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*Full Length Research Paper*

# Giant African land snails (*Achatina achatina* and *Archachatina marginata*) as bioindicator of heavy metal pollution

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It is important to always monitor the bioaccumulation potential for heavy metals by organisms especially the edible ones, to assess their potential risk to human health. This study evaluated the bioaccumulation of heavy metals in the shell and soft tissues of snails. Forty snails each were purchased from Ikire and Ore towns. The snails' shells, feet, digestive tracts and glands were analysed for bioaccumulation of heavy metals using an Atomic Absorption Spectrophotometer. The results showed that the concentration of heavy metals varied with the location and species of the snail. *Archachatina marginata* from Ore accumulated higher concentrations of heavy metals than *A. marginata* from Ikire. The concentration of Pb in *Achatina achatina* and *A. marginata* from Ikire, and Cd in *A. marginata* from Ore are slightly above the FAO/WHO permissible limits. Foot bioaccumulated more heavy metals in *A. achatina* while the digestive gland bioaccumulated more heavy metals in *A. marginata*. The study concluded that the shell and soft tissues of *A. achatina* at Ikire and *A. marginata* at Ikire and Ore bioaccumulated some levels of toxic heavy metals. *A. achatina* and *A. marginata* are capable of being used as a sentinel to study the physiological and biochemical imbalances in living organisms arising from the accumulation of heavy metals.

**Key words:** Bioaccumulation, heavy metal pollution, snails, *Achatina achatina*, *Archachatina marginata*.

## INTRODUCTION

Giant African land snail is the common name for *Achatina achatina* (Linnaeus). It can grow up to 200 mm in length and a maximum diameter of 100 mm in the native range within the northern part of West Africa (Dar et al., 2017). *Archachatina marginata* (Swainson) is also one of the giant African snails with the common name banana rasp, it has the potential to grow up to 210 mm in length and 130 mm in diameter (Awodiran et al., 2012). *A. marginata* native range is within West Africa (Barker, 2001). These two species belong to the family Achatinidae.

Achatinids are generally nocturnal forest dwellers but can fit into disturbed habitats. Hence, they are active more during the period of high humidity and feed on a wide range of living and dead plant materials. When reared in captivity, food materials often consumed by this species include banana, lettuce, papaya and the rind of watermelon (Ajayi and Babatunde, 2022). Achatinids attain sexual maturity at 9 to 10 months and can live up to 5 years (Cowie et al., 2009).

Appenroth (2010) and Oguh et al. (2019a) described

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heavy metals as those metals whose atomic mass exceeds that of Calcium; having relative densities greater than 5 g/cm<sup>3</sup>. Heavy metals are toxic even at low concentrations, not biodegradable but can be assimilated and bioaccumulated in the tissues (Gupta and Singh, 2011). Heavy metals may include some trace elements such as Zinc (Zn), Iron (Fe), and Nickel (Ni) that are nutritionally required for enzymatic reactions and have functional roles in various metabolic processes. They become toxic when their concentrations exceed a certain limit (Gawad, 2018). The other category of heavy metals is nonessential and they are environmental pollutants. They are toxic even at a very low concentration. Examples include Arsenic (As), Cadmium (Cd), Thallium (Tl) and Tin (Sn).

The two major sources of heavy metals are natural and anthropogenic. Natural sources include atmospheric sources, geological weathering, the earth's crust and volcanic emissions while anthropogenic sources are a result of various human activities through effluent from automobiles, weathering, sewage sludge, fossil fuel burning, manufacturing industries, and fertilizer application (Mahmoud and Abu-Taleb, 2013). The probable health hazards posed by heavy metals remain a global concern especially, in developing countries, where treatment and elimination of effluents are inadequate or non-existent (Banaee and Taheri, 2019).

Snail meat is proteinous, rich in essential fatty acids and amino acids, supplies enough essential minerals, and contains less fat and cholesterol (Ademolu et al., 2004). Thus, snail meat holds the potential to bridge the gap of would-be nutritional deficiency owing to its nutritional profile, palatability and availability (Ajayi and Babatunde, 2022). These potentials are being harnessed because snails are easily accessible either by production, purchase or picking (hunting) in the wild (Anthony et al., 2010; Adeniyi et al., 2013).

Though snails are omnivores (Amobi and Ezewudo, 2019), wild snails which are commonly found in the bush, have free access to soil, vegetables, fruits, and plants which might have grown in heavy metals contaminated areas (Nica et al., 2012; Louzon et al., 2021). Domesticated snails fed with plant food materials that have been contaminated can accumulate such heavy metals. This could adversely affect their growth and reproductive capacity. Plants that grow near the roadside, domestic and industrial waste dumpsites tend to absorb and accumulate heavy metals (Singh et al., 2012; Salih et al., 2021). It is worthy to note that some of these elements are essential for the normal functions of the body but could cause acute and chronic poisoning when their concentrations exceed the tolerable limit.

Incessant consumption of fruits and vegetables grown in heavy metal highly contaminated soils and eating of animals that feed on the plants grown on such soil are the main route through which man gets infected (Khan et al., 2014). Heavy metals can bioaccumulate in the tissues of humans and non-humans and wreck great health

havoc. Metal-induced pathologies remain a global public health concern (Hina et al., 2011; Izah et al., 2017). The toxic effects of heavy metals may be due to their interference with normal body biochemistry in the normal metabolic process (Okunola et al., 2011). Metals for instance Pb, Cd, and As may cause toxicity by preferentially interacting with thiol-containing groups of biomolecules, oxygen, or sulphur-containing compounds to induce oxidative stress, causing tissue damage (Lemire et al., 2013). Heavy metals are known disruptors of lipid homeostasis and the antioxidant system such as Pb and As in rats (Ademuyiwa et al., 2010), Cd in crabs (Yang et al., 2013), and Cd and Pb in snails and fish (Banaee and Taheri, 2019; Sarah et al., 2019). Exposure to Pb may cause mitochondrial apoptosis (Jin et al., 2017), disrupt the cellular redox state, inhibit haeme biosynthesis (Mani et al., 2018), and cause convulsion, encephalopathy and hypertension (Iweala et al., 2014). Cadmium has been reported to be hepatotoxic and nephrotoxic (Iweala et al., 2014). Cd may disrupt the metabolism of lipids by altering the levels of triacylglycerol, cholesterol, and lipoproteins via the inhibition of lipogenic enzymes (Yang et al., 2013). Keratosis, mitochondrial damage, disruption of glycolysis, dyslipidaemia, and carcinogenicity are hallmarks of arsenic (As) toxicity (Gupta and Singh, 2011; Afolabi et al., 2015). Furthermore, heavy metals toxicity may lower endogenous antioxidant molecules (such as metallothionein), impede secondary antioxidant enzymes (such as Arylesterase), reduce glutathione levels, increase lipid peroxidation, and induce oxidative stress (Gupta and Singh, 2011; Izah et al., 2017; Banaee and Taheri, 2019).

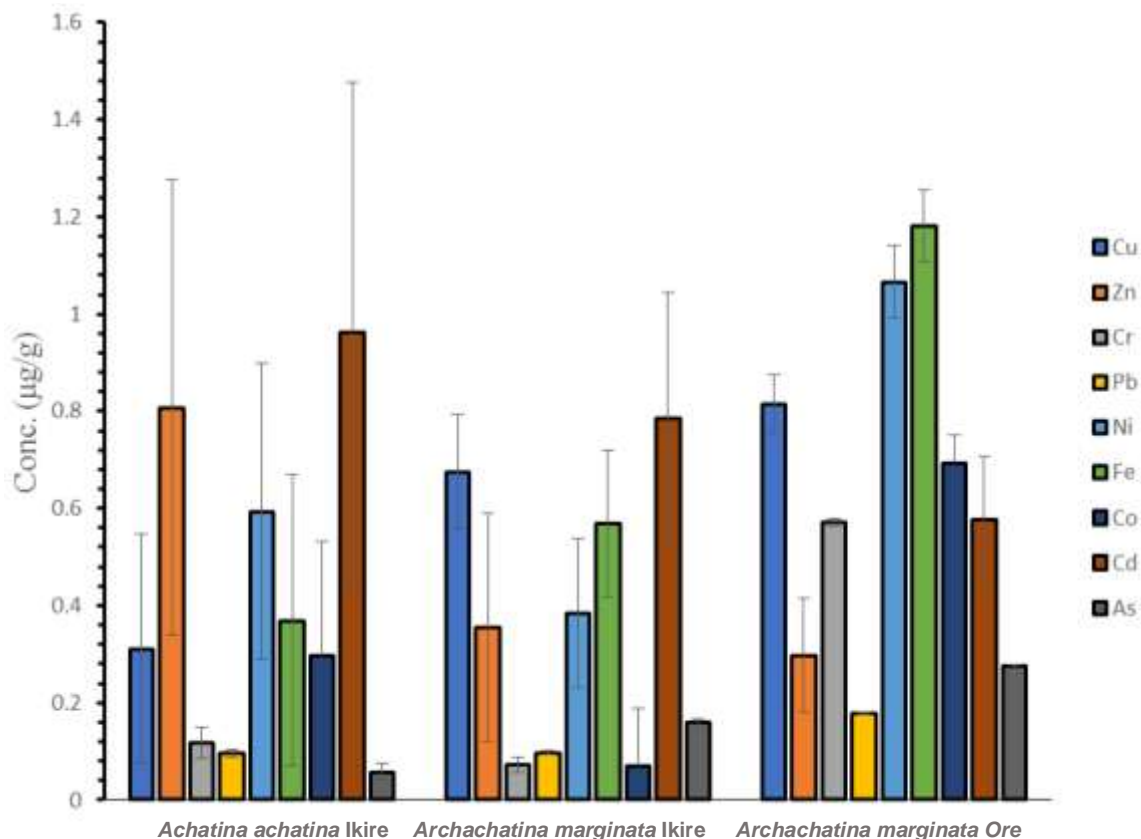
With these dangers posed by heavy metals in mind, it is appropriate to identify organisms that can be used as sentinel in the study of heavy metal pollution in our environment and the level of accumulation of such heavy metals in living organisms along with the physiological and biochemical imbalances arising from the bioaccumulation. This study seeks to evaluate the level of heavy metals (Copper, Zinc, Chromium, Lead, Nickel, Iron, Cobalt, Cadmium and Arsenic) (Figure 1) in selected tissues of *A. achatina* and *A. marginata* with the view to compare the extent of heavy metals bioaccumulation in the tissues of the snails from the two sampling locations and compare the levels of heavy metals with established regulatory standards.

