].

Without changing the legal content of the Directive 2000/53/EC [6], the above GD prohibits the introduction on the market of ″a) all batteries or accumulators that contain mercury in a proportion greater than 0.0005% of their weight, regardless of whether or not they are integrated into appliances; b) portable batteries and accumulators, including those integrated in devices, which contain cadmium in a proportion greater than 0.002% of their weight" [4]. From this prohibition, the national legislation for portable B/As provides two exceptions:

those used for “a) emergency and alarm systems, including emergency lighting; b) medical equipment” [5]. Non-compliance with these legal provisions leads to contraventional sanctions with a fine from 25,000 to 30,000 lei for legal entities and from 2,500 to 3,000 lei for individuals [5].

To have a clear control of the B/As introduced on the market, the Romanian legal authorities established the obligation to register the producer or, as the case may be, the importer in the National Register of producers and importers of B/As, a register managed by the Ministry of the Environment. The omission of registration leads, on one hand, to contraventional sanctions, and, on other, producers and importers must stop selling them, as the legislation forbids distributors to sell B/As from producers who are not registered in the National Register.

To treat and recycle, GD no. 1132/2008, amended and supplemented by GD no. 540/2016, provides that "producers together with the competent authorities of the state must take the necessary measures for the separate collection of waste from batteries and accumulators, without mixing them with municipal wastes" [5]. In addition, wastes recycling allows the recovery of thousands of tons of metals, including precious metals such as nickel, cobalt, lithium, and silver, and Romania, as an EU member state, must ensure that the B/As that have been collected are treated and recycled using the best available techniques, in accordance with Regulation (EC) no. 761/2001 of the European Parliament and of the Council of March 19th2001 regarding the voluntary participation of organizations in a community environmental management and audit system (EMAS).

The calculation of recycling efficiency levels is carried out according to Regulation (EU) no. 493/2012 of the Commission of June 11, 2012, in accordance with Directive 2006/66/EC of the European Parliament and of the Council, which establishes the detailed rules regarding the former.

To protect the environment and to promote recycling, the national legislation establishes a series of obligations for B/As traders, some of them being emphasized:

a) to collect car B/As from end users;
a) to store the car B/As received in exchange for those sold, in specially designed, fenced and secured spaces to prevent uncontrolled leaks;
b) to hand over car B/As to manufacturers or to an economic operator who is authorized to carry out the collection on behalf of the manufacturer;
c) to show in a visible place the announcement with the following content: "Hand over car batteries and accumulators for recycling" [5].

Romania, as an EU member state, can dispose of portable battery waste containing cadmium, mercury or lead by landfill or underground storage if there is no viable market for recycled products or if, based on a detailed environmental impact assessment, but also on economic and social evaluations, it is concluded that recycling is not the best solution.

On the other hand, the storage or incineration of industrial and automotive battery waste is prohibited by the 10th art. from HG 1132/2008 amended and supplemented through HG 540/2016 and the non-compliance with this prohibition is being sanctioned according to 17th art. lit. g) with a fine between 25,000 lei and 30,000 lei [5]. The residues of any battery that have undergone both treatment and recycling can be eliminated by landfill or incineration.

Manufacturers (or third parties acting on their behalf) must bear the net cost of collecting, treating, and recycling industrial, automotive, and portable batteries. Manufacturers of portable batteries must cover the costs for public information campaigns regarding the collection, treatment and recycling of all wastes resulting from portable batteries, an obligation mentioned in the Directive 2006/66/EC on B/As and B/As wastes [4] and transposed at the national level in HG 1132/2008 amended and supplemented through GD no. 540/2016 (art. 12 alin. 3-4) [5]. Small producers can be exempted from this obligation, if this does not prevent the proper functioning of the collection and recycling systems.

The recycling processes of B/As must achieve the following minimum levels of efficiency:

a) recycling 65% of the average weight of lead-acid B/As, including recycling the lead content to the highest level that is technically feasible, while avoiding excessive costs;
a) recycling 75% of the average weight of nickel-cadmium batteries and accumulators, including recycling the cadmium content to the highest level that is technically feasible, while avoiding excessive costs;
b) recycling 50% of the average weight of the other waste batteries and accumulators [5].

In reference to recovery and recycling B/As wastes, they can be carried out outside the territory of Romania or of the European Community, if the transport of wastesrespects the requirements of the Regulation (EC) no. 1.013/2006 of the European Parliament and of the Council of June 14th, 2006, regarding wastes transfers.

4. Debates and challenges

The use of B/As, especially for EVs and light means of transport, but not limited to these, has grown considerably [8] and, in consequence, the need for recycling them, according to the concepts of circular economy. Therefore, on March 10th, 2022, the European Parliament adopted the amendments relating to the proposal for a regulation of the European Parliament and of the Council on batteries and battery wastes, repealing Directive 2006/66/EC and amending the Regulation (EU) 2019/1020 [8]. Thus, an update of the legislation regarding the management of battery wastes is being pursued to take measures to protect the environment and people’s health, preventing or reducing the impact created by the generation and management of hazardous wastes.

5. Conclusions

To avoid or to reduce the considerable impact on both the environment and on people's health caused by hazardous wastes resulted from the use of B/As, the legislation at the EU level and its transposition at the national level, along with the existing legal provisions/rules, pursues to regulate a continuously expanding field – the management of the B/As wastes, given the growing demand of using B/As. Thus, it is mandatory to continuously update the existing legislative norms in the matter, recycling being a sensitive domain that must be regulated and followed carefully, according to the scientific knowledge, to avoid the amplification of the problems caused by using B/As on a large scale.

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ASSESSING THE GREENHOUSE GAS EMISSION REDUCTION FROM THE ANAEROBIC DIGESTION OF WASTE IN HARARE, ZIMBABWE

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Abstract

The management of municipal solid biomass waste has received global attention due to its methane and other greenhouse gas emission generation capabilities when disposed in landfills and open dumps. This study assessed the potential reduction in global warming potential and other impacts that comes along with the management of the BMSW fraction through anaerobic digestion (AD) evaluated against incineration (IN) and the prevailing management practices in Harare, the Capital City of Zimbabwe. Significant reductions in GHG emissions with negative impact potential of -3,67 x 106 kgCO2eq were noted from the AD of the BMSW fractions generated in Harare compared to the prevailing open dumping which has an impact potential of 2.23 x 108 kgCO2eq. The incineration of BMSW also has a negative global warming impact potential of -1.48 x 107 kgCO2eq. The global warming potential reduction that comes with AD of biodegradable MSW fractions generated in Harare provides the needed motivation the establishment of anaerobic digestion systems.

Keywords: anaerobic digestion, life cycle assessment, organic waste, greenhouse gases, global warming potential

1. Introduction

The management of biodegradable municipal solid waste (BMSW) has received global attention due to its methane and other GHG emission generation capabilities when disposed in landfills. In addition, the need to reduce the amount of waste that is sent to landfills has led to the development of alternative BMSW management strategies. Evangelisti *et al.* [1] cited the implementation of the European Commission Landfill Directive of 1999 [2] that required European Member States to lower the quantities of BMSW that goes to landfills to have significantly changed the management of municipal solid waste (MSW). Anaerobic digestion (AD) was introduced to treat the BMSW that includes farm, green garden,

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and food waste having been used widely in the treatment of sewage sludge. It has become a technically proven, environmentally sustainable, and commercially viable technology for treating the BMSW.

AD is receiving widespread acceptance as a sustainable technology for treating the organic fractions of municipal solid waste (OFMSW). It produces biogas together with a solid and liquid digestate. The biogas is a form of a renewable energy that can either be used for heat and electric power generation or upgrade to biomethane for use as fuel for vehicles. The solid and liquid digestate are potential biofertilizers. Globally, the generation of MSW together with the BMSW fraction is anticipated to rise [3]. The European Union BMSW generation per annum has been estimated at between 1.18 x 10^8 and 1.38 x 10^8 tons [1] and is projected to have increased by 10% by 2020 of which 40% still being landfilled signalling the remaining BMSW management challenge despite the noted progress brought by the European Commission Landfill Directive of 1999. The situation can only be worse in developing countries especially in Africa where no such landfill directives have been issued and BMSW is being sent to open dumpsites. This study therefore seeks to assess the potential reduction in greenhouse gas emission that comes along with the management of the BMSW fraction through AD evaluated against incineration (IN) and the prevailing management practices in Harare, the Capital City of Zimbabwe. This work builds upon previous work [4] that compared the composting and AD of the BMSW generated in Harare hence composting was not considered under this study.

2. Methodology

MSW and BMSW generation in Harare

Like in many developing countries where reliable MSW generation and MMSW composition data is scanty, Zimbabwe and its Capital City are no exception hence this study assessed data from Harare municipal records and other MSW generation and characterization studies. The Harare City Council through UN Habitat estimated the annual MSW generation in Harare at 280,000 tons [5] whilst the German Agency for International Cooperation (GIZ) provided an annual estimate of 150,000 tons [6]. Tirivanhu and Feresu [7] provided an annual estimate of 210.000 tons of MSW generated from residential (households) areas in Harare with Kwenda et al [8] giving an estimate of 207, 635, 294±56, 027, 040 tons. An average annual MSW generation of 212,000 tons was therefore used for this study. Biodegradables are estimated to constitute over half of this generated waste with Kwenda et al [8] reporting estimates of between 50 and 62 %. The UN Habitat [5] reported that food and garden waste respectively constitute 27 and 15% of MSW generated from households in Harare, giving a 42 % composition of BMSW. GIZ further provided a 63 % BMSW composition in the MSW generated from households in Harare [6]. Tirivanhu and Feresu [7] provided a BMSW composition in MSW generated within Harare of 62%. An average BMSW composition of 56% was therefore used in this study.

MSW and BMSW management in Harare

Tirivanhu and Feresu [7] estimated that 52 % of the MSW generated within Harare is collected and disposed at the sole official Pomona dumpsite, with 39 %, 6 % and 3 % being illegally dumped, burnt, and separated for recycle and reuse purposes, respectively. However, Harare City Council through UN Habitat [5] reported a 27 % collection for disposal at the official Pomona dumpsite, 2 % collection for management at controlled facilities and 5% recovery rate for reuse and recycle. GIZ [6] reported 44% MSW collection for disposal at the official Pomona dumpsite. However, Kwenda et al [8] noted the highest MSW collection of 72.4 ± 7.5 % (170, 385,600 ± 33,384,209 kg) for disposal at the Pomona dumpsite. Kwenda et al further notes a 9.5 ± 2.8 % (23,498,400±3, 988,817kg) recovery for recycling and reuse purposes.

Environmental Life Cycle Assessment

The greenhouse gases emission or global warming potential of the prevailing management systems for biodegradable waste generated in Harare were estimated using the environmental life cycle assessment (E-LCA) and compared with those from the AD. SimaPro 9.4.0.2 software with its embedded Ecoinvent database and ReCiPe 2016 v1.1 midpoint methods were used. The annual BMSW generation of 118,720 tons was used. For this study it is assumed that 100 % of the BMSW is subjected to open dumping (OD) under the current prevailing management practice. This has been derived from 52% being send to Pomona an open dumpsite, 39% being illegally dumped reported by Tirivanhu and Feresu [7]. Though Tirivanhu and Feresu indicated that 6% of the MSW generated is openly burnt, there are challenges associated with open burning of BMSW due to its moisture content which will likely have the BMSW being dumped in open dumps. The assumption is reasonable considering that reports from other studies provided collection estimates for disposal at the Pomona dumpsite with recovery levels of between 3 and 9.5% having been noted signaling that the uncollected waste is largely illegally dumped. Reported recovery rates are for plastic, paper, and metals with no or little mention about BMSW recycling and reuse. Other options considered 100% AD and incineration of the BMSW generated, 60% AD and 40%

OD and finally the 60% AD and 40% Incineration. Incineration has been considered due to the planned Pomona Waste to Energy project that seeks to incinerate all the MSW generated in Harare for energy generation purposes. Since Evangelist reported that 40% of BMSW is still being send to landfills in the European Union despite implementing landfill directive of 1999, this study also considered a scenario where 40% of the BMSW generated in Harare remain subjected to OD. Table 1 provides the BMSW management options that were considered for the environmental LCA assessment.

Table 1

BMSW management options

BMSW Management Option	Amount of BMSW going to a Treatment Technology (tons)		
	OD	**Anaerobic Digestion**	**Incineration**
100% OD - Current Practice	118,720	0	0
100% AD	0	118,720	0
100% IN	0	0	118,720
60% AD, 40% OD	47,488	71,232	0
60% AD, 40% IN	47,488		71,232

3. Results and discussions

Table 2 and figure 1 show the environmental impact potentials under the different impact categories at mid-point whilst figure 3 provide a damage assessment results at end point. Significant reductions in GHG emissions with negative impact potential of -3,67 x 10^6 $kgCO_{2eq}$ were noted from the AD of the BMSW fractions generated in Harare compared to the prevailing open dumping which has an impact potential of 2.23 x 10^8 $kgCO_{2eq}$. The incineration of BMSW also has a negative global warming impact potential of -1.48 x 10^7 $kgCO_{2eq}$. The energy recovery together with flue gas capture and treatment contributed to the negative potential impacts of incineration. The disposal of biodegradable MSW at dumpsites is responsible for methane formation that eventually escapes into the environment contributing, as a result, to global warming. The renewable energy generation as well as the biofertilizer production capabilities of the AD technology contributed to global warming potential reduction. Combining the AD and IN of 60 % of the BMSW with 40 % OD yielded positive global warming potentials of over 8.0 x 107 $kgCO_{2eq}$ despite the negative impacts that come with AD and IN which shows the severity of OD of BMSW. At mid-point AD had overall negative impact potentials in the global warming, ozone formation, ecotoxicity, human toxicity and resources scarcity with notable positive impact potentials on water consumption, land use, eutrophication, particulate matter formation and ionizing radiation. At end point, AD performed well in the resource and ecosystems damage category with positive damage potential in the human health damage category as shown in Figure 2. IN outperformed AD in the human health and ecosystems damage categories.

Table 2

Environment impact potential of BMSW management options at mid-point

BMSW management option	**Impact category**				
	Global warming (kgCO2eq)	**Fine particulate matter formation (kgPM2.5eq)**	**Freshwater eutrophication (kgPeq)**	**Fossil resource scarcity (kgoileq)**	**Water consumption (m3)**
60% IN-40% OD	8,03E+07	-1,52E+04	-1,13E+03	-2,04E+06	-3,59E+05
60% AD-40% OD	8,69E+07	1,44E+04	2,90E+03	-5,81E+05	4,14E+05
100% OD - Current Practice	2,23E+08	0,00E+00	2,04E+03	0,00E+00	0,00E+00
100% IN	-1,48E+07	-2,53E+04	-3,24E+03	-3,41E+06	-5,99E+05
100% AD	-3,67E+06	2,40E+04	3,48E+03	-9,69E+05	6,90E+05

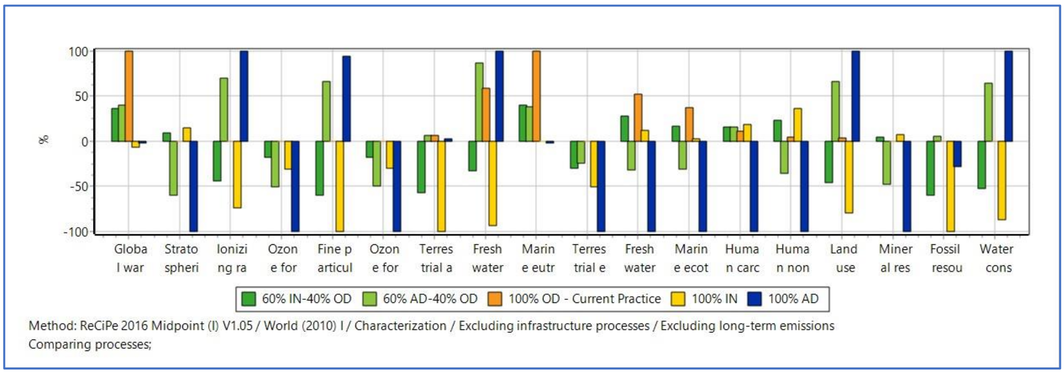

Fig. 1. Comparison of BMSW management options at mid-point.

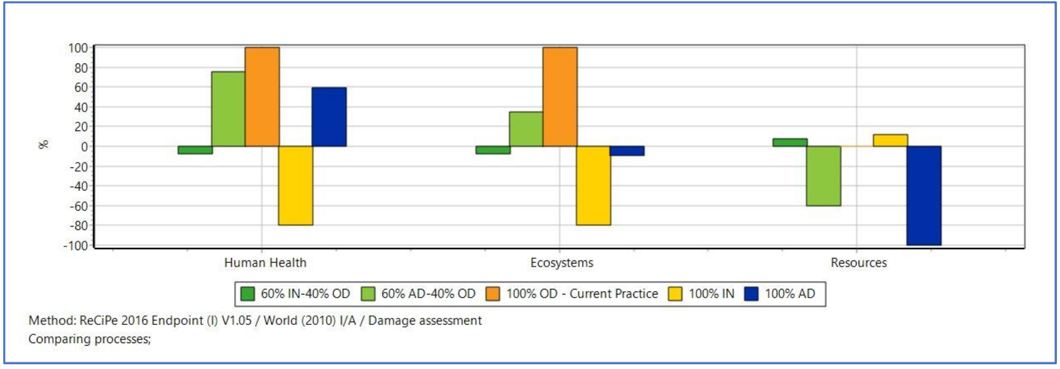

Fig. 2. Comparison of BMSW management options at end point.

4. Conclusions

Life cycle assessment is an important tool that has been widely used in decision making as well as planning for the design, development, and operation of waste management systems. The global warming potential reduction that comes with AD of biodegradable MSW fractions generated in Harare provides the needed motivation for the establishment of anaerobic digestion systems. These reductions in global warming potential contribute to the national low emission development strategy under the nationally determined contributions in response to global efforts towards emission reductions.

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FRESHWATER ECOTOXICITY, MINERAL RESOURCE SCARCITY AND FOSSIL DEPLETION IMPACTS ASSOCIATED WITH VARIOUS PLASTIC WASTE MANAGEMENT SCENARIOS IN JOHANNESBURG, SOUTH AFRICA

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Abstract

Plastic waste management is associated with numerous environmental impacts. An environmental life cycle assessment provides a critical tool to analyse these impacts while simultaneously enabling a comparative evaluation. This paper evaluates the impacts of five plastic waste management scenarios developed for South Africa on freshwater aquatic ecotoxicity, mineral resource scarcity, and fossil resource scarcity using SimaPro software and its databases. A brief overview of transportation impacts is also given. The results showed that landfilling was the most impactful process in all three categories. At the same time, mechanical recycling had the highest net benefit on the environment, followed by incineration with energy recovery to a lesser extent. The energy-intensive lime production process resulted in significant fossil depletion in the gasification process. Brake wear emissions, incineration of automotive shredder residues (ASR) and road construction were not beneficial for the environment in the terrestrial and freshwater ecotoxicity and land use categories, respectively. Overall, the scenario combining recycling, incineration with energy recovery, gasification, and cement kiln use was the least impactful scenario. he paper presents a simulation case of gasoline hydrofining simulating using a simplified model. Considerations regarding the promotion of the simplified model are presented starting from a physical model that considers hydrofining in a three-phase system)

Keywords: freshwater ecotoxicity, fossil depletion, life cycle assessment, mineral resource scarcity, plastic-waste management, transportation impacts

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1. Introduction

The environmental impacts associated with plastic waste management methods have been a subject of discussion by various researchers [1–15]. Comparative assessments of plastic waste management methods using environmental life cycle assessment are beneficial as they assist in identifying environmentally sustainable technologies. At the same time, it allows possible alternatives to be identified to improve the environmental performance of unit processes. The environmental impact categories that have been assessed in various works include freshwater and marine ecotoxicity, human carcinogenic and non-carcinogenic impacts [1–3], global warming [4–7], ozone depletion [8–10], fossil depletion [11–13], and water depletion [14, 15]. This paper assesses the impacts of five plastic waste management scenarios on freshwater aquatic ecotoxicity, mineral resource scarcity, and fossil resource scarcity. Freshwater ecotoxicity is vital to monitor, considering that freshwater is critical for sustaining life. Minerals and fossil resources are non-renewable; hence, their consumption should also be monitored. The main contributions from transport on terrestrial ecotoxicity, land use and freshwater ecotoxicity are also assessed.

Plastic Waste Management in South Africa

Waste management in South Africa hinges on the three pillars of the 2020 National Waste Management Strategy. Pillar 1 aims to minimize waste, including plastic packaging, by promoting reducing landfilling practices, reuse, recycling, recovery and alternative treatment technologies. This reduces the negative impacts on the ecosystem and human population [16]. Pillar 2 hinges on identifying various waste management problems affecting communities, finding solutions to the identified problems, the inclusion of waste pickers and promoting environmental sustainability. Pillar 3 aims to ensure compliance with enforced regulations and to minimize practices such as illegal dumping and littering, which leads to socio-economic and environmental benefits for the country. There are numerous alternatives to plastic waste management, including mechanical recycling, incineration with energy recovery, and the use of plastic waste in cement kilns or blast furnace as solid refuse fuel, gasification, and pyrolysis. However, plastic waste management in South Africa is commonly managed through landfilling and mechanical recycling, with the 2019 statistics showing that approximately 54% of plastic waste was managed through landfilling.

2. Methodology

A life cycle assessment study was conducted following the ISO 14040 and ISO 14044 standardised framework illustrated in Figure 1 [17]. Step 1 involved defining the goal and scope of the study, followed by the collection of relevant data used in the model, modelling various scenarios in SimaPro using the Recipe endpoint, Egalitarian method and interpretation of results, respectively. Input and output data were sourced from peer-reviewed literature, the Ecoinvent database and grey literature as plant data for existing plants were not accessible due to confidentiality, while other processes modelled do not currently exist for plastic waste management in South Africa. These are gasification and incineration with energy recovery while cement kiln use is practised on a small scale.

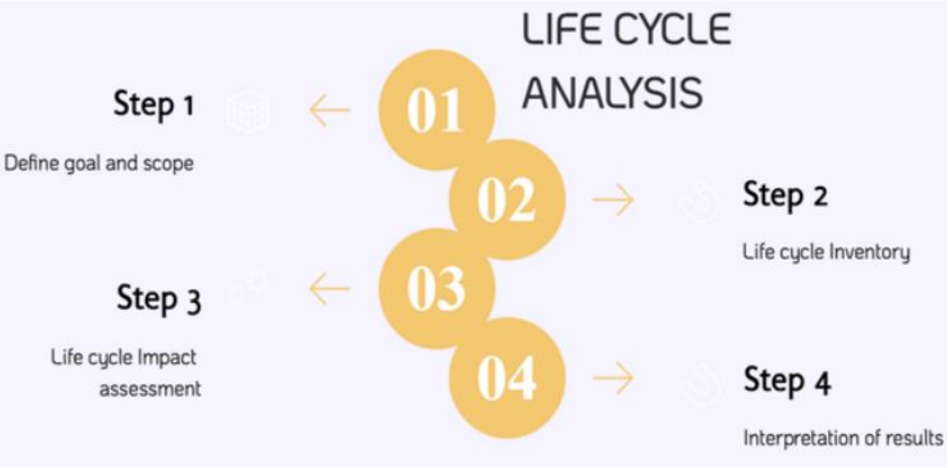

Fig. 1. Life Cycle Analysis Methodological Framework [17]

Table 1

Proportion of plastic waste per scenario [18]

Scenario	Landfilling	Mechanical recycling	Incineration with energy	Gasification	Cement kiln
1 *(Worst-case scenario)*	100%	-	-	-	-
2 *(Current scenario)*	54.3%	45.7%	-	-	-
3 *(European scenario)*	27.3%	31.1%	41.6%	-	-
4 *(Potential future scenario)*	15%	45%	20%	20%	-
5 *(Potential future scenario)*	-	50%	8%	20%	22%

Overly, five plastic waste management scenarios were modelled for South Africa, which are indicated in Table 1 [18]. Scenario development was based on the following:

- Objective knowledge
- The current scenario
- Practices from other regions such as Europe
- National Waste Management Strategy of 2020’s three pillars
- Plastics South Africa

3. Result and discussions

3.1 Freshwater Ecotoxicity

Freshwater ecotoxicity represents the impact that toxic emissions to air, soil and water have on freshwater systems [19]. Table 2 shows the impact potentials and main process contributions in the freshwater aquatic ecotoxicity category for each scenario.

Only scenario 5 had a negative impact potential indicating its net benefit on the environment compared to scenarios 1 to 4, as illustrated in Figure 2, while scenario 1 was the worst performing scenario. This is attributed to the absence of landfilling in the scenario, the increased percentage of plastic waste recycled and the energy recovery from incineration, which minimizes coal consumption and burning and, in turn leads to reduced emissions. In agreement with this study, [15] also found that mechanical recycling and incineration with energy recovery were beneficial for the environment due to the avoided processes of virgin resin production, coal mining and combustion compared to landfilling.

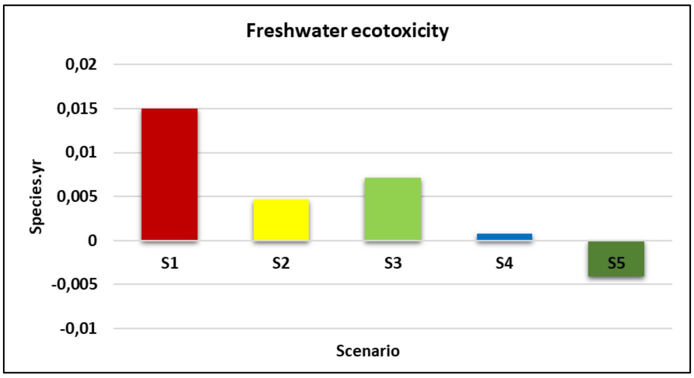

Fig. 2. Freshwater aquatic ecotoxicity

Table 2

Contributions to Freshwater ecotoxicity

Scenario	**Amount (species.yr)**	**Main process contribution to impact**
Scenario 1 (100% landfilling)	0.015	- PE landfilling (60.5%), PP landfilling (15.4%), PET landfilling (10.9%), WEE landfilling (9.9%), PS landfilling (1.9%)
Scenario 2 (Mechanical recycling and landfilling)	0.00495	- PE landfilling (55.3%), PP landfilling (14.1%), PET landfilling (18.3%), WEE landfilling (9.0%) PE recycling (-17.2%), PET recycling (-18.6%), PP recycling (-4.3%) PVC recycling (-4.5%)
Scenario 3 (Mechanical recycling, incineration, landfilling)	0.0072	- PE incineration (34.8%), PE landfilling (21.9%), PP incineration (9.0%), PET incineration (9.1%), PP landfilling (5.6%), PET landfilling (3.9%) WEE incineration (10.1%), PE recycling (-10%), PET recycling (-10%), PVC recycling (-5.6%), Energy recovery in CHP plant (-9.1%)
*Scenario 4 (Mechanical recycling, landfilling, incineration and gasification)	0.00041	- PE incineration (32.1%), PE landfilling (23.1%), PP incineration (8.3%), PP landfilling (5.9%), PET incineration (8.4%), PET landfilling (4.2%), WEE incineration (9.3%), WEEE landfill (3.8%), Gasification (2.6%), PE recycling (-25.6%), PET recycling (-40.1%), PP recycling (-6.4%), PVC recycling (-12.6%), Energy recovery in CHP plant (-8.3%)
Scenario 5 mechanical recycling, incineration, gasification, cement kiln	-0.00435	- PE incineration (11.6%), PP incineration (3.0%), PET incineration (3.0%), WEEE incineration (3.4%), syngas production (2.33%), clinker production (9.1%), PE recycling (-25.7%), PET recycling (-51.4%), PP recycling (-6.4%), PVC recycling (-13.5%), Energy recovery in CHP plant (-3.0%)

* Least environmentally impactful process

Vanadium was the primary contributing substance in scenarios 1 to 5. Vanadium presence in plastic can be attributed to the raw material, petroleum [20], contamination from vanadium catalysts used during the manufacture of plastics [21] or pigments such as bismuth vanadate, which are used to colour plastics [22]. Vanadium toxicity in humans leads to diarrhoea, vomiting, weight loss, kidney and liver damage, as alluded to in an earlier publication by the authors [18].

