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ENVIRONMENTAL IMPACTS OF SUGARCANE PRODUCTION, PROCESSING AND MANAGEMENT: A CHEMISTS PERSPECTIVE

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ABSTRACT

Sustainable sugarcane production and processing requires intensification of benefits and minimization of both short term and long term loses. Identification of long term loses/benefits from sugarcane production and processing is a difficult venture that entails critical scientific analysis based on collected scientific data, historical events and laboratory experiments. Moreover, most companies do not invest in research activities geared towards identifying critical long term loses or benefits. The long term effects of agronomic activities in sugarcane farming are herein discussed. Disposal of processed and unprocessed wastes from sugarcane production and processing activities are also discussed with various possible technical solutions and scientific techniques of effectively generating profits from such wastes summarized. It is hoped that the diverse green technologies of sugarcane production and processing explored herein can be of significant contribution to the management of this vital sector of the economy.

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1. INTRODUCTION

Sugarcane (*Saccharum* spp.) remains to be the world's largest cash crop with estimates of 23.8 million hectares in more than 90 countries, and with a worldwide harvest of approximately 1.69 billion tons by the year 2010 [1]. There are approximately 10 species of sugarcane with *saccharum officinarum*, *saccharum robustum* and *saccharum spontaneum* being dominant [2]. Environmental conditions necessary for sugarcane cultivation include tropical or temperate climatic conditions with plentiful supply of water: approximately for more than six months annually - either from rainfall or irrigation; with frost not favoring its growth and up to altitudes of 1,600 m [3]. Although this type of climate exists between 22 °N and 22 °S and some up to 33 °N and 33 °S, other regions outside this range such as the Natal region of South Africa still grow sugarcane due to anomalous climatic conditions such as warm ocean currents that sweep down the coast [3].

Sugarcane is one of the most efficient photosynthesizers in the plant kingdom categorized as a C4 plant due to its ability to convert up to one percent of solar energy into biomass [4]. In fact, Rolph [3] simply refers to it as '*Sugarcane is nothing more nor less than a concentrated sunshine'*. As such, sugarcane is referred to as a carbon crop since sugar and biomass are harvested rather than its protein-rich grains. Sugarcane is grown on different types of soils including the highly fertile well drained mollisols, heavy cracking vertisols, infertile acid oxisols, peaty histosols, rocky andisols *etc* with plentiful sunshine and water supplies increasing its production [3]. For this reason, arid countries with good irrigation schemes such as Egypt have emerged as excellent sugarcane producers [5].

Although there are documented guidelines for effective and sustainable agronomic practices in sugarcane cultivation [6], there are certain long term effects that can be determined through effective record keeping of events and analytical data of every step involved in cultivation and processing. This chapter attempts to critically analyse some of the data and scientific reports collected over a long period of time with great emphasis on long term effects of sugarcane production and processing to the environment.

2. IMPACT ON ATMOSPHERIC CARBON DIOXIDE CONCENTRATION

Global warming, the unequivocal and continuing rise in the average temperature of earth's climate system, is due to the heat retaining phenomena of greenhouse gases such as CO_2, CH_4, H_2O, O_3, N_2O *etc.* These gases generate an increase in the earth's temperature by about 33^oC, thus in their absence, the average earth temperature would be -19^oC (currently it is 14^oC) [7]. Initially, the gases were naturally generated and maintained through processes such as the water and carbon cycles. However, anthropogenic activities such as land-fills, burning fossil fuels, clearing of forest cover, industrial processes, power stations *etc.* are currently increasing their levels at an alarming rate [8]. Consequently, there has been a remarkable increase in the average earth's temperature by 0.8^oC, and if this continues unabated, then there is high risk of extreme severe consequences of global warming such as rising sea level, decreased snow cover in the northern hemisphere, species extinction, shutdown of thermohaline circulation *etc.* [9,10].

Emission of CO_2 to the environment is considered as a primary factor in causing global warming [11]. In 1999, Schoen reported an increase of 80 ppm in atmospheric CO_2 within a

time frame of 200 years, with most increment occurring in the past 50 years, as compared to the previous 80 ppm recorded over 10 000 years [12]. For this particular reason, efforts have been put in place to control the release of CO_2 into the environment [11-15] as well as its removal from the environment [16]. However, it should be noted that the best CO_2 sequestarators remains to be plants with sugarcane being the most favorable due to its economic importance, early maturity and higher photosynthesizer abilities of category C4 in the plant kingdom [4,17].