## MATERIALS AND METHODS

### Area of study

Forty snails each were purchased from Ikire and Ore in June and July 2021. The month of June is an active farming season in southwest Nigeria when agrochemicals are used on farmlands for plant protection and weed control.

Ikire town is the administrative headquarter of Irewole local government of Osun State, Nigeria. It is the gateway town into



**Figure 1.** Level of heavy metal accumulation in *A. achatina* and *A. marginata*.  
Source: Author

Osun from Oyo State. Ikire is within the basin of River Osun; it lies around latitude 07°21'29" - 07°24'36" North and longitude 004°10'11" - 004°13'43" East. Ore town is the administrative headquarter of Odigbo local government area in Ondo State, Nigeria. It is the major town separating southwestern Nigeria from the southeast; its geographical coordinates are between 06°42'18" - 06°46'30" North and 004°51'18" - 004°54'55" East.

#### Land use

The primary activity in Ikire is farming. The proximity to Ibadan, a major commercial and industrial centre in southwest Nigeria, facilitates the easy movement of goods and services. Ore is a commercial town with agriculture being the mainstay of the economy, cultivating different food crops and cash crops like cassava, plantain, cocoa etc. It is reputable for the large bitumen deposit in Ondo state.

#### Sample collections

Giant African land snails were purchased from farmers who sourced the snails in the wild. Procured snails were immediately taken into the Physiology laboratory at the Department of Zoology, Obafemi Awolowo University, Ile-Ife for identification. Fifteen *A. achatina* and twenty-five *A. marginata* were bought at Ikire; all the forty snail samples from Ore were *A. marginata*. Only fully grown snails were

purchased because this is the preferred size consumed by the local population.

#### Dissection of snail specimens

Snails were dissected according to the method described by Low et al. (2016). The snails were thoroughly washed with distilled water. The snails were dissected to remove the foot, the digestive gland and the digestive tract. These parts were stored in small plastic jars and preserved in the deep freezer ready to be analysed. Snail shells were also kept in polythene bags and later analysed.

#### Determination of heavy metals

Each body part was defrosted for 2 h, weighed into a pre-weighed crucible and dried at 80°C in Gallenkamp hot box oven. The sample weights were taken and recorded at 4 h intervals until a constant weight was obtained. The samples were ground separately to fine particles using clean, dried mortar and pestle and then sifted using a sieve of particle size 0.02 mm. Each powdered sample (0.5 g) was measured into a 100 ml beaker; 5 ml of aqua regia HCL and HNO<sub>3</sub> (3:1) was added to digest the sample. The samples were evenly distributed in the acid using a glass stirring rod. The digested samples were filtrated (using Whatman filter paper No. 1) into a cylinder. The filtrate was made up to 25 ml of distilled water. The concentration of heavy metals: viz. Arsenic, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Nickel and Zinc in the

**Table 1.** Heavy metal concentration in *Achatina achatina* collected from Ikire.

Heavy metals ( $\mu\text{g/g}$ )	Tissues			
	Shell	Foot	Digestive tract	Digestive gland
Cu	0.052 $\pm$ 0.0000 <sup>a</sup>	1.018 $\pm$ 0.0028 <sup>c</sup>	0.088 $\pm$ 0.0028 <sup>b</sup>	0.086 $\pm$ 0.0000 <sup>b</sup>
Zn	2.003 $\pm$ 0.0014 <sup>d</sup>	0.031 $\pm$ 0.0035 <sup>a</sup>	0.087 $\pm$ 0.0021 <sup>b</sup>	1.111 $\pm$ 0.0014 <sup>c</sup>
Cr	0.200 $\pm$ 0.0014 <sup>d</sup>	0.051 $\pm$ 0.0014 <sup>a</sup>	0.099 $\pm$ 0.0092 <sup>b</sup>	0.119 $\pm$ 0.0014 <sup>c</sup>
Pb	0.092 $\pm$ 0.0014 <sup>ab</sup>	0.103 $\pm$ 0.0028 <sup>bc</sup>	0.116 $\pm$ 0.007 <sup>c</sup>	0.078 $\pm$ 0.0035 <sup>a</sup>
Ni	0.083 $\pm$ 0.0028 <sup>b</sup>	1.121 $\pm$ 0.0028 <sup>c</sup>	1.123 $\pm$ 0.0064 <sup>c</sup>	0.047 $\pm$ 0.0042 <sup>a</sup>
Fe	1.265 $\pm$ 0.0007 <sup>c</sup>	0.050 $\pm$ 0.0021 <sup>a</sup>	0.106 $\pm$ 0.0050 <sup>b</sup>	0.057 $\pm$ 0.0042 <sup>a</sup>
Co	0.078 $\pm$ 0.0028 <sup>b</sup>	1.001 $\pm$ 0.0007 <sup>c</sup>	0.055 $\pm$ 0.0042 <sup>a</sup>	0.055 $\pm$ 0.0042 <sup>a</sup>
Cd	0.059 $\pm$ 0.0000 <sup>a</sup>	2.306 $\pm$ 0.1060 <sup>d</sup>	0.258 $\pm$ 0.0042 <sup>b</sup>	1.227 $\pm$ 0.0063 <sup>c</sup>
As	0.061 $\pm$ 0.0000 <sup>ab</sup>	0.037 $\pm$ 0.0021 <sup>a</sup>	0.029 $\pm$ 0.0021 <sup>a</sup>	0.104 $\pm$ 0.0240 <sup>b</sup>

Mean  $\pm$  standard deviation with the same alphabet along the rows are not significantly different at  $p < 0.05$  by Tukey HSD.

Source: Author

**Table 2.** Heavy metals concentration in *Archachatina marginata* collected from Ikire.

Heavy metals ( $\mu\text{g/g}$ )	Tissues			
	Shell	Foot	Digestive tract	Digestive gland
Cu	1.030 $\pm$ 0.0007 <sup>a</sup>	0.549 $\pm$ 0.6378 <sup>a</sup>	1.030 $\pm$ 0.0424 <sup>a</sup>	0.095 $\pm$ 0.0778 <sup>b</sup>
Zn	0.072 $\pm$ 0.0021 <sup>a</sup>	0.058 $\pm$ 0.0028 <sup>a</sup>	0.087 $\pm$ 0.1768 <sup>a</sup>	1.200 $\pm$ 0.0184 <sup>b</sup>
Cr	0.090 $\pm$ 0.0028 <sup>b</sup>	0.102 $\pm$ 0.0028 <sup>b</sup>	0.039 $\pm$ 0.0014 <sup>a</sup>	0.055 $\pm$ 0.0092 <sup>a</sup>
Pb	0.042 $\pm$ 0.0000 <sup>a</sup>	0.190 $\pm$ 0.0007 <sup>d</sup>	0.055 $\pm$ 0.0050 <sup>b</sup>	0.101 $\pm$ 0.0028 <sup>c</sup>
Ni	0.255 $\pm$ 0.0000 <sup>c</sup>	0.023 $\pm$ 0.0050 <sup>a</sup>	1.199 $\pm$ 0.000 <sup>d</sup>	0.060 $\pm$ 0.0042 <sup>b</sup>
Fe	0.331 $\pm$ 0.0028 <sup>b</sup>	0.114 $\pm$ 0.0000 <sup>a</sup>	0.775 $\pm$ 0.0163 <sup>a</sup>	1.055 $\pm$ 0.6647 <sup>c</sup>
Co	0.029 $\pm$ 0.0000 <sup>a</sup>	0.080 $\pm$ 0.0021 <sup>b</sup>	0.087 $\pm$ 0.0014 <sup>c</sup>	0.087 $\pm$ 0.0014 <sup>c</sup>
Cd	0.086 $\pm$ 0.0014 <sup>a</sup>	1.107 $\pm$ 0.0014 <sup>b</sup>	0.087 $\pm$ 0.015 <sup>c</sup>	1.867 $\pm$ 0.2080 <sup>c</sup>
As	0.085 $\pm$ 0.0021 <sup>a</sup>	0.440 $\pm$ 0.0000 <sup>b</sup>	0.063 $\pm$ 0.0021 <sup>a</sup>	0.048 $\pm$ 0.0000 <sup>c</sup>

Mean  $\pm$  standard deviation with the same alphabet along the rows are not significantly different at  $p < 0.05$  by Tukey HSD.

Source: Author

samples was examined using PG 990 model Atomic Absorption Spectrophotometer (AAS).

### Statistical analysis

Data were analysed using one-way ANOVA and Independent-sample T-test in IBM SPSS version 25. Tukey's HSD Post Hoc test was used to resolve differences among means.  $P < 0.05$  indicates significant differences among groups.

