



Alternatives for Valorization of Agricultural Resources of Low Commercial Value in Benin: Production of First Generation's Bioethanol: A Review

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Abstract Currently, the possibilities for energetic valorization of the biomass by biotechnological processes represent a solution of choice for the use of low trading value agricultural products, waste from food industries, crop residues, etc. The valorization of this biomass, especially of organic nature, is realized through various biotechnological processes such as bioconversion into ethanol. The present study is a literature review that aims to encourage the recovery of agro-industrial waste and reducing post-harvest losses through the evaluation of bioethanol fuel production possibilities by using sugar commodities (pineapple peelings, mango, cashew apple) and local starch (cassava, sorghum). The realization of this study is an important challenge in environmental domain and on socio-economic level through employment creation, socio-economic integration of women, and the creation of added value to peasants..

Keywords biomass, energetic valorization, biotechnological processes, bioethanol fuel

1. Introduction

The search for renewable energetic biomasses without food competition, without harmful effects on the environment, nor direct or indirect change in lands, combines with climate change and the scarcity of fossil fuels to envisage new resources and innovative processes [1]. From this perspective, the conversion of biomass into biofuels seems to be a solution of choice to palliate these problems. Bioethanol is the most widely consumed biofuel in the world. It's produced by fermentation from materials rich in sugar or starch such as cassava, corn, sugar cane [2]. However, competition with food products has led industrials to abandon widely consumed food products use to turn to new unconventional materials, agricultural and industrial residues (pineapple peelings, Mangoes, cashew apples, etc.) for bioethanol manufacture. Valorization of agricultural by-products contributes to the resolution of environmental problems, but also represents a significant additional source of income (job creation, income-generating activities, women's socio-economic integration, improved balance of payments, etc.). Possibilities of energy recovery of biomass by biotechnological processes represent a solution of choice for the use of agricultural products of low commercial value, crop residues and agro-industrial waste [3]. Similarly, the promotion of biofuels obtained from neglected biomass contributes to reduction of countries' energy dependency. It therefore creates new agricultural sectors and could offer new battlements for farmers, especially developing countries [4]. Moreover, the interest in producing bioethanol stems from the fact that it is a strategic energy substance whose use covers a wide land of industrial activities (detergents, solvents, disinfectants, pharmaceuticals and cosmetics, etc.). Although second-generation bioethanol obtained from lignocellulosic biomass is recognized as a promising alternative energy



source, ineffectives pretreatment pathways and the high cost of enzymatic hydrolysis constitute major causes that impede bioethanol commercialization. As a result, attempts to produce bioethanol are often directed towards non-edible, high-sugar agricultural resources [5]. Indeed, it is reported that ethanol has a better octane number. It is non-toxic and therefore can't contaminate water sources. Also, it's an excellent chemical synthesis reagent [6]. This bibliographic study aims to contribute to the valorization of agro-industrial waste and the reduction of post-harvest losses through fuel bioethanol production from sugared and starchy substrates.

2. Trends in Bioethanol Fuel Production

The first requirement for the production of bioethanol is the source of sugars. In the production of bioethanol, the usable raw materials are very varied and depending on the progress made in research during last few years [7]. However, choice of each of them depends not only on the cost and profitability of the process, but also on fermentation capacity of the microorganisms associated with bioconversion process [8].

In general, according to the raw materials and the technologies used, the bioethanol production chains are classically divided into four generations [9].

- First generation uses conventional technologies to convert only the food part of crops (sugars and starch) into bioethanol.
- Second generation aims at full valorization of plants, lignocellulosic biomass in bioethanol using advanced technologies.
- Third generation wants to exploit the potential of seaweeds for bioethanol production using more advanced technologies.
- Fourth generation envisages the conversion of plancton vegetal (micro seaweed) to bioethanol using very high processing technologies.

2.1. Evaluation of Bioethanol Production Raw Materials

First generation bioethanol is generally obtained by microbiological conversion of fermentable sugars and starches [10]. Sugars extracted from sugar agro-resources (such as sugar cane, sugary sorghum, fruits) are directly subjected to ethanolic fermentation and the starch obtained from cereals (such as wheat, maize, barley, rye) or tubers (cassava, yam, sweet potato, potato and taro) undergo saccharification (enzymatic or chemical hydrolysis) before ethanol fermentation step [8].

