ENERGY AND MATERIAL RECOVERY FROM ZEBU BONES FOR THE PRODUCTION OF DISTILLATION GAS: ALTERNATIVE FUEL AND ACTIVATED CARBON BY DRY DISTILLATION.

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ABSTRACT

The race to industrialization for good economic growth brings with it several consequences, first of all on the environment and on the sustainable protection of natural resources. This in turn encourages awareness and diversification of energy sources. In this context, the food industry is doubly concerned because it uses fossil fuels but also produces waste. To face this problem related to climate change and for the preservation of the environment, Madagascar has ratified various international conventions on the environment and sustainable development to mitigate the phenomenon of climate change.

In the case of Madagascar, the population is beginning to worry about the importance of waste recovery. Newly created industries all over the island, which are the largest producers of waste, are beginning to be increasingly interested in view of the MECIE Decree "Mise en Compatibilité de l'Investissement à l'Environnement" (Making Investment Compatible with the Environment).

Given the country's wealth of agricultural and livestock products, several companies working in the agri-food sector are currently facing the problem of managing and recovering their waste, particularly zebu bones. The zebu is one of the country's riches. In the sixties, the number of zebus is three to four times the number of the population. At present, this bovine number is close to half of the population given the resurgence of beef stealing.

A beef carcass is composed of 18 to 20% of bones of its weight (http://www.omafra.gov.on.ca/french/livestock/beef/facts/05-076f1.htm). The bones are classified into two categories: category 1 comprising the long bones mainly composed of limbs and ribs and representing 80% of the skeleton. On the other hand, category 2 is composed of the short bones such as the skull and vertebrae and represents 20% of the skeleton's mass.

The city of Antananarivo needs 400 heads of cattle per day for its consumption, that is to say a production of 75.000 Kg per day of bones (https://www.madonline.com/300-a-400-zebus-par-jour-a-trouver-pour-antananarivo/).

The purpose of this research work is to find a technology allowing the energetic and material valorisation of these zebu bones. The result of the research has shown that the appropriate technology is dry distillation in order to achieve the aforementioned objective.
This research work includes respectively: a theoretical study in order to establish mathematical models of the thermal behaviour of the dry process distiller, the realization of the latter working with wood energy. The results of the various tests carried out showed that for 500 g of bone, we can obtain 288 g of bone charcoal with the same behaviour as activated charcoal, 9.88 l of flammable gas for 18 minutes that can be used as an alternative fuel to wood energy and 320 ml of pyrolytic juice that can be used for various purposes (medical, pharmaceutical).
The results of the economic and financial profitability evaluations of the project show the different advantages brought by the dry process distiller in several areas

Keyword: *Dry process distiller, distillation gas, material and energy recovery, pyrroline juice, bone charcoal.*

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1. INTRODUCTION

Waste, whether from domestic, agricultural or industrial sources, is one of the unavoidable problems of the 21st century. Indeed, the increase in the world's population and its concentration in cities, as well as the development of industrial equipment and consumer goods generate large quantities of residues. Waste therefore follows man as the shadow of his presence. Garbage is the traces of his life and technical waste is the traces of his activities. In view of the potential nuisances and dangers conveyed by waste, its rational management and reduction have become essential to preserve the environment and the future of future generations. Faced with this situation, we are currently witnessing the emergence of various research activities into innovative techniques for recovering the energy contained in waste, transforming and/or recycling it.
In Madagascar, particularly in the large cities, the problem of waste management is one of the major concerns of most municipalities, both socially and financially. In this context of waste management, animal waste such as zebu bones are added.
The agri-food company SAVA called "Société Agricole de Valorisation Alimentaire", located in Analakely in the center of the urban municipality of Antananarivo, works in the field of meat processing (pork, meat). This activity generates a lot of agro-food waste creating not only a congestion in the freezer of the said society but also an increase in its consumption of electrical energy. This constitutes an additional burden for the company
Several experiments around the world, supported by scientific studies, have demonstrated the feasibility of recovering waste of agri-food origin. According to these experiments, processes exist that allow society not only to reduce its various costs, but also to open up to other recovery activities.
In addition, energy production and other forms of recycling can be a source of income for the farmer or even the company and can thus contribute to the diversification of activities. In view of these issues, recycling agricultural products contributes to the recovery of organic waste and to the search for resources complementary to food production.
The city of Antananarivo needs 400 head of cattle per day for its consumption, i.e. a production of 75,000 Kg per day of bones. It is a potential renewable resource.
The purpose of this research work is to find an innovative technology allowing the energetic and material valorization of these zebu bones. Dry distillation is one of the most appropriate technologies to achieve this,