## RESULTS

### Concentration ( $\mu\text{g/g}$ ) of heavy metals in *A. achatina* procured from Ikire

The mean concentration of heavy metals in *A. achatina* collected from Ikire is shown in Table 1. Zn, Cr and Fe were accumulated in the shell more than in other organs. The foot accumulated more Cu, Co and Cd than other organs. The digestive tract had the highest concentration

of Pb and Ni. The digestive gland accumulated the highest concentration of As and the lowest concentration of Pb and Ni. There was a significant difference ( $p < 0.005$ ) in the concentration of heavy metals across the organs.

### Concentration ( $\mu\text{g/g}$ ) of heavy metals in *A. marginata* collected from Ikire

The results summarized in Table 2 showed that in *A. marginata* collected from Ikire, the shell had the lowest concentration of Pb, Co and Cd while the foot had the highest level of Cr, Pb and As. The digestive tract had the lowest level of Cr. However, Ni in the digestive tract was higher than in the other organs. The digestive gland had the highest concentration of Zn, Fe and Cd and the lowest concentration of Cu and As. The concentration of Cu and Zn in the digestive gland was significantly different ( $p < 0.05$ ) from the concentration in the shell, foot and digestive tract. Moreover, there was a

statistically significant ( $p < 0.05$ ) difference in the level of Pb bioaccumulated across the organs.

### Concentration ( $\mu\text{g/g}$ ) of heavy metals in *A. marginata* collected from Ore

As shown in Table 3, the mean concentrations of Zn, Ni and As were more in the shell than in other tissues whereas the mean concentrations of Cu, Cr and Cd in the shell were lower than in other tissues. The concentration of Fe and Cd in the foot was higher than in other tissues. The concentration of Co in the foot was the least among the tissues. The highest concentration of Cr was recorded in the digestive tract while Pb, Fe and As in the digestive tract were lower than in other tissues. The digestive gland accumulated more Cu and Pb than other tissues while the level of Zn and Ni accumulated in the digestive gland were lower than in other tissues. There was a significant difference in the level of accumulated heavy metals across the tissues ( $p < 0.005$ ) except Pb.

### Relationship between the levels of heavy metals in the shell, foot, digestive tract and digestive gland of *A. achatina* and *A. marginata* collected from Ikire and Ore

Independent-sample t-test was used to compare the levels of heavy metals in the shell, foot, digestive tract and gland of *A. achatina* and *A. marginata* collected from Ikire and Ore. The result revealed that there was a significant difference ( $p < 0.05$ ) in the level of heavy metals within the shell and foot (except Cu) of *A. achatina* and *A. marginata* in Ikire and Ore. Similarly, there was a statistical difference ( $p < 0.05$ ) in the heavy metal concentrations except for Zn, Pb, Fe, Cd in the digestive tract of *A. marginata* collected from Ikire and Ore; and Zn and Fe in the digestive tract of *A. achatina* and *A. marginata* from Ikire.

Pb, Fe and As in the digestive glands of *A. marginata* from Ikire and Ore; Cu, Ni and As in the digestive glands of *A. achatina* and *A. marginata* from Ikire showed no significant difference ( $p > 0.05$ ). The level of heavy metals in the shell, foot, digestive tract and digestive gland of *A. achatina* and *A. marginata* gathered from Ikire; and *A. marginata* from Ikire and Ore were not significantly different ( $p > 0.05$ ).

Overall, the concentration of heavy metals in snail tissues varied with the location and species of the snail. Cd ( $0.963 \mu\text{g/g}$ ) followed by Zn ( $0.808 \mu\text{g/g}$ ) were the most accumulated heavy metals and As ( $0.058 \mu\text{g/g}$ ) had the minimum accumulation in *A. achatina* from Ikire. The trend of heavy metal in *A. achatina* from Ikire showed that Cd > Zn > Ni > Fe > Cu > Co > Cr > Pb > As. In *A. marginata* from Ikire, Cd ( $0.787 \mu\text{g/g}$ ) and Cu ( $0.676 \mu\text{g/g}$ ) were the most accumulated heavy metals while Co

( $0.070 \mu\text{g/g}$ ) was the least accumulated metal. The concentration of metals was detected in the following order Cd > Cu > Fe > Ni > Zn > As > Pb > Cr > Co. However, the trend of heavy metals in *A. marginata* from Ore revealed that Fe ( $1.182 \mu\text{g/g}$ ) and Ni ( $1.066 \mu\text{g/g}$ ) were the most accumulated heavy metals and Pb ( $0.178 \mu\text{g/g}$ ) had the minimum accumulation following the trend: Fe > Ni > Cu > Co > Cd > Cr > Zn > As > Pb (Fig. 1). Moreover, the trend of heavy metals accumulation in *A. achatina* from Ikire showed that Foot ( $0.635 \mu\text{g/g}$ ) > Shell ( $0.433 \mu\text{g/g}$ ) > Digestive gland ( $0.320 \mu\text{g/g}$ ) > Digestive tract ( $0.218 \mu\text{g/g}$ ). The trend of heavy metals in *A. marginata* from Ikire was Digestive gland ( $0.508 \mu\text{g/g}$ ) > Digestive tract ( $0.380 \mu\text{g/g}$ ) > Foot ( $0.296 \mu\text{g/g}$ ) > Shell ( $0.224 \mu\text{g/g}$ ) while Digestive gland ( $0.713 \mu\text{g/g}$ ) > Shell ( $0.655 \mu\text{g/g}$ ) > Foot ( $0.615 \mu\text{g/g}$ ) > Digestive tract ( $0.531 \mu\text{g/g}$ ) was observed in *A. marginata* from Ore (Figure 2).

### Comparison of inherent heavy metals with regulatory standards

The level of heavy metals in the tissues of *A. achatina* and *A. marginata* collected from Ikire and Ore were compared with the established regulatory safety standards for human consumption concerning the edible parts (Table 4). The concentrations of heavy metals recorded in the edible parts of *A. achatina* and *A. marginata* are lower than the FAO/WHO (2016) regulatory limits except for Pb ( $0.105 \mu\text{g/g}$ ), Ni ( $1.123 \mu\text{g/g}$ ), Co ( $1.002 \mu\text{g/g}$ ) and Cd ( $2.314 \mu\text{g/g}$ ) in *A. achatina*; Pb ( $0.190 \mu\text{g/g}$ ) in *A. marginata* from Ikire, and Cd ( $2.100 \mu\text{g/g}$ ) in *A. marginata* from Ore which is slightly above the permissible level.

## DISCUSSION

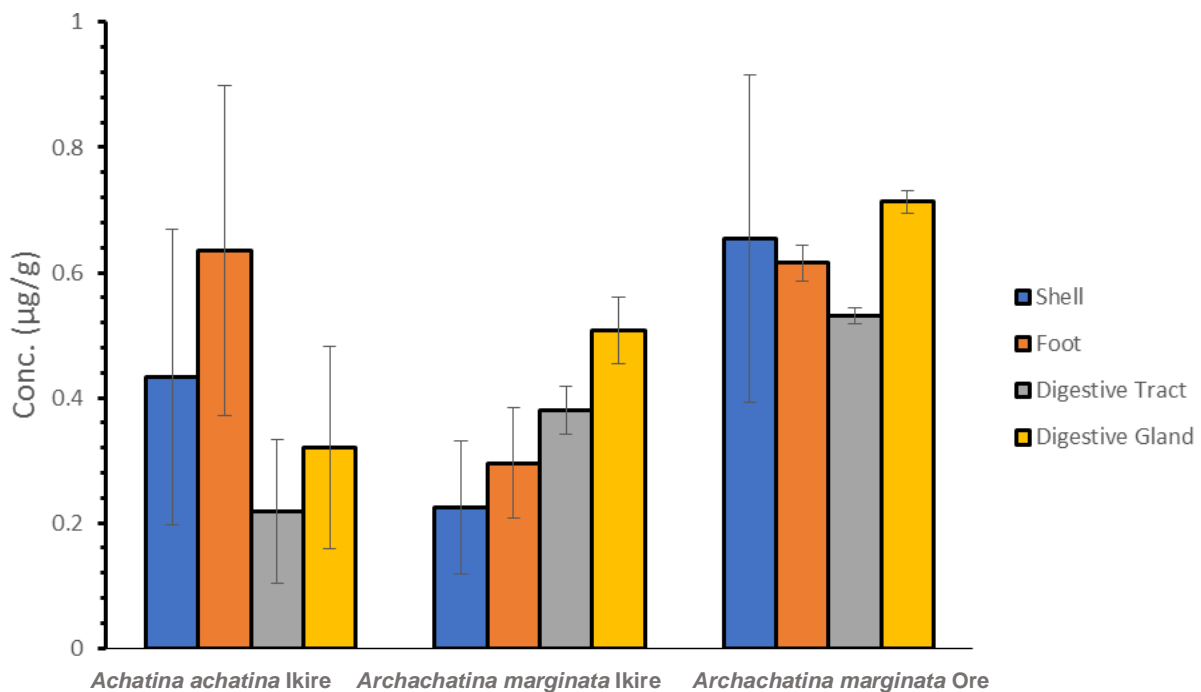
Bioaccumulation of heavy metals in tissues varies significantly amongst the taxa and conspecifics (Iwegbue et al., 2009). The concentration of heavy metal in the tissues depends on the form in which the metal is bound (Mariam et al., 2004). Other factors that influence the accumulation of heavy metals are metal concentration in the soil, soil pH, and the physiological characteristics of the species which include assimilation and excretion capacity (Purchart and Kula, 2007). The giant African land snails are omnivores that feed on the debris from the soil surface which may have been contaminated with heavy metals and organic pollutants; therefore, they may accumulate the pollutants to harmful levels.