In scenarios 1 and 2, zinc emanating from the landfilling of plastic waste was the second contributing substance in this category. Zinc is used in plastic products as a heat stabilizer, flame retardant (zinc borate), inorganic pigment (zinc sulphide and zinc oxide), filler (zinc oxide) or metallic stearate slip agent (zinc stearate) [23]. Zinc toxicity effects are similar to those reported for vanadium [24] and can result in copper and iron deficiency in the body [25, 26]. Antimony from WEEE and PET landfilling and incineration was noted in scenarios 1 to 5. Antimony toxicity results in gastrointestinal-related problems and is potentially carcinogenic [27, 28]. Reference [29] found antimony in the urine of workers managing electrical and electronic waste in Ghana, which they attributed to the open burning of this waste. Antimony is used in plastics as; a biocide, a synergist in brominated flame retardants, a pigment and a catalyst in the production of PET [23, 28]. According to [28], the fate of antimony is determined by how plastic waste is managed. In incineration, antimony reduces the usability of bottom ashes due to its toxicity while in landfilling, the metalloid is detected in landfill leachate. Another substance found to contribute to freshwater aquatic ecotoxicity was copper in scenarios 1 and 5. For scenario 1, this was attributed to WEEE and PE landfilling while for scenario 5, gasification and clinker production were the main contributors. In a life cycle assessment of WEEE waste carried out by [30], the authors noted that landfilling accounted for 50% towards the freshwater aquatic ecotoxicity category compared to other waste management methods. This was due to copper and nickel groundwater contamination.

Reference [31] compared the impacts of landfilling and gasification and found that copper was among the main contributors to freshwater ecotoxicity impact in both processes. These results on copper also agree with [32]. Landfill leachate contributes significantly to adverse environmental impacts while solid residues from gasification can harm the environment when metals leach out. In cement production processes, [33] found copper among the main emissions to water. However, [34] highlighted that the magnitude of freshwater aquatic ecotoxicity impact could be reduced by substituting coal with alternative fuels, which minimizes fossil fuel consumption and burning of coal. In this category, transportation impacts were negligible.

3.2 Mineral Resource Scarcity

Mineral resource scarcity refers to the depletion of minerals under each scenario. Table 3 shows the results from the analysis of this impact.

Table 3

Mineral resource scarcity

Scenario	Amount (USD2013)	Main process contribution
Scenario 1 (100% landfilling)	2 760	PE landfilling (32.8%), PP landfilling (9.9%), PET landfilling (12.9%), Transport (38.4%)
Scenario 2 (mechanical recycling and landfilling)	-81 700	PE recycling (-35.6%), PET recycling (-42.6%), PP recycling (-12.1%), PVC recycling (-9.8%)
Scenario 3 (mechanical recycling, incineration, landfilling)	-70 800	PE recycling (-28.1%), PET recycling (-33.6%), PP recycling (-9.5%), PVC recycling (-18.0%), Incineration with energy recovery (CHP plant) (-10.8%), Transport (1.7%), Landfilling (0.6%)
*Scenario 4 (Mechanical recycling, landfilling, incineration and gasification)	-97 500	PE recycling (-26.9%), PET recycling (-46.5%), PP recycling (-9.1%), PVC recycling (-14.0%), Incineration with energy recovery (-3.4%), Gasification (10.7%), Transport (1.3%), Landfilling (0.2%)
Scenario 5 mechanical recycling, incineration, gasification, cement kiln	-16 400	Cement kiln (85.2%), Gasification (8.6%), PE recycling (-24.2%), PET recycling (-53.3%), PP recycling (-8.2%), PVC recycling (-13.3%)

*Shaded row represents the least environmentally impactful scenario

In the mineral resource category, mechanical recycling and incineration with energy recovery were beneficial for the environment as indicated by the negative impact potentials. These findings agree with [35] and [36], who observed a significant net benefit with recycling and incineration respectively in contrast to landfilling. However, in [3] and [37], incineration with energy recovery had a higher net benefit on the environment than recycling. In [10], landfilling performed better than recycling and incineration with energy recovery in the category.

The net benefits associated with recycling and incineration with energy recovery, in scenario 5, were lowered by the presence of cement kiln and gasification processes. Their contributions to the final impact potential value were 85.2% and 8.6% respectively. In [38], a scenario combining the cement kiln option and 10% incineration, led to adverse effects in this category compared to tertiary recycling. Although the authors did not document the process contributions. In this work, the main burdens in the cement kiln process were bauxite mining, electricity production and magnetite mining. Their contributions were 83%, 6.5% and 5% respectively. As corrective materials during clinker production, bauxite and iron are added in minute quantities. This ensures that the required chemical composition of the raw mix is achieved [39].

The main burdens in the gasification process were lime production and electricity generation. These burdens were higher than landfilling burdens, leading to scenario 2 outperforming scenario 5 as illustrated in figure 3.

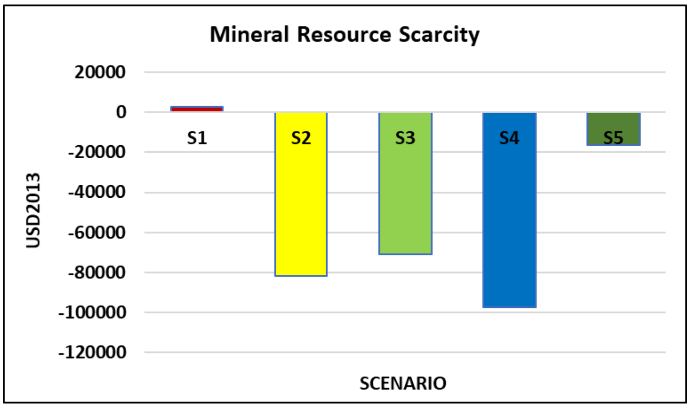

Fig. 3. Mineral resource scarcity

A few studies have investigated the mineral resource depletion category in contrast to other impact categories including fossil resource scarcity. For scenario 4, net benefits associated with recycling and incineration with energy recovery offset the negative impact of gasification, transport, and landfilling.

3.3 Fossil Resource Scarcity

Table 4 shows the LCIA results for the fossil resource scarcity category, which highlights the impact of scenarios on fossil resources.

Table 4

Fossil resource scarcity

Scenario	**Amount (USD2013)**	**Main process contribution**
Scenario 1 (100% landfilling)	4.86E5	PE landfilling (34.9%), PP landfilling (10.5%), PET landfilling (13.6%), Transport (34.8%)
*Scenario 2 (Mechanical recycling and landfilling)	-3.82E7	PE recycling (-54.6%), PET recycling (-19.7%), PP recycling (-16.9%), PVC recycling (-4.1%), Landfilling (0.5%), Transport (0.5%)
Scenario 3 (Mechanical recycling, incineration, landfilling)	-2.77E7	PE recycling (-48.8%), PET recycling (-17.6%), PP recycling (-15.1%), PVC recycling (-8.5%), Incineration with energy recovery (CHP plant) (-1.1%), Transport (0.6%), Landfilling (0.3%)
Scenario 4 (Mechanical recycling, landfilling, incineration and gasification)	-3.92E7	PE recycling (-47.2%), PET recycling (-24.6%), PP Recycling (-14.6%), PVC recycling (-6.7%), Incineration with energy recovery (-0.3%), Gasification (9.8%), Transport (0.5%), Landfilling (0.1%)
*Scenario 5 mechanical recycling, incineration, gasification, cement kiln	-4.7E7	PE recycling (-44.2), PET recycling (-29.4%), PP recycling (-13.7), Gasification (8.3%), Cement kiln (-0.8%), Transport (0.5%)

*Shaded row represents top environmentally performing scenario

Mechanical recycling was the least impactful individual process in this category, whilst incineration with energy recovery though negligible had a net benefit. In [1, 12, 26, 11, 40] mechanical recycling had considerable benefits in the fossil depletion category compared to incineration with energy recovery. Reference [11], observed a higher net benefit on the environment with energy recovery in a CHP plant than in a power plant. Landfilling (scenario 1) had the worst environmental impact since it had no avoided processes to offset its impact in this category. In [10, 15, 35, 41, 42], the negative impact of landfilling in comparison to recycling, incineration with energy recovery and thermal cracking was also highlighted. In [1], landfilling, pyrolysis and incineration respectively performed poorly in this category. Reference [1] also found that the use of plastic waste as solid refuse fuel in a cement kiln outperformed other processes, followed by mechanical recycling while in this work, although the cement kiln benefited the environment, this was to a small extent. Reference [13] assessed plastic waste management methods in India and noted that recycling was more beneficial in reducing fossil depletion than cement kiln and incineration options.

In this study, gasification had a negative impact on fossil depletion, and this was attributed to lime production, which accounted for 91.7% towards the gasification impact. The production of lime requires a significant amount of energy as it involves unit processes such as limestone quarrying/blasting, crushing and screening, calcination, hydration, packing and transportation [43–45] which require electricity, diesel and fuel oil. Reference [43], mentions that the calcination process consumes the highest amount of energy, in the range 92% to 97%. Consequently, utilising renewable energy sources, including solar and hydroelectricity, improving the plant's energy efficiency and using alternative sorbents during syngas scrubbing may lower the negative impact of gasification on fossil depletion [43, 46]. Overall, scenario 5 outperformed all the other scenarios, followed by scenarios 4, 2 and 3, respectively, as indicated in figure 4. This is attributed to mechanical recycling, which offset the negative impacts of landfilling, gasification, and transport.

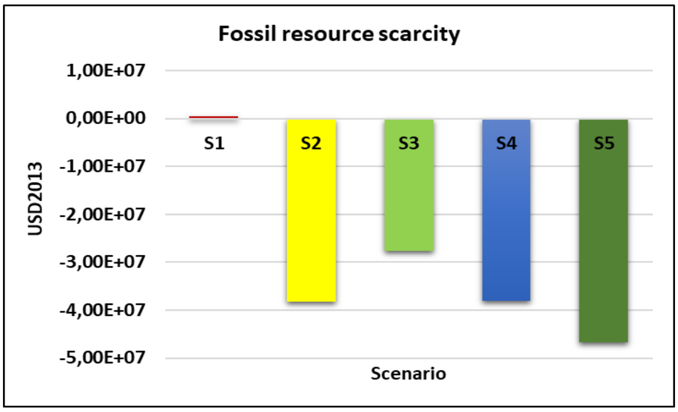

Fig. 4. Fossil resource scarcity

3.4 Contributions to Transportation Impacts

Transportation impacts on global warming, eutrophication and fine particulate matter have been a subject of research by several authors [47–50]. However, this study assesses the main contributions to terrestrial ecotoxicity, land use and freshwater ecotoxicity. This helps to determine hotspots, which can then be mitigated to reduce environmental harm. Table 5 shows the primary contributing processes in the stated categories.

Table 5

Main process contributions to transport

Impact category assessed	**Top contributing processes**	**% Contribution**
Terrestrial ecotoxicity	Brake wear emissions	87.4%
Land use	Road market	91.8%
Freshwater ecotoxicity	Lorry market	52.4%

In the terrestrial ecotoxicity category, brake wear emissions were the major contributor accounting for 87.4% towards the overall impact. The elements contributing to these emissions included copper, antimony, zinc, tin, barium, molybdenum, and lead. Substances such as barium sulphate are used as fillers, while antimony or molybdenum-based sulphidic compounds are used as reinforcement materials or solid lubricants. These results are in with other researchers, including [51-53], who are cited in [54]. The emissions from brake wear depend on the driving conditions and material manufacture of the brakes. For example, aggressive driving generates more emissions. A considerable amount of the generated emissions goes into the air, while some settle on the road or the vehicle. The emissions range from nano, micro or submicron in size [54].

When land use impact was considered, the main contributing process to the impact was the road market, accounting for 91.8% of the overall impact. The road market involves land transformation to enable road construction and other infrastructure development, including bridges or tunnels. Reference [55] highlights the destruction of green spaces, including wetlands and forests, due to road construction. This in turn results in habitat destruction and can affect groundwater quality or the aesthetics of an area. There is also heightened flooding risk, siltation and erosion as road construction affects the surface water, groundwater flows and recharging by concentrating storm water.

Reference [56] cite [57], [58], who highlighted the formation of heat islands on roads and the subsequent ambient temperature increase. Furthermore, land is scarce in South Africa, so existing roads and infrastructure should be used when siting the proposed plastic waste management technologies where possible. In Germany, targets have been set to reduce daily land usage to approximately 30 hectares per day from 120 hectares per day in 2003 to minimise environmental degradation [59, 60]. However, other authors argue that road construction is advantageous in that it leads to economic development in an area [61, 62].

The primary offending process in the freshwater ecotoxicity category was the lorry market, including manufacturing the transporting vehicle. The lorry market accounted for 52.4% of the impact category. Contributing substances in this category were copper, antimony, zinc, nickel, and chromium. Zinc emissions were from automotive shredder residue (ASR) incineration at the end of the transporting vehicle's life. ASR consists of plastic, rubber, and heavy metals. Sources of metals include plastic additives, plastic-coated metals or PVC-coated electrical wires [63], [64, 65]. In [64], the authors noted that incinerator bottom ash contained 15g/kg and 28g/kg zinc and 32g/kg and 160g/kg copper in tests conducted in 2007 and 2008 respectively. Reference [64], mentions the necessity of recovering and recycling these metals. In the same study by [64], zinc concentrations in the fly ash and air pollution control residues (APC) were 180g/kg and 655g/kg, respectively. Copper concentration in the boiler and bag filter ash was around 45g/kg. In [66], the author found copper and chromium in ASR leachates, while in [67, 68], traces of nickel were detected. In [64], leaching tests revealed that zinc emissions from APC residues and fly ash were higher compared to the set limits for hazardous waste landfills in the European Union Directive 2000/53/EU, which recommends that 95% by weight of an ELV should be recovered. Such high metal content leachates indicate the toxic nature of these residues, and therefore it is necessary to pre-treat them before landfilling.

In South Africa, the treatment pathway of ELVs is not clear. However, EPR regulations targeted at ELVs are being pursued. Reference [69] highlights current challenges in the country, which include limited regulations, the uncertainty on the number of ELVs available and the existing recyclers, the proliferation of informal recyclers and the adverse environmental impacts that may occur [69]. Numerous authors [70–73] have investigated ASR gasification under various conditions. This should also be done in the South African context to assess the suitability of the process in managing such wastes, which will lead to the minimization of impacts associated with landfilling practices.

4. Conclusions

Landfilling of plastic waste significantly adversely affects freshwater ecotoxicity due to various metals including vanadium, zinc, and antimony, found in leachate. These metals negatively affect humans and aquatic life. In tandem with the country's waste minimisation goals, increasing the current mechanical recycling rate would be beneficial in protecting freshwater systems in a country that is regarded as water-scarce. Gasification, incineration with energy recovery and cement kiln use also had a net benefit in this category. However, in processes such as incineration and gasification, pre-treatment of bottom ashes is necessary to recover metals before the ash is beneficiated to reduce the risk of similar metals including copper leaching out and contaminating water bodies. Recycling and energy recovery had a net benefit on the environment in the mineral resource scarcity category while landfilling, gasification, and the cement kiln option were among the most impactful processes. In the Fossil resource scarcity category, recycling was the least impactful process, followed by incineration with energy recovery and cement kiln use, although to a lesser extent. Due to the energy-intensive nature of the lime production process, a reduction in the use of lime and its potential replacement options in processes should be considered. This will result in a corresponding decrease in fossil resource consumption in processes where it is employed. Overall, the only scenario with net benefit to the environment in the 3 assessed impact categories was scenario 5, involving 50% mechanical recycling, 8% incineration with energy recovery, 20% gasification and 22% cement kiln use. This performance is attributed to the absence of landfilling in the scenario, an increased mechanical recycling rate, and incineration with energy recovery to a lesser extent. On transportation impacts, brake wear emissions influenced by driving conditions and brake wear material, transporting vehicle's life cycle and road construction, negatively impacted the terrestrial and freshwater systems and land use, respectively. Eco-friendly alternatives that can be used as fillers or reinforcement materials should be evaluated in the production of brakes. If scenario 5 is implemented, utilising gasification to treat automotive shredder residue, could result in the sustainable management of end-of-life vehicles in South Africa. Lastly, the use of existing roads when siting the proposed technologies in plastic waste management will minimise land utilisation and preserve green spaces.

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A REVIEW OF DECISION-MAKING TOOLS IN WASTE MANAGEMENT: PROS AND CONS

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Abstract

Decision-making tools can assess the environmental, economic, and social acceptability of waste management processes. This paper reviews 11 decision-making tools to determine the best-performing tool when conducting comparative assessments of waste management processes. Among the tools studied, environmental life cycle assessment (e-LCA) had the highest number of benefits compared to the other tools. One of the main advantages is the tool's ability to assess numerous environmental impacts which encompass human health, ecosystems, and resources. LCA methodology will help to provide a thorough evaluation of processes and products and thus potentially uncomplicate the decision-making process. However, some limitations associated with the tool need to be addressed to ensure that generated models are accurate.

Keywords: decision-making tools, waste management, environmental assessment, life cycle assessment, social acceptability

1. Introduction

Several decision-making tools exist, that are used to determine the environmental sustainability, economic viability, and social acceptability of waste management processes. Morrissey and Browne (2004) evaluated the benefits and limitations of cost-benefit analysis, life cycle assessment (LCA) and multicriteria decision analysis models. Turner and Kemp (2016) assessed a solid waste management system using a combination of material flow analysis and life cycle assessment while Milutinovic et al. (2014), Achillas et al., (2013) and Vučijak (2016) used multi-criteria decision analysis in their assessments. Authors that have evaluated the LCA tool include, Rebitzer et al. (2004), Guinée et al. (2010) and Curran, 2013) while (Herva and Roca, 2013) evaluated the benefits of combining ecological footprint (EF), LCA and risk assessment (RA). This review focuses on

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11 environmental tools, their pros and cons to select the best-performing profiling tool that can be used to assess and compare the environmental sustainability of processes. Such tools include Strategic Environmental Assessment (SEA), Environmental Impact Assessment (EIA), Risk Assessments (RA), Multi-Criteria Decision Models (MCDM), Material Flow Analysis (MFA), Ecological Footprint (EF), Environmental Management System (EMS), Impact Pathway Approach (IPA), System of Economic and Environmental Accounts (SEEA), environmental-life cycle assessment, and Intergovernmental Panel for Climate Change (IPCC) guidelines.

2. Methodology

This review study was conducted by accessing several academic databases, including Science Direct, Scopus and Springer Link. Google Scholar was also consulted. The keywords/phrases used in combination included “decision-making tools”, “waste management”, “inception year”, plastic waste, and “pros and cons”. No period restrictions were put; to enable capturing of the developments that have occurred since each tool's inception. Peer-reviewed and grey literature were considered in the review.

3. Results and discussions

Among the tools studied, e-LCA, governed by ISO 14040:2006 and ISO 14044:2006 standards (ISO, 2006a, 2006b) had the highest number of benefits which outweighed its disadvantages compared to other decision-making tools. One of the primary advantages is the tool’s ability to assess various environmental impacts encompassing human health, ecosystems, and resources (Hill, 2013). Other advantages include its ability to calculate the emissions to air, soil and water per each life cycle stage, the possibility of identifying and improving areas most impactful to the environment, its ability to quantify material and energy flows, possible use for ecolabelling and its versatility which enables it to be used in conjunction with other tools. These findings agree with Arena et al. (2003), who highlight that LCA is the ideal tool for evaluating environmental sustainability in municipal solid waste management. The utilisation of this tool by policymakers and other stakeholders has been increasing, for example, in regions such as Europe.

Table 1

Comparative assessment of decision-making tools in waste management (adapted from Mazhandu 2022, PhD thesis)

Tool and sources	Inception Year	Advantages	Disadvantages
Environmental impact assessment (EIA) (Alshuwaikhat, 2005; Morgan, 2012) (Assia, 2019)	Early 1970s	- Well-established, applied extensively and is supported by several organisations such as the United Nations (UN), World Bank, World Health Organisation (WHO). - It is commenced early on in the process -More mandated and a stringently monitored method compared to other tools. -The process is open and is participatory in nature. It provides a structure which enables the simultaneous assessment of location, design and environmental-related aspects. Therefore, potential adverse impacts can be averted by implementing modifications to the design. - It allows transparency early in the project, between its custodians and the	- Ancillary developments on a project may cause accumulative impacts and these may not be addressed adequately. - Activities that are regarded as minor and therefore ignored, may adversely affect the environment. - Decisions on forecasted impacts might be irreversible. - Environmental challenges arising from activities that are not regulated may not be addressed by conducting an EIA. - The tool may fail to adequately address social and health-related impacts associated with a project. - There is a risk of prematurely rejecting alternatives before conducting extensive sustainability assessments.

Tool and sources	Inception Year	Advantages	Disadvantages
		community, resulting in a smooth implementation.	
Risk assessments (RA) (Garrick, 2002) (U.S. EPA, 2009) (Weekes, 2017; *IIRSM*, 2016)	Late 1970s and early 1980s	- The environmental impacts associated with different anthropogenic drivers can be assessed. - The process is transparent and peer-reviewed and includes the participation of the public. -Financial savings can be realised since the process is proactive and not reactive.	- Absence of a standardised method to conduct solid waste management risk assessments is a limitation. - Possible hazards may be missed, due to lack of knowledge or limited experience.
Environmental life cycle assessment (e-LCA) (Ekvall, 2000) (Torabi and Ahmadi, 2020; Cossu et al., 2017) (Farjana *et al.*, 2021) (McManus and Taylor, 2015)	1960s	- Product or process environmental footprints can be evaluated across numerous impact categories that cover human health (carcinogenic and non-carcinogenic effects), resource depletion and the ecosystem. - Material and energy flows can also be quantified. - Emissions can be calculated for each stage in the life cycle. - Can be used in hotspot analysis to identify and improve areas in a process	- A lot of data is required and the process of conducting an LCA can be time-consuming. - Results from an LCA study are location- specific as data varies between different areas. - Expertise is required when conducting an LCA.

Tool and sources	Inception Year	Advantages	Disadvantages
		that are more impactful to the environment. - Comparative assessments can be done for products or processes. -This tool is standardised and is also endorsed by the United Nations. - In marketing of products, LCA can be utilised in ecolabeling or assessing a company's sustainability profile. - Due to its flexibility, LCA can be used in conjunction with other tools.	
Multi-criteria decision models (MCDM) (Morrissey and Browne, 2004) (Nautiyal and Goel, 2021) (Mosadeghi *et al.*, 2013)	1972	-Utilised when single criteria tools cannot be used. -Robust decisions can be made. -Various problem-solving ways can be identified. - Quantitative and qualitative methods can be used.	- A lot of data is required for this tool. - It requires both experience and personal opinions. - Its application is complex.
Intergovernmental Panel for Climate Change (IPCC) guidelines (Yona *et al.*, 2020)	1996	- IPCC guidelines enable transparency between various countries when they report inventories. - The IPCC guidelines can be used in policy	- There is a disparity between reported and actual emissions as guidelines are dated. The developmental process associated with these

Tool and sources	**Inception Year**	**Advantages**	**Disadvantages**
(Sala *et al.*, 2019)		formulation aimed at reducing the carbon footprint of a country.	guidelines has not been modified since inception. - The guidelines are susceptible to bias as they rely on expert synthesis of data. - It only evaluates climate change and does not consider toxicity impacts.
Ecological Footprint (EF) (Nautiyal and Goel, 2021)	1990	- The environmental performance of products and processes can be determined. - The rate of consumption of raw materials and rate of waste production can be evaluated.	- Important environmental monitors may be missed since minimum criteria are used. This leads to inaccuracies in the results when comparative assessments are conducted.
Environmental management system (EMS) (Zilahy, 2017) (El Haggar, 2005)	Early 1990s	- Implementing this tool in a company improves its image and competitiveness. - There is continuous monitoring of environmental impacts resulting from the business, which in turn leads to financial savings for the company.	-The performance of Environmental Management Systems differs depending on the regulatory or cultural perspective. - Increased production will offset indicators like eco-efficiency and this can lead to erroneous results. - The use of the EMS tool is voluntary. Also, a company sets its own criteria for evaluating environmental

Tool and sources	**Inception Year**	**Advantages**	**Disadvantages**
			performance, and therefore its application is narrowed.
Material flow analysis (MFA) (Björklund, 2000) (Zhang, 2019; Boer and Abokersh, 2022) (Graedel, 2019)	Late 1980s and 1990s	- MFA can be used to identify areas where raw material usage can be reduced; thereby minimising the associated negative environmental impacts. - A process's substance transfer factors can be determined. - Hidden flows and their environmental impacts can be identified.	- In contrast to LCA, its scope is limited. - Due to the subjective nature of weight application to materials, a change in weighting, will alter the results. - Since the quality of materials is not taken into consideration, this may result in inaccurate results.
Strategic Environmental Assessment (SEA) (Tetlow and Hanusch, 2012) (Alshuwaikhat, 2005; Lee and Walsh, 2012)	1969	- Environmental sustainability of current and future policies, plans or programmes can be assessed to identify the preferred option. -In contrast to EIA, SEA can assess cumulative environmental impacts.	-The success of SEA depends on the availability of data and its accessibility. However, developing countries are riddled with data availability and access challenges. -Can be resisted by governments as it highlights their inadequacies.
Impact pathway approach (IPA) (Bickel and Friedrich, 2005; Jorli *et al.*, 2018) (Hainoun, Almoustafa and Seif Aldin, 2010)	The early 1990s	- It is multidisciplinary and generally recognised by the scientific population. -Financial costs can be determined from damages to society.	- Complexities in the model arise when the need to calculate ingestion dosages of harmful metals and organic compounds arises. - If data on the acidification and eutrophication of ecosystems or other

Tool and sources	Inception Year	Advantages	Disadvantages
			information is unavailable, the application of the model is limited. - Although it can be used to evaluate point source emissions, LCA is the recommended tool when comparing various processes since it can take into consideration the whole life cycle. - Results are site-specific as they are impacted by weather patterns and plant productivity.
System of Economic and Environmental Accounts (SEEA) (Cavalletti and Corsi, 2021) (Vardon *et al.*, 2018) (Nagy, 2018)	Early 1990s	-SEEA improves the quality of data. This in turn lowers the level of uncertainty. - This tool aids in data gap identification and can connect both economic and environmental information.	- Since SEEA requires a significant amount of economic and environmental data; its implementation in developing countries can be challenging due to the lack of data. - It does not have a broad scope and is not an established tool.

4. Conclusions

The LCA methodology will help to provide a thorough evaluation of processes and products and thus potentially uncomplicating the decision-making process. However, it should be noted that some drawbacks associated with the tool need to be adequately addressed to ensure the accuracy of the generated models.

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EVALUATION OF BOTSWANA COAL FOR SYNGAS PRODUCTION

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Abstract

This paper explores the quality and quantity of synthetic gas from Botswana coal when exposed to different operating parameters: gasification temperature of 750˚C and 900˚C, residence time of 1 and 2 hours, and particle size ranges of 1 – 10 mm and 10 – 40 mm. The coal used was collected from Mabesekwa coal field. Experiments were performed in a bench-scale fixed bed reactor using the 2^3-factorial method to determine a better combination of these parameters and how each of them influences the product of interest. LHV for producer gas from BIUST was calculated to be at least 28 MJ/kg based on the gas composition. 1 kg of Botswana coal produces $3.14 \cdot 10^{-2}$ m^3 volume of raw synthetic gas. Residence time has a greater impact on the amount of gas produced in the gasification process. Increasing the residence time by 1 hour will increase the yield by 6.46 L.

Key words: coal gasification, syngas production, fixed-bed reactor, quality analysis, factorial design

1. Introduction

Botswana has approximately 212 billion tons of coal of which less than 6 million tones is mined annually by Morupule Coal Mine (MCM) and Minergy Mine. Mabesekwa is a sampling site that was explored by Shumba coal company. Botswana is in the region called the Karoo Supergroup which is the most widespread stratigraphic area in Africa south of the Sahara Desert [1]. These resources have been found to have high ash, medium calorific value, and low-medium quality bituminous coal [2]. Despite vast coal reserves, Botswana has only two power plants adjacent to (MCM) which generate and supply electricity meeting only 50% of Botswana's electricity demand. Botswana is developing at a high rate

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with increased infrastructure expansion which increases its power demand. Hence, the significance of this work to evaluate electricity generation using syngas as a product of Botswana coal gasification.