Studies have been done through incorporation of radioactivity ($^{14}CO_2$) into sugarcane leaves as a function of time in order to determine a steady state of photosynthesis under physiological conditions of concentration of carbon dioxide and light intensity [18,19]. The results showed the presence of large proportions of ^{14}C in 3-phosphoglycerate, hexose monophosphates and sucrose. The ^{14}C appeared first in C-4 of the dicarboxylic acids and C-1 of 3-phosphoglycerate. The labelling pattern in hexoses were consistent with their formation from 3-phosphoglycerate. The reaction giving rise to C4 dicarboxylic acid appeared to be the only quantitatively significant carboxylation reaction in sugarcane leaves. This research findings based on successful incorporation of ^{14}C into the C4 dicarboxylic acid pool and its subsequent transfer to sugars via 3-phosphoglycerate (Figure 1) prove that sugarcane is a C4 photosynthesizer [18].

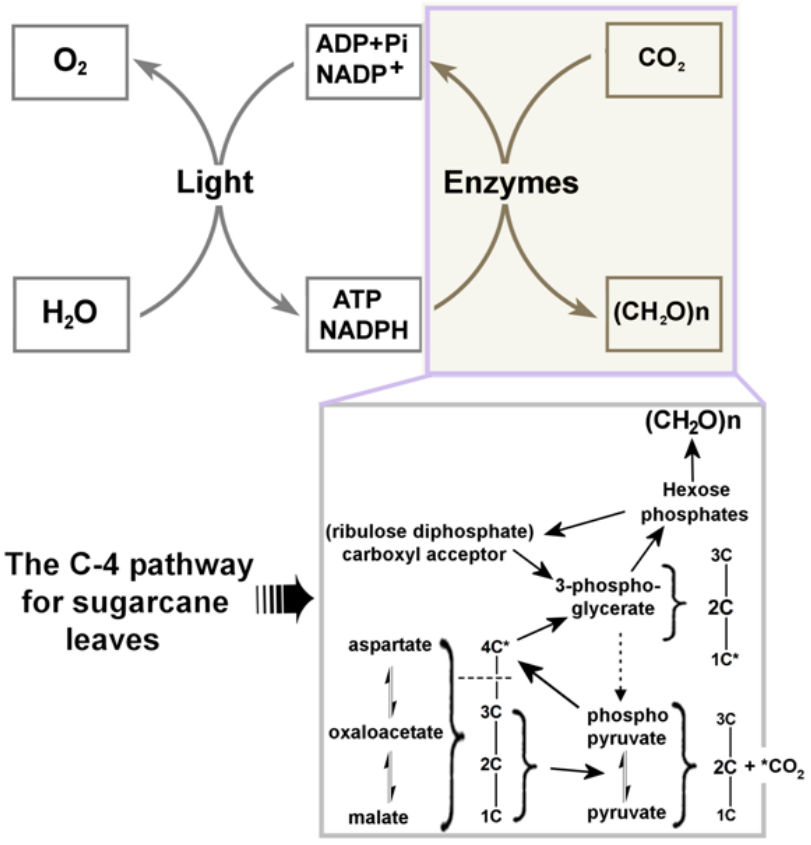

Figure 1. The C4 photosynthetic pathway for fixation of atmospheric carbon dioxide in sugarcane leaves. The dotted arrow indicates a minor pathway [18].

Technically, C4 photosynthesizers fix atmospheric carbon at the β-position of phosphoenolpyruvate (PEP) by the action of phosphoenolpyruvate carboxylase (PEPC) in the cytoplasm of mesophyll cells. The oxaloacetate so formed is then reduced to malate in the chloroplasts by NADP-malic dehydrogenase (NADP-MDH) or transformed to aspartate by transamination. These acids are then exported to the bundle sheath cells, where decarboxylation occurs (via malic enzyme or PEP carboxykinase) to yield CO_2 that is re-fixed by the reductive pentose phosphate (RPP) pathway operative in these cells. The other three carbon atoms are recycled to the mesophyll cells in the form of pyruvate or alanine, where PEP is generated by the chloroplast enzyme pyruvate, Pi dikinase (PPDK) [20].

However, it should be noted that sugarcane farming activities including use of bio solids as fertilizers increase soil carbon stock hence increasing the release of the same carbon dioxide gas being fixed by plants [21-23], although this is considered insignificant as compared to the fixing rate.