In *A. marginata* from Ikire, Cu was highest in the shell ( $1.030 \pm 0.0071 \mu\text{g/g}$ ), Ni was predominant in the digestive tract ( $1.199 \pm 0.000 \mu\text{g/g}$ ), the foot ( $1.107 \pm 0.0014 \mu\text{g/g}$ ) and the digestive gland ( $1.867 \pm 0.208 \mu\text{g/g}$ ) accumulated highest level of Cd. The results recorded in this study were within the tolerable limit of FAO/WHO

**Table 3.** Heavy metals concentration in *Archachatina marginata* collected from Ore.

Heavy metals ( $\mu\text{g/g}$ )	Tissues			
	Shell	Foot	Digestive tract	Digestive gland
Cu	$0.071 \pm 0.0021^a$	$1.106 \pm 0.0042^b$	$0.075 \pm 0.0042^a$	$2.010 \pm 0.0014^c$
Zn	$1.025 \pm 0.0350^b$	$0.082 \pm 0.0035^a$	$0.046 \pm 0.0000^a$	$0.036 \pm 0.0021^a$
Cr	$0.051 \pm 0.0000^a$	$0.065 \pm 0.0028^a$	$1.105 \pm 0.0063^c$	$1.070 \pm 0.0120^b$
Pb	$0.070 \pm 0.0028^a$	$0.051 \pm 0.0000^a$	$0.037 \pm 0.0050^a$	$0.553 \pm 0.6480^a$
Ni	$2.161 \pm 0.0000^d$	$0.089 \pm 0.0014^b$	$2.000 \pm 0.00071^c$	$0.016 \pm 0.0007^a$
Fe	$1.433 \pm 0.0014^c$	$2.008 \pm 0.0028^d$	$0.045 \pm 0.0020^a$	$1.241 \pm 0.0370^b$
Co	$0.054 \pm 0.0021^a$	$0.024 \pm 0.0000^a$	$1.346 \pm 0.0760^b$	$1.346 \pm 0.0760^b$
Cd	$0.030 \pm 0.0021^a$	$2.096 \pm 0.0056^d$	$0.112 \pm 0.0021^c$	$0.075 \pm 0.0160^b$
As	$1.000 \pm 0.0021^c$	$0.017 \pm 0.0021^a$	$0.011 \pm 0.0000^a$	$0.074 \pm 0.0150^b$

Means  $\pm$  standard deviation with the same alphabet along the rows are not significantly different at  $P < 0.05$  by Tukey HSD. Source: Author



**Figure 2.** Level of heavy metal accumulation in the tissue of *Achatina achatina* and *Archachatina marginata*. Source: Author

(expect Ni in the digestive tract). Ogidi et al. (2020) reported ( $0.14 \pm 0.001 \mu\text{g/g}$ ), ( $0.032 \pm 0.002 \mu\text{g/g}$ ) and ( $0.96 \pm 0.007 \mu\text{g/g}$ ) for Cd, Ni and Cu, respectively in the tissue of *A. marginata* from Ekowe community and observed that *A. marginata* bioaccumulate high levels of Zinc when compared with other metals such as Cu, Cd, Ni, Cr. Iwegbue et al. (2009) recorded higher levels of Pb ( $6.53 \pm 1.03 \mu\text{g/g}$ ), Fe ( $7.86 \pm 0.36 \mu\text{g/g}$ ), Ni ( $0.18 \pm 0.16 \mu\text{g/g}$ ) and Cd ( $1.47 \pm 0.55 \mu\text{g/g}$ ) in the tissues of *A. marginata* in industrial sites of Warri.

The main sources of heavy metal contamination are vehicle exhaust and untreated industrial wastes that find their way through irrigation channels, therefore polluting the soil layers (Mariam et al., 2004). An increased Pb content may be found in crops and animals at distances of 50 m radius from highways, depending on weather conditions and traffic volume (Eltier and Sivacioglu, 2021). The level of heavy metals in the tissues of *A. marginata* from Ore is relatively higher than in *A. marginata* from Ikire (except Zn and Cd). Cadmium is

**Table 4.** Permissible maximum limit ( $\mu\text{g/g}$ ) of heavy metals in regulatory standards.

Heavy metals ( $\mu\text{g/g}$ )	<i>Archachatina marginata</i>		<i>Achatina achatina</i> Ikire	Acceptable Maximum Limits ( $\mu\text{g/g}$ )
	Ikire	Ore		
Cu	1.000	1.109	1.020	NL
Zn	0.060	0.085	0.033	3.000
Cr	0.104	0.067	0.053	0.300
Pb	<b>0.190</b>	0.051	<b>0.105</b>	0.100
Ni	0.026	0.090	<b>1.123</b>	0.500
Fe	0.114	2.010	0.051	NL
Co	0.081	0.024	<b>1.002</b>	1.000
Cd	1.108	<b>2.100</b>	<b>2.314</b>	2.000
As	0.044	0.018	0.038	0.500
References	This study	This study	This study	FAO/WHO (2016)

NL: No limit given by FAO/WHO. The bold values represent the concentration of metals above the permissible limit by FAO/WHO (2016).

Source: Author

closely related to Zinc and is found wherever Zinc is found in nature. Cd may occur as a contaminant in phosphate fertilizers and municipal sludges and so enter the food supply. Shell ( $2.161 \pm 0.0000 \mu\text{g/g}$ ) and digestive tract ( $2.000 \pm 0.0007 \mu\text{g/g}$ ) in *A. marginata* from Ore have a higher accumulation of Nickel. The foot accumulated Cd ( $2.096 \pm 0.0056 \mu\text{g/g}$ ) than other tissues while the digestive gland has a rich deposit of Cu ( $2.010 \pm 0.0014 \mu\text{g/g}$ ). Although, Cr and Co (in the digestive tract and gland), Ni (in the shell and digestive gland), Pb (in the digestive gland) and As (in the shell) outstripped the FAO/WHO permissible limit yet this finding is comparatively low to studies recorded by other authors. Moreover, heavy metal concentration in the muscular foot (the main constituent of snail meat) did not exceed the FAO/WHO regulated limit. Therefore, *A. marginata* from Ore may be tenable for human consumption. Awharitoma et al. (2016) reported higher values for Fe, Pb, Cd and Co in the range between ( $38.61 - 70.49 \mu\text{g/g}$ ), ( $0.39 - 0.71 \mu\text{g/g}$ ), ( $0.19 - 0.35 \mu\text{g/g}$ ) and ( $0.04 - 0.007 \mu\text{g/g}$ ), respectively in infected *A. marginata* from three communities in Edo State while Oguh et al. (2019b) reported that the concentration of heavy metals (As, Cd, Cr, Cu and Pb) in snails treated with dumpsite soil were 3.05, 3.89, 3.60, 2.89 and 2.55 mg/kg, and snails treated with mining site soil recorded 2.73, 2.74, 3.91, 4.96 and 4.82 mg/kg, respectively.

Lead (Pb) has no beneficial biological function and is known to accumulate in the body (Assi et al., 2016). Ingestion of Pb through the consumption of contaminated foods may cause mental retardation among children, inhibit haemoglobin synthesis; distort the cardiovascular system and hypertension in humans (Bello et al., 2015; Nkpaa et al., 2016). Cadmium is a toxic element because it can be absorbed through the alimentary tract and damage membrane and DNA (Maobe et al., 2012). In comparison with levels of heavy metals recorded in *A.*

*achatina* by previous authors, the mean concentration of heavy metals in *A. achatina* collected from Ikire is low. Zn was predominant in the shell ( $2.003 \pm 0.0014 \mu\text{g/g}$ ), Cd recorded ( $2.306 \pm 0.106 \mu\text{g/g}$ ) in the foot, Ni ( $1.123 \pm 0.0064 \mu\text{g/g}$ ) was more accumulated in the digestive tract while Cd ( $1.227 \pm 0.0063 \mu\text{g/g}$ ) and Zn ( $1.111 \pm 0.0014 \mu\text{g/g}$ ) had higher accumulation in the digestive gland. Ugbaja et al. (2020) reported  $1.80 \mu\text{g/g}$  of Cd in the foot of *A. achatina* collected from the Papalanto cement factory area. Eneji et al. (2016) recorded (0.42 - 2.80 mg/kg) of Cd in *A. achatina* from Abak, Akwa Ibom, Nigeria. However, Adedeji et al. (2011) had earlier recorded a low concentration (0.01 mg/kg) of Cd in snails from Alaro River in Oluyole Industrial Area Ibadan, Oyo State.

The levels of heavy metals across the tissues in *A. achatina* and *A. marginata* from Ikire and Ore were relatively within the FAO/WHO (2016) benchmarks limits except for Pb, Ni, Co and Cd in *A. achatina*; Pb in *A. marginata* from Ikire, and Cd in *A. marginata* from Ore which are slightly above the permissible level. This shows that the environment is gradually being polluted with toxic waste. It is important to always determine the bioaccumulation capacity for heavy metals by organisms especially the edible ones, to assess the potential risk to human health and other animals that feed on the organisms. Though, the level of heavy metals in *A. marginata* from Ore was comparatively higher which could probably be due to overdose of agrochemical application, higher traffic emission and higher concentration of toxic wastes from the activities of industrial presence in the Ore axis. Heavy metals often find their way into the soil and vegetation through an overdose of agrochemical application, pollution from traffic emissions and sewage from industrial estates (Adedeji et al., 2011; Eltier and Sivacioglu, 2021; Salih et al., 2021). The ability of snails to bioaccumulate essential

heavy metals enables them to acquire other non-essential heavy metals from the soil and vegetation.