At the 26th United Nations Climate Change Conference (COP26) which was held in Glasgow, Scotland in October – November 2021, countries had a draft agreement to end the use of coal and other fossil fuels [3]. This agreement was important in reducing the effects of global warming, with countries tasked to submit their plans in reducing global warming. There is an ongoing plan to limit global temperature rise from 2.4 °C to 1.5 °C in the 2020s decade [4]. With 40 countries signed up to move from coal, China and the US have not signed up mainly because they still depend largely on coal as the major source of energy. These two giants have abundant coal resources, and the ever-rising natural gas and fuel prices, China and the US have no choice but to continue depending on coal as an energy source. Africa contributes a negligible amount to the global warming compared to other continents (less than 4%) [5]. Botswana is one of the African countries with abundant coal and mainly depends on this coal for its electricity generation and other energy applications. This paper looks to explore the production of synthetic gas from Botswana coal through gasification process which is more efficient and more environmentally friendly. The gas can be used for several applications including fuel for electricity, as chemical feedstock in the production of methanol, dyes, and other chemical processes.

A fixed bed reactor plant running at atmospheric pressure consisting of coal feeding system, steam supply, oxygen inlet, a fixed bed reactor equipped with two condensers, a cyclone, gasometer system, gas sampling point, and data acquisition unit will be used for this study. This plant is connected to a SCADA and excel spreadsheet for process manipulation, process operation, process monitoring and data capturing.

2. Experimental

2.1. Coal Gasification Process

Sample selection and preparation

Coal samples were collected from Mabesekwa coal sampling site, near Tonota in the northern part of Botswana. Approximately 10 kg of coal was collected from the coal barrels which stored coal samples. The ultimate and proximate analysis of this coal are shown in **Error! Reference source not found.**.

Table 1

Proximate and ultimate analysis of Mabesekwa coal samples

Proximate analysis						Ultimate analysis			
AC	MC	VM	FC	Total S	GCV	C	H	N	O*
37.75	4.45	23.40	34.45	0.34	81.90	37.22	2.09	0.83	17.40

*by difference

The samples were crushed in a primary jaw crusher (at 12 mm gap size) and then a gyratory crusher (at 7 mm gap size). They were then sieved to the required size ranges according to the design of experiments (1 – 10 mm, 10 -40 mm. Oversize from this sample preparation was crushed using a primary jaw crusher (at 12 mm gap size) and further crushed using a gyratory crusher (at 7 mm gap size), while undersize was kept for briquetting and processing later. The desired sample was stored in well labelled sample bags for the gasification process.

Oxygen and steam supply system

Gasification process requires oxygen at the right stoichiometric ratio for the partial combustion of coal. Oxygen was introduced into the reactor through the spouting nozzle at room temperature and atmospheric pressure. Steam was generated in an Italian Elettronica Veneta SPA SCT04/EV steam generator which introduced steam into the reactor at 500°C and 4 bar pressures.

Fixed bed reactor plant

Fixed bed reactor:

A scheme of fixed bed reactor is shown in Fig. 1. The main component of this system was a porous mild steel gasifier with a 150 mm internal diameter and length of 300 mm. The reactor was well insulated to avoid any major heat losses. Coal was fed into the reactor and allowed to heat up for 60 minutes. Oxygen and superheated steam were introduced after the required temperature was reached.

Scrubber and condensers:

Product gas is a combination of condensable and non-condensable gases as well as solid particles that are carried through to first a wet scrubber then a series of 3 condensers. The scrubber is used for the removal of harmful components (including Sulphur dioxide, SO_2 and acid gases) of the exhausted flue gases by spraying water through the gas. Condensers are operated at 150°C, 100°C, room temperatures and atmospheric pressure to remove condensable gases from the product gas.

Gasometer

The flowrate of the product gas was measured in a gasometer that uses Bernoulli's principle to measure the amount of gas produced per run. There was a gas sampling point just before the gasometer to collect samples for quality analysis using gas chromatography (GC).

Induction heating

Bratina *et al.*, (2011) filed a patent which involved providing an induction heated screw conveyor with an auger and transporting the mixture through the induction heated screw conveyor while inductively heating the auger so that it heated the mixture in the induction heated screw conveyor [6]. It was from this idea that gasification reaction method using induction heating was adopted. Electromagnetic induction heating is a method of heating electrically conducting materials using electrical current. Components that are necessary to have an induction heating system are AC power source, induction coil, component circuit and workpiece according to Skill Lync [7].

As alternating current of high frequency passes through the coil, it causes alternating magnetic field to surround the coil. A workpiece (material to be heated) is placed inside the coil causing the magnetic field to induce electromotive force as well as eddy current [7]. The workpiece heats up when eddy currents within the material experience resistance to flow which is explained by Faraday's law of electromagnetic induction. Heat transfer in induction heating is highly efficient as heat can be transferred uniformly throughout the material instead of a certain point [6].

Gasification

Fixed bed reactor system at BIUST consists of mainly the gasifier (1), cyclone (6), Knock-out drum (4), scrubber (7) and steam generator (3). A schematic diagram of the auger reactor is shown in Fig. **1**.

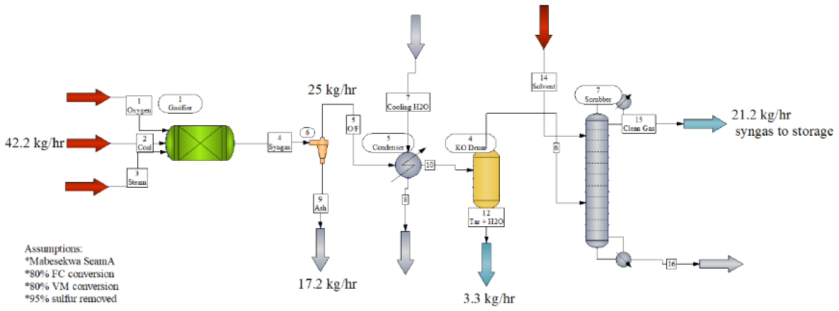

Fig. 1. A schematic diagram of the reactor plant

Coal feedstock was manually fed into the reactor. The reactor is an induction heated horizontal batch reactor on a bench-scale. The reaction zone has induction coils around, covering a length of 400 mm. Several temperature transducers (T1 to T4) measured temperature variations along the reactor. These transducers measure the temperature at the reaction zones. The reactor was equipped with oxygen and steam flow inlets.

Product gas from the reactor went through a scrubber which was used to remove harmful gases and cool it followed by a series of three condensers to remove condensable gases as well as to further cool the gas before collection and measuring in the gasometer.

Design of Experiments

Different operating parameters were varied to understand how the process variations affected the response of interest. While steam flow rate, oxygen flow rate, temperature and pressure were fixed as in **Error! Reference source not found.**; residence time, granulation and temperature were varied to see how they affect the quality and quantity of the syngas produced. The coal used was collected from Mabesekwa coal field. Experiments were performed using the 2^3-factorial method.

Table 2

Gasification process input parameters

Parameter	Range
Particle size range	1-10 mm and 10-40mm
Residence time	1 and 2 hours
Temperature	750 and 900ºC
Oxygen Pressure	4 bars
Oxygen flow	3.42×10^{-4} kg/s
Steam flow	13.7 g/min
Steam pressure	4 bars

The experimental conditions for the initial screening of the affecting parameters are given in **Error! Reference source not found.**. The repeatability of the gasification tests was evaluated by performing three repeat tests of the upper and the lower limits of the factorial design tests.

Table 3

Levels and factors used for the factorial design experiments in this study

Parameter	(-) = low limit	(+) = high limit
Res. Time (hr)	1	2
Granulation (mm)	1 – 10	10 – 40
Temperature (°C)	750	900

Product gas samples from gasification runs were collected in tedlar bags as per the standard guidelines and samples were sent to Betach in Francistown, Botswana for quality analysis. The results for syngas composition at different operating parameters (feed rate, residence time and granulation) are presented in figure 2 and figure 3. The experiment consisted of two levels and three factors which are residence time, granulation, and temperature.

3. Results and discussions

Qualitative & Quantitative Analysis of Syngas

Residence time was varied between 1 and 2 hours, followed by granulation with size ranges 1-10mm and 10-40mm and lastly temperature variation between 750°C and 900°C. There were eight experiments repeated three times for accuracy of results.

Table 4

Factor combinations for volume of gas produced from coal through gasification in a fixed bed reactor.

A	B	C	Interactions				
Res.Time (hr)	Granulation (mm)	Temp (C)	AB	BC	AC	ABC	Quantity of gas (L)
-1	-1	-1	1	1	1	-1	50
1	-1	-1	-1	1	-1	1	82
-1	1	-1	-1	-1	1	1	42
1	1	-1	1	-1	-1	-1	68
-1	-1	1	1	-1	-1	1	71
1	-1	1	-1	-1	1	-1	80
-1	1	1	-1	1	-1	-1	40
1	1	1	1	1	1	1	47
-1	-1	-1	1	1	1	-1	52
1	-1	-1	-1	1	-1	1	74
-1	1	-1	-1	-1	1	1	52
1	1	-1	1	-1	-1	-1	72
-1	-1	1	1	-1	-1	1	85
1	-1	1	-1	-1	1	-1	82
-1	1	1	-1	1	-1	-1	52
1	1	1	1	1	1	1	53
-1	-1	-1	1	1	1	-1	54
1	-1	-1	-1	1	-1	1	75
-1	1	-1	-1	-1	1	1	51
1	1	-1	1	-1	-1	-1	75
-1	-1	1	1	-1	-1	1	85
1	-1	1	-1	-1	1	-1	82
-1	1	1	-1	1	-1	-1	52
1	1	1	1	1	1	1	51

Random was chosen through excel spreadsheet by using the code =1+INT (8×RAND ()). Excel software was used to generate the runs for the interpretation of the responses, table 4.

Table 5

Factor combinations for volume of gas produced from coal through gasification in a fixed bed reactor

Summary Output

Regression Statistics	
Multiple R	0.96325
R Square	0.927851
Adjusted RSquare	0.896286
StandardError	4.86912
Observations	24

Anova

	df	*SS*	*MS*	*F*	*Significance F*
Regression	7	4878.292	696.8988	29.39468	5.53E-08
Residual	16	379.3333	23.70833		
Total	23	5257.625			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	63.625	0.993905	64.01517	1.03E-20	61.51802	65.73198	61.51802	65.73198
Res. Time (hr)	6.458333	0.993905	6.497938	7.35E-06	4.351349	8.565318	4.351349	8.565318
Granulation (mm)	-9.04167	0.993905	-9.09711	1.01E-07	-11.1487	-6.93468	-11.1487	-6.93468
Temp (C)	1.375	0.993905	1.383432	0.185532	-0.73198	3.481985	-0.73198	3.481985
AB	-0.04167	0.993905	-0.04192	0.967079	-2.14865	2.065318	-2.14865	2.065318
BC	-6.79167	0.993905	-6.83332	4.02E-06	-8.89865	-4.68468	-8.89865	-4.68468
AC	-5.625	0.993905	-5.65949	3.55E-05	-7.73198	-3.51802	-7.73198	-3.51802
ABC	0.375	0.993905	0.3773	0.710909	-1.73198	2.481985	-1.73198	2.481985

Analysis of regression model

Excel software was used to generate the runs, table 4, and for the interpretation of the responses, table 6. Analysis of the data collected in the study shows that temperature is more significant than granulation and residence time in coal gasification for gas collected. Their extent of influence was measured by the p-values and t-ratios. Temperature shows larger positive p-value followed by residence time and then granulation. The effect of temperature on coal gasification and liberation of gases in coal is found to be the highest compared to the other parameters because heat acts on the weak and strong bonds (aliphatic and ether bridges, and aromatic rings); breaking the strong cross linkages and causing the elements to bond together forming different product gases with composition from H_2 to low chain alkane molecules. The granulation provides more surface area for the heat to act on the coal samples while the residence time allows for the heat to work on these bonds.

To find factors that have a significant effect on the response and to determine by how much these factors affect the yield also, and how they interact with each other, a regression analysis was designed, table 5, a model in equation (1):

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{23} X_2 X_3 + \beta_{13} X_1 X_3 + \beta_{123} X_1 X_2 X_3 \quad (1)$$

Where X_1 is residence time [hr], X_2 is granulation [mm] and X_3 is temperature [°C]

This model tells us what the yield is if we feed different combinations and different interactions. It also tells total interaction when the three factors are combined.

A contrast matrix was applied as a systematic way to assign all levels for all the three factors. Interactions were computed by multiplying levels. A total of 24 experiments were performed.

From the data collected, a regression analysis was derived using excel software to find the model and see factors that have significant effect and what effect they have on the yield.

From the regression analysis, table 5, the coefficient of residence time is higher with a positive value which implies residence time has a greater impact on the amount of gas produced in the gasification process. Increasing the residence time by 1 hour will increase the yield by 6.458 L.

From the regression analysis the model fitting data in this research is

$$\begin{aligned} y = 63.625 + 6.458X_1 - 9.042X_2 + 1.375X_3 - 0.0417X_1X_2 - 6.792X_2X_3 \\ - 5.625X_1X_3 + 0.375 \end{aligned} \quad (3)$$

Temperature has a smaller coefficient of 1.375 which means temperature has a significant and positive impact on the quantity of gas produced. Increasing the temperature by 1°C will increase the yield by 1.375 L while increasing granulation by 1 will lower the yield by 9.042 L according to the regression model in equation (3).

Analysis of plots

An average of 564 ppm of carbon dioxide was produced from this process which brings the calorific value of the gas down since CO_2 is not a combustible gas. Carbon dioxide is a greenhouse gas and must be disposed carefully to avoid harming the environment. According to figure 3 an average LHV of the product gas is at least 28 MJ/kg which shows to be a good quality gas according to Ghenai (2010) [8] who described the range of LHV for syngas to be between 10 and 28 MJ/kg.

From a total of 8 sets of experiment with each having 8 runs the highest amount of product gas was observed to be obtained at temperature of 900°C, particle size range of 1 – 10 mm and at residence time of 1 hour. Figure 2 shows the average of product gas produced from each run for the three experiments and 8 runs from each experiment.

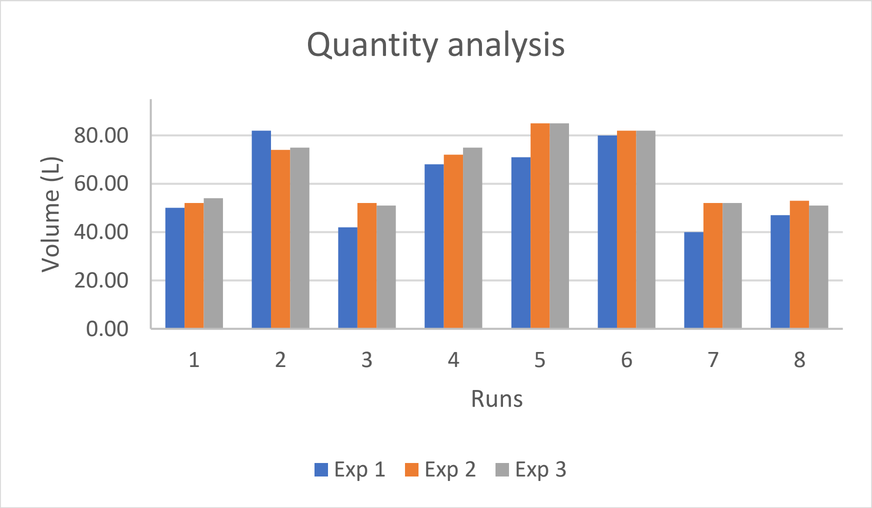

Fig.2. Quantitative analysis of coal representing 3 experiments and 8 runs

Fig. 3. LHV of product gas from the fixed bed reactor

Thermal energy calculations

Within specified operating conditions presented in table 2, the product gas is produced in the presence of a gasification medium (oxygen and steam) during the gasification process. From the (Federal Energy Regulatory Commission, 1980) [9] relationship between the lower heating value of a fuel and the higher heating value of that fuel is:

$$LHV = HHV - 10.55(W + 9H) \quad (5)$$

where:
LHV = lower heating value of fuel in Btu/lb.,
HHV = higher heating value of fuel in Btu/lb.,
W = Weight % of moisture in fuel, and
H = Weight % of hydrogen in fuel.

Short chain hydrocarbons that occur in gaseous phases such as ethylene, benzene and toluene increase the heating value of coal to improve its combustion properties.

Research by Ponzio (2008) [10] states that LHV of syngas is calculated based on the composition of combustible gas components; CO, CH_4 and H_2. Table 6 illustrates heat technical characteristics of these combustible gases.

Table 6

Heat technical characteristics of combustible gases (Engineering Toolbox, 2003)

Gas	Molar mass M (g/mol)	Density ρ (kg/m^3)	Gross heating value (HHV) Q_s (MJ/Nm^3)	Net heating value (LHV) Q_i (MJ/Nm^3)
CO	28.010	1.250	12.64	12.64
H_2	2.016	0.090	12.77	10.76
CH_4	16.042	0.717	39.85	35.80
C_2H_6	30.068	1.356	70.42	64.35
C_3H_8	44.094	2.019	101.82	93.57
C_4H_{10}	58.120	2.590	134.02	123.55

The combustible components found in synthetic product gases are CO, CH_4, H_2 and unsaturated hydrocarbon while non-combustible components include N_2, CO_2, O_2, H_2O and SO_x. Calorific value is defined as the heat released by complete combustion of fuel, without condensation of water vapor in the combustion gases – LHV.

For gaseous fuel, the calorific value of the fuel (Q_{tot}) is given by equation below:

$$Q_{tot} = \sum_i \varphi_i \cdot Q_i \left(\frac{MJ}{Nm^3}\right) \quad (6)$$

Where Q_{tot} is the calorific value of the syngas, φ_i is the volume fraction of each gas and Q_i is the LHV for each gas component in the syngas.

Sample calculation is as follows:

$$Q_{tot} = 12.64\varphi_{CO} + 10.76\varphi_{H_2} + 35.80\varphi_{CH_4} + 59.52\varphi_{C_2H_4} + 64.35\varphi_{C_2H_6} + 93.57\varphi_{C_3H_8} + 123.55\varphi_{C_4H_{10}} \,(\mathrm{MJ/Nm^3}) \quad (7)$$

By dividing with the density of each component the lower heating value becomes 41.9163 MJ/kg. Gases detected from Mabesekwa coal product gas are CO, H_2, CH_4 and CO_2. This results in the LHV estimation as:

$$Q_i = 12.64\varphi_{CO} + 10.76\varphi_{H_2} + 35.80\varphi_{CH_4} = 59.20 \text{ MJ/Nm}^3 \quad (8)$$

CO_2 is non-combustible; therefore, it is not included in the LHV calculations. Compared to results where air was used as an agent, oxygen-based environment produces less percentage nitrogen in the gasification process because air composition has nitrogen as an element.

Table 6

Calorific value calculations for gases produced during gasification process

Gas	M (g/mol)	ρ (kg/m^3)	V (m^3)	x	HHV (MJ/Nm^3)	LHV (MJ/Nm^3)	
					Q_s	Q_i	Q_{LHV}
CO	28.01	1.25	22.41	0.33	12.64	12.64	4.22
H_2	2.02	0.09	22.40	0.33	12.77	10.76	3.59
CH_4	16.04	0.72	22.37	0.33	39.85	35.80	11.92
		Total Vol	**67.18**			Q_{tot}	**19.73**

From table 6 calorific value of the product gas in this study is 19.73 MJ/Nm^3 after substituting volume fractions using equation (8).

Gasification efficiency

The gasification efficiency is explained as the ratio of energy content of synthesis gas (LHV) to energy content of fuel (HHV). It is computed as below:

$$\eta_{gasification} = \frac{Y_{gas} LHV_{syngas}}{LHV_{fuel} + \frac{h_{agent} V_{agent}}{m_{fuel}}} \quad (9)$$

Where Y_{gas} is the gas yield; LHV_{fuel} is the general heating value of the fuel in MJ/kg. This can be applied in calculating heating value for coal product gas; h_{agent} is the latent and sensible heat in the agent in MJ/Nm^3; V_{agent} is the volume flow of agent in Nm^3/h and m_{fuel} is the mass flow of fuel in kg_{fuel}/h [10].

Limitations

There are limitations in operation of the fixed bed gasifier. Coal is fed before preheating the gasifier; to discharge in preparation for the next run, the reactor is opened to remove ash/coal left after a run. There are no flowmeters in the syngas exit line, and steam and oxygen feed lines. Pilot plant requires frequent disassembling and reassembling when feeding and discharging which may temper with settings and the equipment seals.

Gasifier problems reside in uncontrolled fluctuation of coal/oxygen, unstable and slow heating of the induction coil and syngas leakage. Smooth feeding is an essential part in all chemical reactions, and it is important in coal gasification by maintaining good feed ratios for consistent product quality. The reactor flange is frequently reassembled inherently posing the possibility of loosening and eventual leakage with time. Syngas composes of CO and H_2 which are both combustible and can easily to ignite with atmospheric oxygen in the cases of loss joints and syngas leakage.

Optimization and cube plots in factorial design could not be achieved due to limitations in variations of parameters. Only two levels per factor could be achieved.

4. Conclusions

Botswana coal is preferable for application in gasification process as it produces better syngas yield compared to caking high rank bituminous coals, therefore our coals from Mabesekwa and Masama, qualify for gasification based on the obtained results and the discussions that followed.Residence time has a greater impact on the amount of gas produced in thegasification process.

Increasing the residence time by 1 hour will increase the yield by 6.46 L. Granulation provides more surface area for the heat to act on the coal samples while residence time allows for the heat to work on these bonds. Temperature has a smaller and positive coefficient which means temperature has a significant and positive impact on the quantity of gas produced. Increasing the temperature by 1°C will increase the yield by 1.4 L while increasing granulation by 1 will lower the yield by 9 L.

1 kg of Botswana coal produces 3.14×10^{-2} m^3 of raw synthetic gas while in China a typical raw gas analysis of 1 kg of coal yields 3.27×10^{-2} m^3 volume of gas [11].

Table 7

Quantities of product gas from different countries

Country	Gas quantity (Nm^3/kg)	Reference
China	0.033	[11]
Indonesia	0.001	[12]
South Africa	0.153	[13]*
Botswana	0.031	

*South Africa's Sasol Lurgi Fixed Bed Gasifiers have the capacity to operate at 30 bar pressure which takes its production two orders of magnitude above lab scale plants that they are compared with.

LHV for producer gas from BIUST was calculated to be at least 28 MJ/kg based on the gas composition. The Russian black coal LHV is approximately 25 MJ/kg, which is a factor 1.8 lower than the heating value of petroleum and natural gas [14]. Swedish and Colombian coals have LHV and HHV of 27.99 and 32 MJ/kg, respectively [10, 15]. Botswana coal syngas falls within the defined coal syngas quality according to [8] with LHV range of 10 and 28 MJ/kg.

Table 8

Comparison of Lower Heating Values for different countries producing syngas

Country	LHV (MJ/kg)	Reference
Russia	25.00	[14]
Sweden	27.99	[10]
Colombia	32.00	[15]
Botswana	30.95	

Botswana coal produces a good quality syngas with a high concentration of methane which contributes to high heating value of the gas. This coal can be concentrated first for higher gas yield. Syngas from Botswana coal can be used, as in South Africa, for gasification to produce synthetic gas. This gas will then be a chemical feedstock to many chemical engineering productions, e.g., methanol, alcohols, olefines, power generation.

Table 9

Gas composition analysis of Botswana compared with other countries.

	Volume fraction (%)				
Country	**H_2**	**CO**	**CO_2**	**CH_4**	**Reference**
China	30.0	60.0	5.0	-	[16]
South Africa	58.0	29.0	1.0	11.0	[17]
Indonesia	34.9	47.3	13.3	2.2	[12]
Botswana	23.6	9.0	13.0	54.3	

The obtained gas has a competitive heating value with other countries that are advanced in coal gasification technologies. This gas can be used as fuel or as a chemical feedstock in the chemical and process industry. Operations of the presented technology of coal gasification has been applied in a proof-of-concept plant for a national fund. There is a plan to fully commercialize this process to increase supply of electricity from local sources upon the success of the pilot plant.

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ECONOMIC FEASIBILITY AND ENVIRONMENTAL SUSTAINABILITY ASSESSMENT OF BIOGAS USE AS A SOURCE OF ENERGY FOR RURAL COMMUNITIES IN ZIMBABWE

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Abstract

This study reviewed and assessed the economic feasibility and environmental sustainability of biogas use as a source of energy for rural communities in Zimbabwe. Literature including published literature on the production of biogas from cow dung and national livestock assessment were reviewed. The average annual cattle population is at 5 million producing and an average of 8 cattle per household. The biogas digesters sizes of between 4 -13 m3 are suitable for household energy supply, installed at a total cost between USD 900 and USD 1800. The major available feedstock amongst rural communities is cow dung with a biogas yield estimated at 0,04m3 per kg giving a gas production 438,730, 1095 and 1600 m3/year of biogas daily from a substrate feed rate of 30, 50 ,75 and 110 kg for the 4, 6, 9 and 13 m3 respectively. The financial analysis indicated that the LOCE for the digesters are 0.11, 0.07, 0.05 and 0.03 USD/kWh for the 4, 6, 9 and 13 m3 respectively. Above the 4 m3 digester, the biogas digester provides a better cost per kWh against a grid tariff of 0.10 USD/kWh for grid electricity. Total amount of CO2 emissions per annum from the 6 m3 biogas system is1,374.35 kgCO2. Study findings indicated biogas as economically feasible and environmentally friendly option for rural energy supply.

Keywords: anaerobic digestion, biogas, greenhouse gases, global warming potential

1. Introduction

Globally, climate change has been identified as one of the key challenges hindering the attainment of sustainable development goals especially in developing countries [1]. The impacts of climate change have reduced the progress made by countries in sustainable development [2]. The Paris Agreement aims at reducing global temperature rise to below 2 $^{\circ}$C with the aim of keeping it below 1.5 $^{\circ}$C to

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reduce the impacts of climate change [3]. For countries to meet the global commitment under the Paris agreement, the rapid deployment of sustainable engineering practices is imperative. Green technologies that mitigate climate change by reducing emissions are at the center of the development agenda. According to the Paris agreement Article 14, countries shall develop national commitments for both mitigation and adaptation under the nationally determined contributions (NDCs) as parties to the accord [4]. Anaerobic Digestion (AD) has been identified as a sustainable energy technology to drive energy access, reduce deforestation and improve quality of life by reducing indoor pollution in rural areas. Anaerobic digestion refers to the biochemical conversion of organic matter in the absence of oxygen to produce a combustible gas (biogas) and digestate. The biogas from AD is composed of 53-70% methane, 30-50 % carbon dioxide and other trace elements including water vapor (5-10%), hydrogen sulphide (0-20.000 ppm), siloxanes (<0.008 -0.5 mg/g-dry), nitrogen (2-6%) and other hydrocarbons. The methane quality depends on the organic fraction reduction in the anaerobic reaction. and carbon [5]. Biogas has an energy content of 9 kWh/m^3 compared to liquefied petroleum gas (LPG) of 12.8 kWh/m^3 [6].

National statistics indicate that 60.7% use firewood as the main source of energy for cooking and 38.7% use clean energy services including electricity, biogas, LP gas and ethanol for cooking with other additional energy sources available include coal and charcoal and dried animal dug that is used by 0.5%. The projected continued reliance on firewood as a source of energy in the foreseeable future in rural areas requires urgent solutions. Such strategies include the deployment of AD systems, which uses animal waste and agricultural residues as feedstock. This study assessed the economic feasibility and environmental sustainability of the deployment AD systems in rural communities in Zimbabwe.

Biogas production depends upon the operating temperature range, the mesophilic (20 -45°C) and thermophilic (50- 70°C), pH range of between 6.8 and 7.2, Carbon to Nitrogen ration of the biomass feedstock of between 20 and 30, organic loading rate, hydraulic retention time, total solids, substrate quality etc. The adopted operating range for rural AD in Zimbabwe is the mesophilic range. Despite its lower gas production compared to thermophilic, it is cost effective at lower sizes as it does not require additional heating and temperature control. The digestion process involves a series of chemical reaction including hydrolysis, acidogenesis and methanogenesis propagated in a controlled environment within optimum pH and temperature parameters.

Various designs are available for production of biogas digesters. The ministry of energy and power development in Zimbabwe and the Rural Electrification fund have adopted the modified CARMATEC biogas digester model for adoption in Zimbabwe. The adoption was based on a cost benefit analysis with an emphasis on the use of locally available materials for construction of digesters.

The design of biogas systems includes assessing the energy demand, availability of feedstock, sizing of a digester based on the quantity of energy demand and available feedstock, retention time of the specific organic matter. The determination of the sizes of digester suitable for household energy supply thus is based on the availability of feedstock that meets the minimum energy requirements. Economic feasibility of biogas digesters is based on the CARMATEC design and identifies the material requirements for the 4 -20 m^3 digesters. Costing is based on the bill of quantities, labor and other legislative requirements for biogas development as well as the levelized cost of energy (LOCE) of the energy generated. The LOCE is a financial parameter that measures the cost of electricity or energy generation over the lifetime of the project. The parameters can be used to compare energy generated by biogas digesters against other alternatives such as the grid, solar PV and diesel generation in USD/kWh.