2. METHODOLOGIES

2.1. Study area: urban commune of Antananarivo, Madagascar

2.1.1. Geographical location

The urban commune of Antananarivo is located in the center of the Antananarivo region and covers an area of 78 Km2. It contains an important agglomeration area and is limited by the districts namely:
- Antananarivo Avaradrano to the North and East
- Antananarivo Atsimondrano to the south and west
- Ambohidratrimo in the North and West

Being the capital of Madagascar, it is the point of convergence of the main national roads such as RN1, RN 2, RN 4 and RN 7 connecting the city with the other regions.

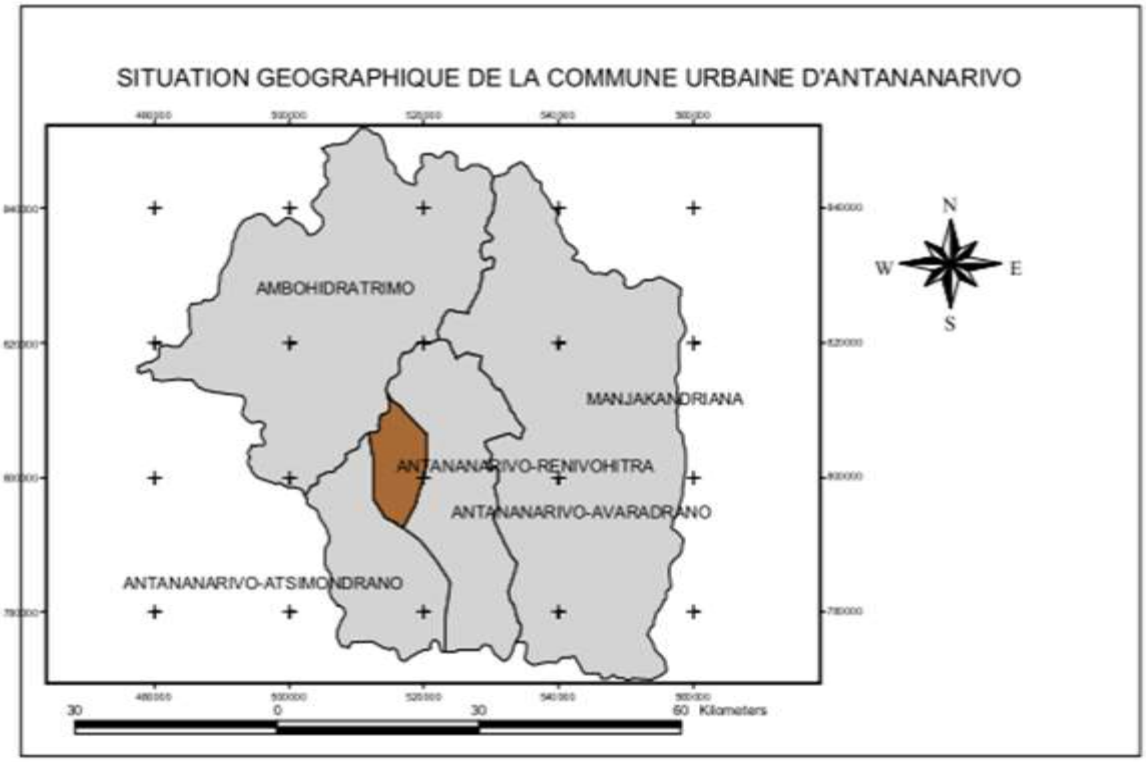

Figure 1: Map of the geographical location of the AUC

2.2. Activated carbon

Activated carbon, also known as activated carbon or activated carbon, is a material made of carbon with porosities.
It has the ability to fix and retain certain molecules in contact with it thanks to the pores. It generally has a large specific surface area which gives it the power of adsorption. Adsorption is a surface phenomenon by which molecules are fixed on the surface of the adsorbent by weak bonds, the production of activated carbon is divided into two important stages:

-Pyrolysis

-Activation of coal

2.2.1. The properties of activated carbon

Activated carbon is a non-hazardous carbonaceous product with a porous structure and a very large internal surface area. The chemical structure of activated carbon can be defined as a rudimentary form of graphite with an extremely porous amorphous random structure, with pores of various sizes, from molecular size to holes and crevices visible to the naked eye.