## Conclusion

This study has shown that giant African land snails *A. achatina* and *A. marginata* can accumulate high levels of heavy metals in the shell and soft tissues. Thus, *A. achatina* and *A. marginata* serve as good bioindicators of heavy metal pollution in the terrestrial ecosystem. The results of this study provided baseline data on the levels of heavy metals in *A. achatina* in Ikire and *A. marginata* in Ore. Very close monitoring of heavy metal levels in Ore and Ikire towns is recommended. Snails need to be thoroughly screened to make sure that unnecessarily high levels of toxic heavy metals are not being transferred through them to the human population that depends on the snail meat for their protein requirements. Therefore, proper monitoring of agrochemical application is recommended to reduce the level of heavy metals built-up which will contribute to further environmental pollution in the not-too-distant future.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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*Full Length Research Paper*

# Investigation of parameters influencing gas production and gasification kinetics of Ziguinchor biomass

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**This study presents the gasification of three types of biomass residues (wood, stem and shells) under CO<sub>2</sub> and water steam, using the different analyses X-ray fluorescence (XRF). Generally, the experiments are carried out using XRF installations and a fixed bed reactor system. The tests are carried out on wood, stems, and shells, because of their energy contents (Lower heating value LHV), and their high availability in the Ziguinchor region (Senegal). The solid residues obtained after pyrolysis were used to carry out the gasification tests. Thus, several gasification tests were carried out and the results were interpreted using the Arrhenius equation. Two kinetic models (Volume Reaction Model, and Shrinking Core Model) were used to explain the influence of experimental parameters (nature of biomass, reagent type, and temperature) on synthesis gas production. From the experimental results, it is found that the nature of the sample, the reagent, and the variation in temperature have significant effect on the char kinetics conversion. In addition to the differences in the chemical composition of the raw sample, ash and char density, an explanation on the parameters effects, which vary the conversion kinetics during the gasification tests is given. The purpose of this work is to understand the kinetic variations of raw materials in the fixed bed reactor during gasification.**

**Key words:** Biomass residues, gasification, kinetic conversion, ash chemical composition.

## INTRODUCTION

The impact of climate change has many implications for the world's natural system (lower agricultural yields, irregular rainfall patterns with serious human and agricultural consequences). To overcome this struggle cash on climate change, community and governmental initiatives (United Nations Framework Convention on Climate Change 1992, Kyoto Protocol signed in 1997,

Intergovernmental Panel on Climate Change, and recently the "Conference of Parties" 2015-2023) and so many other bodies are being taught around the world. These aim to fight the limitation of the use of fossil resources through the development of renewable energies and for the control of energy demand. Even if awareness of this phenomenon may seem slow in view of

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the stakes on the planet, it is nonetheless real and is becoming more and more integrated into the world's energy landscape. However, developing and promoting renewable energies, and biomass, is becoming a priority because of the many environmental and energy benefits. In the logic of the use of biomass as a source of energy, it will be very difficult to take wood as a raw material, because its overuse may lead to an unfortunate cause of deforestation.

Given the low rate of electrification in rural areas, and given that the quantity of various increasingly important and unrecovered bio-resource waste delivered to the open air is considered a loss, it is more indicative that the thermochemical recovery of this diversity of biomass is a promising process. Processes known as "thermochemical conversion" are still explored in this research direction and development phase. They combine a thermal conversion (under the effect of heat) and a chemical conversion (reaction between two bodies). Then, gasification is a thermochemical conversion of a fuel, which consists in a thermal degradation of the char at a high temperature ( $> 600^{\circ}\text{C}$ ) to obtain a synthesized gases composed mainly of  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CH}_4$ . These products can be used for electrification and/or cogeneration. The design and operation of a reactor requires an understanding of the gasification process, how its configuration, its size, its raw material preparation, and experimental conditions influence installation unit performance. A good understanding of the basic reactions is fundamental to the planning, design, operation, and process improvement of a gasification unit. In order to obtain a complete char conversion and an improved product yield, several experimental protocols have been presented in the literature. The work conducted by (Kamble et al., 2019; Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016) have different studies on the effect of temperature on biomass char conversion kinetics and have considered temperature as a fundamental parameter for the conversion of different biomasses. These authors indicated that the temperatures used have a positive effect on biomass conversion kinetics, that is, the higher the temperature ( $750 - 1350^{\circ}\text{C}$ ), the better will be the conversion kinetics of the biomass. Other researchers such as (Kamble et al., 2019; Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Schneider et al., 2021) presented the study of thermochemical conversion of biomass by evaluating the effect of the type of reagent on the conversion kinetics and that they point out that  $\text{CO}_2$ -char and  $\text{H}_2\text{O}$ -char reactions have different conversion kinetics effect, in addition the mixture of these reagents has a slowing conversion kinetics and that could be due to the competition effect between the different reagents. Finally, more advanced studies of the effect of char and ash chemical composition on conversion kinetics have been

carried out by (Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Schneider et al., 2021; Wang et al., 2016; Zhang et al., 2017; Wu et al., 2022; Lv et al., 2004; Prestipino et al., 2018; Ling et al., 2022a; Wu et al., 2022b; Zhang et al., 2008; Yao et al., 2020; Parikh et al., 2007; Gao et al., 2017).

The latter had different conclusions, according to some the chemical components of the ash have a significant effect on the biomass conversion rate. According to the study by Zhang et al., 2008, which compared the gasification reactivity of biomass samples under K-, Na-, Ca- and Mg-catalyzed steam, the results indicate that alkali metal-catalyzed char (K and Na) has a much higher reactivity than alkaline earth metal-catalyzed char (Ca and Mg). Secondly, despite the advantages of biomass fuel in reducing carbon emissions from the power sector, during the co-combustion process, many unexpected interactions between the ash-forming elements (such as K, Na, Ca, Si, Al, Cl, P, Mg and S, etc.) occur during the co-combustion process. It is inevitable that many ash-related problems, such as ash deposition, fouling and corrosion of heat transfer surfaces, could be due to the high alkali and alkaline earth metal content (Yao et al., 2020).

In this study, we are looking for a specific understanding of the kinetic sensitivity conversion of samples vs experimental conditions. To achieve the objectives, we seek to better understand the effect of the temperature, of the chemical composition of the ashes and samples on the kinetics gasification.

## MATERIALS AND METHODS

### Presentation of samples

Sorghum stems (St.sorghum), cotton stems (St.cotton), teak wood (W.teak), kaicédrat wood (W.kaicédrat), palm shells (Sh.palm) and peanut shells (Sh.peanut) were used. These samples were collected from the Ziguinchor region in southern Senegal. The samples were selected on the basis of their energy content (high heating values, Table 1) and their high availability in this area (in terms of recoverable quantity). The main properties of all these biomass samples were subjected to immediate and elementary analysis in accordance with ASTM D 3172-73 (84) and ASTM D 3176-84 standards (Zhang et al., 2008), the results are listed in Table 1.

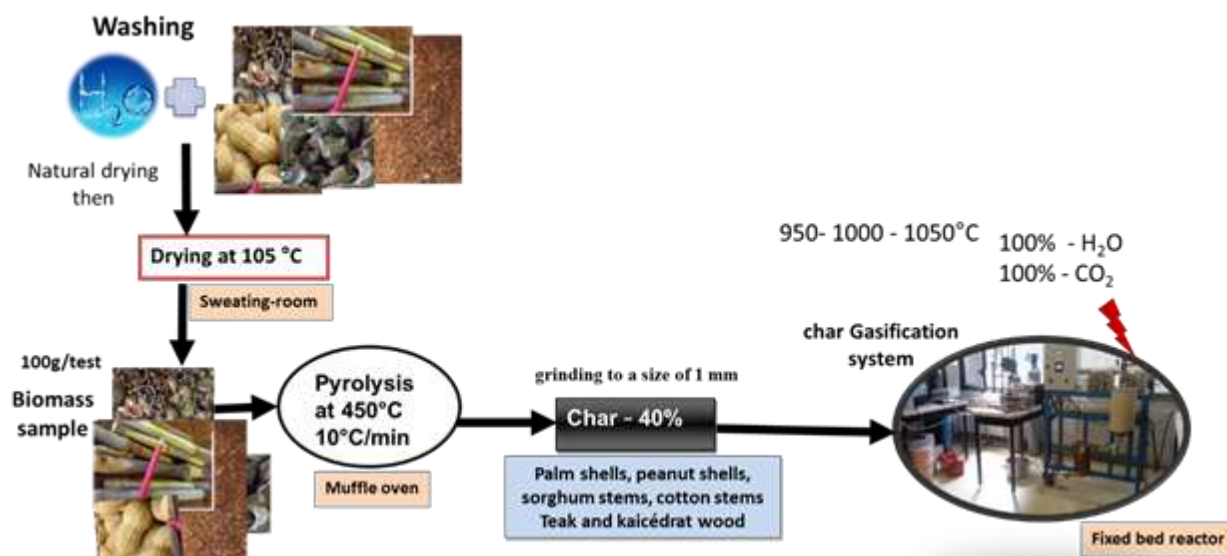
Table 1 shows very good lower heating value (LHV) of our samples, which allowed us to select these samples in order of their energy content (LHV) among several other biomass. A variety of chemical component values of these biomass residues were also noticed. This noted difference can play a fundamental role during thermochemical conversion (Hu et al., 2022; Zhang et al., 2023). However, in order to characterize our biomass samples during gasification and to analyze their ashes, the tests were carried out using micro gas chromatography ( $\mu\text{GC}$  or micro-GC) and XRF, respectively. The results obtained from the ash analysis, in accordance with ASTM E 1755-1 (Zhang et al., 2008), are shown in Table 3.