3. IMPACT ON SOIL PH

Continued use of agronomic inputs such as nitrogenous fertilizers in sugarcane farming eventually lowers the soil pH [22,24]. In Papua New Guinea, the pH of top soils under sugarcane cultivation decreased from 6.5 to 5.8 between 1979 and 1996 [24]. In Fiji, a decline in soil pH from 5.5 to 4.6 was recorded over the first 6 years of cane cultivation while in Philippines, a reduction from 5.0 to 4.7 was recorded over 19 years [24]. This change in soil pH is mainly due to the use of acidifying nitrogenous fertilizers such as urea and ammonium phosphates, coupled with nitrate leaching that occurs under the high rainfall conditions that often prevail in cane cultivation areas.

Changes in soil pH are usually accompanied by other chemical changes in both the soil and the receiving waters. For instance, a reduction in soil pH makes heavy metals more soluble, bioavailable and mobile [25]. Hence, continued use of nitrogenous fertilizers affects the acidity of soils and makes heavy metals readily available for transportation from soils to the aquatic environment; especially during long rainy season accompanied with large surface runoffs, leaching and erosion of the soils [26,27]. Furthermore, the use of biosolids as fertilizers in sugarcane farming increases the total organic carbon of the soil hence influencing heavy metal transport in soil [28].

In addition, it has been scientifically proven that nitrogenous fertilizers are contaminated with heavy metals that accumulate in soil with repeated application [22,29]. Lawrence and Brian from Oregon State University point out that contamination of nitrogenous fertilizers with heavy metals has drawn the attention of farmers, environmental organizations, consumers, and public policymakers [30]. In his book, Alloway clarifies that inorganic fertilizers contain traces of heavy metals that accumulate in soils with repeated applications [25].

Most importantly, the use of these fertilizers affects the soil pH, which is one of the chemical conditions of soil and a significant secondary determinant of heavy metal transport and fate at the application site [31]. Firstly, ionization of metals increases at low pH thereby increasing their water solubility and mobility. Secondly, hydroxonium ions (H_3O^+) displace most other cations on negative surface charges. These mechanisms have been clearly shown to reduce metal adsorption by cation exchange and organic complexation [32].

Once heavy metals find their way into aquatic environments, a large amount of them get deposited into the sediments due to other factors like dilution factor, sedimentation and precipitation [33]. Heavy metal analysis of sediments and water samples collected from contaminated sites show the concentration in sediments to be of several orders of magnitude greater than in water [33]. Sediment associated heavy metals pose a direct risk to detrital and deposit feeding benthic organisms, and may also represent a long-term source of contamination to higher trophic organisms. Bioaccumulation and bio concentration of toxic heavy metal residues in aquatic environments can result in their transfer into food chains putting terrestrial consumers including humans and birds at risk [34-37]. Contaminated food webs can also cause health and economic disadvantages to people as contaminated commercial foods like fish become restricted or banned due to high metal burdens [37].

Heavy metal solubility can be affected by several factors including temperature and pH changes [38]. However, the presence of heavy metals in aquatic environment will affect its electrical conductivity, chemical oxygen demand and dissolved oxygen [39]. Adverse effects including death of animals due to lack of oxygen may arise if the above physicochemical parameters exceed the allowable limits [40,41].

However, another major concern is the fact that not all the applied fertilizers are utilized in the soils. Most of the inorganic nitrogen and phosphates applied find their way into aquatic environments due to surface runoffs and leaching into ground water. Previous studies have shown that addition of these nutrients into water systems results in large proliferations of algae and other aquatic weeds such as water hyacinth, which have detrimental effects on the water quality [42,43]. Algal blooms and water hyacinth deplete oxygen supply in the water system and are also harmful to other aquatic species. Additionally, nutrients cause taste and odor problems that result in reduced recreational use, and increased water treatment costs [42].

3.1. The Process of Soil Acidification

Soil acidification (declining soil pH due to net proton (H^+) accumulation) is a natural process that occurs during pedogenesis and is often associated with high rates of leaching. However, the rate of acidification can be accelerated through farming activities with the result that the soil resource may become significantly degraded. Under intensive agricultural production, continual acidification of these soils is likely to occur through the use of high inputs of ammonium-based nitrogen fertilizer, the high level of base removal as a result of crop uptake and subsequent removal and the generally high rainfall environment of the region which facilitates losses of basic cations through leaching [44]. Acidification of soils is usually accompanied with fertility loss and declining productivity [45], hence placing the products of farming systems operating in acidifying environments subject to scrutiny under the recent ISO 14000 treaty [44].