Activated carbon treatment is mainly based on a phenomenon called adsorption, in which molecules of a liquid or gas are trapped on the surface, external or internal, of a solid substance. Activated carbon has a very large internal surface area (up to 1500 m^2/g) and is therefore an ideal material for adsorption. Activated carbon can be treated with chemicals to improve its properties for certain applications.

2.2.2. Advantages and disadvantages:

In this research work, activated carbon will be used for water clarification, so its use has different advantages and disadvantages:

Disadvantages:

-Powdered activated carbon is 2 to 3 times cheaper than granular carbon.

-Additional quantities may be added in case of accidental or temporary pollution peaks.

-Adsorption is rapid as a large part of the contact surface is directly available.

Advantages:

-Activated carbon cannot be regenerated when mixed with hydroxide sludge.

-It is difficult to remove the last traces of impurities without adding a very large amount of powdered activated carbon.

-The detection of pollution peaks is problematic and its applicable concentration is limited to 80 mg. L-1
-their use requires only a reduced investment when the treatment consists only of a flocculation-settling stage

2.3 Sources of activated carbon

Currently, several technologies exist but they differ from each other in terms of the raw materials they use to produce them:
- Vegetable coal
- Animal coal

Vegetable coal:

It comes from a production or any organic vegetable matter rich in carbon: the raw materials used in this manufacture come from: bark, wood pulp, coconut shells, peanut shells, olive pits, or from coal, peat, lignite, oil residues. It is the most widespread technology at present.

Animal coal:

It comes from the bones of fresh animals; fish bones are to be excluded.
It can be recycled and thus be used for several years. When it has lost its adsorptive power, it is treated with Sulphur acid to form superphosphate for soil fertilization.

2.4 Uses of Activated Carbon

Activated carbon is used in several areas in everyday life as listed below
Field of Medicine:
-It fights viruses and bacteria
-It whitens teeth
-Relieves stomach aches
Industry:
-Gold mining
-Manufacture of super-capacitors
-Hydrogen storage
-Industrial hygiene
Chemistry:
-Sugar decoloration
-Removal of oil from water
-Water discoloration

2.5. Characteristics and origin of the raw material

Choice of raw material:

When choosing the raw material used, it was necessary to know statistically the potential of the raw material. Several factors entered during this phase:
- Availability: Is the material available at all times or is its presence conditioned by other factors?
- Moral barriers: Since we are in the field of food and we are in a developing country, the question remains about food insufficiency.
- The value: Does the material have a remunerative value without transformation? since in the field of recycling the most important thing is that the source is something unusable or to be thrown away.

After several days of study the choice was made between: Bone and unusable meat.
The choice was quickly made on the "bone" since it answers the 3 factors posed above.

Composition of the bone:

Generally speaking, the bone is formed by mineral and organic matter.
Inorganic molecules represent two thirds of the bone mass. They are mineral salts such as calcium phosphates. Calcium salts give bone its hardness and strength. It contains about 60% carbon
Bone is therefore a "composite" material of great resistance.

The yield and availability of raw materials:

According to studies made in several documents a beef carcass is composed by 18-20% of bone of its weight. " http://www.omafra.gov.on.ca/french/livestock/beef/facts/05-076f1.htm "
The different types of bone can be categorized into two distinct categories
- Category 1 :
It classifies the long bones mainly composed of limbs and ribs; it represents 80% of the skeleton.
- Category 2:
It classifies the short bones with different forms composed by the skull, vertebrae etc., it represents 20% of the skeletal mass.

In our study, the SAVA company uses 600 Kg of carcass per week to run the company. It represents 100 Kg of bones every week, including:

Table 1: Availability of raw materials

categories 1	80Kg
categories 2	20 kg

During their transformation process the bones accumulate easily in the freezer and are almost to be thrown away because there are so many of them.

In 1 month, the company produces 400 Kg of bones or waste if we take it as the data above in table 1.