The experimental protocol for the sample preparation, pyrolysis,

**Table 1.** Chemistries compositions of ash and of the samples.

Biomass Samples	Elementary analysis (Wt. %)					Proximate analysis (Wt. %)			
	C	H	N	S	O	CF	MV	Ash	LHV (MJ/kg)
Sh.peanut	49.8	8.50	1.30	0.40	40.00	19.60	65.40	5.7	17.98
W.teak	48.75	8.97	0.27	0.01	42.00	20.11	80.72	0.17	18.80
W.kaicedrat	50.12	7.01	0.50	0.02	42.35	17.27	82.00	0.73	18.80
Sh.palm	49.50	6.00	1.10	0.70	42.60	13.40	84.90	1.20	21.20
St.Sorghum	49.69	3.87	0.60	0.04	45.80	21.57	74.18	4.25	16.98
St.cotton	51.41	4.05	1.31	0.02	43.21	23.78	65.41	5.74	16.65

Source: Authors

**Figure 1.** Simplified diagram of the experimental protocol.  
Source: Authors

and gasification study is described in a simplified manner in Figure 1. In Figure 1, a sample washed with tap water was performed to reduce impurities. These mineral impurities have a significant influence on the thermochemical conversion process of the sample. After washing, the stems, wood and shells were dried naturally for 24 h and then steamed at 105°C for 24 h.

After this sample preparation, a mass of 100 g per test was used to carry out sample pyrolysis. The objective during the pyrolysis was to obtain a high proportion of char (carbon-rich solid) with a low porous surface. In order to achieve this, a temperature of 450°C is used with a heating rate of 10°C min<sup>-1</sup>. The pyrolysis tests were carried out in a muffle furnace under an inert atmosphere. About 40% char was obtained. The char was crushed to an average size of 1 mm and the samples were then used for the gasification tests. Several gasification tests of the samples were carried out in a fixed-bed reactor at different experimental conditions (three temperatures, two reactive media, and five samples).

#### Fixed-bed reactor presentation

The fixed bed reactor system (36 mm internal diameter and 350 mm internal height) consists of a sample thermal conversion system

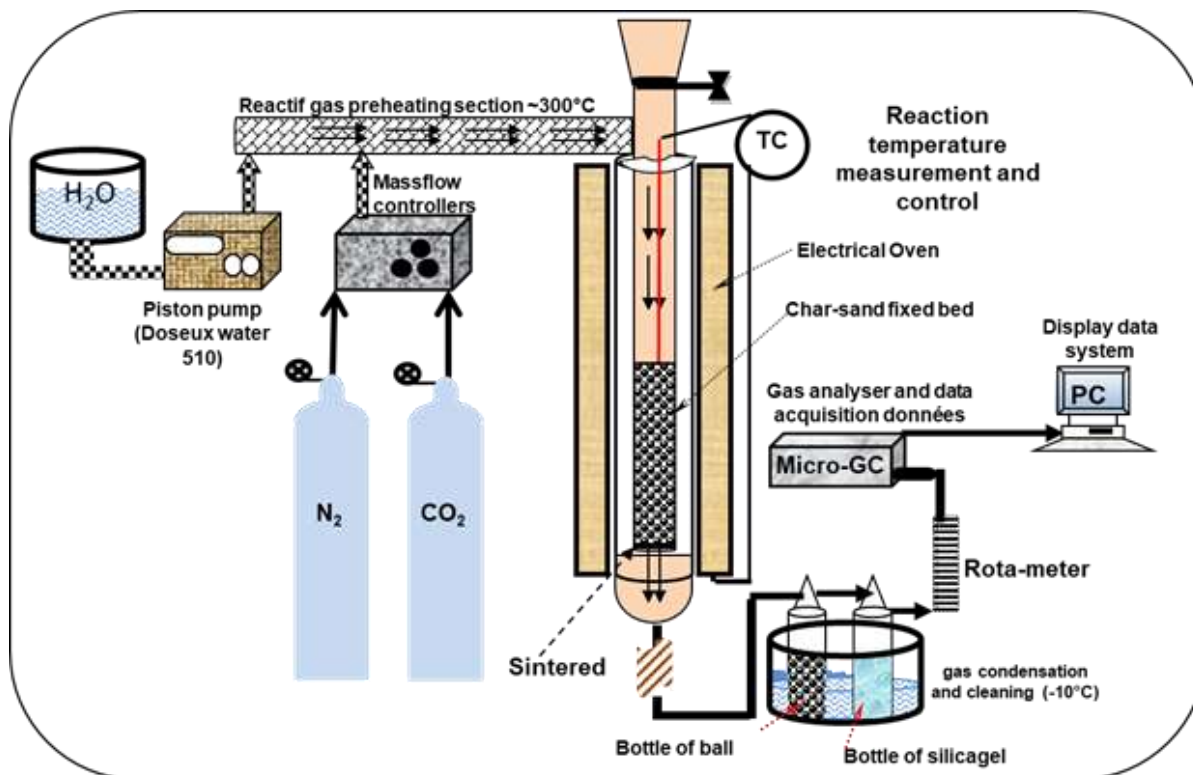
and a gas analysis system. The reactor is simplified in Figure 2.

The operating principle of this fixed bed reactor is summarized as follows: the gasification temperature is controlled by a thermocouple. The flow rate of nitrogen and CO<sub>2</sub> is fixed by a mass flow regulator, and the water vapour is adjusted by a "Water 510 Doser" type pump. These reagents are first preheated to a temperature of 300°C before being injected into the reactor. The reactor is loaded with 15 g of char mixed with 70 g of sand. The sand plays the role of heat transfer, maintaining the temperature and limiting the preferential passage of gases. At the outlet of the reactor, there is a system for cleaning and condensing the gases. This system consists of two flasks immersed in a cold bath (≈ -10°C). At the outlet of the cleaning system, the gases are analyzed by gas phase micro-chromatography and the data are displayed on a computer.

The tests are repeated and the average is presented subsequently.

## RESULTS AND DISCUSSION

In order to study the effect of temperature on char



**Figure 2.** Simplified representation of the fixed bed reactor system.  
Source: Authors

conversion, several gasification tests were carried out on the wood char, stem and shells samples at 950, 1000 and 1050°C.

### Effect of gasification temperature on conversion

In order to evaluate the effect of temperature, the half-reaction index ( $R_{0.5}$ ) described in (Guizani et al., 2013) is used:

$$R_{0.5} = \frac{X_{0-0.5}}{t_{0-0.5}} \quad (1)$$

where  $t_{0.5}$  is the half-conversion time of the char (50%). To better see the effect of temperature on the gasification reaction rate of the chars resulting from the pyrolysis of the different samples, we plotted the variation of this half-conversion rate of Equation 1 as a function of time using the half-conversion rate data (from  $X=0$  to  $X=0.5$ ). The result obtained is as shown in Figures 3 and 4. In Figures 3 and 4, we can see that the variations in the trend of the half-conversion rate of the char at a temperature of 1050°C is above those obtained at 1000 and 950°C. Similarly, the trend of the conversion rate at 1000°C is also above those obtained at 950°C. It is clear that the char kinetic conversion rate from "kaicacedrat" wood, teak wood, peanut shells, palm shells, cotton, and

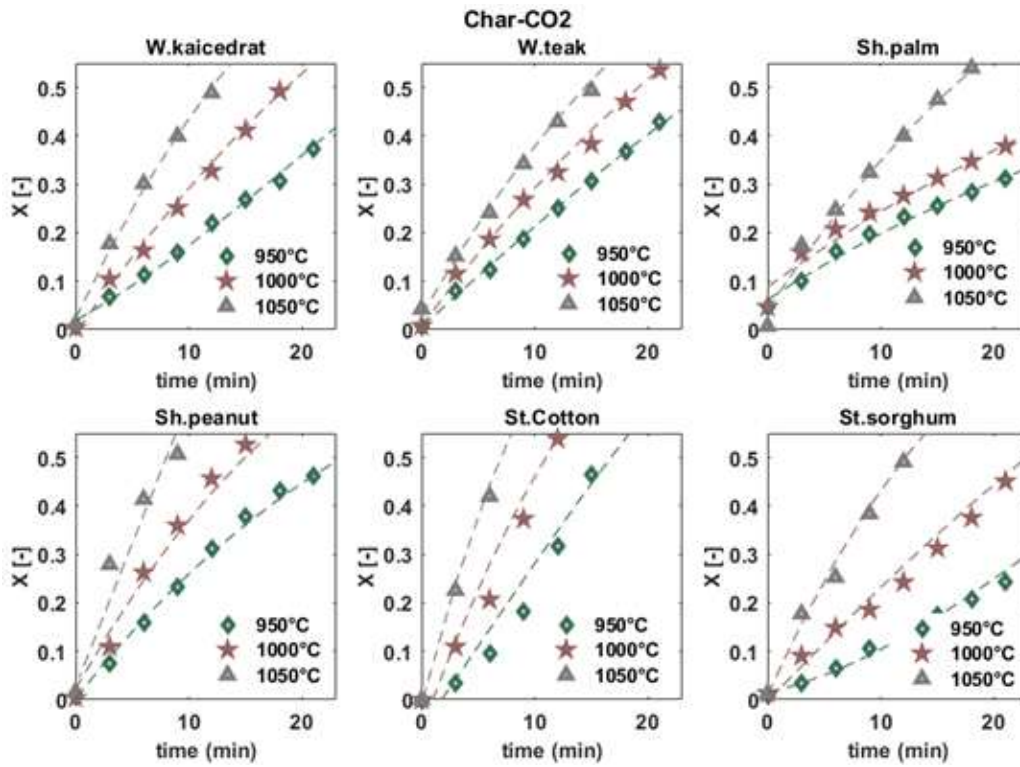
sorghum stems during the gasification process under  $\text{CO}_2$ , or under steam is improved at high temperature (that is, the higher the temperature the better the conversion of the char), thus reflecting the fact that temperature has a positive effect on the reactivity of the char. It is concluded that the reaction temperature has a precursor effect on the reactivity of the char.