2.1.1. Availability of sweet substrates

2.1.1.1. Mango

Non-food valorisation of mango is still an unknown activity and occupies a very limited place in research. It constitutes a real opportunity to create added value and an asset for the fight against the fruit fly. In addition to mangoes infested and discarded, valuable mango wastes are mango peels from peeling in drying units and cores [11].

Benin possesses the ecological conditions necessary for an intensive cultivation of the mango: suitable climate, favorable soil, absence of strong winds. There is little attention paid to the cultivation of mango in national agricultural development programs. Nevertheless, intensification of production will in principle pose no major problems, owing to the favorable climate and the availability of land (especially in the departments of Borgou, Zou and Atacora). Mango is available during the two rainy seasons: the small season (December to February) which seems to promise because the mango plantations bloom very well while there is a drastic reduction of the fly infestation and the great season, when infestation threatens the quality of export mangoes (May - July) [12]. Few producers process mangoes infested and discarded into non-food derivatives, except for composting or for feeding livestock. In the latter case, the infested mangoes are rather given free of charge by the producer to the breeders. The producer does not profit thereby. Hence the justification once again of non-food valorisation idea of mangoes to meet two expectations: income supplement for small producers and means to combat the development of fruit fly. Infested and therefore non-marketable mangoes can be discarded for non-food valorization [11].



Moreover, during the mango season, the population does not manage to consume all mango production. The fruits drag under the mango trees and also, the sellers, disappointed with the slump in sales, pour their goods on the outskirts of the streets. Flies infect mangoes abandoned and the environment is probably threatened. This could lead to several undesirable illnesses within the population. The implementation of new strategies for bioconversion of these mangoes into bioethanol would certainly contribute to the improvement of producers' incomes and to environmental and public health problems resolution.

2.1.1.2. Cashew apple (*Anacardium occidentale* L.)

In several regions of Benin, and particularly in the Department of Hills, a large cashew production area, producers only market cashew nuts, but this tree also supplies the apple to which nut is attached [13]. However, in spite of its high content of fermentable sugars, vitamin C, phenolic compounds [14], carotenoids [15], aromatic compounds [16], almost all of Benin's cashew apple production is often abandoned, due to its astringency due to tannins presence in the fruit [17]. The cashew apple is considered a waste in cashew nuts' industry and is left in decomposition on the ground in the fields [3, 18]. Producers hardly benefit from the cashew apple attached to this nut because of their ignorance of this abundant raw material's valorization techniques. To reduce this important loss in order to increase producers' incomes and add value to the cashew industry, it is necessary to develop a valorization technology of cashew apple without detracting from nut quality. This apple contains astringent compounds which give a disagreeable sensation to its consumption, which limits its use on juice's world market [19]. The artisanal transformation of the apple into alcohol or juice is still embryonic [20]. This under-utilization was telling Karuppaiya et al. [21] that apple cashew has no commercial value, with the exception of its use by people living in rural areas for alcoholic beverage production at the household level. For some people, the real value is hidden in the cashew apple to the point where some producers focus their attention on the income potential of cashew apple compared to nuts [22]. Indeed, its richness in fermentable sugars and in mineral elements and vitamins, makes it a substrate of choice in sugar materials bioconversion into bioethanol by fermentation [4]. Using this agro-resource as a feedstock of modern bioethanol production units through improved yield technologies would provide a boost to the economy while solving a major environmental problem.

2.1.1.3. Pineapple peelings (*Ananas comosus*)

Like cashew apple and mango, pineapple is a very perishable product because of its high water content, rich in fermentable sugars and generates 25 to 35% of waste during its transformation [23]. The government of Benin, in its policy of development of the agricultural subsector has oriented in recent years, its strategy towards the development of the pineapple sector through the establishment of processing plants in different production areas of this fruit in Benin. The fruits and by-products of the pineapple processing industries are obtained every year in significant quantities all over the world [24]. Unfortunately in Benin, these by-products are not recycled and are often crammed into wild dumps located in the vicinity of processing centers [25]. The promotion of the pineapple spinneret in Benin is an important issue, not only in the field of environmental protection, but also in socio-economic terms (job creation, income-generating activities, socio-economic integration of women, improved balance of payments, etc.). The valorization of agricultural by-products contributes to the resolution of environmental problems but also represents a not negligible additional income source [4]. Fruit waste such as pineapple peel containing fermentable sugars should no longer be abandoned in our environment but should be converted to useful products such as bioethanol [26]. Nadzirah et al. [27] found that sucrose was the most important sugar present in the pineapple waste extract.