2.6. Principle of activated carbon production

The different stages of animal coal production:

-Degreasing

-Pyrolysis

-Physical Activation

-Chemical activation

- Bone degreasing:

The principle followed to degrease the bone is to boil it for a certain time to remove impurities on the bone and so that the pyrolysis can take place more quickly.

- Pyrolysis

Pyrolysis or calcination or carbonization is a high temperature process that creates pores or the area in which molecules will be blocked, as elements other than carbon leave pores in the carbon matrix when they carbonize.

Pyrolysis is the thermal decomposition of organic matter in an anaerobic environment.

It is the first stage of thermal transformation after dehydration.

It allows the production of a carbonaceous solid and oil and gas, the proportion of the three different compounds depending on the temperature.

- Activation of activated carbon:

Activation is divided into two distinct stages:

- Physical activation:

New combustion with thermal shock (at 900 to 1,000 °C) it increases the adsorption surface of the carbon. This process produces a narrow pore carbon.

- Chemical activation:

Put the carbon in contact with phosphoric acid at a temperature of 400-500 C. This process gives a coal with larger pores.

2.7. Physical and chemical conditions

Due to its varied origins and manufacturing processes, activated carbon is known for its

To be a material of heterogeneous structure and composition. In order to better define its properties, different techniques

Structure

Thus, the structure of activated carbons can be likened to an assembly of hexagonal and pentagonal sheets, comparable to crumpled paper. This structure explains the large surfaces developed by activated carbons.

Texture

The texture of a solid is defined by the porous structure and the specific surface.

This porous structure is at the origin of the large surface area developed by activated carbons and these textural parameters can be determined from the isotherms of physical adsorption of an inert gas on this solid.

The adsorption:

Adsorption is a physical phenomenon where a solid is used to remove a soluble substance from water. In this process, activated carbon is the solid. Activated carbon is produced specifically to cover a very large internal surface area (between 500 and 1500 m2/g).

That is to say 5 g of activated carbon can cover three football pitches.

The specific surface:

The specific surface area is the total surface area per unit mass of the product accessible to atoms and molecules. It is thus a matter of considering the entire surface of each particle, including porosity.

The physical principle, recognized for the determination of the mass surface area, is based on the adsorption of gas at low temperature. Knowledge of the specific surface area is of great use in the production of activated carbon. It can be experimentally known from the B.E.T. method. "These authors have shown that there is a relationship between the quantity of gas adsorbed per unit mass of the solid studied, the equilibrium pressure, the temperature, the nature of the gas and that of the solid itself. »

The formula for knowing the specific surface area is given by the following formula:

$$S=n.Sm$$

Or:

S= Total sample area= Specific surface area in m2/g

n = number of gas molecules adsorbed in a monolayer

Sm = surface area of a gas molecule.

S = [(6.1023. Vm / 22214) Sm] / mass of the sample

2.8. Optimizing the furnace to raise the temperature

Principle and purpose of insulation

In order to increase the carbonization temperature in the crucible, it was noted that radiation losses are significant. It is necessary to insulate the system to reduce the heat losses present.

The principle consists in coating the furnace with an insulating material capable of considerably reducing heat loss. The aim is for the system to reach 800-900 °C in the crucible.

To achieve this goal (800 - 900°C), good insulation is required, usually using the chosen material such as glass wool or stone wool (specific for high-temperature industries).

Stone wool:

Stone wool protects against cold and heat, and stores the ambient temperature in a certain way. It also allows significant savings in heating costs. Stone wool is the guarantee of a healthy and pleasant (and advantageous) indoor atmosphere and is a natural product with remarkable properties:

- low thermal conductivity (0.033-0.045 W/(m-K))
- Optimum heat absorption capacity (870 J/(kg-K))
- Permeable to water vapor (diffusion resistance µ: 1-2)
- Resistant to mold, mildew, rot and vermin
- Non-combustible and high melting point (> 1'000 degrees Celsius)

3. RESULTS

3.1. Conduct of the tests

The test took place as the device was completed.

In the first trial, no distillation column was used, just the lid was closed so as not to dissipate too much of the foul odour from the experiment.

During the 2nd trial, the manufacture of a distillation column was necessary after the knowledge of a by-product that could be recovered. The column was quickly built up using an unused gutter slice.

It was easily deformed under the action of heat but the by-product was more or less recovered.

For further tests, a distillation column and a solid condenser were built for the prototype and the system worked well.