Nitrification of ammonium based fertilizers such as urea and organic N in crop residues (Organic Matter) is an acidifying reaction which occurs through the microbial conversion of NH_4^+ to NO_3 with the consequent production of protons (H^+). The extent of acid generation by fertilizers is a function of the fertilizer type, environmental and edaphic factors [46]. Estimates of potential net acidity generated by frequently used fertilizer sources in the sugar industry are presented in Table 1, with diammonium phosphate being the most acidifying and

urea the least on the basis of N per kg fertilizer applied. In view of the potential acidity generated by nitrogenous fertilizers, the equivalent amount of $CaCO_3$ required to neutralize this acidity is also shown (Table 1).

Table 1. Estimated potential acidity produced as a result of nitrogenous fertilizers in sugarcane plantations [47]

Source	Nitrification reaction	Net potential acidity generated (kmols H^+.kgN)	Potential acidity generated from 180 kg N ha^{-1} (kmoles H^+ ha^{-1})	[a]Amount of $CaCO_3$ required to neutralize acidity generated by an application of 180 kg ha^{-1} (kg ha^{-1})
Urea	$(NH_4)_2CO + 4O_2 = 2H^+ + CO_2 + H_2O$	0.072	13.0	650
Diammonium Phosphate	$(NH_4)_2HPO_4 + O_2 = 3H^+ + 2NO_3^- + +H_2PO_4 + H_2O$	0.0107	19.3	965
a: assuming that 1 kmol requires 50 kg $CaCO_3$ to neutralize				

The theoretical amount of $CaCO_3$ required to neutralize the acidity generated by application of 180 kg N $ha^{-1}y^{-1}$, typical for the NO_3^- from ammonium-based fertilizer is a significant source of acidity generation in these production systems. In contrast, the addition of basic nitrate fertilizers such as $Ca(NO_3)_2$ causes little change in pH due to the absence of nitrification and may in some cases result in an increase in soil pH [46,47].

Although the production of NO_3^- through nitrification process for nitrogenous fertilizers is a net proton accumulating reaction, the subsequent leaching of nitrate can lead to a significant decline in exchangeable bases because Ca^{2+} and Mg^{2+} will move downwards as counter ions for the very mobile NO_3^-, resulting in an accumulation of protons at the point of nitrification [48]. Consequently, there is spatial disjunction between the production of NO_3^- and its subsequent uptake by the plant. The result is an accumulation of H^+ at the point of production and net alkalization due to the uptake of NO_3^- by the plant at some other point in the profile.

The uncoupling of these two processes results in net proton accumulation at one point in the profile and net alkalization at some other point. As long as nitrate is taken up at the point of production, the outcome will always be neutral [47].

3.2. Scientific Evidence of Accelerated Acidification under Sugarcane Production

Soil acidification rates can be measured in terms of absolute changes or relative to some control soil. In the former case, acid addition rates can be estimated from analyses of soils before and after a given period of acidification- long-term study [47]. However, relative rates of acidification can also be derived from survey data (e.g. fence line contrasts of developed and undeveloped sites). This approach has been used in a number of studies in the sugar industry [44,49]. The use of fence line comparisons essentially results in a conservative estimation of the net acidification rate.

As part of a wider study on the possible role of changes in soil properties over time on sugar yield decline [50], differences in soil chemical properties between new land and land which had been under sugarcane monoculture for more than 20 years were examined in detail by Bramley *et al.* [49]. They found that there was no consistent effect of time under sugarcane monoculture on soil chemical properties across sites located in the Burdekin, Herbert and Tully Districts of North Queensland, Australia; either when the distribution of properties through the soil profile, or property values at specific depths were considered. However, marked effects were observed in some sites with respect to some soil properties and these were generally consistent with soil acidification.

The changes included reduced topsoil pH in old land (0.5-1.5 pH units); increased exchange acidity and aluminum saturation in soils under old land, especially in Herbert where percent Al saturation increased from approximately 5 to 20 %. However, although little change was noted in the Tully soils where much higher Al % (45 %) in both old and new land soils were measured, decreased cation exchange capacity (CEC) and increased anion exchange capacity (AEC) were observed in old land soils in some sites of each region. Wood obtained similar results in a paired sites study in the Herbert River District, North Queensland, Australia; where he found that many of the differences in soil chemical properties between new cane land and land that had been under sugarcane for several years could be associated with soil acidification [46]. Sugarcane soils were found to have a lower pH, lower cation exchange capacity and lower levels of exchangeable base cations (calcium, magnesium and potassium).