2. Modelling

The study assessed the economic feasibility and environmental sustainability of deploying AD systems to provide rural household with energy. The cost of establishing a $4m^3$, $6m^3$, $13m^3$, and $20m^3$ household AD system together with the associated operating costs were estimated and evaluated against the amount that could be used to purchase equivalent power generated from the biogas produced to determine the simple payback period. The environmental sustainability assessment was based on the emission that came from the use of biogas against the use of firewood. The size of the digester, which is the digester volume V_d, is determined using the daily substrate available for input for digestion S_d and the chosen retention time RT of the specific substrate as shown in Equation 1. Hydraulic Retention time defines the period required for the organic substrate to be fully fermented in the anaerobic digester. The retention time of the process is determined at a specific digestion temperature and the digestion process can be defined as thermophilic (50 - 70 ^oC) and mesophilic processes (20-45 ^oC)

$$\boldsymbol{Vd = Sd * RT\ [\,m3 = \frac{m3}{day} X\ number\ of\ days]} \qquad (1)$$

Sources of feedstocks for rural AD system in Zimbabwe

The two major probable AD feedstocks in Zimbabwe are cow dung and maize crop residues. The communal cattle herd per household has decreased over the last 20 years due to increased pressure on the limited availability of grazing land, prevalent of livestock diseases and erratic rainfall patens due to climate change. Communal household now have between 4 – 25 cattle per household with an average herd of 8 per Household[7]. Which is a national agriculture sector census with the national beef herd reported to have increased to 5 509 983 in 2021 from 5 478 648 in 2020[8]. Zimbabwe has an average cattle population of 5 million for the period 2012 -2021.

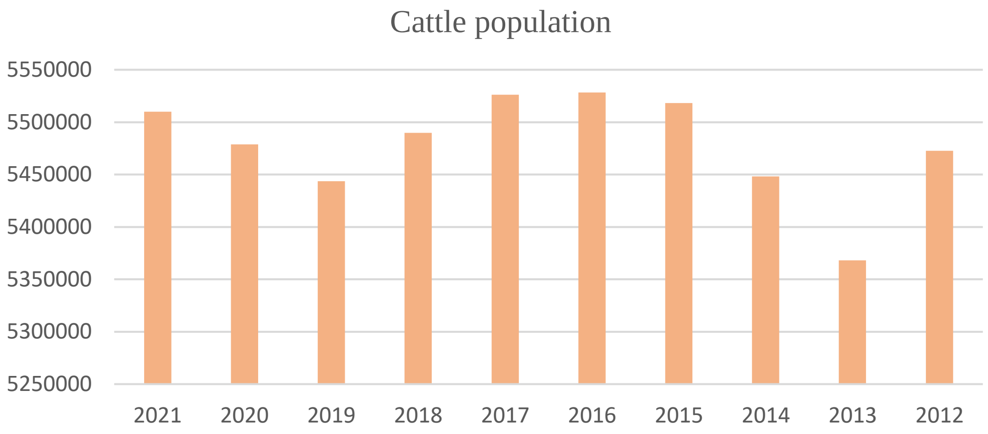

Fig. 1. Cattle head population in Zimbabwe

Using the available organic waste and a water to dung ratio of 1:1 for the modified CARMATEC Design (MCD)

Table 1

Biogas Digester sizing

Plant size(m^3)	**MCD**					**SSD**				
	Cattle		**Dung per day (Kg)**	**H_2O (litre)**	**Daily gas production (m^3)**	**Cattle**		**dung per day (Kg)**	**H_2O (litre)**	**Daily gas production (m^3)**
	Full stable bound	**Half stable bound**				**Full stable bound**	**Half stable bound**			
4	**02.apr**	**06.dec**	**20-40**	**20-40**	**0.8-1.6**					
	(Av 3)	(Av 9)	(Av 30)	(Av 30)	(Av 1.2)					
6	**04.iun**	**dec.18**	**40-60**	**40-60**	**1.6-2.4**	**06.oct**	**18-30**	**60-100**	**16-24**	**2.4-3.6**
	(Av 5)	(Av 15)	(Av 50)	(Av 50)	(Av 2.0)	(Av 8)	(Av 24)	(Av 80)	(Av 20)	(Av 3)
9	**06.sept**	**18-27**	**60-90**	**60-90**	**2.4-3.6**	**oct.14**	**30-42**	**100-140**	**24-36**	**3.6-5.4**
	(Av 7)	(Av 21)	(Av 75)	(Av 75)	(Av 3.0)	(Av 12)	(Av 36)	(Av 120)	(Av 30)	(Av 4.5)
13	**sept.13**	**27-39**	**90-130**	**90-130**	**3.6-5.2**	**14-20**	**42-60**	**140-200**	**36-52**	**5.4-7.8**
	(Av 11)	(Av 33)	(AV 110)	(AV 110)	(Av 4.4)	(Av 17)	(Av 51)	(Av 176)	(Av 44)	(Av 6.6)

Financial and economic feasibility

The study assessed financial and economic feasibility of household biogas digesters as a substitute for grid electricity, LPG and fuel wool used for cooking in rural households. The evaluation is done based on the gas production of a 4 - 13 m^3 digesters. The most common size, the 6 m^3 biogas digester, which is also the smallest unit to supply adequate gas for a household of 8 people. An average family requires 465 m^3 of biogas per year and the unit produces 730 m^3 per year.

The considered design and installation for this assessment is the fixed dome biogas design constructed from brick and mortar. Other prefabricated designs can be used such as high- density polyethylene (HDPE), Teflon, acrylonitrile butadiene styrene and fiber reinforced plastic. The choice of material in the study was based on durability, availability of material, low carbon footprint. The cost of construction per m^3 reduces as the volume increases. The major economic parameter analyzed is the Levelized cost of energy (LOCE). The LOCE determines the cost of energy generation over the life of the project and was calculated using equation 2.

$$LCOE = \Sigma\,[(It + Mt + Ft) / (1 + r)t] / \Sigma[(Et/(1 + r)t] \qquad (2)$$

Where **It** is the Investment Cost / Capex, **Mt** is the maintenance and operations expenditure, **F** is the fuel expenditures if applicable, **E**t is the energy generated, **r** being the discount rate.

Table 2

Biogas digester technical and financial parameters

Parameters	4 m^3	6 m^3	9 m^3	13 m^3
Amount of Fresh Dung (kg)	10950	18250	27375	40150
Amount of Dry matter (76%) (kg)	8322	13870	20805	30514
Biogas produced (m3)	438	730	1095	1606
Energy value MJ (	10512	1440	2160	5568
Thermal energy (kWh)	2628	4380	6570	9636
Energy over 25 Years (kWh)	65700	109500	164500	240900
Capex USD	900	1200	1400	1800
OPEX	240	240	240	240
Capex + 25year CAPEX	6900	7200	7400	7800
LOCE (USD/KWh)	0.11	0.07	0.05	0.03

Environmental Sustainability Assessment

Zimbabwe's revised nationally determined contributions (NDC) commit to a reduction of GHG emissions form the energy sector. A 33% reduction of GHG emission from the 2017 business as usual scenario. The deployment of biogas technology is expected to reduce reliance of energy from the grid and replacement of fossil fuel use. Anaerobic digestion has shown potential to meet the sustainable engineering approach to rural energy development. The major environmental management potential from AD in rural areas is in the replacement of emissions from electricity and fuel wood as domestic fuel supply. In addition, emission reduction of deforestation rate in rural areas reducing the much-needed carbon sinks in climate change mitigation.

Emissions from firewood

The average monthly consumption of biogas for rural household is 3.2kg/capita/day [8]. A rural Zimbabwean household is estimated to have an average of 5 people. The annual average wood biomass consumption per household is calculated as follows.

$$W_{yr} = Q_w * N_p * 365 = 3.2kg/capita/day * 5 * 365 = 5840kg \tag{3}$$

Where W_{yr} is the estimated average amount of wood used per household per year, Q_w is the daily consumption per capita of the wood and N_p the number of people per household.

Emission of GHG from use of wood fuel per annum using an emission factor of 1.73 kg CO_2 per kg of firewood gives total GHG emission of 10,103.2 kg CO_2e per year for each household.

Biogas systems reduces the amount of methane emitted during the storage of animal waste which has a 21 times carbon dioxide equivalence once emitted in the atmosphere. A cow is estimated to produce about 10kg manure per day hence the emission per kg of manure per day is 1.29kg CO_{2e}. Assuming the biogas cow dung feeding rate of 50 kg per day gives an annual feeding rate of 18,250 kg after multiplying daily feed rate by the number of days in an annum.

$$E_{cd} = 18{,}250 * 1.29 = 23{,}500kgCO_2 \tag{4}$$

Where E_{cd} are the annual emissions that would be generated from the cow dung that is fed into a 6 cubic m biogas digester.

Biogas production from cow dung is estimated at 0,04m^3/kg of cow dung. The annual production of biogas (G) in m^3 from the biogas digester is calculated as follows

$$G = 18{,}250 * 0{,}04 = 730\ m^3 \tag{5}$$

Biogas from cow dung is estimated to be constituted by 58% CH_4 and 42% CO_2 on a volume basis hence the mass of methane $M_{methane}$ and that of M_{CO2} in the biogas are calculated as follows using their densities. Density of methane is 0,657kg/m^3 and that of CO_2 is 1,98kg/m^3.

$$M_{methane} = 0{,}58 * 730 * 0{,}66 = 279\ kg \tag{6}$$

$$M_{CO2} = 0{,}42 * 1460 * 1{,}98 = 607.10\ kg \tag{7}$$

From equation 7, 1 mole of CH_4 produces 1 mole of CO_2

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{8}$$

The molecular mass of CH_4 is 16 hence the number of moles of methane in the biogas n_{ch4} is calculated as follows

$$n_{ch4} = \frac{279*1000}{16} = 17{,}437.50\ moles \tag{9}$$

These are the same number of moles of CO2 produced hence the mass of CO2 produced from burning methane in biogas produced (M) is given by

$$M = \frac{17{,}437.50*44}{1000} = 767.25\ kg \tag{10}$$

Total amount of CO_2 emissions per annum from the biogas system is

$$m = M_{co2} + M = 607.10\ kg + 767.25\ kg = 1{,}374.35\ kgCO2 \tag{11}$$

The difference between Ecd and m is 22,168.50 kgCO_2

3. Results and discussions

The capital together with operating costs for the different biogas systems assessed ranged between USD 900 and USD 1800. The major available feedstock amongst rural communities is cow dung with a biogas yield estimated at 0,04m^3 per kg giving a gas production 438,730, 1095 and 1600 m^3/year of biogas daily from a substrate feed rate of 30, 50 ,75 and 110 kg for the 4, 6, 9 and 13 m^3 respectively. The gas production for the 4 m^3 is below the energy demand for households of 465 m^3 per year. The 6 m^3 was therefore recommended as the minimum digester size for rural household. The financial analysis indicated that the LOCE for the digesters are 0.11, 0.07, 0.05 and 0.03 USD/kWh for the 4, 6, 9 and 13 m^3 respectively. Above the 4 m^3 digester, the biogas digester provides a better cost per kWh against a grid tariff of 0.10 USD/kWh for grid electricity. The agricultural crop residues and food waste are the other potential feedstock for possible co-digestion that could improve the AD process stability and biogas yield[9]**.** However agricultural crop residues are mainly available during the harvesting period after the rain season. Simple pay back periods of between one year and two years were estimated. The use of biogas for heating and cooking gives almost 99% emissions reduction.

4. Conclusions

Biogas use for cooking and heating in Zimbabwe rural households brings about environmental together with human health benefits considering the reduction in emissions and less than two years payback period. However, the estimated installation and operating costs are way beyond the reach of majority of rural households hence the need for financing strategies to be in place.

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COAL UTILIZATION TRENDS AND OPTIONS FOR CLEAN COAL TECHNOLOGY IN ZIMBABWE

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Abstract

The coal reserves in Zimbabwe are assessed and subsequent coal utilization trends are explored. Zimbabwe revised NDC (Nationally Determined Contribution) has been expanded to include emissions reduction in industrial processes and product use, from an initial emission reduction in the energy sector only. The NDC aims to reduce greenhouse gas (GHG) emissions by 40% per capita compared to business as usual by 2030 and though laudable, this target may be a challenge for a developing nation like Zimbabwe where coal remains a major player in the energy profile. In 2020, bituminous and anthracite ranked coals were estimated to be 502 million tons and have been exploited for export and for local use in power generation and in industrial and manufacturing processes, generating up to US$9.03 million. Coal is a readily available and cheap resource, and it is difficult for countries rich in this resource to refrain from exploiting it. It is against this background that this paper explores coal utilization trends in Zimbabwe while suggesting viable options for clean coal technology (CCT) in an effort to meet the pledged emission reduction targets. Of particular interest for Zimbabwe are high-efficiency combustion, CO_2 capture and utilization and flue gas cleaning technologies as they are related to coal utilization trends in Zimbabwe.

Key words: clean coal technology, coal utilization, emissions reduction, Zimbabwe

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1. Introduction

Coal has been a major source of energy for 1000 years BC [10]. In the 18th century, coal was already dominating as the major source of energy surpassing other sources like wood and charcoal and this was attributed to its high calorific value aiding more heat output and better performance. As technology advancement has gradually gained momentum in line with green fuel technology and renewable energy, there are efforts aiming at reducing emissions related to carbon in the form of CO_2. According to the International Atomic Energy Agency (IAEA) bulletin of September 2020 [38] on Nuclear Power and the Clean Energy Transition, it was revealed that nuclear power was gaining momentum in low carbon electricity generation ranging up to one third in the world. Such alternative sources of energy have resulted in a slight decline in the utilization of coal even though it remains the second largest source of energy worldwide until 2030-2040 as predicted by the Energy Information Administration [9].

Coal is the most abundant fossil fuel in the world, with recoverable reserves in over 70 countries worldwide, and currently provides the cheapest and most convenient source of carbon [12]. In addition, coal has a higher reserve to production ratio compared to natural gas and oil, which are at 55 and 53 respectively, approximately half of the global coal reserve to production ratio which is at 115 years (BP, 2014). Africa is estimated to hold about 3.7% of world reserves and Zimbabwe is reported to hold 553 million short tons of recoverable anthracite and bituminous ranked coals [9]. At current consumption rates, Zimbabwe is estimated to have a reserve-to-production ratio of 315 years [22]. With more coal reserves being discovered and advancements in mining techniques that make previously inaccessible resources economically viable, the current reserve-to-production ratios can potentially be extended.

From the 18th century, coal was used primarily in the iron and steel industry, in locomotives for transport, and for household heat. From the discovery of electricity in the 19th century, coal became the primary source of energy in electricity generation and remains a major player in the electric power matrix in the 21st century.

In this century, coal remains useful in iron and steel production and has also found use in cement and chemical industries. In the steel industry, coal is the source of metallurgical coke which is one of the vital raw materials in blast furnace operations in which iron ore is smelted to produce molten iron. In cement manufacture, coal is the primary source of energy and the by-products such as fly ash from coal combustion is useful in enhancing the properties of cement [26]. The fly ash from coal contributes to improved workability, increased compressive strength, and reduced hydration of cement. In other industrial processes such as in the manufacture of ferroalloys and nonferrous metals such as aluminum, lime and in brick production, coal is also used as a primary energy source, particularly in the production of steam.

Coal is also a source of feedstock for carbon-related materials that can be derived from it such as activated carbon which is used in air and water treatment alongside oils, tar, plastics, and pharmaceutical products. Advances in technology have seen emerging innovations to the functionality of coal allowing for liquefaction to make synthetic fuels similar to petroleum or diesel [27].

Coal uses are influenced by its quality, that is, from low-rank coals that are characterized by high ash and volatiles to high-ranking coal with low ash and low volatiles.

Zimbabwe consumes about 2.9 million tons of coal annually, in power generation (60% of the total consumption) and in the manufacturing and processing industry (30%). Only 10% is used as coking coal in the iron and steel industry. Even though this is a small fraction compared to other major global coal producers, the contribution to greenhouse gas (GHG) emissions is quite significant. As the country has a lot of fossil fuel-based technologies in power generation and in the processing and manufacturing industry Zimbabwe has to explore options for clean coal technologies if it is to meet the revised nationally determined contribution (NDC) target of a 40% reduction in emission by 2030.

The global increase in clean coal utilization is a result of more environmental awareness and concerns regarding energy supply and global energy prices with many countries aiming to achieve energy security and stability. The development of clean coal technology (CCT) in the world has been focused on improving combustion efficiency and emissions reductions [22]. An increase in environmental awareness has prompted countries across the globe to put more stringent regulations on emissions in coal-utilizing industries, including power generation sectors since parties are required to meet their NDC targets as stated in the Paris Agreement. Research and development in advanced combustion technology not only increased efficiency in thermal fired power generation but significantly lowered pollutant emissions. Environmental control technology development aimed at lowering SO_x and NO_x with reduction efficiencies of over 95%.

The objective of this study is to explore viable options for CCT in line with the utilization trends of the country. The recommendations made in this review were derived from a desktop assessment of global trends in CCT with a comparative benchmark of various countries who are global leaders in terms of clean coal utilization. Maintaining a low cost of energy where there is an increase in demand requires the development of new technologies that can sustain socio-economic growth, as is the case in Zimbabwe. Coal utilization technology is constantly improving to cope with economic and environmental demands and Zimbabwe can potentially adopt some of the already tested and commercialized clean coal technologies.

2. Coal utilization trends in Zimbabwe

Coal utilization is defined as the combustion or conversion of coal into useful gaseous, liquids, or solids products. Utilization is dependent on the quality and properties of the coal. As aforementioned, Zimbabwe utilizes coal mainly for power generation in several of its coal-fired power stations, in agriculture, and in the manufacturing and processing industry.

2.1 Power generation

According to a 2021 report by the International Renewable Energy Agency [39]. on Zimbabwe, in 2018 coal contributed 16% of the total primary energy supply while renewables contributed 72% and oil 12% as shown in figure 1.

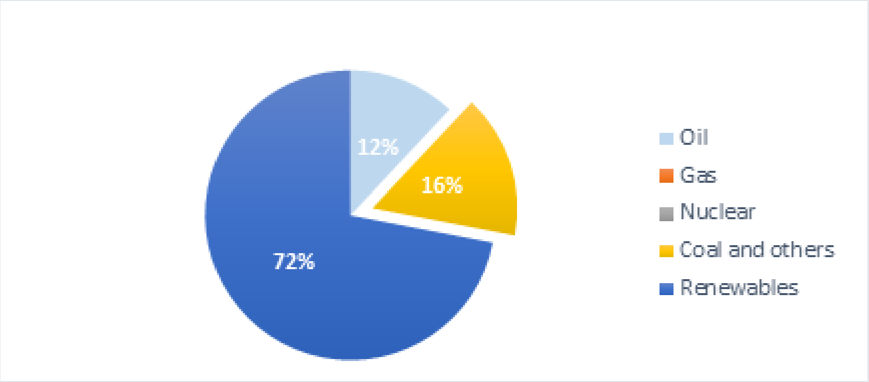

Fig. 1. Total primary energy supply in Zimbabwe [39]

The electricity supply industry is mainly dominated by state owned power entities, namely the Zimbabwe Power Company (ZPC) and the Zimbabwe Electricity Transmission and Distribution Company (ZETDC). Incorporated in 1996, ZPC has been in operation since 1999 focusing on electricity generation and supply. It has four coal fired power stations and one hydro power station. The hydro power station is located in Kariba and is guided under the statutory body called the Zambezi Regulatory Authority (ZRA) which emerged as a result of a coalition between Zimbabwe and Zambia. ZRA thus, regulates the water supply to Kariba South and Kariba North power stations in Zimbabwe and Zambia respectively. Kariba South power station after undergoing a series of renovations and upgrades is labeled the biggest power generating plant in the country with a capacity of

1050MW. The other four coal fired power stations are located in Harare, Hwange, Munyati and Bulawayo. While ZPC is responsible for power generation, ZETDC on the contrary manages the logistics in the supply of electricity through the system/network operator function. ZPC is licensed with the Zimbabwe Energy Regulatory Authority (ZERA) along with other independent players. Among the independent power generating companies is Zimbabwe Zhongxin Electrical Energy (Private) Limited aimed at generating electricity from coal [35].

2.1.1 Harare Power Station

Located in the Workington area of Harare, the power station is one of the coal fired power stations in Zimbabwe with generation currently rated at 11MW according to ZPC generation statistics as of September 2022. It comprises 3 stations: Station 1 commissioned in 1942, Station 2 commissioned in 1955 and Station 3. Station 1 had a capacity of 21MW when it was commissioned but was decommissioned in 1970. Station 2 initially had a capacity of 75MW when it was commissioned consisting of nine chain-grate boilers and six turbo-alternators. It was however de-rated to 20MW due to uneconomical units which facilitated the decommissioning of five boilers and three turbo-alternators. Station 3 comprises pulverized fuel-fired boilers and two large turbo-alternator machines each with a capacity of 30MW adding up to give a total capacity of 60MW [40].

2.1.2 Hwange Power Station

Hwange Power Station is the largest coal-fired power station in the country and rated 14th largest thermal station in the Southern African region having 920MW installed capacity. It is located in the Northwestern, part of Zimbabwe adjacent to Hwange Colliery Open Cast Mine. With the envisaged expansion works through the construction of a 600 MW coal fired thermal power plant under Hwange 7 and 8 expansions currently underway, the station is expected to increase its capacity from 920MW to 1520MW. The station consists of three staged units; the 4 x 120 MW unit commissioned between 1983 and 1986, the 2 x 220 MW unit commissioned between 1986 and 1987, and the envisaged upgrade of 2 x 300MW units which is yet to be commissioned upon completion. Coal is delivered to the station by a 6 km long overland conveyor belt from Hwange Colliery Company Limited (HCCL) and also by trucks from Makomo and Coalbrick mines. [43].

2.1.3 Bulawayo Power Station

Bulawayo Thermal Power Station is located in Zimbabwe’s second largest city, the city of Bulawayo. Commissioned between 1947 and 1957 the plant had initial capacity of 120MW later to be refurbished in 1999 to a capacity of 90MW. According to ZPC generation statistics reports the plant currently generates 14MW as of September 2022 [41].

2.1.4 Munyati Power Station

Munyati Power Station is located about five kilometers off the Harare-Bulawayo Road at the 183-kilometer peg. The plant was constructed in stages between 1946 and 1957 with initial capacity of 120MW but currently operates below 100MW. Coal which is the main raw material for the process is railed from Hwange Colliery, about 618 kilometers away. Water is harnessed from Sebakwe River through a 23-kilometer-long canal and the Munyati Weir through a 3-kilometer pipeline [42].

2.1.5 Zimbabwe Zhongxin Electrical Energy (Private) Limited

Zimbabwe Zhongxin Electrical Energy (ZZEE) is a subsidiary of the Zimbabwe ZhongXin Coking Company (ZZCC). The project is a joint venture between Qualisave Mineral Resources of Zimbabwe and Yuxia ZhongXin Coking Company of China. The plant is located approximately 10km west of Hwange Town in Matabeleland North Province. The establishment was set with a target of 6 x 50 MW units and started with construction of a 50 MW unit in 2019. Upon completion, the plant is expected to consume 0.3 Mega tons of coal for electricity generation [36, 37].

2.2 Agriculture

The agricultural sector is one of the main pillars that drives the economy of Zimbabwe with the weather being favorable for farming activities [15]. This sector has the potential of implementing the use of coal in fertilizer manufacture. Research done previously saw the benefits brought by availability of carbon in the soil [16]. Thus, further research is yet to be done to incorporate carbon use in fertilizers as bonding agent to the nutrients in order to introduce trace for organics to the soil which increases soil fertility.

2.3 Manufacturing and processing

The manufacturing and processing sector uses coal and or coal derived products in many instances. The major consumer of coal is the iron and steel industry where iron ore is reduced into molten cast iron in the blast furnace, which is further alloyed to produce steel. Steel industries in the international community are currently operating at nearly 100 percent capacity and research conducted on Zimbabwe steel industry performance showed that the capacity was well below the threshold ranging from 14 % to 60 % and giving an average of 3 1% [14]. However, there are positive developments being currently conducted in the country to foster industrialization. Located southwest of Chikomba district in Manhidze area is an emerging Iron and Steel works giant, the Dinson Iron and Steel Company (DISCO) which will incorporate the processing of iron ore into steel. Manhidze area has iron rich ore ranging from 45 to 55 percent grade. The project is envisaged to produce 1.2 million tons in the first phase of its operation and anticipated to be upgraded to reach 3 million tons in the later phases. This is an interesting development adding to the already existing iron and steel manufacturers alongside foundry industries. The processing of iron ore comprises three main raw materials which are: iron ore, limestone and coke which are subjected to high temperatures in blast furnaces. The iron ore consists of iron oxide among other elements like silica embedded in the ore in minute amounts. Limestone therefore behaves as a slag forming component with its function being the removal of the embedded impurities by slag formation. Limestone decomposes into quicklime which later reacts with the impurities. Coke on the other hand has unique physical and chemical properties which advocate for three major purposes: fuel source, permeable support and reducing agent. The coke is derived from coal and is not only used in the iron and steel industry but also in platinum and chromite reduction among other minerals.

3. Global Clean Coal Technologies

Globally, a lot of development and innovation has been made to make coal conversion more effective, efficient, safe and environmentally friendly. From simple combustion and pyrolysis to complex gasification and liquefaction processes [32], clean coal utilization aims to minimize the impact of coal use on the environment, especially in terms of GHG emissions. Continuing research and development on clean coal utilization globally is an indication of the inevitable use of coal in modern day industries and the near future.

CCT is a broad term used to describe technologies that focus on making coal use less polluting regarding GHG emissions [32] as well as oxides of nitrogen (NO_x) and sulphur (SO_x), mercury and particulate emissions. These technologies incorporate more efficient and ‘cleaner’ combustion, gasification, and liquefaction processes. Different combinations of these technologies are used globally, depending on the quality and characteristics of the coal. Different CCTs are used at different stages of coal use, including CO_2 capture and storage, high-efficiency (advanced) combustion technology, integrated gasification combined cycle technology, pollution control and reutilization and flue gas cleaning technologies. Leaders in CCT are Japan, the US and some EU countries with China quickly closing the gap as it is one of the global leaders in coal based electric power generation [19]. Each of these countries classify CCT differently according to its utilization trends.

3.1 Japan

Several researchers refer to Japan as having the most advanced CCT and the government of Japan has been promoting research and development in CCT since it is the second largest importer of coal [3]. Japan has classified its CCT into high – efficiency combustion technology, CO_2 recovery and utilization, flue gas cleaning technology and advanced gasification technology. Some new innovative technologies include novel integrated coal gasification combined cycle technology, chemical looping combustion and advanced ultra-super critical power generation technology that are still in development [11].

3.1.1 High -efficiency combustion

Of importance in the high-efficiency combustion technology class is the internal circulating fluidized bed combustor (ICFBC) which is an adaptation from the circulating fluidized bed technology of the US. The circulating fluidized bed is a very flexible technology offering an economic and efficient coal combustion process that lowers NO_x and SO_x emissions. The general operating principle of the circulating fluidized bed is that an inert substance, usually sand, is introduced into the bed whose primary function is to disperse fuel and distribute heat throughout the bed.

The operating principle of fluidized bed combustion is that a fuel, together with inert material (sand or ash), referred to as bed material and limestone are suspended in a combustion chamber due to air velocity. The purpose of the bed material is to disperse material throughout the bed, for uniform and efficient heat transfer as well as provision of enough resident time for complete combustion and other reactions taking place in the chamber [21].

In Japan, the internal circulating bed is divided into 2 compartments, a combustion chamber, and a heat recovery chamber. Circulation flow is created by the recycling of unburned fuel and unreacted limestone (which is the SO_2 sorbent). Silica sand is used as the inert bed material. Temperature control is essential to ensure that operating conditions inhibit NO_x formation. Advantages of the ICFBC are that different rank coals can be efficiently combusted, desulfurization efficiency can be as high as 90%, combustion efficiency is very high lowering NO_x formation, and the structure of the bed makes it easy to maintain [11].