Similar conclusions were made by (Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Almeida et al., 2019). This effect of temperature could be due to the endothermic reaction phenomenon char- $\text{CO}_2$  or char- $\text{H}_2\text{O}$ . Indeed, during this reaction according to chemical principles, the production of synthesis gas is favorable at high temperature. Further, this temperature effect during the gasification of char under steam or  $\text{CO}_2$  can be interpreted by the Arrhenius correlation.

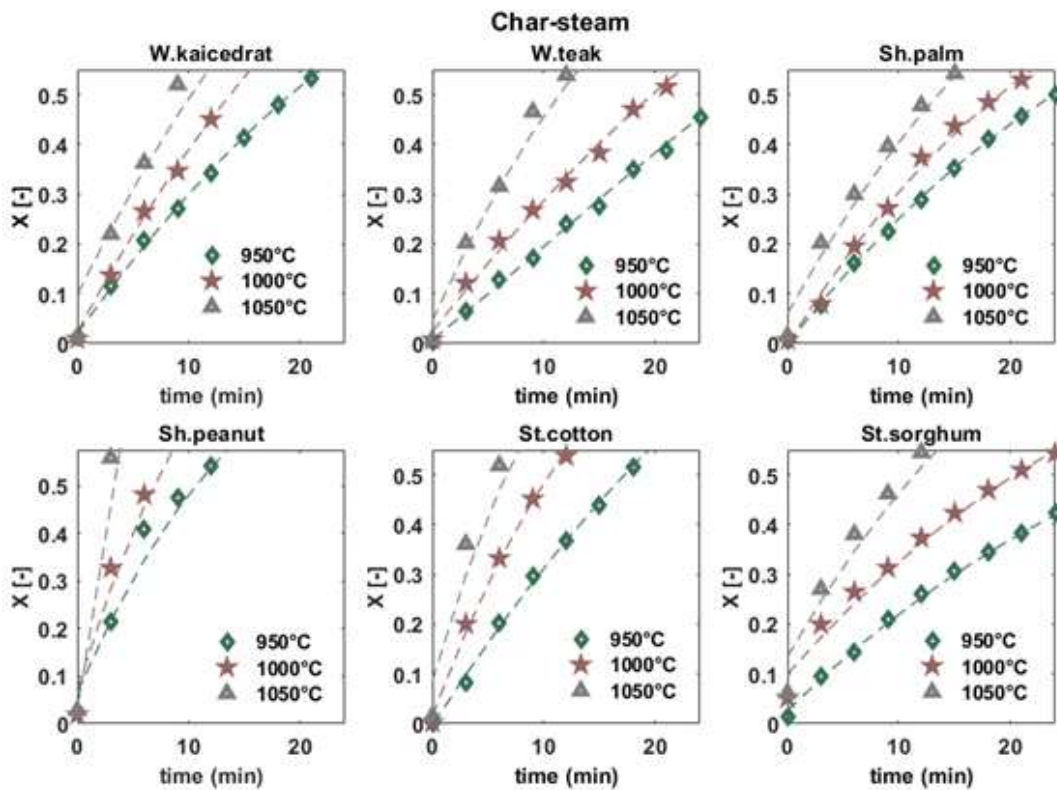
On the basis of this Arrhenius equation, we used the "Volumetric Reaction Model (VRM)" and the "Shrinking Core Model (SCM)" to study the effect of the nature of the char on the conversion kinetics.

### Char nature effect on conversion kinetics

The char kinetic conversions have been the subject of many studies as they are of crucial importance in



**Figure 3.** Influence of temperature on conversion kinetics with CO<sub>2</sub> presence.  
Source: Authors



**Figure 4.** Influence of temperature on conversion kinetics with steam presence.  
Source: Authors

describing the evolution of char conversion (Li et al., 2017; Hernowo et al., 2022; Ansoumane et al., 2018; Zuo et al., 2015). The gasification kinetics of the char remains complex, when it is linked to several parameters defining the structure and char composition; for example the nature of the char (granulometry, porosity, chemical composition, dispersion of minerals in the char, etc). This complexity of the gasification kinetics of the char is at the origin of the varying properties of the char and is also a function of the process used to form the char. Therefore, it is still difficult to establish a universal mathematical expression to describe the gasification kinetics of the char, however we will use the most widely used models in the literature. Models are developed as research progresses, but each model is valid and practical on a case-by-case basis (Zuo et al., 2015). It has been described in the literature (Schneider et al., 2021; Wang et al., 2016) that each model gives its own interpretation of the kinetics of the char during thermochemical transformation.

The Volumetric Reaction Model (VRM) defined by Equation 2 is used to describe the chemical evolution of the conversion of char particles (Zhang et al., 2017; Prestipino et al., 2018; Yao et al., 2020). These authors stipulated that with VRM, the reaction is uniform for a given particle size. They added that with this model, the porosity of the particles increases linearly with the conversion of the char.

$$\frac{dX}{dt} = k_{VRM} (1 - X) \quad (2)$$

The Shrinking Core Model (SCM, Equation 3) consists of a reaction that first occurs on the outer surface of the particle and then continues progressively inside the particle (Jeong et al., 2014). For this model, the particle porosity remains constant and the particle size decreases with the conversion kinetics of the char (Yang and Chen, 2015).

$$\frac{dX}{dt} = k_{SCM} (1 - X)^{2/3} \quad (3)$$

We have seen that an increase in temperature leads to an increase of the conversion speed of the char. Thus, to evaluate the effect of the nature of the biomass on the reactivity of the gasified chars, the kinetic parameters were determined using the two models described earlier.

These different models made it possible to determine the rate constants  $k$  of the Volumetric Reaction Model ( $k_{VRM}$ ), and  $k$  of the Shrinking Core Model ( $k_{SCM}$ ) for each reaction temperature used (950, 1000 and 1050°C). The principle of determining the reaction rate constant as a function of temperature is based on the use of the results of the variation of the conversion rate ( $X=0$  to  $X=0.5$ ) as a function of time. The results are as shown in

Figure 5.

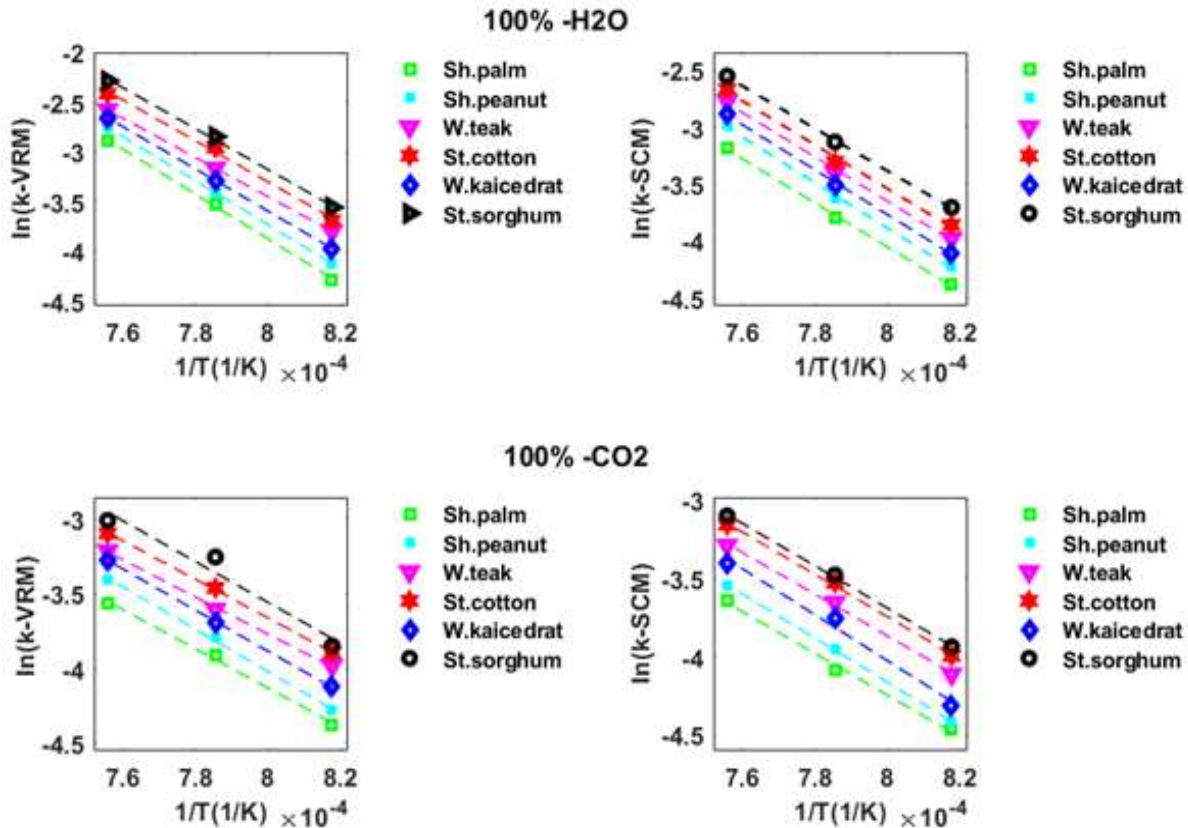
From these results, we can see that the experimental data were well represented by both models (VRM and SCM), with quite high regression coefficients ( $R^2 > 0.9$ ). Table 2 summarizes the kinetic parameters obtained for each sample during their gasification.