3.2. Results of each test :

The following table 2 summarizes the results obtained during the various trials of charcoal production:

Table 2: Test results

Tests	**Nature**	**Initial mass (g)**	**Final mass (g)**	**Quantity of coal (kg)**	**Start (testing)**	**End (testing)**
1^er^	Category 1	650	255	4	10h15	11h30
2^ème^	Category 2	950	350	3,8	10h	12h
3^ème^	Category 1	650	360	3,8	10h	12h30
4^ème^	Category (1 + 2)	1 300	460	3,5	11h	13h30
5^ème^	Category 1	500	300	3	10h	12h

This table gives the results of the five tests carried out. It highlights for each test: the duration of the experiment, the categories of bones treated, the mass of sample and the weight of charcoal used.

For the first test, the equipment is not yet complete:

We used it:
- a manual fan to reach the temperature of 700°C and a yellow-orange colored smoke was observed, accompanied by an odour emission. The yellow-orange gas is called carbonaceous hydrogen gas.
We obtain oil, seen on the lid, the pyrolytic liquid, which is used for traditional medicine.
The product obtained is not very homogeneous, i.e. part of the bones is not well cooked.

The second attempt:

During this test, after the presence of an oil on the lid, it was necessary to make a distillation column with a gutter, i.e. tinplate.
The condensation was done manually by cooling the condenser with a sponge.
- The dark brown pyrolytic liquid, but also another very viscous beige liquid from the bone marrow was collected.
- The heat passing through the distillation column is very high, since the column that was made up was completely damaged, even though it still resisted until the end of the experiment, but could no longer be used.

The third attempt:

From this third test, the system was completely made up as described previously as:
- The distillation column was made with a black body, in order to avoid its deformation in contact with a very high temperature.
- The improvement of the condenser, so that the heat exchange taking place in the condenser only takes place by activating the tap water.
- Increasing the cooking time.
- It has been noted that the majority of Category 1 bone by-products are pyrolytic juices.
- Increasing the cooking time has made it possible to homogenize the bone charcoal.

The fourth attempt:

It was from this test that we started to insulate the furnace:
- We completely filled the crucible and the whole height of the distillation column, to know its real capacity and the ideal quantity of bone to put for the best possible yield.
- Simultaneous use of the manual fan and an electric fan delivering 150 m³ of air/ h, i.e. use of a constant source.
- Only part of the bone quantity has been processed and the ideal quantity is therefore 500 g.
- The temperature of 900 C was reached and maintained for 2 hours.

3.3 Post-production control tests

The following curve represents the variation of temperature versus time during the bone activation and gas recovery process- At the start of the fire, the temperature is 23°C,
- The appearance of flammable gas is observed at the surrounding temperature: 700°C.
- At 800°C, one can easily notice the presence of a 2-hour stage, corresponding to the characteristic temperature of the activation of an activated carbon.

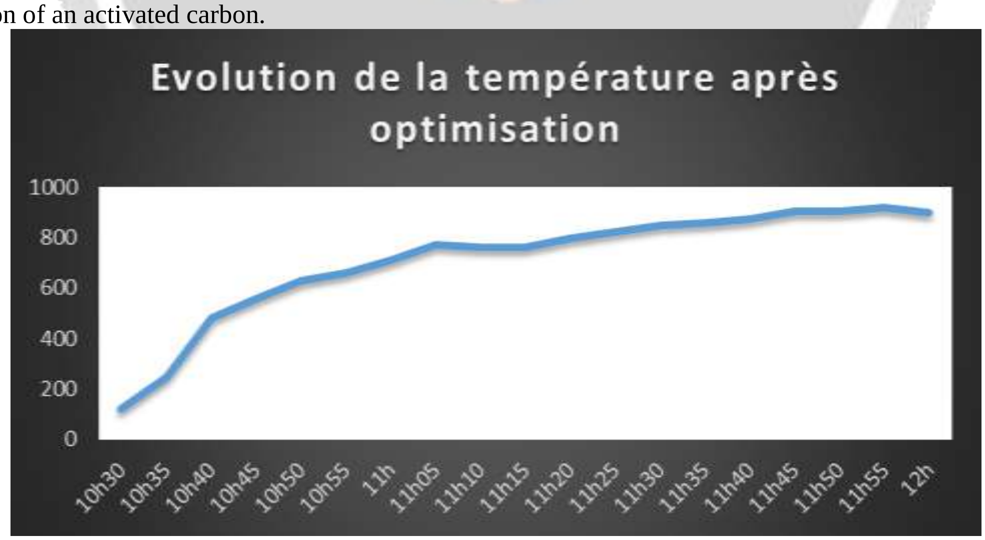

Figure2: Evolution de la température

At the end of the various distillation tests of 500 g of raw bone, we have recorded in the following table the quantities of activated bone produced.