3.1.2 CO_2 capture, storage and utilization

Although Japan is ranked top among countries that have significantly lowered GHG emissions, coal use is still the highest emitter of CO_2 compared to other fossil fuels. Power generation in coal fired stations is where most GHG are generated and even though the country is using high efficiency technology, there is still a need to capture, store and utilize CO_2. Carbon dioxide capture technologies can be classified into pre-combustion, oxy – fuel combustion and post combustion technologies.

Pre-combustion carbon capture is realized in the integrated gasification combined cycle (IGCC) and is the most advanced pre-combustion CO_2 capture technology to date. IGCC is a combination of coal gasification chemistry and the combined power cycle in electric power generation technology. In IGCC technology, coal gasification produces syngas at a high pressure followed by CO_2 enrichment in a shift reaction which occurs in the presence of a catalyst. The high pressure and an increase in carbon dioxide concentration acts as a driving force for the separation of CO_2. After the shift reaction, molar concentrations of H_2 and CO_2 increase to 55% and 40% respectively thus the higher partial pressure and chemical potential of CO_2 promotes separation and capture. Separation of carbon dioxide is done using physical absorption using a solvent. Removed CO_2 is dried, compressed and sequestered while the H_2 rich gas is fired for electricity regeneration [20]. Japan has optimized this technology by integrating the gasification process, air supply systems and the separation process in a bid to lower energy consumption [11]. IGCC offers high efficiency and produces less carbon dioxide per unit fuel compared to other systems at higher capital costs, however.

Oxy - fuel combustion entails the separation of air to remove nitrogen and combusting fuel using nearly pure oxygen to produce CO_2 and water vapor. The flue gas after removal of water vapor is mostly carbon dioxide [19] is subsequently purified and stored. Pulverized coal is normally used in oxy - fuel combustion with oxygen purity or between 95 to 99%. The oxygen which is normally from an integrated cryogenic ASU is mixed with about two thirds of the flue gas stream to maintain conditions similar to air fired boilers and for efficient heat transfer. Flue gas normally goes through a desulphurization process before recycling [21]. The advantage of oxy - fuel combustion technology is that it can be retrofitted into existing power plants.

Post combustion CO_2 capture is mostly used in manufacturing and processing industries. This technology involves physical/ chemical solvents, membranes, adsorption onto solids and cryogenic separation. Post combustion capture is not economically viable for processes with large gas volumes and low CO_2 concentration and as such, Japan has developed amine-based solvents with longer life cycles and lower regeneration energy requirements. Selectivity and permeability are key performance indicators for membrane separation processes which have limited industrial application for carbon capture because of low permeability [11]. Japan has since developed facilitated transport membranes with high carbon dioxide permeability and selectivity against N_2, a major post combustion gas component.

Storage is the final stage of carbon dioxide management where it remains stored or sequestered permanently. Because Japan is an earthquake prone island, available storage options such as geological formations is not viable and so it has leaned more towards utilization rather than storage after recovery. Recovered carbon dioxide is used in the production of methanol, dimethyl ether and kerosene or light oils.

3.1.3 *Flue gas cleaning*

The government of Japan has put in place very stringent laws that make flue gas cleaning necessary for industry and as such much research and development has been made towards economically viable gas cleaning technology. Limestone and gypsum-based systems and selective catalytic reduction are used for desulphurization and denitration respectively in pulverized - coal fired power plants. Efficiency of selective catalytic reduction (using metal catalysts such as vanadium and tungsten) is between 80 to 90% [11]. Because flue gases normally contain both SO_x and NO_x, effective reaction of NO_x with ammonia is affected by the presence of SO_x (because of catalyst poisoning/deactivation) Japan has developed a system enabling removal of both SO_x and NO_x simultaneously, namely active carbon adsorption process. In this process, ammonia is injected onto activated carbon and reacts with sulfur oxides to form NH_4HSO_4 allowing the remaining nitrogen oxides to be selectively reduced to nitrogen and water. The NH_4HSO_4 can be thermally desorbed to reuse the active carbon [11]. Ammonia can also be regenerated, and the sulfur oxides are used for sulphuric acid production.

For particulate cleaning, Japan was one of the pioneer countries to use electrostatic precipitators for collection of fine particles in coal fired power plants and this technology has since been adopted by many other countries [11].

3.2 The United States of America

The United States of America (US) is considered to be the global leader of CCT and has some of the most stringent environmental laws addressing coal use in particular. The Department of Energy (DOE) is committed to achieving near – zero emissions technology for coal fired power plants. The US is reported to have 275 billion short tons of recoverable coal reserves and acknowledges the role played by coal in meeting the energy demand required to sustain the economic growth in the country [23]. A 1984 energy policy allowed for a more balanced system in achieving energy security and stability, where fossil fuels played a key role in sustainable energy production, thus funds were channeled towards research and development in CCT [7]. Over 20 projects in the clean coal technology development program (CCTDP) between 1985 and 2006 reached commercialization [2]. CCT in the US can be classified into four groups: industrial application technology, advanced electric power generation, coal processing for clean fuels and environmental control. A few technologies in advanced electric power generation and environmental control classes will be reviewed.

3.2.1 Advanced electric power generation

The development of advanced electric power generation technologies puts emphasis on upgrading existing old power plants in terms of emissions control and the ability to meet the ever-increasing power demand. These systems can lower GHG emission by more than 20% and are characterized by reduced carbon dioxide emissions, enhanced economics, thermal efficiency and low pollutant emissions. They include fluidized bed combustion, IGCC, integral gasification fuel cell, and slagging combustion.

Fluidized bed combustion (FBC) is an advanced combustion technology which can be operated under high pressure or at atmospheric pressure. Atmospheric pressure operated fluidized beds include the bubbling fluidized bed (BFBC) and the circulating fluidized bed (CFBC), which was adopted and modified by Japan [11]. Similar circulating fluidized bed combustion technology was also adopted and commissioned in Poland in 2009, making it the largest hard coal fired (CFBC) power generation unit [34]. The high turbulence resulting from high gas velocity results in effective heat transfer and allows fuel particles to ignite rapidly thus lowering combustion temperature. The entire mass of solids is fluidized by the intense turbulence and operation temperatures are lowered to values where thermally induced production of NO_x is significantly inhibited. The sorbent added (limestone) reacts with SO_2 consequently removing sulfur pollutants from the flue gas. Operating conditions in the bed are such that it is thermodynamically and kinetically feasible to lower NO_x production and capture SO_2. A high-efficiency cyclone is used to recycle entrained solids back into the combustion chamber [30]. CFB can be cofired with biomass as a way of lowering carbon dioxide emissions [23].

Fluidized bed combustion can either be bubbling or circulating and they are distinguished by gas velocity. Circulating beds operate at much higher gas velocities and promote solids elutriation, unlike bubbling beds where gas velocity is lowered to avoid solids being carried over. Circulating beds, therefore, are favorable and are characterized by a refractory-lined solid separator (cyclone) for the recycling of entrained solids.

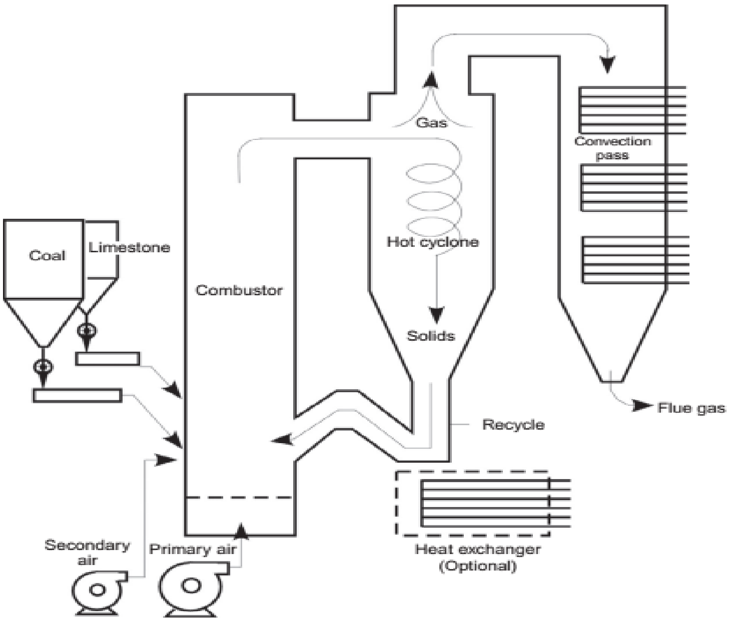

Fig. 2. Schematic Representation of a Circulating Fluidized Bed [22]

In pressurized FBC technology, elevated pressures result in a high gas pressure stream which can be used to drive gas turbines and the steam generated from the heat in the FBC can be further used in steam turbines creating an efficient combined cycle [23]. Good heat and temperature distribution and higher heat transfer rates makes both pressurized and atmospheric FBC technology ideal new generation clean coal technology. The US has successfully implemented the pressurized FBC in Ohio, where sulfur dioxide removal efficiency can be up to 90% [25] and in Colorado where old stoker boilers were replaced with atmospheric FBC technology where 99.9% removal efficiency has been recorded for SO_x, NO_x and CO_2 emissions [7].

3.2.2 Environmental control

Environmental control technologies in the US are concerned with the removal of SO_x, NO_x, CO_2 and particulate matter from flue gasses in power generating facilities in a cost-effective manner [8]. Developed SO_x capture technologies that reached commercialization are sorbent injection systems, advanced flue gas desulphurization technology and spray reactors with integrated sorbent particulate recycle, with desulphurization efficiencies of between 50 and 90% [21]

The simplest form of SO_x capture technology is the furnace sorbent injection system, which involves the injection of pulverized sorbent, calcium hydroxide or limestone into the upper part of the furnace to react with the flue gas. The sorbent is uniformly distributed through the entire cross section of the upper furnace where temperature ranges from between 760°C and 1300°C. Residence time for reaction is 1 to 2s. When calcium hydroxide is used as sorbent, a calcium to sulphur-in-the-flue-gas ratio of 2.0 is employed to achieve sulphur removal of 15 - 40% [21]. The calcium sulfate formed is collected with fly ash and unreacted sorbent in a particulate removal device integrated into the system downstream. When limestone is used, optimum injection temperatures are around 1100°C. Humidification increases SO_x capture to approximately 80% and can be achieved using hydrated lime as the sorbent. This may, however, result in scaling. The advantages of furnace sorbent injection technology are its simplicity, low capital cost and ease of operation and maintenance which makes it ideal for retrofitting into already existing power generation facilities [7].

Spray scrubbers are the most widely used duct injection technologies SO_x capture in coal - fired power generation facilities, especially in the western parts of the US. This technology was first introduced in 1981 and has been developed further to reach upto 50% sulfur dioxide removal. Lime or sodium carbonate is usually used as the sorbent. Slaked lime slurry is injected into the duct which should be long enough to allow for enough residence time for SO_x capture. The water in the slurry improves sulfur dioxide capture. Unreacted sorbent may react with carbon dioxide to form calcium carbonate. This technology is also fitted with particulate control devices that capture products of the sorbent and flue gas reactions, as well as fly ash and other particulate matter.

A modification to this technology is the atomization of the slurry, in a process known as confined zone desulphiration (CZD). In this case, the slurry is confined and allows for better SO_x capture because there is better mixing of the flue gas and the sorbent. CZD has the advantage of being more controllable, having adjustable water flow rates (for humidification purposes), low maintenance costs and higher reliability.

A combination of furnace and duct injection technologies are referred to as hybrid systems. These provide higher sulfur dioxide capture and better sorbent utilization [29]. Hybrid systems allow for different configurations in terms of the sorbent injection points and sodium compounds can also be used as sorbent. Humidification of flue gasses is possible in hybrid systems and gives higher SO_x capture efficiencies. Advantages of hybrid systems are that they have low capital and operational costs and can easily be retrofitted into existing power generation facilities as they do not require a lot of space [29].

It is difficult to remove or reduce nitrous oxides. Available technologies for NO_x capture in the US are based on combustion modification to suppress NO_x formation or post-combustion control, i.e. flue gas treatment. Commercialized NO_x capture technology includes low NO_x burners (LNB), selective catalytic reduction (SCR), and selective non catalytic reduction (SNCR), with several others still under study or in development. These technologies generally operate on the following principles; lowering peak flame temperature, lowering residence time at peak flame temperature, chemically reducing $NO_{x,}$ and using sorbents to revolve nitrogen. NO_x removal in these technologies vary between 30% and 80% [8].

In LNBs, there is rapid devolatilization of coal in a fuel rich but oxygen-starved environment producing NO. The production of NO_x is suppressed by the limited oxygen, and this results in a lower flame temperature. Hydrocarbon radicals then reduce the NO to nitrogen. More air is then added after primary combustion for the complete burning of coal where the flame temperature is still low enough to suppress the formation of NO_x [21]. This principle is referred to as staging oxygen and effectively reduces the production of NO_x in the combustion of coal.

3.3 China

China is one of the largest consumers of coal in the globe and with the increasing global environmental awareness and a drive towards zero emissions, it has made some great strides in CCT. Coal accounts for 64% of primary energy consumption, in power generation, industry and household heating and in energy intensive industries such as the cement and steel industries [4]. 83% of GHG emissions in China come from the direct combustion of coal [13] hence the need for clean coal utilization. CCT in China is divided into 5 main categories, according to Na and colleagues [5]; advanced power generation (high-efficiency combustion), coal conversion, pollution control and utilization, clean and efficient coal utilization and coal processing.

3.3.1 Advanced power generation (high efficiency combustion)

China's focus has been to replace old power generation technology with new generation technology with higher efficiency and lower pollutant emissions [4]. Optimization of the thermal power industry was done to meet a targeted 10% reduction in GHG emissions [4]. Supercritical and ultra-super critical coal fired power generation technology were developed, designed and fabricated in China, and optimized towards emissions reduction and energy saving. Supercritical power generation plants operate at much higher temperatures and pressure than subcritical plants. China developed alloys that can withstand these higher parameters, reportedly the highest supercritical operating parameters globally [4] with further development focusing on operating temperatures higher than 700℃. This robust technology, deemed high efficiency combustion, has since been exported to other countries.

China has coal resources with high sulfur content and has developed and designed the largest CFB power generation plant (600MW) in the world [4]. Considering CFB technology's wide range fuel scope, lower cost of desulphurization and low NO emissions, supercritical CFB designed in China is meant for high ash high sulfur coals found in China [3].

3.3.2 Pollution control

China has put in place strict regulation to control emissions from thermal power plants since 2004 which resulted in a significant reduction in GHG emissions [4]. Desulfurization technologies in China are similar to the globally commercialized technologies, including wet scrubbers, spray dry scrubber and sorbent injection technologies. The most used is the wet flue gas desulfurization technology which China has optimized and works on the principle of increased residence time and improved gas - liquid mixing. Wet flue gas desulphurization technology in China is optimized to remove particulate matter as a result of humidity eliminators integrated and because of the high liquid drop removal efficiency. SO_x emissions were lowered from 62.7% in 2005 to 38.4% in 2014, as reported by Xia and colleagues [31].

Denitrification is dependent on the coal type, combustion technology and the operating conditions. Commonly used denitrification technologies in China include LNB, SCR and SNCR. Air pollutants standards established in China in 2012 for thermal power plants resulted in 80% of power plants installing denitrification technology that can 95% denitrification [17]. Stricter regulations required more efficient denitrification technology which was done by increasing the amount of catalyst in the SCR which resulted in reduction efficiency of up to

90%. Flue gas reheating systems was also another modification used to further improve efficiency in SCR using vanadium - tungsten - titanium catalysts. It is difficult to meet the NO emission standard (below 50mg. Nm) [4] and so a combination of LNB and SCR technologies are integrated to control NO emissions and has since been proven to be both technically and economically viable.

Coal comes with trace heavy metal elements such arsenic, nickel, cobalt and mercury. Most mercury emissions come from the combustion of coal and are released as Hg^0 in flue gas. The removal of Hg^0 from flue gas has been the focus of research in China in recent years. Mercury removal is done through the injection of oxidizers such as ozone or halogens that transform Hg^0 to Hg^{2+} which can be removed from flue gases via WFGD technologies with efficiencies of between 40 and 90%. SCR can also capture $Hg^{2+}$with efficiencies of 89% when used in combination with WFGD [4].

4. Options for CCT in Zimbabwe

Zimbabwe is committed to meeting its GHG emissions reduction target and clean coal utilization is the first step towards attaining this goal. Most CCTs require huge capital investments but by implementing the US and China models, Zimbabwe can start by integrating some of the commercially available technologies in its thermal power plants and commissioning environmental control technologies that lower pollutant emissions. Japan, on the other hand, was able to adopt and modify some of the US technologies since the government had set aside funds for research and development into clean coal technologies, pushing Japan to be one of the most advanced countries globally, in terms of CCT. Despite the Zimbabwean government's commitment to lower GHG emissions by 40% per capita by 2030, the Japanese model for transition to CCT may not be economically possible for Zimbabwe.

According to Bezdek and Wendling, who evaluated the return on investment of the clean coal technology program in the US, the cumulative return on investment to the US DOE was favorable and continued to grow rapidly because of the reduction in environmental costs, capital, and technological cost savings by integrating CCT into already existing thermal power plants and an annual average of 60000 jobs created. ROI was estimated to be 13 [2].

China replaced old direct coal combustion technology with new generation technology in its power plants. It also shut down small-scale power plants and replaced them with larger thermal plants to meet the growing energy demands while introducing CCT [4].

While shutting down small power plants may not be economically viable for a developing nation with an electrical energy deficit, replacing old coal combustion technology with cleaner, more efficient technology is potentially feasible and will certainly lower operational costs. China, like the US, was able to develop, design and commercialize some CCTs that are exported to other countries and Zimbabwe can take advantage of commercially available technology for integration in local power plants and other coal-utilizing sectors.

4.1 Power generation

In its integration of CCT in existing power plants, Zimbabwe should focus on more pressing environmental concerns and the elimination of the electrical energy deficit. The Zimbabwean energy and power development minister lamented how power generation technology in Zimbabwe is basically obsolete [24] causing the massive electrical energy shortage Zimbabwe is facing. Advanced combustion technology would address the growing energy demand and environmental concerns simultaneously. Advanced combustion technology can serve to repower old thermal power plants that have the need to meet the growing energy load and lower pollutant emissions. Apart from a reduction in pollutant emissions of greater than 20%, [7], high thermal efficiency and low waste problems, advanced combustion offers enhanced economics [23]. Of the commercially available advanced combustion technology, Zimbabwe can adopt fluidized bed combustion technology for power generation.

As aforementioned in section 3.3.1, fluidized bed combustion technology can potentially lower cost, is more effective and is a cleaner form of coal utilization. It has a wide fuel scope, that is, even low-quality fuel can effectively be utilized in a fluidised bed.

Combustion efficiency can be defined as the ratio of heat released by fuel to heat input by fuel [23] and is affected by factors such as bed temperature, fuel type, gas velocity [28]. In new generation FBC technology, combustion efficiencies are higher even with low quality fuels which are sometimes co-fired with coal. Low combustion temperature and higher residence time results in a lower risk of the challenges associated with the use of lower quality fuel which are characterized by high ash and moisture content.

4.2 Pollution control

Environmental control is focused on the treatment of flue gasses to remove all pollutants. Flue gas treatment can be applied in power generation technology as well as other coal utilizing sectors. Flue gas treatment focuses on the control of SO_x, NO_x, CO_2 and particulate matter. Carbon dioxide capture can be pre- combustion, post combustion or through oxy - fuel combustion as alluded to earlier and are capital intensive. Challenges and barriers to commercial pre combustion capture in the form of IGCC technology are mainly due to cost associated with installation and extensive support systems required.

Although oxy - fuel technology is normally used in power generation, it is an effective means of pollution control. As explained earlier, pulverized coal is combusted in near pure oxygen to give a flue gas consisting of mainly carbon dioxide (about 89%) and water which is easily removed, and the carbon dioxide is purified for utilization or storage [23]. The advantages of oxy - fuel combustion technology for Zimbabwe is that it can be easily retrofitted into existing power plants because of its simplicity and can operate within the range of conditions of conventional power plants, i.e. air fired systems. Oxy - fuel combustion technology can potentially produce near zero emissions, which is what Zimbabwe needs to meet its NDG targets within the set time limits.

Another advantage of oxy-fuel combustion for Zimbabwe is that boiler and auxiliary equipment for oxy fuel combustion technology uses conventional designs and material as opposed to other technology like ultra-supercritical power generation technology which requires special alloys that can accommodate the high temperatures and pressures. This is a competitive technology that's more cost effective compared to pre and post combustion carbon dioxide capture technology. The disadvantage, however, is that the power needed for the ASU and compression of carbon dioxide in the separation unit adds to the energy load when compared to conventional air fired plants without carbon dioxide capture of the same size.

Combined SO_x - NO_x control technologies are best suited for flue gas treatment in Zimbabwe because of the commercial availability of these technologies which have achieved reduction in NO_x and SO_2 of 40 - 94% and 50 - 95% respectively. As explained in section 3.3.2, available denitrification technology uses the principle of modified combustion, in LNB and when used with SCR (with a vanadium - tungsten - titanium catalyst) can efficiently control NO_x emissions. These two technologies combined with sorbent injection in the exhaust stream can effectively lower SO_x - NO_x emissions. In addition, SCR can effectively lower heavy metal pollutants (mercury) by up to 89% [4]. Of importance in sorbent injection technology is residence time to ensure that all the SO reacts with the chosen sorbent, normally limestone or calcium hydroxide. Another viable option in sorbent injection technology is to combine furnace injection with exhaust stream injection to ensure efficient SO_x capture. Combined SO_x - NO_x control technologies are not limited to power generation plant pollutant control only; it can be used in any coal utilizing sector. This is an advantage for Zimbabwe because coal utilizing sectors include agriculture and manufacturing and processing industries.

5. Conclusion

Zimbabwe, like most governments have set its goals in line with attaining net zero emissions, which has resulted in transition to renewable energy production accompanied by CCT in power generation and decarbonization of hard-to-electrify heavy industry sectors. CCT technologies recommended for Zimbabwe will not only improve combustion efficiency in power generation and provide the much-needed energy security for a country already facing an electrical energy deficit due to economic growth, but it will also significantly lower pollutant emissions and give Zimbabwe a chance to meet its emissions reduction target. Recommended clean coal technologies can be retrofitted into existing conventional combustion technology without much complexity, and as such, capital costs are significantly lowered. Denitrification technology, carbon dioxide capture and desulfurization technology are environmental control-based technologies that are not suitable for emissions reduction in power generation, but in manufacturing and processing and agriculture, the other two main applications of coal in Zimbabwe. There is a potential for a quick return on investment, as was the case for the US, if the country focuses on adoption of commercialized CCT rather than on design and development.

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REVIEW ON OPTIMISATION OF BLAST FURNACE PERFORMANCE IN IRON AND STEEL PRODUCTION USING BLENDED COKE FROM BOTSWANA AND ZIMBABWE

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Abstract

Most chemical processing and metallurgical industries operations exploit and use coal/ coal derived products. Coal is mainly used in the iron and steel industry through metallurgical coke which serves as the heat source, reducing agent and permeability support provider. Zimbabwe is known to have good grade coking coal while Botswana on the contrary has poor coking grade coal reserves [1]. This research focused on reviewing the possibility of blending the Botswana non coking coals with Zimbabwe coking coals to produce metallurgical coke.

Key words: coking coal, blast furnace, optimization, coal blending, metallurgical coke

1. Introduction

Zimbabwe has vast coal reserves which are used for power generation and a greater percentage exported to other countries. According to statistics conducted in 2016 on available coal reserves, Zimbabwe was ranked in the top 40 with 553 million tonnes of proven coal reserves in the world. The percentage consumption of coal was rated at approximately 0.52% [1]. Relatively large coal reserves estimated at over 12 million tonnes have been found located in the Lower Karoo of the mid Zambezi and the Save-Limpopo basin [2]. The Hwange coal deposit has large reserves of both coking and thermal coals [2], with the coal being mined by Hwange Colliery Coal Company Ltd ranges from steam quality to coking coal [2]. Botswana on the contrary has approximately between 106 and 212 billion tonnes of proven coal reserves with the consumption rate at approximately 1.2% [3]. The major supplier of coal in Zimbabwe since 1985 is Hwange through the state partially owned Hwange colliery plant [4]. Morupule colliery located in Palapye is

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the main source of coal in Botswana and has been in operation since 1973 [4]. Coal utilisation in Zimbabwe and Botswana has been realised in power generation with a greater percentage exported to other countries. Figure 1 shows the railway link for the exportation and distribution of coal in the southern African region [5].

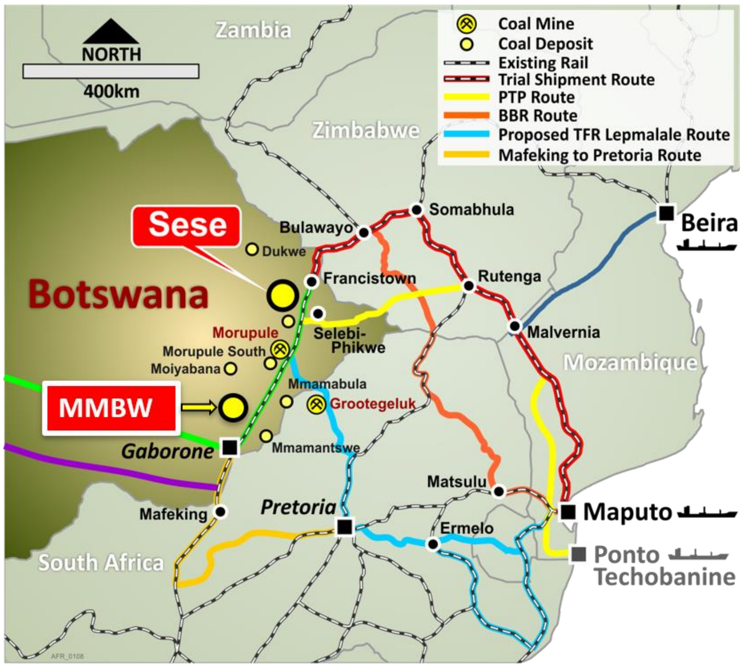

Fig. 1. Railway line for coal exports [5]

Despite a few locations like Mmamantswe where some best quality coal has been discovered [5], the general coking potential of Botswana coal has been rated as poor advocating for the need for blending measures and techniques to be researched and experimented [6].

2. Geology of Zimbabwean coal

The geology of Zimbabwe mineral locations is a product of three main eras namely; Archean, Proterozoic and the Phanerozoic [7]. Approximately 60 percent of the country is covered by the Zimbabwe craton, comprising of rare-metal granites and granitic rare-element pegmatites which have become a promising exploration target in the twenty first century. The Great Dyke of Zimbabwe, a NNE- trending mafic encroachment of layered metal-bearing rock falling under the Proterozoic era is also the country's promising source of valuable minerals. It spans about 550 km in length and 4–11 km in width across the Zimbabwe craton in the North South direction [7]. Covering the peripheries of the Zimbabwean Archean crust are a series of sedimentary rocks, cretaceous sediments and the Karoo Supergroup all being intricate of the Phanerozoic era. Coal resources in Southern Africa are categorized in the Middle Ecca group which is a section of the Karoo Supergroup and Zimbabwe consist of coal deposits in the Lower Karoo sediments of the mid Zambezi and the Save-Limpopo basins [8, 9]. The two basins are separated by the Zimbabwean craton as shown in figure 2.

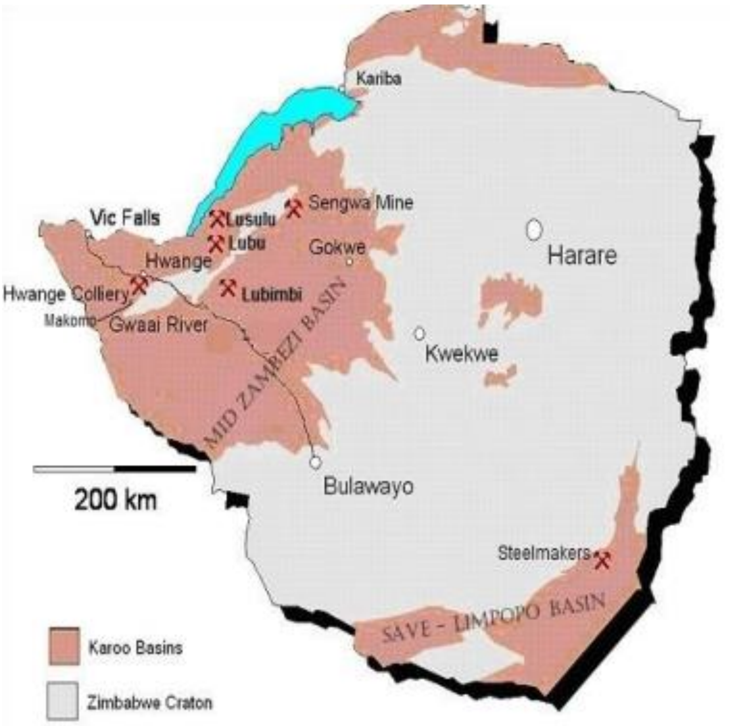

Fig. 2. Sediments of the Mid Zambezi and the Save-Limpopo basins [9]

3. Geology of Botswana coal

Located at the centre of Southern Africa, the country’s intrinsic geological features are an integration of the earth geological records thus from the Archean crust to the shallow regional depression geographically referred to as the Kalahari Desert [10]. Botswana thus constitutes the Kaapvaal craton located in the Southeastern part, sedimentary rocks of the Karoo Supergroup lastly but not least, the Kalahari Desert covering the central and western part of the country. Figure 3 shows locations of major deposits of coal in Botswana.