2.1.2. Availability of starch substrates

Starch is a generic term for saccharide types consisting of complex molecules consisting of hundreds or even thousands' glucose molecules chains. These chains can be decomposed into simple glucoses by hydrolysis. Sorghum (*Sorghum bicolor*) is the oldest source of starchy material used for the production of two types of local beers that are widely consumed in Benin: Tchoukoutou and Tchakpalo [28]. The most suitable raw material for the production of ethanol fuel is manioc (*Manihot esculenta*). With an average production of 2.8 million tonnes of cassava per year, Benin could be able to produce 20 000 m³ of ethanol by valuing only 5% of the crops (no competition with food



needs) and cassava is available throughout the year [29]. One of cassava's great qualities is that it does not have a specific harvest season. Tuberous roots can be harvested at any time, from six months to two years after planting. In general, fermentation substrates' choice depends on cost, process profitability and fermentation capacity of microorganisms associated with the bioconversion process.

2.2. Processes for Converting Sugars into Bioethanol

Depending on raw material used and the required purity of ethanol, one or more steps may be omitted. For example, sugar-containing feedstocks can be directly fermented if sugars are available, whereas starched products must first be hydrolyzed. Sugars from fruit juices or fermentable agro-industrial by-products are directly converted to bioethanol by alcoholic fermentation, and starch from tubers and cereals, as well as agro-industrial wastes, undergo an enzymatic or chemical pre-treatment before alcoholic fermentation stage [8].

2.2.1. Hydrolysis process

The process for producing ethanol consists in recovering by hydrolysis maximum sugars obtained from starch and then fermenting these sugars into ethanol. The first hydrolysis processes used were mainly chemical, but at present they aren't very competitive, due in particular to reagents cost and formation of numerous by-products and inhibitor compounds making hydrolysates less fermentable. They are now competing with more specific enzymatic processes, which permit better hydrolysis yields under less severe conditions [30]. Enzymatic hydrolysis constitutes a specific method, carried out under relatively mild conditions of pH and temperature, and allowing hydrolysis yields greater than those obtained from chemical processes by dilute acid hydrolysis (80-90%) [8]. SFS process development (Simultaneous Saccharification and Fermentation) makes it possible to improve enzymes efficiency by minimizing inhibition reactions of the enzymes by formed products. Its disadvantage is related to the differences between enzymatic hydrolysis' and fermentation's optimum temperatures. The search for microorganisms maintaining good fermentative performances at high temperature therefore constitutes an important research axis.

2.2.2. Alcoholic Fermentation

Alcoholic fermentation is sugars' biological transformation (mainly glucose and fructose) into ethanol and carbon dioxide. This alcohol production is accompanied by secondary products formation such as glycerol, acetic acid, lactic acid, higher alcohols, esters, etc. [31]. Alcoholic fermentation is carried out by inoculation with biological microorganisms.