Table 3: Quantities of bone charcoal

Number of distillation tests	1	2	3	4	5
Weight of bone (g)	500	500	500	500	500
Bone charcoal (in g)	295	278	280	289	260

This table shows the evolution of the charcoal obtained for the five tests carried out. For the five tests carried out, the average mass of bone charcoal was obtained as follows:

average mass of bone charcoal (g)=1402/5=280.4 g

For 500 g of bone, we will have 205 g of bone charcoal with the same behavior as activated charcoal.

3.4. Bone charcoal efficiency test

a) Roles of the form of activated carbon:

Several documents state that the finer the molecules of activated carbon, the more its adsorption surface does not increase any more.

To prove this hypothesis, three (3) different forms of bone charcoal were taken, one of which is in its natural form, a second granular sub-form and finally another powder sub-form.

In this experiment, the measurements taken will be the same:

Alcohol: 200 ml

Activated carbon: 25 g

Exposure time: one night

<u>Results</u>:

The hypothesis was demonstrated since the alcohol, which initially turned orange, was transformed into a transparent solution comparable to the water in the solution where the powdered coal was found.

Therefore, the finer the carbon is in the form of fine molecules, the greater its adsorption capacity.

b) Bone charcoal in the role of filtration:

In frequent use, but also in its use, activated carbon is used for the filtration of a solution and for deodorization.

Therefore, in the test that follows, we will test its ability to filter the alcohol solution to be cleaned.

First, we will take the same measurements for each one:

-Bone charcoal: 15 grams.

-Alcohol: 250 ml

<u>Results Achieved</u>:

The figure shows the filtration stage and the results obtained after the solution has passed through the filter.

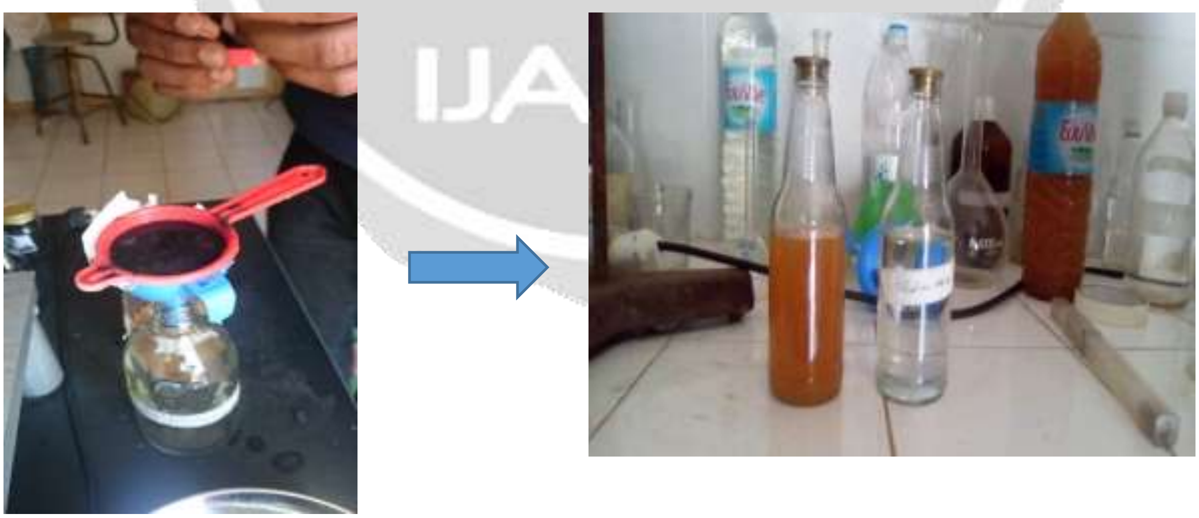

Figure3: Step and result of the filtration process

In Figure 2, we can see that the alcohol that has just been filtered becomes visually very clean like water. In addition, it can be seen that even the smell of alcohol disappears, i.e. the alcohol becomes odourless. This confirms that the deodorization hypothesis has been proven.