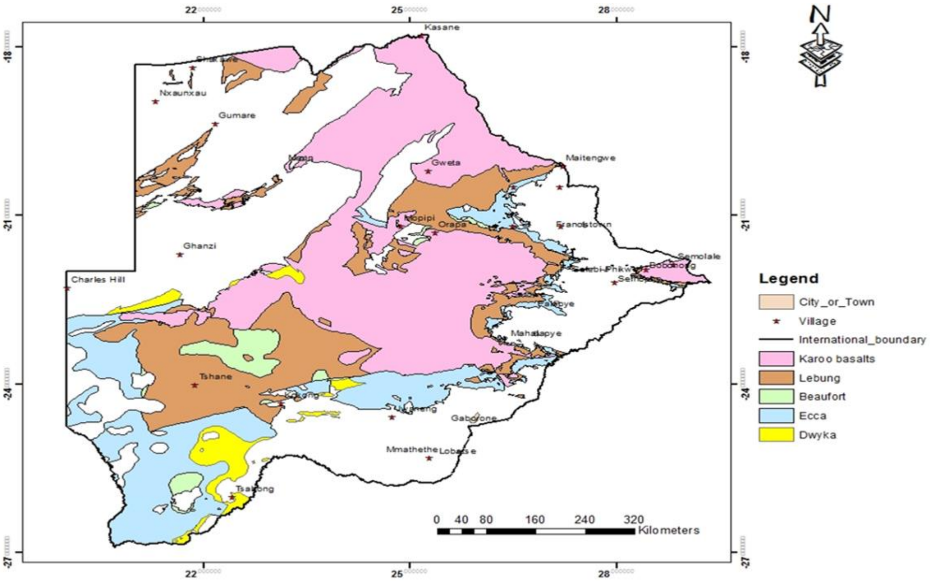

Fig. 3. Distribution of the Karoo supergoup in the Botswana region [11]

4. Coal Characterisation

The properties of coal that influence the quality of metallurgical coke have been identified and can be categorised as chemical and physical properties [12]. Chemical properties include moisture content, composition of volatile matter, gross calorific value, ash content, sulphur content, phosphorous content and alkalies [13]. The physical properties comprise of; Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) and the procedures used to determine these have been outlined in the International standard document ISO 18894:2018. Table 1 shows the chemical properties and standard permissible range for the coal to be considered as good quality for metallurgical coke.

Table 1

Chemical Properties for good quality metallurgical coke [12-16]

Chemical property	Recommended range
Moisture (wt.%)	<10
Sulphur (wt.% db)	0.5 – 0.9
Ash (wt.% db)	11 – 16
Volatile matter (wt.%)	20 – 35%
Phosphorous (wt.% db)	0.02 – 0.06
Nitrogen (wt.% db)	<2%
Alkalies (wt.% db)	< 0.3
GCV/ MJ/kg	>24MJ/kg
db = dry-based	

Table 2 gives the physical properties of coal and the permissible range constituting good quality metallurgical coke. Depending on design and operating conditions of the blast furnace the optimum values for CRI and CSR would vary but the recommended specifications are between 20 and 30% and greater than 60%, respectively [12].

Table 1

Physical properties for good quality metallurgical coke [12, 13, 15, 17]

Physical property	**Recommended range**
Mean size (mm)	47 – 70
M_{40} (+ 60 mm)	>78 – >88
M_{10} (+ 60 mm)	< 5 – < 8
I_{40}	53 – 55
I_{20}	>77.5
CSR	>60
CRI	20 – 30
CSN	2 – 8
RoV_{max}	>1.15%
Total reactives (esp. vitrinite)	>50%

The mentioned parameters amongst others, are of importance in analysing the coking potential of coals which define their quality of performance in the blast furnace. Determination of these parameters is conducted through proximate analysis, ultimate analysis, and petrographic and rheological analyses.

4.1 Characterisation of Zimbabwean coal

Research has been underway to investigate the characteristics of Zimbabwean coal in line with metallurgical coke production [6]. Six coal seam samples (Chaba, Hwange Thermal Power Station, Galpex investments, Hwange Coking Coal and Coal Zim) were collected and analysed for the physical and chemical properties to assess their coking suitability. Chaba Hilltop, Galpex Investiment, Hwange Thermal Power Station and Hwange Coking Coal fall under Hwange coal seams located in the north-western part of Zimbabwe approximately 335 km from Bulawayo and 100 km (by road) from the scenic Victoria Falls in the Zambezi basin. Coal Zim is located in the south-eastern part of Zimbabwe in Chiredzi which fall under Save-Limpopo basin. Ultimate, proximate and petrographic analysis results are presented in Table 3. The highlighted areas represent unconformity to the set ranges.

Table 2

Ultimate analysis of Zimbabwean coals [6]

Element	Hwange thermal Power Station (HTPS)	Chaba Hilltop	Hwange Coking Coal	Galpex Investments ROM	Galpex Investments Washed Coal	Coal Zim ROM
Ultimate analysis						
C%	66.85	72.7	75	67.05	73.25	63.3
H%	3.71	3.77	4.14	3.53	4.03	2.73
N%	1.53	1.6	1.67	1.29	1.39	1.38
O%	3.97	2.37	3.25	0.9	4.06	4.23
S%	1.89	3.16	2.04	5.29	1.27	0.37
P%	0.16	0.035	0.073	0.44	0.213	0.025
Proximate analysis						
MC%	1.4	1.5	1.3	1.3	1.4	1.4
Ash%	20.85	15	12.7	20.8	14.7	20.8
VM%	21.7	19.55	23.25	19.85	21.95	11.4
GCV/ MJ/kg	26.77	29.25	29.54	26.67	29.12	24.35
Petrographic and Rheological analyses						
CSN	1.0	1.0	1.0	1.0	1.0	0.0
Total reactives (esp. vitrinite)	33.7	17.6	58.8	10.1	43.3	7.1
Total Inerts	66.3	82.4	41.2	89.9	56.7	92.9
RoV $_{random}$	0.88	1.03	0.89	0.94	0.89	2.03
RoV$_{max}$	0.94	1.10	0.95	1.01	0.96	
Total abnormal conditions	29.2	14.2	20.8	23.3	30.0	
CSR	69.5	72.2	72.9	62.8	54.2	54.2
CRI	16.6	16.5	18.6	21.8	29.8	17.6

4.1.1 Ultimate analysis of Zimbabwe Coal Samples

Five of the six coal seam samples had their sulphur content exceeding the required set threshold. Thus sulphur, having strong catalysis on both carbon dioxide (CO_2) and air reactivity of coke which facilitate organic sulfur→H_2S→SO_2→COS and elemental sulfur (S_x)→SO_2 and organic sulfur→H_2S→COS→S_x→C_2S→COS reaction systems during coke–O_2 and coke–CO_2 reactions respectively. Such scenario results in enlarged coke specific surface area and increased consumption carbon which is not an ideal situation for the blast furnace operation [18]. In the long run it has adverse effects on steel mechanical properties and is responsible for red-shortness, which is brittleness of the metal in the heated state [14]. Further results on the ultimate analysis indicated significant amounts of phosphorus from four out of the six coal seam samples. This advocates for tendency of the metal becoming cold-short, which is brittleness at reduced temperatures [14].

4.1.2 Proximate Analysis of Zimbabwe Coal Samples

The proximate analysis indicated that half of the coal seam samples tested had ash content and amount of volatile matter falling outside the set threshold. Ash content, being an essential parameter in the coking process affect coke quality in that, higher stamping energy will be required for compacting high ash-coals to attain the desired cake density [19]. Volatile matter also plays a role in the coking process in that the lesser the volatile matter the greater the bulk density thus, facilitating formation of stronger inter particle bonds which advocate for higher coke strength and quality [20].

4.1.3 Petrographic and Rheological Analyses of Zimbabwe Coal Samples

A number of outlier parameters were observed for the Zimbabwe coal seam samples. Among these was the crucible swelling number CSN which determined the swelling properties of the coals. All coal samples were below the threshold set range even though five out of the six exhibited some swelling potential [21]. One out of the six samples (Hwange Coking Coal) had the total reactives within the specified range, but however had some shortcomings in terms of mean maximum reflectance (RoV_{max}) and CRI. Other coal samples showed nonconformity for the total reactives and their conformity to the other parameters were alternating. Thus, the coking potential of the tested Zimbabwe coal seam samples indicated that they had at least one or more parameters falling out of the set threshold specifications thereby advocating the necessity for blending as the samples showed potential for improvement to meet coking requirements.

4.2 Characterisation of Botswana coal

Coal samples were collected from Masama and Morupule coal mines for analysis of their properties in line with metallurgical coke properties. According to the ultimate analysis of samples from the two coal mines whose results are shown in table 4, show that phosphorous content was higher exceeding the set threshold range [6].

Table 3

Analysis of Botswana coal [6]

Element	**Masama washed composite**	**Masama ROM**	**MCM Composite washed**	**MCM ROM**	**Masama washed 0–10mm**	**Masama washed 10–28mm**	**Masama washed 28 – 50mm**
Ultimate analysis							
C%	65.4	57.5	65.2	56.1	66.1	64.4	63.3
H%	4.5	3.94	4.02	3.53	4.42	4.37	4.2
N%	1.44	1.29	1.5	1.31	1.44	1.37	1.35
O%	8.94	5.87	5.04	8.22	8.53	9.4	9.56
S%	0.42	3.4	0.34	1.44	0.31	0.56	0.59
P%	1.18	0.85	0.39	0.12	1.21	1.01	0.95
Proximate analysis							
MC%	7.3	7.9	5.0	5.8	7.4	7.4	7.2
Ash%	20.7	11.4	24.4	18.1	11.8	12.5	13.8
VM%	23.8	26.3	23.1	22.5	25.5	26.5	26.2
GCV/ MJ/kg	22.08	25.09	21.68	25.21	25.34	24.78	23.85
Petrographic and Rheological analyses							
CSN	0	0	0	0	0	0	0
Total reactives (esp. vitrinite)	64.1	65.6	36.2	22.1	Not tested (NT)	NT	NT
Total Inerts	35.9	34.4	63.8	77.9	NT	NT	NT
RoV $_{random}$	0.56	0.60	0.60	0.62	NT	NT	NT
RoV$_{max}$	0.60	0.64	0.64	0.66	NT	NT	NT
Total abnormal conditions	26.7	24.2	24.2	25.0	NT	NT	NT
CSR	16.2	22.7	40.4	44.8	NT	NT	NT
CRI	48.9	60.6	37.0	63.2	NT	NT	NT

4.2.1 Ultimate analysis of Botswana Coal Samples

The results for run of mine ROM indicated significant amounts of sulphur in comparison with the washed coal samples. Phosphorous content was relatively higher

than that from Zimbabwe coal samples and well above the set threshold specifications. As alluded earlier high phosphorous results in metal cold-short characteristics which is a symbol of poor quality [14].

4.2.2 Proximate analysis of Botswana Coal Samples

Proximate analysis for Botswana coal, unlike Zimbabwean coal the deviations were noticeable for ash content and Gross Calorific Value (GCV). The amount of volatile matter fell within the required specifications. GCV is of importance in that it determines the potential characteristics of coal as a fuel that is, in line with provision of heat thus higher GCV is preferred [22]

4.2.3 **Petrographic and Rheological Analyses of Botswana Coal Samples**

Botswana coal samples showed no swelling potential with a recording of zero which when interpreted is an indication that Botswana coals did not form coherent and agglomerating masses upon being subjected to heat [23], thus confirming their sub-bituminous nature. Therefore, the caking capability and fluidity for Botswana coal is negligible with narrow margin for thermo-plasticity. Both MCM washed and ROM had low percentage of total reactives but the ranges for Masama coal samples were within the specifications. None of the RoV_{max}, CSR and CRI for Botswana coal samples showed conformity with the set specifications.

5. Coal Blending

The limited availability of coking coal and increasing demand due to the drive for industrialisation in the Southern Africa has led to high cost of prime coking coals. Thus, there is need for innovative methods and techniques to produce high quality coke at low cost. Results obtained from the ultimate, proximate, and petrographic analyses provided the background on basic idea potential of coal from Botswana and Zimbabwe. Here it could be noticed that Botswana coal is non-coking in nature. This was sufficed by the values of the key parameters; CSN, CSR, CRI and $RoV_{max.}$ Zimbabwe on the contrary exhibited some coking potential, thus the slight nonconformities can be addressed through incorporation of blending strategies and techniques. Research have been done on coal selection and blending in modern pre-carbonization methods. Prediction of the optimum ratios of coals to be considered in blending has been done mainly by comparison of the conformity of their respective parameters, and models for such operations have been in use.

Further research by Tiwari et al, unveiled that generalizing prediction models without the adequate context of the coals of interest would not give a conclusive answer [24]. Thus, carbonizing the coal samples and analyzing the resulting properties would attribute to the coke quality.

5.1 Coke quality and the pre-carbonization techniques

Technologies aligned to coke quality improvement in coal blends have been explored as the demand for quality coke has been significantly rising. One of the major properties of coal considered for enhancing coke properties is the bulk density. Increase in bulk density of the charged coal facilitates the formation of stronger inter particle bonds which advocates for higher coke strength and quality [25]. Among these pre-carbonization techniques are selective crushing, coal preheating or pre-caking, partial briquetting, and stamp charging. Research by Gangopadhyay et al show significant improvement in the CSR and CRI values on coal samples with different coking properties after hot stamping [26].

In relation to the gathered information, chemical properties that constitute a good fuel are high carbon, low sulphur, low ash, low moisture, and low alkalis [13]. The reducing agent parameters which foster optimum reactivity are good combustibility and adequate reactivity to CO_2 (CRI) and H_2O. The coke physical properties that can facilitate the movement of molten material and radiation of hot gases are coarseness with a narrow size distribution, high CSR, and high cold coke strength [6]. In the blast furnace, the metallurgical coke contributes as a stock column skeleton, heat source, as well as carburizing and reducing agent [27]. The basis for conducting experiments on coal to coke for use in the blast furnace were based on the research from various pre-carbonization techniques which included stamping, stamp charging, preheating and briquetting [24, 28, 29-31]. The concept incorporated in the carbonization method applies the principle of high temperature carbonization (HTC) with temperature ranges of 900-1200 ℃. A series of transformations occur as the coking coal is carbonized at increasing temperature regime and Figure 4 illustrates the transitions involved [32].

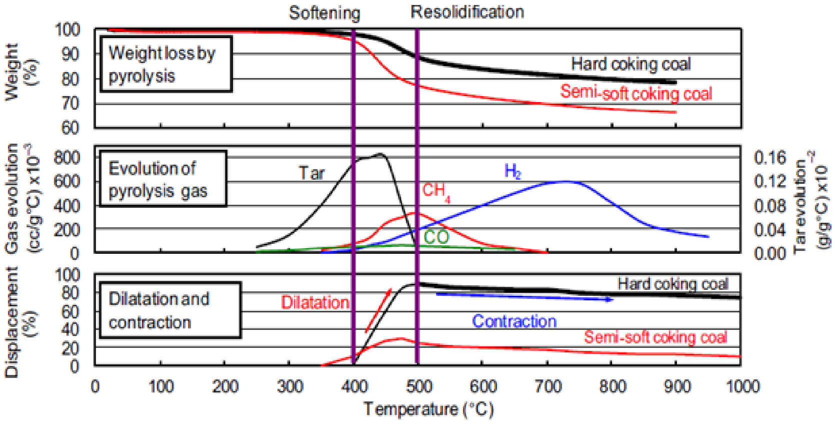

Fig. 4. Transformations of coking coal or blends during the carbonization process [32]

5.2 Conceptual Framework

A typical framework can be established with the necessary unit operations for blending of coal from the two countries based on the fundamental concepts gathered from literature. The pyrolysis of the individual Botswana and Zimbabwe coals was considered the first step for possible blending. Laboratory scale pyrolysis were conducted for the Zimbabwe and Botswana coal seam samples. Figure 5 gives an illustration of the pyrolysis steps.

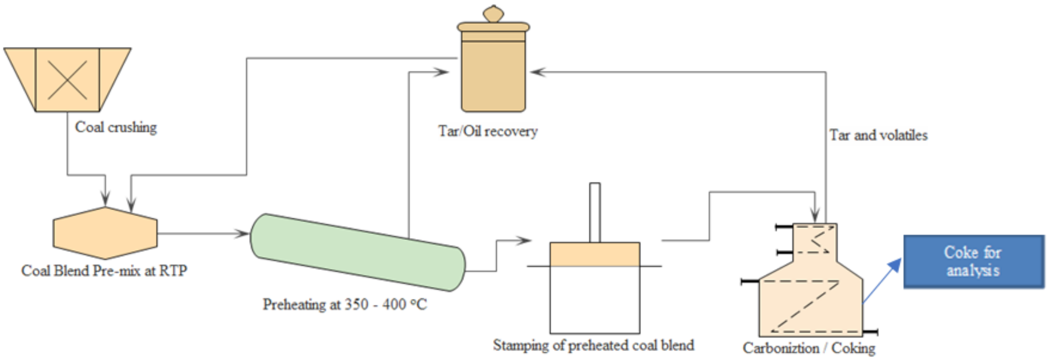

Fig. 5. Pre-carbonization and carbonization experimental steps

Step 1: Variation of coal particle sizes in the range of 50μm to 20mm thus allowing for determination of the optimum size with the potential to produce coke of the desired quality.

Step 2: Premixing of coal blend in varying ratios at room temperature and pressure (RTP).

Step 3: Preheating sample to temperatures ranging from 350°C - 400°C to facilitate tarrification of the blended coal sample.

Step 4: Hot stamping commence after the preheating step. The bulk density before stamping is recorded along with the final bulk density after stamping.

Step 5: The carbonization (coking) step will resemble the retort reactor developed by Gajic et al. This step is conducted at varying heating rates with the temperature profiles being recorded for analysis.

Fig. 6, Morupule a) and Galpex washed coal b) char

Figure 6 shows coal char formed after the first attempt of pre-carbonization. The porosity features of coal from Galpex Investments were visible in comparison with Morupule washed coal upon visual inspection.

The pre-carbonization experiments conducted gave results that were in sync with the data gathered on the behavior of coal upon carbonization. Thus, coal samples from Zimbabwe exhibited coking potential while those from Botswana were non-coking in nature. Blending techniques to be implemented need to follow the set procedures in accordance with international standards ISO11760:2018. Two routes are worth considering as shown in figure 7. The first route follows the sequence; sampling, blending pyrolysis and finally coking (represented by red lines). The second route, represented by blue lines involves the pyrolysis of coal to produce char, blending and then coking.

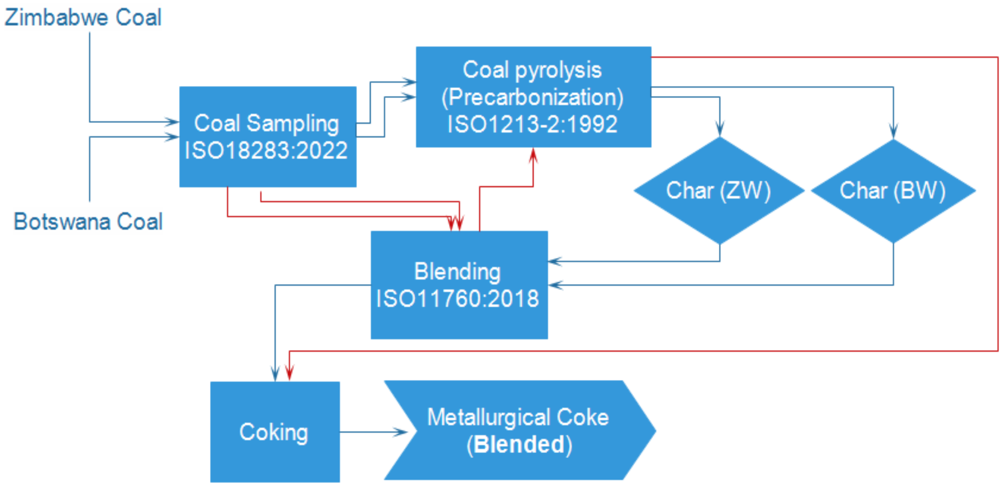

Fig. 6. Flow diagram for blended coal/char coking

6. Conclusions

The results from the preliminary experiments clearly provide evidence that the coal from the two countries can be blended and blending techniques can be implemented in line with ISO11760:2018. The Iron and steel industry is continuously developing and growing nationally, continentally and globally which advocates the need for joint collaboration between countries. Both Zimbabwe and Botswana have vast coal reserves which would benefit and sustain the iron and steel industry if blended. Coal blending and optimization of coke blends will provide breakthrough to the effective use of Botswana coal and will help sustain coal use in Zimbabwe.

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REVIEW OF MWANESI, RIPPLE CREEK AND BUCHWA IRON ORE DEPOSITS AND IDEAL PRETREATMENT PRACTICES OF THE ORES FOR BLAST FURNACE IRON BURDEN

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Abstract

The purpose of this review is to assess the characteristics of Zimbabwean iron ore reserves, with a special focus on the Mwanesi, Ripple Creek and Buchwa deposits and determine ideal treatment methods of the ores to be a suitable ferrous burden for the blast furnace. Zimbabwe is known to have large amounts of iron ore reserves with grading above 40%. Mwanesi, Ripple Creek and Buchwa mines are known to have 43%, 52.2%, and 61% grade iron respectively. Blast furnace iron-bearing burden should enable reliable hot metal production of the optimum quality and quantity at minimum costs. By reviewing archetypal ferrous burden preparation methods and analyzing how burden quality affects the reduction efficiency in the blast furnace, ideal preparation methods for Mwanesi, Ripple Creek and Buchwa ores are subsequently recommended.

Keywords: blast furnace, iron ore deposits, ferrous burden, Zimbabwe

1. Introduction

Zimbabwe is reported to hold 553 million tonnes of proven coal reserves of which 10% is used as coking coal in the iron and steel industry [1] particularly in the blast furnace where coke acts a fuel for the endothermic process, as a reducing agent for iron oxide and as permeable support for molten material to trickle down the furnace while hot gases rise [2].

The blast furnace to this day plays a pivotal role in iron ore processing and steel making and remains a relevant technology in the 21st century in the production of pig iron. The blast furnace (BF), basically, is a cylindrical furnace used for smelting ores into molten metal. The word ‘blast’ is indicative of air being

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forcefully supplied into the furnace. The smelting process itself is complex with a series of chemical and thermal reactions taking place, coupled with mass and heat transfer within different phases. Iron making in a modern blast furnace is referred to as a moving bed characterized by high temperatures with counter-current, cross, and co-current flow of powder (normally as pulverized coal), gas, liquid and solid [3]. Even though many alternative ironmaking technologies have been developed globally, the blast furnace remains the most cost effective and highly productive process for hot metals, responsible for approximately 70% of all global steel production, and is predicted to remain so in the future [4]. Iron is referred to as one of the most geochemically abundant metals in the earth's crust, together with Mg, Al, Mn and Ti, contributing more than 0.1% by weight [7].

Impurity elements in iron ore deposits can affect the quality of pig iron from the blast furnace and the efficiency of the blast furnace operation. Geological, geographical, and commercial factors require customization of each iron-bearing material for efficient blast furnace operation. Critical parameters for understanding the characteristics of an ore include chemical composition and oxygen fugacity, which directly influence subsequent processing as iron ore burden in the blast furnace. For instance, according to Kress and Carmichael [8], the Fe_2O_3/FeO melting ratio is linked to oxygen fugacity. This ratio is significant in blast furnace operation because the reduction–disintegration of blast furnace burden (which occurs at lower temperatures in the shaft zone of the furnace) results in the generation of fines which reduces the void fraction in the shaft zone [9]. A reduction in the void fraction in the shaft zone lowers reduction efficiency since the bulk flow of reducing gases through the furnace burden is dependent on the void fraction.

2. Research

Zimbabwean Iron Ore Characteristics

Zimbabwean iron ore deposits are associated with banded iron formations (distinctive layered sedimentary rocks of alternating iron oxides and chert), hosted by deformed Archaeon greenstone belts within an estimated 800km long and 500km wide Zimbabwean craton [10]. Buchwa and Ripple Creek are the country's most important deposits of high-grade ores, while Mwanesi deposits are also significant with lower-grade ores. The Midlands greenstone belts, where the Ripple Creek deposits are located, are known to have approximately 200Mt iron ore resources with between 56 to 65% and 4 – 12% hematite and SiO_2 respectively [11]. The Belingwe greenstone belts host iron band formations of Buchwa mine with an estimated 134Mt of iron resources in the form of hematite with 60 - 63% grade iron, and associated SiO_2, S, and P at 4 – 6%, 0.02%, and 0.03% respectively [11]. The

Mwanesi greenstone belts are located 130km SSW of Harare and the banded iron formation is known to have 43% grade iron also in the form of hematite [11].

The main impurities occurring in these ores are silica, alumina, calcium, phosphorus, sulphur, and titanium. The three deposits considered in this paper are in the form of hematite as mentioned earlier, with the exception of Ripple Creek which has used limonite in the blast furnace in the past. Limonites are complex hydrated oxides or ores with the general formula $Fe_2O_3{\cdot}nH_2O$ [13].

Blast Furnace Ferrous Burden

The blast furnace process requires a rich ferrous burden, preferably an excess of 58% Fe for high efficiency [9], though a minimum of 50% is acceptable [5]. Ores require beneficiation and processing before they can be classified as suitable BF charge in terms of physical and chemical composition. Processing of ores generally requires the liberation of iron minerals (crushing and grinding) from gangue minerals and the extent of processing depends on the specific requirements of the ore deposit. The liberation size influences the extent of crushing and grinding that must be done to unlock iron minerals. For low-grade ore, fine grinding is often required, which results in the generation of fines.

Ferrous burden in the blast furnace can be pellets, roughly spherical thermally or chemically bounded agglomerates of between 5- and 10-mm diameter, sinter which consists or irregularly shaped partially fused agglomerates of size range 5 to 30mm, or lump ores which are large particles of 5 to 30mm size range [5]. The iron-bearing burden is reduced in a typical sequence from hematite (Fe_2O_3) to magnetite (Fe_3O_4) and then to wustite (FeO).

Quality demands for blast furnace iron burden extend beyond chemical composition to physical aspects related to durability and properties in cold and hot states, which are partly influenced by ore treatment methods. The major quality demand for BF ore burden is the limitation of fines to as low as possible as alluded to earlier. Burden material is in the range of 5 – 30 mm and material below 5 mm is classified as fines [9]. Fines in the furnace are introduced as part of the burden charge or they are generated in the shaft zone. Fines in the furnace charge can be minimized by efficient screening and processing of ferrous burden material with good reduction disintegration properties. The generation of fines in the shaft zone is a result of reduction disintegration [9], where the reduction of hematite to magnetite changes the structure of the burden material, weakening it and resulting in the generation of fines. Sinters are more prone to this phenomenon, and it can be minimized by either increasing the percentage of FeO by cooling the sinter in an oxygen-depleted environment or by adding more fuel during the sintering process [9].

Another quality demand of the BF burden is melting properties which are influenced by the slag composition of the ore burden. The reducibility of ore burden is dependent on the bulk flow of the reducing gases and the contact between the gases and ferrous burden to allow for the reactions to take place. In order for gases to flow, the burden material has to be permeable and once the furnace charge starts to melt, permeability is lowered, and it is important that melting starts at high temperatures. The period between softening and melting of the iron burden should be short so that the flow of gas is not impeded resulting in low reduction rates. Acidic pellets and lump ores melt between 1050℃ and 1100℃ and fluxed pellets and sinter at higher temperatures [9].