2.2.2.1. Microorganisms adapted to bioethanol production

The microorganisms often used are: yeasts of *Saccharomyces* genus [32], *Kluyveromyces* genus [33] and bacteria as *Zymomonas mobilis* [34]. The major disadvantage of bacteria is that they often produce other by-products such as higher alcohols, polyols, organic acids, ketones and gases (CH_4 , CO_2 and H_2). In fermentation processes using yeasts, oxygen is required for reasons of maintenance of cellular integrity. Unfortunately, aerated conditions will also favor the production of biomass [35]. To palliate for this phenomenon, *Zymomonas mobilis* has advantage of being cultivated in strict anaerobiosis and therefore producing little biomass but more ethanol [36]. It would therefore be more tolerant to ethanol than *Saccharomyces cerevisiae* [37]. On other hand, *Zymomonas mobilis* is very effective for glucose fermentation but produces many by-products (especially organic acids) when sucrose is used as sugary substrate. Indeed, microorganisms studied exhibit significantly lower performances than those obtained, for example, with yeast *S. cerevisiae* on glucose. This is one of weak points of the process. In general, *Saccharomyces cerevisiae* is used for a broader spectrum of substrates. It is the most efficient in terms of ethanol production at a relatively low pH ($\text{pH} \approx 4$). This makes it possible to avoid contaminations or parasitic reactions due to others microorganisms presence, whereas sterilization is still necessary before using *Zymomonas mobilis* [35]. Currently, *Saccharomyces cerevisiae* is bioethanol production's main yeast, given that it can produce high ethanol concentrations from glucose and sucrose with high ethanol tolerance [38, 39].



2.2.2.2. Alcoholic fermentation processes using yeasts

Currently, there are four types of fermentation (batch, semi-continuous, continuous and perfused) achievable in bioreactors, also known as fermenters (biosynthesis culture medium) with different configurations (mono-stage, bi-staged or with membrane recycling). The choice of fermentation type depends not only on kinetic properties of microorganisms, on substrate type to be fermented but also on economic aspects envisaged in order to optimize production yields [40, 41]. Batch fermentation is commonly used in basic research laboratories as well as in the agro-food and pharmaceutical industries [42]. During the process of ethanolic fermentation, glucose is easily transformed into ethanol by the yeast *Saccharomyces cerevisiae* used by all industries of alcoholic fermentation. Currently, no other microorganism achieves its performances on glucose under non-sterile conditions, namely a yield of the order of 0.47 g of ethanol per g of glucose, a productivity greater than or equal to 5 g/L/h and final ethanol concentrations close to 10% by volume. *Saccharomyces cerevisiae* has many additional advantages resulting from many years of selection: resistance to ethanol, easy industrialization, etc. [30].

2.2.3. Alcoholic distillation

At fermentation stop, the wine obtained was distilled (Figure 1) in order to extract the bioethanol in condensed form by fractional distillation while maintaining the temperature at approximately 79 °C at the vigreux column head [8]. Fractional distillation is a well-known technology for separation of mixtures of liquids with different boiling points. The vigreux column serves to separate vapors from two phases. Indeed, one will be more volatile than the other, so it will evaporate more easily. But there will always be traces of the other product. Since the temperature in the vigreux column decreases by gradient, the less volatile product will tend to condense before reaching the column top. The mixture thus becomes more and richer in the more volatile product as and when one moves up the column and at the end a pure product is obtained. At column's top, at the thermometer, vapor obtained's temperature is read. If the distillation is well done, a pure product is obtained. The vapor temperature is then the product's boiling temperature. The latter is therefore easily identifiable. The distillation makes it possible to obtain an ethanol content of up to 96% per volume unit.



Figure 1: Distillation process [36]

2.2.4. Dehydration Process

In this last step, the distilled bioethanol must be dehydrated beforehand to obtaining very low water levels, less than 0.3% per unit volume corresponding to ethanol with a degree of purity of more than 99.7% and compatible with its end-uses. Demands for anhydrous ethanol includes biofuels (in direct blend or for ETBE production), industrial chemicals, and various food and pharmaceutical ingredients. For this separation, conventional technologies are employed as successive fractional distillation operations, membranes or molecular sieves. Molecular sieves use for the dehydration of bioethanol is a technique that is still less widespread, uses less energy and is more environmentally respectfully than benzol or cyclohexane traditional techniques [43].

3. Conclusion

In a controlled environment, in oxygen absence, genetically modified microorganisms or not transform fermentable sugars into bioethanol. Simply select the appropriate microorganism, monitor its metabolism and growth and be able to use it on a large scale. The production of first-generation ethanol by fermentation is a mature technology. One of



the best ways of producing bioethanol can be through anaerobic fermentation with *Saccharomyces cerevisiae* with sugary and starchy unconventional's agro-resources without competition with food. Thus, these agro-resources' bioconversion into bioethanol fuel by fermentation would be opportune in agro-industrial products valorization with low market value in order to promote agriculture and the biofuels sector.

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