3.5. Demonstration on the specific surface

As seen previously, activated carbon has the ability to adsorb. This capacity is measured using the technical method of B.E.T. (Brunauer, Emmet and Teller). However, this experiment is not possible due to a lack of material and financial means.

Therefore, in order to know the specific surface of the bone charcoal, we will proceed by the observation test and visual comparison to know its efficiency.

The principle of the test is simple:

Carbon black is an activated carbon with a specific surface of 120 m²/g, which is easily found in chimneys and especially on the bottom of pots.

We will therefore compare the effect of carbon black and bone charcoal in a solution to be cleaned, here in the test, of the alcohol residue at 02° Alcohol.

We will put in the test the same values for each, that is to say:

-Mass of charcoal: 20 grams.

-Alcohol: 200 ml

-Observation time: one night

-The activated carbons will both be powdered.

-The same solution

It should be pointed out that even when the solution is put to rest, no settling phenomenon occurs.

Results obtained:

After several hours of rest, the solution cleaned itself thanks to the effects of the activated carbon. We notice on the pictures a cleaned alcohol shown in figure (17).

Thus, according to the data, the carbon black has a specific surface area of 120 m²/g. When viewing the results, it can be seen that the bone charcoal has a better cleaning power since with the same time allowed, the solution to be cleaned is clearer in the one where it was used.

It can be estimated that bone charcoal has a specific surface area of 400 m²/g.

Figure4: Comparison of the two coals (on the left the bone charcoal)

3.6. Gas recovery tests

After dry distillation of the bone, the by-products from this distillation are of two types: solid and liquid.

One can have activated carbon and distillation gas or Rano Mena.

As a matter of principle, priority is given to by-products that can be used to produce energy.

Objectives of the trials:

The aim of the experiment is to determine the potential of the distillation gas if it has a real plus in production:

- The gaseous by-products (distillation gas) of bone can be used as an additive for the dry distillation of raw bone, reducing not only the consumption of charcoal for its transformation but also the emission of greenhouse gases harmful to the environment.

3.6.1. Distillation Gas Recovery Sequence

Methodological approach:

To be able to determine the volume of distillation gas rejected at each dry process distillation process, our approach consists of the following steps:

Step One:

Start the charcoal production process but using the tap instead of the distillation column.

Second step:

Look for a standard flask;
Fill with tap water;
Measure the volume of water filling this balloon;

Third step:

Start the distillation by lighting the fire;
Record the flammable temperature of the gas.
Record the flammable temperature of the gas.
Take several readings of the filling time of the standard flask as a function of temperature.

Test results:

Tests No.	Bone mass (g)	Bone charcoal mass (g)	Distillation gas volume (l)	Flammability time (min)
1	500	280	10,01	20,01
2	500	280	9,04	21,02
3	500	276	9,54	19,02
4	500	276	9,45	19,01
5	500	288	11,4	21,9
		280	9,888	20,192

This table summarizes the results of the different distillation tests on zebu bones. It highlights that for a well-defined mass of bone, the quantity of bone charcoal is about 56%, i.e. a little more than its initial mass. The flammability time for the different tests carried out varies around 20 minutes on average.

In short, for a bone mass of 500 g, we were able to obtain 280 g of bone charcoal, 9.88 l of flammable gas for an average duration of 20 minutes.

4. DISCUSSION AND CONCLUSION

The aim of this research work is to find a solution to get rid of zebu bones, waste from the activities of the agro-industrial company SAMVA. These bones are a nuisance in the company's refrigerator and disrupt the smooth running of their daily activities. Faced with this problem, the search for a solution is a priority. Questions arise among others:

-Is energy and material recovery the appropriate solution to solve the problem of the said society?

The three principles of waste recovery are:

-reduce
-reuse
-recycle

Taking this principle into account, we can say that first of all, zebu bones have been reduced because the fact of transforming them into bone charcoal has led to the reduction of the volume of waste in society. Bone charcoal is a new and much sought-after product for water treatment. In addition, gas was also obtained that could be used as a new source of energy, an alternative to wood energy. In short, recovering these zebu bones in the form of energy and new material is the appropriate solution for the SAMVA company, the object of this research work.

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