The amount of SiO_2 in the ferrous burden is also important as it determines the amount of slag that will be produced in the furnace and the physical and metallurgical properties of the iron-bearing material. Slag is essential for the removal of impurities such as S, K_2O and Na_2O but excessive slag amount can result in an unnecessary thermal load on the furnace and cause increased fuel consumption. CaO/SiO_2 is often designed to yield the best physical and metallurgical properties in the processing of ferrous burden [5].

Lump Ores

Lump ores are generally high-grade ores (>60% Fe) that are processed through coarse crushing and fine grinding and screening. They may be water sprayed to remove ‘piggyback’ fines and dried. Lump ore usually constitutes only 5 – 20% of mined ore [5] with the rest reporting to the -10mm screen as fines that require upgrading to produce suitable BF ferrous burden. Hydraulic techniques are used to upgrade the fines and after dewatering, they make suitable feedstock for sintering plants. -1 mm fines are ground further and used as feedstock for pelletizing processes. Lump ores are not very common as high-grade ores are scarce, being found in Australia (Pilbara region), Brazil (Caracas), and South Africa (Sishen).

Lump ores are cheaper compared to sinter and pellets but metallurgically speaking, they make poor BF ferrous burden material due to the following reasons. They generate more fines in the upper stack of the blast furnace and during handling, resulting in poor reduction-disintegration properties and low reducibility [9]. Lump ores also have low melting temperatures, and this lowers reduction efficiency. They are generally not suitable for high productivity because they are in their naturally occurring state with SiO_2, CaO, and S levels at 0.5 – 3.6%, 0.1 – 0.15%, and <0.04% respectively [5]. They can, however, be blended with pellets or sinter to minimize their disadvantage in the BF process, because of their affordability in comparison to other iron-bearing materials [12].

Sinter

Sinter is made from heterogeneous materials including fine ore, and recycled waste from iron and steel-making industries making it a more profitable way of ferrous burden preparation. Recycling waste also minimizes the environmental liabilities of waste disposal [9]. Limestone and dolomite are also added to provide the desired sinter composition. The most important parameters that determine the quality of the sinter are size distribution, cold strength, and reduction disintegration properties.

Sinters can be classified as acidic, fluxed, or super fluxed based on the basicity ratio, B/A which is given by CaO + MgO/ SiO_2 + Al_2O_3. B/A ratios of <0.1, 1 -2.5 and >2.5 are classified as acid, fluxed and super fluxed respectively [12]. BF operations generally used fluxed sinter as ferrous burden material. The use of CaO and MgO, which are normally added as carbonates in the form of limestone ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$), is useful in achieving the required chemical and physical composition of the sinter. Slag bonds are easily formed when CaO is used instead of MgO, and the sinter can also be made at lower temperatures. Sinters made at high temperatures have glass-like structures and are difficult to reduce. The use of dolomites as fluxes in sinter processing results in sinters with poor reduction disintegration qualities [12].

Reduction disintegration is also related to the amount of hematite and wustite in the sinter. It is important to remember that sinter is made from different materials including primary and secondary magnetite and controlling the chemical and physical properties of the final product is a challenge. At high temperatures, secondary magnetite is formed, and it lowers areas in close proximity to the coke. High percentages of primary magnetite give very stable structures in the presence of SiO_2 that can only be reduced at high temperatures. Burnt CaO and iron oxides also result in the formation of calcium ferrites further complicating the chemical composition of the sinter [12].

The basis of low-temperature reduction disintegration is the reduction of hematite to magnetite which results in an alteration of the crystalline structure of the sinter, making this phenomenon related to the amount of hematite present. As is the case for magnetite, there is primary and secondary hematite in the sinter, and secondary hematite is a more effective driving force of reduction disintegration. A high FeO percentage will minimize reduction disintegration. The precise relationship between FeO and sinter quality depends on the ore blend. However, the percentage of FeO can be increased by cooling the sinter a in gas-air mixture with 12 -14% oxygen or by adding more coke breeze which is used as fuel during the sintering process as aforementioned.

The cold strength of the sinter should be high enough to minimize the formation of fines both in the furnace shaft/stack zone or during handling. Cold strength can be determined through tumbler tests.

Pellets

Pellets involve size reduction of mined ore and agglomeration to produce spherical particles, as well as thermal induration for metallurgical properties impartation. Pellets are made from generally low-grade ores of 25 to 30% iron [12]. Pellet quality is based on cold strength, swelling properties, softening and melting, and reduction disintegration properties. The main types of pellets are acidic (SiO_2 between 1.5 and 2.5%; CaO <0.5%; MgO <0.2%), basic with about 14% SiO_2 and olivine doped pellets (SiO_2 is 2.5 –.3.5%; CaO <0.5%; MgO 1.3 – 1.8%) [9].

Pelletizing is a series of stages starting from crushing and grinding for the liberation of iron minerals from gangue, and concentration may follow thorough fine screening, flotation, or using hydro cyclones [9]. Flux preparation follows, like in the case of sintering, limestone and dolomites are used with a particle size range of 5 – 50mm. Dewatering and filtration leave a cake mixture with the right moisture content which is then rolled in the presence of a binder to form spherical pellets in a process referred to as balling. Bentonite clay is also added to assist in pellet growth and strength [9]. The pellets are dried and heat-treated during induration using gas, pulverized coal, or oil, where chemical changes occur in the pellets, all changes previously having been physical. After the induration, the pellets are screened again, and fines are recycled.

During induration, the chemical changes that occur include the exothermic oxidation of magnetite to hematite, the calcination of limestone /dolomites, and the reactions between iron oxides and gangue and the binder to produce silicates and aluminates of iron and the subsequent crystallizing of iron-bearing phases. Time, temperature selection, and control are very crucial at this stage to ensure that the desired physical and chemical properties are obtained [12].

Swelling is an important parameter in determining pellet quality because pellets tend to swell during the BF process unlike lump ores or sinters. An increase in volume can be up to 20%, which is considered critical (measured according to ISO 4698) [9]. Swelling occurs during the reduction of wustite to iron, and tends to improve the opportunity to generate fines, and increases in alkali conditions. Factors influencing swelling are basicity and gangue content and operation temperatures during induration. Pellets with basicity between 0.2 and 0.7 are prone to swelling.

Average strength on the other hand had no major drawback on the BF operation if it is not a result of weak pellets. This factor can be affected by the pellet production rate. Olivine-doped pellets, because they have mostly MgO (added in the form of olivine or serpentine) instead of CaO are generally weak in terms of cold compression strength.

Ideal ore preparation methods for Zimbabwean ores

BF operations require high grades of about 60% Fe for efficiency and of the deposits considered only Buchwa ore deposits fit into that class. Buchwa ores can be prepared by crushing and screening to form lump ore since lump ores are cheaper compared to sinter and pellets. Lump ores on their own make poor BF ferrous burden charge because they have poor reduction disintegration properties, low reducibility, low melting points, and up to 6% SiO_2. The fines generated from crushing and grinding can then be sintered and blended with Buchwa lump ore to make a suitable BF ferrous charge. Aptly produced sinters can provide the proper chemical and physical properties needed to make the optimum ferrous burden for high reduction efficiency.

Ripple Creek mines ore deposits are considered high grade (>50% Fe) and just like Buchwa ores, a blend of lump ores and sinters can be used to produce the suitable ferrous burden charge.

The low-grade ores of Mwanesi (43% Fe) require the liberation of iron-bearing material from gangue minerals which necessitate crushing to finer liberation sizes and subsequent agglomeration to produce optimum blast furnace iron burden. Concentration techniques can also be used to upgrade the ores to an excess of 60% as ideal for BF operation. Sintering and pelletizing the ores will produce a suitable ferrous burden charge. Even though acidic sinters have a higher cold strength compared to fluxed sinters, fluxed sinters are more suitable for Mwanesi ores because the ores are characterized by silica and calcium-based impurities, and they can be formed at lower temperatures. Pellets can then be used to blend with the sinter to form an optimum BF ferrous burden. Because of the induration process, pellets will provide the necessary physical and chemical properties required in BF charge and minimize the disadvantages of fluxed pellets.

3. Conclusion

Quality demands for blast furnace iron burden extend beyond chemical composition to physical aspects related to durability and properties in cold and hot states, which are partly influenced by ferrous burden preparation methods. Reduction–disintegration properties, size distribution, melting points, acidity, and basicity are the main parameters influencing the reducibility of ferrous burden in the BF. Suitable pretreatment methods of iron ores are essential for efficient blast furnace operation and as established, Ripple Creek and Buchwa mines ore deposits are considered high grade (>50% Fe) and can be easily converted to blast furnace feed by beneficiation through sintering to produce the suitable BF charge. Lower-grade ores of Mwanesi require the liberation of iron-bearing material from gangue material which necessitates crushing to finer liberation sizes and subsequent agglomeration by sintering as well as pelletizing. A blend of sinter and pellets provides the optimum metallurgical physical and chemical properties suitable for BF ferrous burden.

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A SIMPLE MODEL FOR GASOLINE HYDROFINING

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Abstract

The paper presents a simulation case of gasoline hydrofining simulating using a simplified model. Considerations regarding the promotion of the simplified model are presented starting from a physical model that considers hydrofining in a three-phase system)

Keywords: Gasoline hydrofining, mathematical modeling, formal kinetics, catalytic hydrogenation

1. Introduction

The French chemist, Paul Sabatier found that unsaturated hydrocarbons in the vapor phase could be converted into saturated hydrocarbons by using hydrogen and a catalytic metal (nickel powder). His work was the foundation of the modern catalytic hydrogenation process [1].

In the decades that followed 1950, various proprietary catalytic hydrodesulfurization (HDS) or hydrofining processes, such as the one depicted in the schematic process flow diagram [2] below, have been commercialized. Currently, virtually all the petroleum refineries world-wide have one or more HDS units. After 2005, miniature HDS units had been developed for treating jet fuel to produce clean feedstock for synthesizing hydrogen for a fuel cell. Around 2010, this had been integrated into a small operating fuel cell system.

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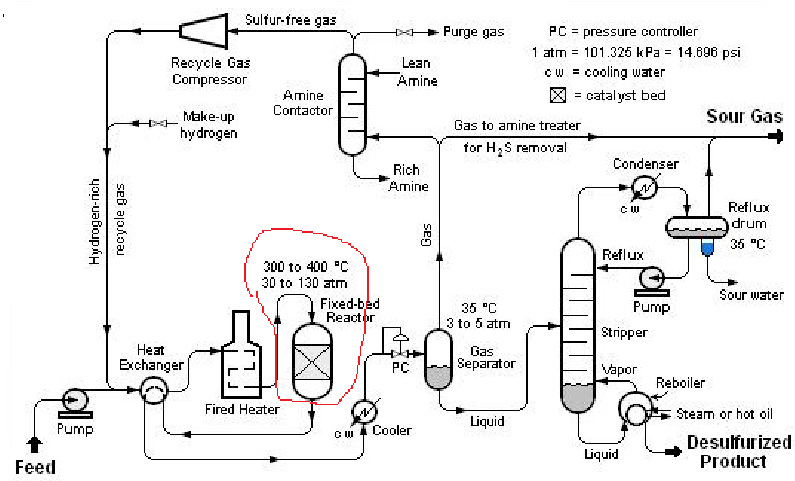

Fig. 1. Scheme of a typical hydrodesulphurization unit from a refinery [3]

Referring to gasoline the hydrofining represents the catalytic hydrogenation of commercial gasoline to remove sulfur and nitrogen compounds and to reduce the gasoline content in unsaturated hydrocarbons (alkenes and aromatics). With respect to figure 1, the process occurs in the red market reactor. If we consider, written below, that we have only four species in hydrogenation and that each reaction's kinetics can be expressed in a simple or complex manner then we have the possibility to build a mathematical model for gasoline reforming reactor [4-6].

$$R_1 - CH = CH - R_2 + H_2 \xrightarrow[cat]{} R_1 - CH_2 - CH_{12} - R_2 \quad (1)$$

$$R_3 - CH_2 - SH + H_2 \xrightarrow[cat]{} R_3 - CH_3 + H_2S \quad (2)$$

$$R_4 - CH_2 - N \quad + H_2 \xrightarrow[cat]{} R_4 - CH_3 + NH_3 \quad (3)$$

2. Modeling

On kinetics of refining process

From a concrete point of view, the hydrofining reactor is considered a three-phase reactor. Thus, the solid phase, containing the specific catalyst (most frequently molybdenum sulfide on alumina (Al_2O_3)), is covered with a film of the liquid phase, which is in contact with the gaseous phase, where the H_2 reactant is in excess. Hydrogen diffuses from the gaseous phase through the liquid phase to reach the reaction centers of the catalyst. Here it meets the reactants that come, by diffusion, from the liquid phase. The reaction products diffuse into the liquid phase and, as the case may be (H_2S, NH_3) end up in gas. Using two film mass transfer theory figure 2 try to explain, graphically, the above describe process.

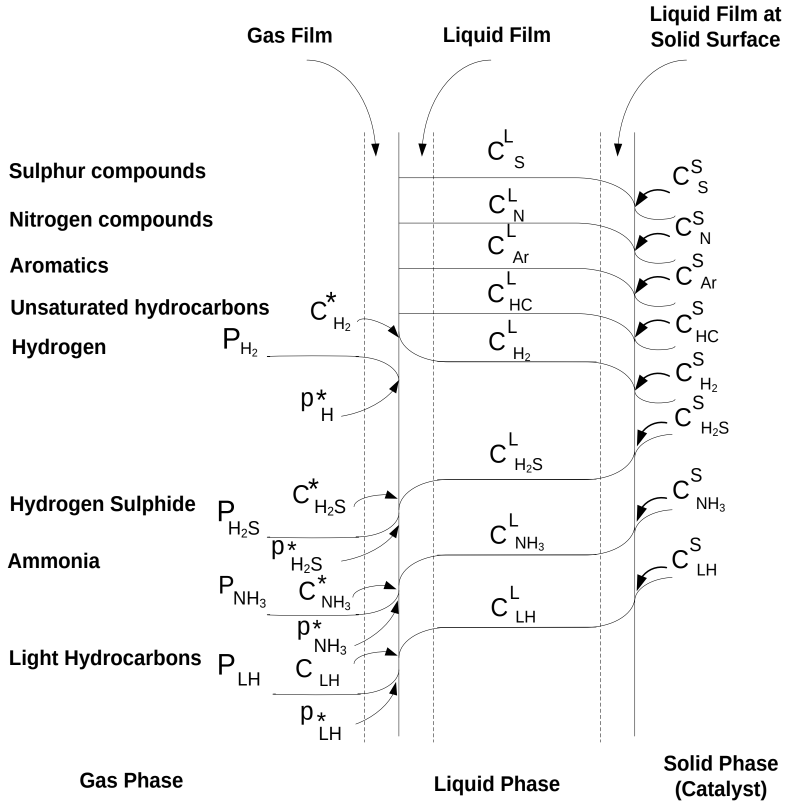

Fig. 2. Scheme of a typical hydrodesulphurization unit from a refinery

Modeling

Those in figure 2 leave open the possibility of expressing a fairly large number of kinetic expressions for the hydrofining process. An interesting limiting case is the one in which, with reference to those in figure 2, it is admitted that the surface chemical reaction(s) (reaction(s) from the active catalytic center) is the slowest. In this way, the speed of the process is determined by the speed of the catalytic chemical reactions. By extension, the expression of the speed of these reactions is used through formal kinetics. If referring to a reactant species, it admits a first order reaction kinetic then it can use the relation (4) for these kinetic. It is implicit that in relation (4) a hydrogen excess is admitted

$$v_{Ri} = k_{oi} \exp\left(\frac{E_i}{RT}\right) c_i \quad i = 1, 2, 3, 4 \tag{4}$$

In the reaction rate expression, the indices *1, 2 ... , 4* show the presence in the treated gasoline of alkenes, aromatics, thiols, and amines. For a reactor, working with hydrogen excess and without recirculation rate of liquid phase, it can be accepted that it behaves like a reactor with plug flow mixing. In this case the operation of the reactor is described in the set of relations (5) - (6)

$$\frac{dc_i}{dV} = -\frac{v_{Ri}}{G} \quad i = 1, 2 \dots ,4 \tag{5}$$

$$\frac{dT}{dV} = \frac{\sum_1^4 (v_{Ri} \Delta H_i)}{G c_{pam}} \tag{6}$$

As it is normaly, the pre-exponential k_{oi} and activation energy E_i depends of reactant species. With table 1 it gives [6] values for four alchenes, aromatics, thiols and disulphures respectively amines and other *N* compounds.

Table 1

Values of pre-eponential factor and activation energy for hydrogenation of some gasoline compounds

Species	Pre-exponențial factor (kg/m^{3}h)	Activation energy (J/Kmol)
Alkenes	5.05 10^8	7.021 10^7
Aromates	6.77 10^7	6.351 10^7
Sulphur compounds	2.17 10^7	5.17 10^7
Nitrogen compounds	4.44 10^6	4.131 10^7

For mathematical model integration of the gasoline composition at reactor entering must be known. Table 2 presents such a case.

Table 2

Entering reactor composition of a typical gasoline

Species	Assumed molecular mass (kg/kmol)	Composition mass (%)	Fluctuations
Alkenes	110	17.5	± 2.2
Aromates	98	14.5	± 1.8
Parafines	130	44,5	± 3.3
Naftenes	105	23.4	± 2.5
Sulphur compounds	115	3500 ppm	± 100
Nitrogen compounds	80	50 ppm	± 10

3. Results and discussions

Has been show that using literature data for kinetics (table 1) and reaction activation energy (table 1), the hydrofining reactor can be simulated, taking into account a real device and a real input operating conditions (as example: reactor volume 70 m^3, inlet temperature 335 ºC, operating pressure 52 bar, feed flow rate 10000 kg/h, hydrogen flow rate 3000 kg/h, and the gasoline composition having around of 3500 ppm sulfides (table 2)). The goal is to have sulfur in reactor gasoline exit under 5 ppm, according to imposed sulfur content for pump delivered gasoline.

If it assumed an isothermal reactor (we control by heating or cooling the reactor temperature) the model accepts the analytical solution (7)

$$\frac{c_i}{c_{0i}} = exp\left(-\frac{k_{0i}exp\left(\frac{E_i}{RT}\right)V}{G}\right) \tag{7}$$

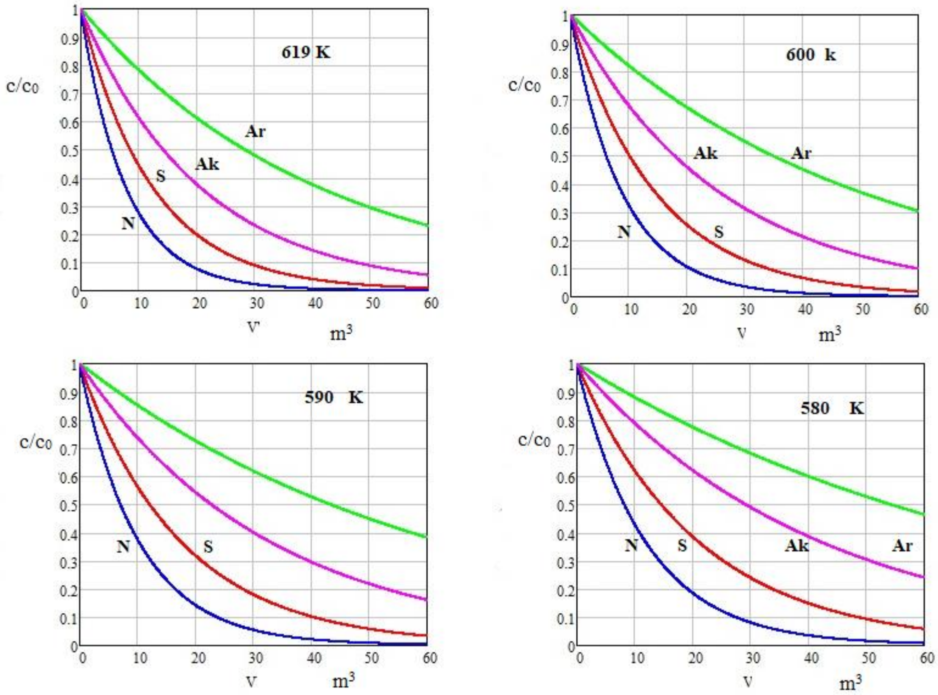

Fig. 3. Refining efficiency (c/c$_0$) versus reactor volume and temperature
(G= 10000 kg/h of gasoline with composition from table 2 (N-Nitrogen compounds, S-Sulphur compounds, Ak = alkenes, Ar-aromatics)

Figure 3 shows that it is not possible, for the given gasoline flow rate, to reach below 3.5 ppm sulfur compounds into hydrofined gasoline without reactor volume over 60 m^3 and operating temperature of 610 ^{0}C. A detailed reading of the sulfur content into hydrofined gasoline, according to operating temperature and reactor volume, also results from table 3.

Table 3

Reactor volume and operating temperature effect on sulphur s content into refined gasoline

V (m^3) / T (K)	620 ^{0}K	610 ^{0}K	600 ^{0}K	590 ^{0}K
50	30.02	61.788	116.134	201.069
60	11.59	27.559	116.134	113.554
70	4.475	12.292	29.738	64.129
80	1.728	5.483	15.049	36.217

Those from figure 3 and table 3 very clearly show how difficult it is to reach the required standards (5 ppm) respect to sulfur content in the hydrofined gasoline. At a given reactor volume and basic operating conditions (gasoline flow rate, hydrogen flow rate, reactor pressure etc.) the temperature is the only control process factor. And this is completely consistent with the operating practice of these reactor types.

4. Conclusions

The three-phase models of gasoline hydrorefining accept, for the case of process controlling through the reactions from the active centers of the catalyst, simplified models, characterized even by formal 1st order kinetics.

In isothermal operation, these models have analytical solutions that highlight the influence of the process factors on the final content in sulfur and nitrogen compounds of the processed gasoline. A concrete example was presented in this regard.

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STATIC CORROSION TESTING OF BIO-CERAMIC MATERIALS IN ARTIFICIAL SALIVA

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Abstract

In-vitro experiments have been conducted on ceramic biomaterials used for oral implants to determine their behavior when immersed in simulated saliva having 2 pH (acid pH=2 and basic pH=10). Thus, 2 different types of ceramic biomaterial samples already available on the market were purchased and immersed in simulated saliva and kept at 37°C for 30 days. In-depth characterization consisted of a wide series of structural characterization of both samples and fluid. Sample analysis consisted of: scanning electron microscopy (SEM) in order to establish the surface and deep corrosion, mass gain/loss assessment for determining the metallic ions loss and/or protective layer formation, pH and electrical conductivity measurements for the artificial saliva in order to determine the ions release phenomena. The key findings of the research are: during the 30 days while kept in artificial saliva, the samples show surface corrosion degradation and ion generation. Considering that it is highly improbable for such large area of metal to be exposed to real body fluids and all the samples have formed protective oxide films is making them appropriate for use.

Key words: artificial saliva, SEM, ceramic biomaterial

1. Introduction

Corrosion of biomaterials used in dentistry is a process that implies modification or destruction of these materials, in the interaction with the oral environment. In general, all dental materials are subjected to aggression in the oral environment. These materials are chemically degraded in a certain period, no matter if this period is longer or shorter [1].

The oral environment is considered an extremely aggressive environment, characterized by frequent and important changes in pH due to both the different types of food and microbial flora. In this environment, dental materials can undergo several degrading processes like, the release of their constituents into saliva through diffusion processes, erosion if acids are present, colour change or corrosion. The oral cavity is a dynamic environment where changes occur constantly. It is also a warm and humid environment, provided with numerous factors that can negatively affect the mechanical properties of ceramic

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*Corresponding author: email address: laurentiu.ceatra@comoti.ro restorations, as like: (a) water in the saliva; (b) water from dental cement and dentinal tubules; (c) masticator stress; (d) the stress determined by the differences in thermal expansion coefficients of restorative materials; (e) temperature variations; (f) pH variation.

The usual pH of saliva is 6.8-7.2, but it can be slightly lowered or raised depending on food and drink consumption. For example, every time a carbohydrate-rich food is ingested - the organic acids lower the pH of the oral cavity to an acidic pH of about 4.5. In response, salivary flow increases, and therefore an increase in bicarbonate flow, would raise the oral pH to normal levels again. However, acidic products such as lemonade and other soft drinks can lower oral pH determination an acidic environment in the oral cavity without bacterial involvement [2].

Glass ceramic materials used for dental prostheses are susceptible to corrosion. The oral environment presents a major challenge for restorations in dentistry due to alternating pH environments. The oral environment is typically subject to pH fluctuations varying in a range from 2 to 14, determining therefore acidity, neutrality, or alkalinity [3]. Ingestion of both, food stuff such as spinach (pH 8.3), beans or soy (pH 12) and antacids (pH 10-14) can raise the pH of the local oral environment, while soft drinks (pH 2.6), apple juice (pH 3.8) and various candies (pH ≤ 3) can decrease it.

Dietary habits and buffering capacity of saliva have also a significant effect on the pH of oral fluid [4] and challenges the chemical durability of ceramic-based restorations. In addition, ceramic corrosion has been shown to adversely affect the fracture toughness of these materials [5,6] and their surface [7].

These effects can reduce the longevity of ceramic-based restorations and consequently, a damage to adjacent oral structures will be observed as a result of enamel wear, plaque build-up and periodontal disease. In addition, rougher surfaces are more likely to cause abrasive wear of opposing tooth structures. Ceramics undergo both degradation and corrosion of its surface through a complex mechanism, involving the decomposition of the glass phase and the release of composing ions from its microstructure. This process is influenced by several factors, including among them mechanical abrasion and a competing loss of ions as a result of the reactions with the environment.

Results of in vitro chemical corrosion studies suggest that acidic media adversely affect the micro hardness, flexural strength, and surface roughness of ceramics during prolonged exposure. Additionally, it has been shown that surface roughness determines the following: a decrease flexural strength, an increasing wear of opposing enamel surfaces, and last but not the least the occurrence of the plaque build-up that can ultimately lead to secondary caries and periodontal disease. The studies performed until now brought evidence suggesting that acidic or basic solutions increase surface degradation and reduce structural strength.

2. Experimental – Method and Materials

The experiments were performed by the Physical-Chemical Testing Laboratory and respectively the Physical-Mechanical Testing Laboratory of INCDT COMOTI using the necessary equipment and materials, being focused on the following:

- Highlighting the corrosion of the studied bio ceramic materials, after immersing the samples in the simulated saliva solution, with pH=2 and pH=10, at a temperature of 37°C, for different time ranges (SEM),
- Monitoring both, the pH and conductivity of the simulated saliva solutions, at different periods of immersion of the studied samples,
- Monitoring the surface characteristics of the studied samples at different time ranges: the initial immersion moment, after 24 h of immersion, after 72 h of immersion, after 168 h of immersion, after 360 h of immersion and after 720 h of immersion(SEM).

The bio ceramics corrosion rate can vary, depending on many factors as: the pH of the immersion solution, the chemical composition of the immersion solution, the temperature of the environment, the composition of the biomaterial and respectively its structure.

Since different foods and drinks with a variety of pH levels are constantly ingested into the mouth they are constantly buffered by saliva, therefore simulations of saliva pH were performed to highlight their similarity.

The performed experiments aimed to test the way that simulated saliva solutions with different pH values accelerate the corrosion of dental ceramics. Therefore, the investigated samples were immersed in the solutions prepared in the laboratory for the time ranges previously mentioned above.

The surfaces of the immersed biomaterial samples were carefully scanned at each time moment stated above by electron microscopy (SEM).

The pH and conductivity of the analysed immersion solutions were determined by the means of a pH/conductivity measuring device at each time moment stated above while the weight of the investigated samples was determined using an analytic balance. These investigations regarding the ceramic biomaterials degradation in solutions miming saliva, aim to determine their degradation rate from the moment they are used as dental crowns.

The main steps, that were attended for the smooth running of the experiments, are presented further on.

2.1. Preparation of both, the ceramic materials samples subjected to laboratory experiments and the artificial saliva solutions used for their immersion

For the deployment of the experimentalplan there were used 4 samples of dental ceramic materials. These 4 samples come from two different unused materials deposited on chrome-cobalt metal alloy, purchased from a dental technique workshop.