In addition, there was no significant difference in the kinetic parameters calculated using the two different models, as the difference between the results was less than 3%. The results also show that the increase in gasification temperature is linearly correlated with the increase in char conversion kinetics (Figure 5). Further, we have activation energies of the reaction of our samples ranging from 100 to 135 kJ/mol (Table 2). It was that the chemical composition of the char corresponding to the different samples influences the kinetic parameters of the gasification of the char under  $H_2O$  or  $CO_2$ . Also, it was noted that the sorghum stem char is more reactive than the cotton stem char, which is in turn more reactive than the teak wood char, then latter in turn becomes more reactive than the "kaicédrat" wood char, the latter remains more reactive than the peanut shell char, which is finally more reactive than the palm shell char in general in a reaction environment.

This effect could be due to the difference in the chemical composition of the raw material, and the chemical composition of the ash (Table 3). Then, the biomass char generally contains a wide variety of predominantly metallic species (Zhang et al., 2008; Jeong et al., 2014; Feroso et al., 2009; Lahijani et al., 2013).

Research shows that the mineral composition of the char has a strong impact on the processing, application and environmental, technological concerns associated with these fuels (Zhang et al., 2008; Skodras et al., 2015; Qian et al., 2015; Yang and Chen, 2015). For biomass, the variability in the mineral content of plants can be considerable, as it depends on genetic and environmental factors or origins, it also depends on physico-biological differences between crops (Xie et al., 2012). The results obtained from the analysis of the ash raw material are listed in Table 2.

It clearly shows that the composition of the biomass ash is different from one biomass to another. The sample ashes are mainly composed of K, Na, Mg, Al, Fe, Ca and P, in the form of oxides, silicates and chlorides. We paid particular attention to the contents of alkali metals, alkaline earth metals and silicon in the biomass ashes and their roles in controlling the char reactivity during the gasification. According to the study carried out by Zhang et al. (2008), comparing the gasification reactivities of biomass samples under steam catalyzed by K, Na, Ca and Mg, the results indicate that the alkali metal-catalyzed char (K and Na) has a much higher reactivity than that catalyzed by alkaline earth metals (Ca and Mg). With K being the most active chemical species for carbonized gas, hence, we can say that the difference in the reactivity of our samples could be due to this



**Figure 5.** Reactivity of the chars samples (plot of  $\ln(k)$  versus  $f(1/T)$ ).  
Source: Authors

difference in the chemical composition of the raw material and the ashes.

In all processes of gasification biomass, ash must be collected and disposed of in an acceptable manner. Depending on the specific process and the properties of the biomass ash, some will produce particulate residues solidifies. Numerous uses have been proposed for ash, ranging from the manufacture of building materials (bricks, concrete and asphalt agglomerates) to agricultural products (fertilizer supplements). Any potential value of a given ash is related to the quantity produced and its physical and chemical properties.

### Sample gas performance

In order to know the performance of the gases obtained from our samples as a function of the experimental conditions, we used the equation described by (Xie et al., 2012; Kong et al., 2022).

$$LHV = (30 \times [CO] + 25.7 \times [H_2] + 85.4 \times [CH_4] + 151.3 \times [C_nH_m]) \times \left(\frac{4.2}{1000}\right) MJ/Nm^3 \quad (4)$$

The results obtained from Equation 4 are listed in Table 4. In this table of variation of gas LHV values as a

function of temperature and reaction medium, we can see that the higher the temperature, the better the gas LHV value. This effect could be due to the principle described by Le Chatelier. According to the latter, in char- $CO_2$  or char- $H_2O$  reaction (endothermic reaction), the production of gases is favourable at high temperature. We note that the LHV values of wood gases (8.06-11.95 MJ/Nm<sup>3</sup>) are approximately equal to those of stems (7.78-12.17 MJ/Nm<sup>3</sup>) and shells (8.93-12.14 MJ/Nm<sup>3</sup>). Therefore, given the seasonality (stems are available from January to April and shells can be available all year round) of biomass residues and the fight against deforestation, it may be recommended to substitute white or red wood with unused biomass waste (burnt in the open air) such as sorghum stems, cotton stems, palm, and peanut shells for energy purposes.

### Conclusion

In this study of thermochemical conversion under  $H_2O$  or  $CO_2$  of wood residue, stems and shells, the conversion kinetics of the samples increase with temperature. The latter remains a determining parameter for the thermochemical valorization of bio-resources. It was also concluded that, based on two kinetic models (VRM and

**Table 2.** Kinetic parameters of char gasification under CO<sub>2</sub> or H<sub>2</sub>O.

Sample	Reactive	Model	E <sub>a</sub> (kJ/mol)	K <sub>0</sub> (min <sup>-1</sup> ) xE <sup>+4</sup>	R <sup>2</sup>
Sh.peanut	CO <sub>2</sub>	SCM	111.81	1.40	0.973
W.teak			109.21	3.36	0.964
W.kaicedrat			108.81	0.62	0.986
Sh.palm			134.24	3.20	0.968
St.Sorghum			101.95	0.89	0.998
St.cotton			102.01	1.01	0.985
Sh.peanut	CO <sub>2</sub>	VRM	112.70	1.06	0.995
W.teak			108.28	1.67	0.998
W.kaicedrat			107.18	0.95	0.998
Sh.palm			127.41	2.36	0.975
St.Sorghum			100.97	1.35	0.942
St.cotton			101.84	2.39	0.996
Sh.peanut	H <sub>2</sub> O	SCM	108.08	1.14	0.999
W.teak			103.03	2.18	0.999
W.kaicedrat			105.16	1.14	0.999
Sh.palm			116.07	1.71	0.951
St.Sorghum			100.58	0.27	0.905
St.cotton			101.45	0.88	0.997
Sh.peanut	H <sub>2</sub> O	VRM	110.63	1.29	0.999
W.teak			103.53	2.24	0.993
W.kaicedrat			104.02	0.90	0.995
Sh.palm			116.80	2.08	0.919
St.Sorghum			100.15	1.03	0.975
St.cotton			100.87	1.11	0.995

Source: Authors

**Table 3.** Biomass ash chemical compositions obtained from our samples using XRF.

Sample	Chemical compositions (Wt. % of ash mass)							
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	Cl
Sh.peanut	0.20	4.76	8.21	23.11	22.69	11.07	6.07	0.12
W.teak	12.82	5.56	6.50	16.47	25.76	20.84	4.57	1.08
W.kaicedrat	10.31	12.72	4.97	19.50	23.30	18.09	1.78	0.01
Sh.palm	6.21	15.34	11.30	34.02	20.23	11.42	8.23	3.01
St.Sorghum	15.08	4.13	2.38	17.43	30.57	6.14	15.11	2.15
St.cotton	12.43	6.40	5.82	18.21	28.07	26.09	3.80	0.08

Source: Authors

SCM), the conversion reactivity of our samples follows the kinetic order: (more reactive) St.sorghum > St.cotton > W.teak > W.kaicedrat > Sh.peanut > Sh.palm (less reactive). We found activation energies of the reaction of our tanks between 100 and 135 kJ/mol. This difference in the conversion kinetics of the char may be due to the

difference in the chemical composition of the material itself and the chemical composition of the ashes. The values of the lower calorific value of the gases obtained vary from 7 to 12 MJ/Nm<sup>3</sup> and are a function of the experimental conditions. This agrees with what is reported in the literature. The gases obtained with the experimental



**Table 4.** Effect of temperature on the LHV value of gases (MJ/Nm<sup>3</sup>).

Sample	Reactive	950°C	1000°C	1050°C	
LHV of gas (MJ/Nm <sup>3</sup> )	Sh.peanut	CO <sub>2</sub>	9.55	11.08	11.61
		H <sub>2</sub> O	9.58	11.48	12.03
	W.Teak	CO <sub>2</sub>	8.06	10.66	11.07
		H <sub>2</sub> O	9.23	11.10	11.95
	W.kaicedrat	CO <sub>2</sub>	9.01	9.91	10.36
		H <sub>2</sub> O	9.54	10.14	10.81
	Sh.palm	CO <sub>2</sub>	8.93	9.48	11.32
		H <sub>2</sub> O	9.76	10.24	12.14
	St.Sorghum	CO <sub>2</sub>	7.78	9.08	9.78
		H <sub>2</sub> O	8.22	9.49	9.78
	St.Cotton	CO <sub>2</sub>	9.03	10.75	11.04
		H <sub>2</sub> O	10.81	11.37	12.17

Source: Authors

conditions of this study can be used to operate an engine or a gas turbine. By comparing LHV values from these different samples, we can conclude that residues of cotton stalks, sorghum, palm shell and peanuts can act as a substitute for the wood used. This distorts the comparison of the LHV values of the gases found. This study therefore focuses on the control of wood cutting and the use of residues of agricultural biomass (cotton stems, sorghum stems and peanut shell) and plant biomass (palm shell) for energy purposes.

It would be desirable to test these samples in a semi-industrial unit under the same experimental conditions. Finally, it would also be necessary to make tests of the mixtures of mass stems, shells, etc., to know the effect of the various conditions on the kinetics of conversion.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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