Ceramic material No. 1 is divided in 2 samples:

- sample 1.10 - will be immersed in an artificial saliva solution with pH=10
- sample 1.2 - will be immersed in an artificial saliva solution with pH=2

Ceramic material No. 2 is also divided in 2 samples

- sample 2.10 - will be immersed in an artificial saliva solution with pH=10
- sample 2.2 - will be immersed in an artificial saliva solution with pH=2

The four samples are presented below in figure 1

Fig. 1. Dental ceramic samples used in the experimental plan

The dental ceramic samples were subjected to ultrasonication in ethanol for 2 minutes to achieve a cleansing as good as possible, further on were washed with distilled water and finally dried in a warm air stream.

Table 1

Initial weight of the immersed samples

Immersed samples	Sample 1.2	Sample 1.10	Sample 2.2	Sample 2.10
Weight after drying (g)	0.731	1.5359	0.3837	0.547

Fig. 2. Preparation of artificial saliva solution:left- with neutral pH; middle- with pH = 1.98; right- with pH = 10.

The pH of the prepared artificial saliva solutions was measured with the METLER TOLEDO pH meter existing in the Physical-Chemical Testing Laboratory. The equipment is also provided with a conductivity measuring cellthat allowed us to measure the conductivity of the preparated artificial saliva solutions.

Table 2

Reagents and corresponding quantities used in the preparation of artificial saliva immersion solutions

Crt. No.	Reagents used for artificial saliva preparation	The necessary amount of reagents for preparation of one liter of artificial saliva pH ≈ 6.5 - 7.4	The necessary amount of reagents for preparation of one 2.10 liters of artificial saliva pH ≈ 6.5 - 7.4
		g/L or mL/L	g/L or mL/L
1	Potassium chloride	0.72	1.512
2	Calcium chloride dihydrate	0.22	0.462
3	Sodium chloride	0.6	1.26
4	Potassium phosphate monobasic	0.68	1.428
5	Di-sodium hydrogen phosphate dodecahydrate	0.866	1.8186
6	Potassium bicarbonate	1.5	3.15
7	Potassium thiocyanate	0.06	0.126
8	Citric acid monohydrate	0.03	0.063
9	1M HCl solution or 1M KOH solution		

The 4 samples of dental bioceramics were immersed into 4 vessels provided with a threaded cap, containing each one the prepared artificial saliva solutions with the corresponding pH.

Fig. 3. The vessels with the prepared solutions and the studied samples

These 4 vessels were placed in the thermostatic bath at (37±1)°C, in accordance with the EN ISO 10271 standard. The bath is equipped with a support frame and a shaking device that provides a shaking frequency of 35 - 160 movements per minute (forward/backward horizontal movement. The shaking frequency was set to the first step, and the bath lid is kept closed during the experiment.

Fig. 4. The vessels with the studied samples, immersed in the solutions of artificial saliva with pH=2 and respectively pH=10

3. Results and discussions

3.1. Results obtained in the static corrosion of the samples originating from studied dental bioceramics

Sampling of artificial saliva solutions and the specified analyzes were carried out at different time periods, as will be seen in the tables and graphs that will be presented further on.

These results imply the following:

- The parameters of the artificial saliva solutions used for immersion of the samples - the sampled volume, the pH and respectively the conductivity,

- The parameters of the immersed samples of biomaterial - their weight and the monitoring of the surface modifications of each studied sample by the means of scanning electron microscopy (SEM).

The parameters of the artificial saliva solutions used for immersion of the samples.

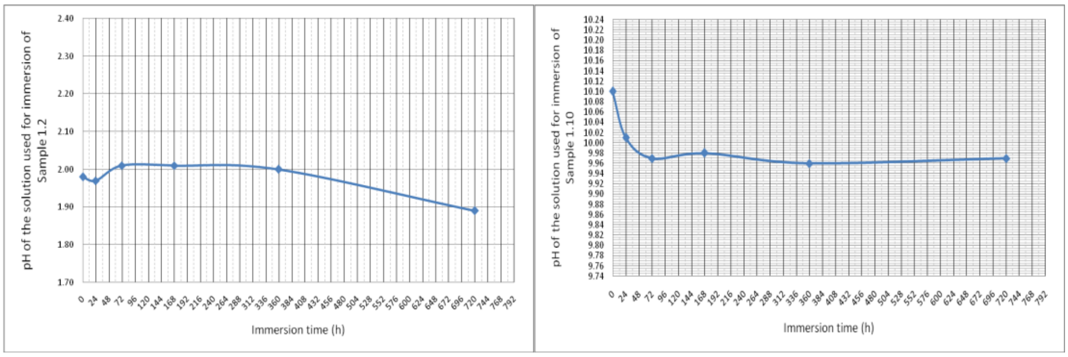

Fig. 5.pH evolution of the solution used for immersion over time:left - Sample 1.2; right - Sample 1.10

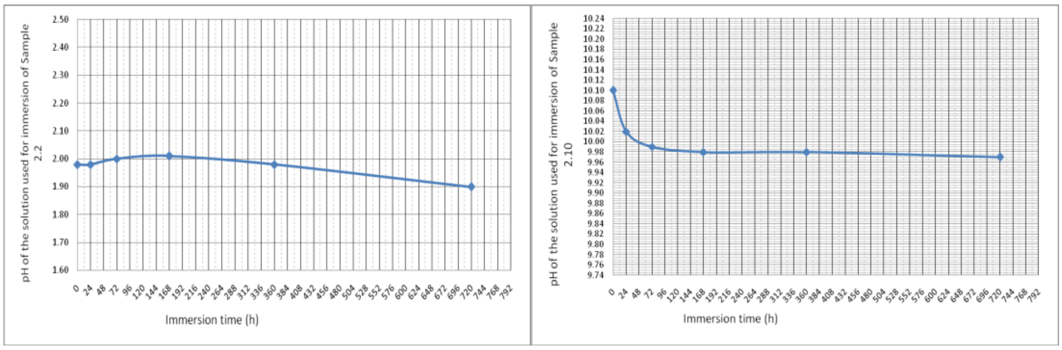

Fig. 6. pH evolution of the solution used for immersion over time:left - Sample 2.2; right - Sample 2.10

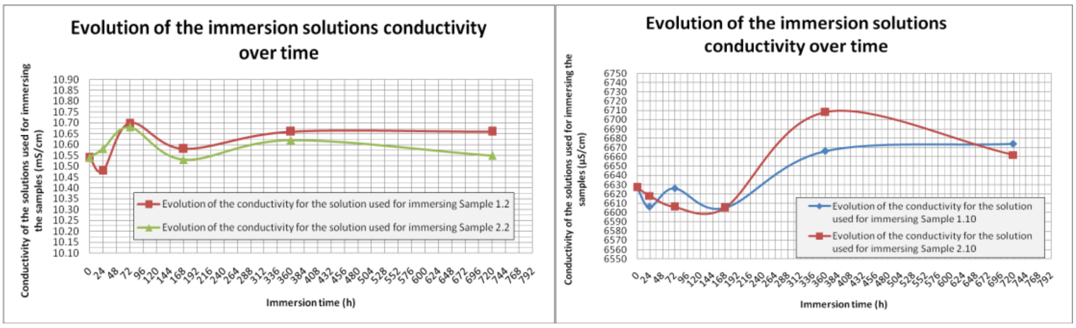

Fig. 7. Conductivity evolution of the solutions used for the immersion over time:left - samples 1.2 and 2.2; right - samples 1.10 and 2.10

Table 3

The weight evolution of the immersed samples, periodically weighed

Immersed samples	Sample weighing date	Immersionperiod (hours)	SAMPLE 1.2	SAMPLE 1.10	SAMPLE 2.2	SAMPLE 2.10
Initial weight (g)	18.05.2022	0	0.731	1.5359	0.3837	0.5470
Sample's weight after drying (g)	19.05.2022 (1 day of immersion)	24	0.7308	1.5353	0.3817	0.5465
Sample's weight after drying (g)	21.05.2022 (3 day of immersion)	72	0.7305	1.5351	0.3828	0.5467
Sample's weight after drying (g)	25.05.2022 (7 day of immersion)	168	0.7305	1.5348	0.3837	0.5457
Sample's weight after drying (g)	02.06.2022 (15 day of immersion)	360	0.7306	1.5347	0.3828	0.5478
Sample's weight after drying (g)	17.06.2022 (30 day of immersion)	720	0.7301	1.5351	0.3826	0.5469

3.2. SEM analysis

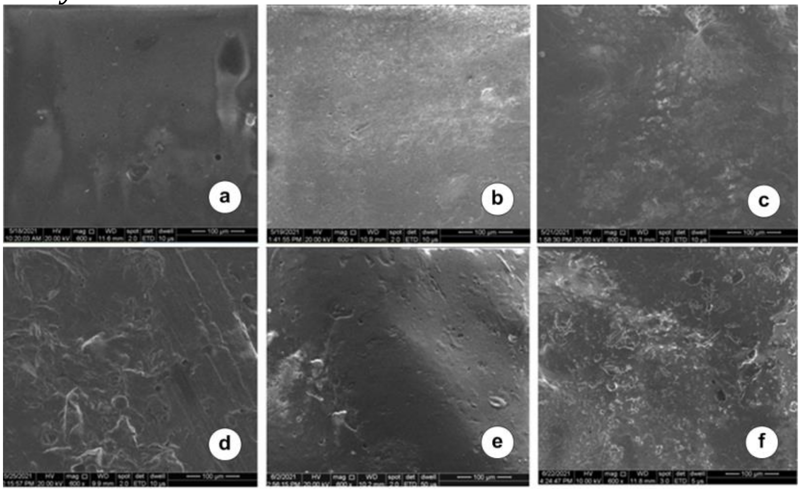

Fig. 8. SEM images SAMPLE 1.2 (x 600):a) Moment 0; b)After 24 hours of immersion; c)After 72 hours of immersion; d) After 168 hours of immersion; e)After 360 hours of immersion; f)After 720 hours of immersion.

In the following figures (Fig. 8-11), there are exposed the most representative images obtained by the means of SEM, when minutiously scanning the surface of the 4 samples.

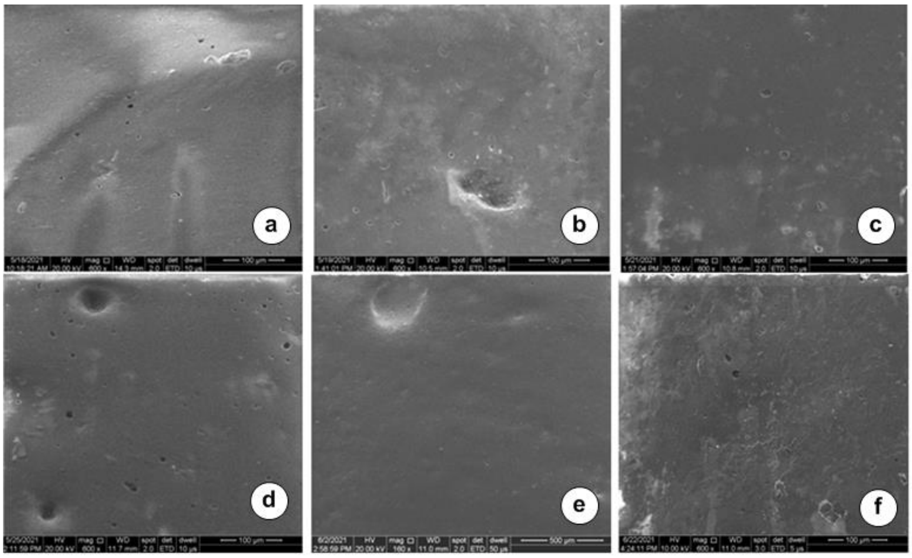

Fig. 9. SEM images SAMPLE 1.10 (x 600):a) Moment 0; b)After 24 hours of immersion; c)After 72 hours of immersion; d) After 168 hours of immersion; e)After 360 hours of immersion; f)After 720 hours of immersion.

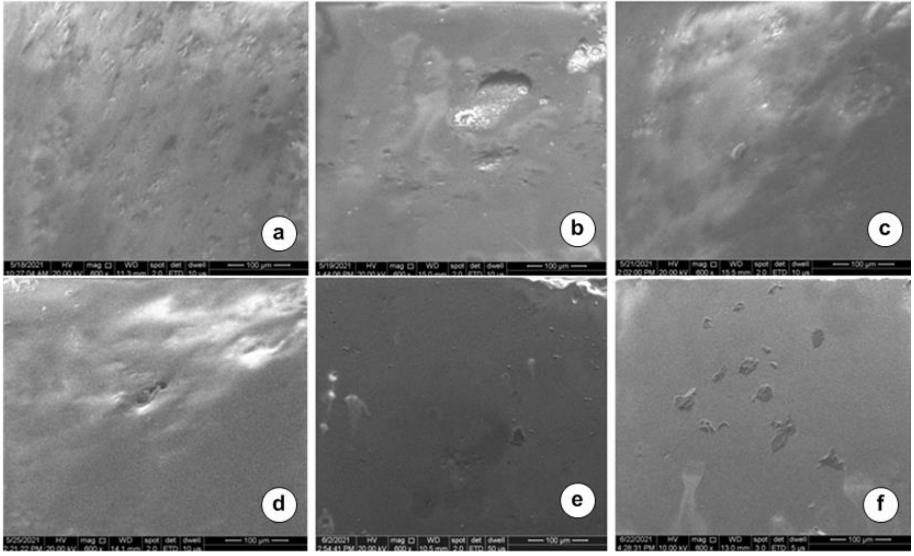

Fig. 10. SEM images SAMPLE 2.2 (x 600):a) Moment 0; b)After 24 hours of immersion; c)After 72 hours of immersion; d) After 168 hours of immersion; e)After 360 hours of immersion; f)After 720 hours of immersion.

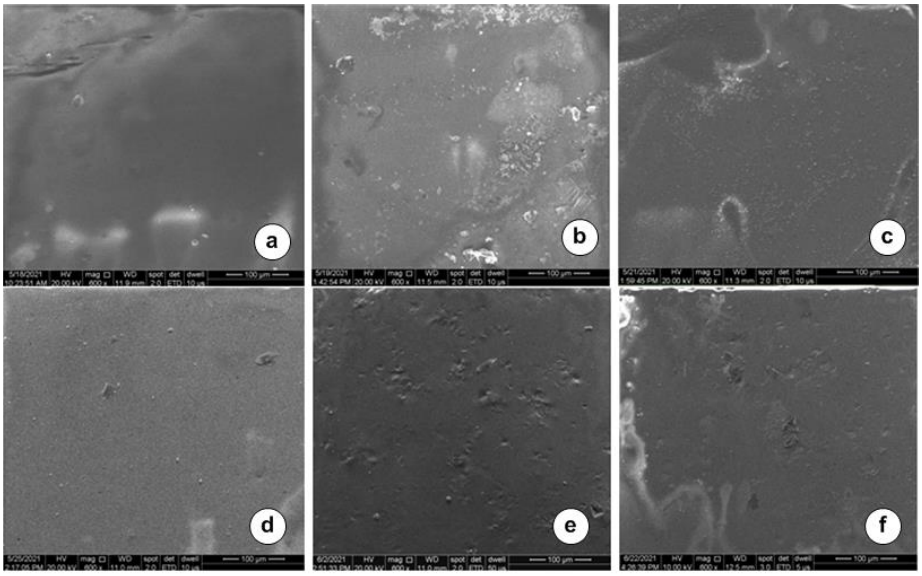

Fig. 11. SEM images SAMPLE 2.10 (x 600):a) Moment 0; b)After 24 hours of immersion; c)After 72 hours of immersion; d) After 168 hours of immersion; e)After 360 hours of immersion; f)After 720 hours of immersion.

4.Conclusions

- Ceramic based biomaterials have been characterized within this paper in terms of surface corrosion and metallic ions while immersed in artificial saliva by using advanced investigation techniques aiming to highlight even more the biocompatibility of these materials.
- The type of corrosion that occurs was different (corrosion spots, pitting and/or mixture) as well the moment they appear. This fact can be attributed to the internal structure of the biomaterial as well as its composition. The corrosion types and formation mechanisms have been in-depth assessed by to optical and scanning electron microscopy, proving that the microscopy can be a very useful "instrument" in material characterization.
- The concentration of metallic ions dissociated from the biomaterial into the SBF solution was assessed by measuring solution's electrical conductivity which highlights that it varies during SBF solution exposure.
- Even though the material has a large area in direct contact with artificial saliva, the ions dissociated within the solution pose no threat to medical use.

- The testing protocol and the equipment used within this paper are complementary to the already used ones for assessing the behaviour and corrosion of metal-based biomaterials in artificial saliva.

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HYPERSPHERE COORDINATES ON CALCULATION OF THE DIHEDRAL ANGLES FROM CARBON CHEMICAL SHIFT

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Abstract

The transformation from 4D - 3D - 2D, from hypersphere - sphere - circle, otherwise from torus to Dupin cyclide, can be demonstrated with NMR data (carbon chemical shift δ_{Cn}[ppm], vicinal coupling constant $^{3}J_{HH}$[Hz]) applied on 3-Sphere theory. The shape of the iminocyclitols with D, L-ribitol stereochemistry was analyzed with trigonometric equations, the calculation of the dihedral angle θ_{HnHN+1}[deg] from δ_{Cn}[ppm] giving different system of equations from every curves. From δ_{Cn}[ppm] with hypersphere and Hopf equations can be calculated the trans-ee $^{3}J_{HH}$[Hz] recorded as bs.

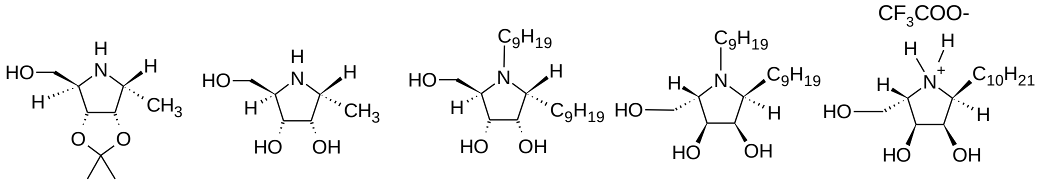
Key words: 3-sphere, dihedral angle, hypersphere coordinates.

1. Introduction

3-Sphere, a hypersphere in 4D, enable calculation of the dihedral angles[1, 2] and tetrahedral angles[3] from carbon chemical shift δ_{Cn}[ppm] and/or vicinal coupling constant $^{3}J_{HH}$[Hz][1] with application on conformational analysis[4]. A method able to give all the isomers with right stereochemistry and sign for every vicinal constant coupling. A method build and explain step by step from the mathematical point of view with - Lie algebra - Hopf fibration.[2]

2. Experimental and/or Modelling:

Dihedral angles of iminocyclitols **1**-**5** (Fig. 1)[5] are calculated in table 1 from δ_{Cn}[ppm], and in close relationship with the recorded $^{3}J_{HH}$[Hz] establysed the trigonometric equations for every stereochemistry.



1 **2** **3** **4** **5**

Fig. 1. Iminocyclitols with α-D-ribitol (**1**-**3**) and β-L-ribitol (**4**, **5**) stereochemistry.

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Table 1

Dihedral angle $\theta_{H_nH_{n+1}}$[deg] and vicinal coupling constant $^3J_{HH}$[Hz] calculated from carbon chemical shift δ_{C_n}[ppm] of iminocyclitols 1-5.

Entry	Im	$^3J_{HH}{}^a$ [Hz]	θ_{HH} [deg]	$\delta_{Cn}{}^a$ [ppm]	$R_m{}^{b,c}$ [π]	Hypersphere equations	θ_{HH} [deg]	$^3J_{HH}$ [Hz]
1.	**1**	H_1H_2: 4.1	22.76	55.8	1.563	$[\tan^{-1}\sin(\cos^{-1}-1/Rm)/2]/2$ $\tan^{-1}\sin[(\cos^{-1}1/Rm)/2]$	21.08 22.99	4.15 4.09
2.		H_2H_3: 5.4	-26.64	83.5	2.338	$\tan^{-1}\sin-[(\cos^{-1}1/Rm)/2]$	-28.14	5.43
3.				84.3	2.361	$\tan^{-1}\sin-[(\cos^{-1}1/Rm)/2]$	-28.23	5.43
4.		H_3H_4: 0	-89.96	65.9	1.845	$2x\{\tan^{-1}\cos[-(\sin^{-1}1/Rm)/2]\}$	-87.62^c	0.77
5.	**2**	H_1H_2: 3.1	51.56	57.4	1.607	$[\cos^{-1}1/Rm]$	51.54	3.1
6.		H_2H_3: 3.9	29.16	71.5	1.995	$[\cos^{-1}1/Rm]/2$	29.96	3.87
7.				71.7	2.008	$[\cos^{-1}1/Rm]/2$	30.06	3.87
8.		H_3H_4: 8.8	-168.7	66.8	1.871	$[\tan-(Rm)^{1/2}]/4$	-166.5	8.74
9.	**3**	H_1H_2: 4.8	-2.159	63.7	1.784	$2\{\tan^{-1}\cos-[(\sin^{-1}1/Rm)/2]\}^d$	-2.57^c	4.67
10.		H_2H_3: 5.2	-18.16	72.5	2.030	$2x[\tan^{-1}Rm^{1/2}]^d$	-19.8	5.24
11.				74.0	2.072	$2x[\tan^{-1}Rm^{1/2}]^d$	-20.43	5.25
12.		H_3H_4: 0	-89.96	69.3	1.941	$2x\{\tan^{-1}\cos[-(\sin^{-1}1/Rm)/2]\}$	-87.87^c	0.73
13.	**4**	H_1H_2: 4.8	-2.159	63.7	1.915	$2x\{\tan^{-1}\cos[(\sin^{-1}1/Rm)/2]\}^d$	-2.18^c	4.68
14.		H_2H_3: 5.2	-18.16	72.5	2.284	$[\tan^{-1}1/Rm^{1/2}]/2$	-16.74	5.18
15.				74.0	2.036	$[\tan^{-1}1/Rm^{1/2}]/2$ $2x[\tan^{-1}Rm^{1/2}]^d$	-17.52 -19.95	5.16 5.24
16.		H_3H_4: 0	89.96	69.3	1.985	$2x\{\tan^{-1}\cos[(\sin^{-1}1/Rm)/2]\}$	87.98^c	0.71
17.	**5**	H_1H_2: 2.8	58.64	63.3	1.773	$2x\tan^{-1}1/Rm$	58.84	2.79
18.		H_2H_3: 3.6	38.16	72.1	2.019	$2x\tan^{-1}1/Rm^d$	37.31	3.62
19.				73.4	2.056	$2x\tan^{-1}1/Rm^d$	38.12	3.60
20.		H_3H_4: 8.8	167.44	63.9	1.789	$[\tan-(Rm)^{1/2}]/4$	166.6	8.75

a. δ[ppm] ^{13}C-NMR, 75[MHz], ^{1}H-NMR 400[MHz]: **1**, **3**, **4**-$CDCl_3$, **2**-D_2O, **5**-CD_3OD; b. $R_m = \Delta\delta_{Cn}x\omega_Lx4x10^{-3}/10.71$[gauss], $\Delta\delta_{Cn}$–chemical shift[ppm], ω_L – Larmor frequency[MHz], gyromagnetic ratio $\gamma = 10.71[MHzxT^{-1}] = 6.7[10^7xradxT^{-1}xs^{-1}]$, c. R_m dodecahedron 1.618, icosahedron 2.618: 1.7 – 1.9 θ_{HnHn+1} or $\phi = \theta^3$ or θ^4[deg], d. ϕ[deg].

3. Results and discussions

Having in mind the 2D trigonometric functions distribution around the five membered ring: C_1 *cotan*, C_2 and C_3 *cos* or *sin*, C_4 *tan*, C_5 *cosec* or *sec*, the calculation of the dihedral angles under hypersphere theory open a door on the influence of the substituents/protective groups on the shape of the iminocyclitols **1**-**5**. In table 1 are presented dihedral angles θ_{HnHn+1}[deg] calculated from carbon chemical shift δ_{Cn}[ppm] in close relationship with vicinal coupling constants $^3J_{HH}$[Hz], and the corresponding trigonometric equations. Torus to Dupin cyclide coordinate, *sin/cos* to *tan/cotan*, set A and set B of the units C and T, are under 3D on unit C or T and under 4D as hypersphere coordinate (Table 1, entry 1-4, 9, 12, 13, 16). Dihedral angles with *cis*/*trans* stereochemistry on hypersphere after translation from higher dimension space to two dimension can be drown on seven sets angles calculated from *sin* or *tan* functions on one unit, or six sets angles on two units for all stereochemistry[2]. The first angle of set A is equal with half ϕ_1 of set B and first angle of set B equal with half ϕ_1 of set A resulting Villarceau circles[6], charactersistic circles of torus. Dihedral angles resulting at intersection of two disks in close relationships with vicinal angles, angle results from vicinal coupling constant $^3J_{HH}$[Hz] under algebraic rule[2].

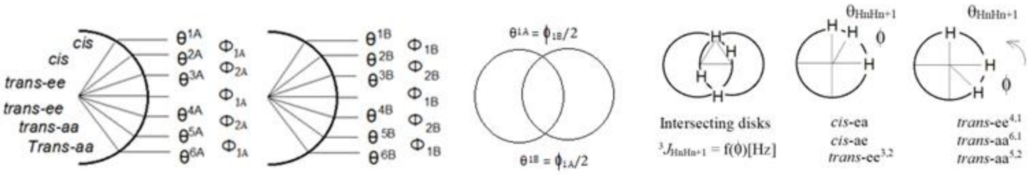

Fig. 2. Dihedral θ^{nN} – vicinal ϕ^{nN} angles (n = 1-6, N = A, B) on Villarceau circles.

The torus or Dupin cyclide equations for calculation of the dihedral angles in 3D from vicinal coupling constant become hypersphere equations in 4D in case of calculation of the dihedral angles from carbon chemical shift *without building units*. In 3D dihedral angles with *cis*/*trans* stereochemistry on two units are calculated from *sin* and *cos* functions (CU and CS), or from *tan* and *cotan* functions (TU and TS). *In 4D the hypersphere equation result from angles of five sets calculated from sin and cos functions and two sets angles calculated from tan and cotan functions.* The 4D coordinates of isopropylidene iminocyclitol **1** (Table 1, entry 1-4) after deprotection (**2**) become 2D (Table 1, circle equations: entry 5-

7, circle inversion entry 8), relative to trifloroacetate salt iminocyclitols **5**, bearing decyl group at C_1 instead of methyl (**2**), with all equations under circle inversion (Table 1, entry 17-20). The iminocycitols **3**, **4**, bearing alkyl chain at C_1 and nitrogen, have C_1 and C_4 under 4D and C_2 and C_3 under 2D, with antiral activity evaluated in BVDV, IC_{50} 4.6 and 8.2µM. Analog to **5**, with nonyl at C_1 has an IC_{50} value of 1.5 µM relative to 10 µM *N*-*n*-nonyl DNJ[5]. The phase angle of the pseudorotation P[deg] calculated with Altona-3-Sphere model[4] shown change on conformation between $^4T_3$ and $^3T_4$ for **1**-**4** and ^3E for **5**, since with molecular models was simulated in case of **5** two atoms of carbon down of plane ($_{32}E$), or gradually out of plane at smaller differences. Introduction of the tangent function[3] change the sign and stereochemistry of θ_{HnHN+1}, the number of isomers increasing from two to six.

The $^3J_{HH}$ recorded as bs[5] can be calculated from R_m with hypersphere equation eq. 1(Table 1, entry. 4, 12, 16) and 3-sphere eq. 2[1, 3] without building units.

$$\text{Eq. 1: } \theta_{H3H4} = 2x\{\tan^{-1}\cos[-(\sin^{-1}1/R_m)/2]\}$$

$$\text{Eq. 2: } \sin^{-1}\cos\theta_{H3H4} = \phi,\ ^3J_{H3H4} = (\phi)^{1/2}/m$$

where: R_m – carbon chemical shift δ_{Cn} transformed from ppm in gauss, θ_{H3H4} *trans-ee* digedral angle[deg], ϕ – vicinal angle[deg], $^3J_{HH}$ – vicinal coupling constant[Hz], m = 1 *trans-aa*, m = 2 *cis*, *trans-ee* stereochemistry.

4. Conclusions

The method presented in this paper for calculation of the dihedral angles from δ_{Cn} don't gives the sign, the $^3J_{HH}$[Hz] established the sign, but demonstrate the influence of the substituents/protective groups on the geometry of iminocyclitols, and no at list on theier reactivity or biological activity[5]. The isopropylidene iminocyclitol **1** have all the trigonometric equation under torus – Dupin cyclide coordinates relative to iminocyclitols **2** and **5**, 4D relative to 2D or 3D relative to 2D?

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