In addition, the analysis of soil samples from 1064 sites in the Herbert sugarcane area, taken as part of the CSR (Central Sugar Refinery, in Malaysia) Herbert River soil survey has shown that mean topsoil (0-20cm) pHw (pH in 1:5 soil:water) is 4.97 and mean subsoil (40-60cm) pHw is 5.28 [51]. Schroeder et al. [52] have also reported marked acidification in a range of sugarcane soils in South Africa. The effects of soil acidification on sugarcane growth have received little attention from Australian researchers, presumably because Hetherington [53] concluded that cane was tolerant of low pH-induced aluminum toxicity. However, Schroeder *et al.* [52] reported marked differences between South African varieties in terms of their response to lime application suggesting that not only was cane affected by the effects of low soil pH, but that these effects may be variety specific. In general, most crops perform better when the soil pH is approximately 5.6 to 6.0 [54].

From the previous discussion it can clearly be seen that soil acidification is a continuing problem confronting the Australian sugar industry and that the largest potential acidifying component is the contribution derived from the use of nitrogen fertilizers [47]. The contribution to the total proton pool arising from the export of millable cane is relatively smaller compared to that derived from the nitrification of ammonium and urea based fertilizer sources, assuming that significant leaching occurs [47]. Most researches on acidification of sugarcane farms have been on sugarcane production with little being done on environmental effect. Alloway [25], points out that reduction in acidity of soil leads to naturally occurring heavy metals in the soils becoming more soluble, bioavailable and enhances their mobility.

Another long term impact of using fertilizers in sugarcane production is the production of N_2O that is a greenhouse gas causing global warming. Specifically, production of N_2O gas from soils in sugarcane plantations occurs after application of vinasse fertilizer followed by urea [55,56].

4. IMPACT OF SURFACE RUNOFFS FROM SUGARCANE FIELDS ON AQUATIC ECOSYSTEM HEALTH

The health of aquatic systems within and or near sugarcane production and processing zones is increasingly threatened due to exposure to pollutants from both agronomic inputs and processing wastes [27,57,58]. The Australia's Great Barrier Reef and Lake Victoria are examples of such threatened aquatic systems within sugarcane plantation catchments being affected by a range of pollutants such as nutrients and pesticides [26,57,59]. Among other aquatic effects, eutrophication that is associated with uncontrolled aquatic plant growth; algal blooms; biodiversity loss and/or death of aquatic animals; destruction of water transport; and poor quality of domestic water are the major challenges facing sugarcane production and processing. Several management strategies have been suggested to reduce pollutant loading into aquatic systems. Drewry et al. proposed reducing N fertilizer applications, reducing tillage and changing management of fallows prior to planting between sugarcane crops [60]. Omwoma et al. have demonstrated an efficient way of trapping these nutrients from canals draining the sugarcane plantations before they are transferred into aquatic systems [26]. Fulcher et al. have also shown that application of pesticides according to label recommendations greatly reduces pesticides wash-offs [61]. The use of recommended levels of both pesticides and fertilizers [62] is very important and should be accompanied with precise timings so as to avoid rainfall wash offs.

Although the suggested methods do not take care of ground water pollution due to leaching [63] and base flow discharge [64], a great pollutant reduction to other aquatic systems such as rivers and lakes can be avoided as runoffs are the major transport agents of these pollutants. However, factories should invest in weather forecast equipment and personnel, critical soil analytical methods to determine region specific fertilizer suitable requirements and strict management to achieve high crop production within a clean environment [65].

In the Everglades Agricultural Area of Florida, soil subsidence and phosphorus runoff from sugarcane fields to aquatic systems are serious problems being addressed in order to have sustainable sugarcane farming. The management uses rice as a rotational crop in sugarcane fields in order to remove PO_4^{2-} from soils. The rice is grown on sugarcane fields every 4 to 5 years under flooded conditions. Specifically, rice crop absorbs excess phosphorus, and flooding the fields halts subsidence, controls pests, and provides a wetland habitat for native animal species [66].

The weighted global average indicates that only 50 % of N fertilizer applied in crop fields are consumed by crops [67]. The reasons provided for the low fertilizer use uptake include high soil nitrification rates (Table 1) and extreme weather conditions that promote N leaching and denitrification processes [67]. It should be noted that sugarcane plants have higher preference for NH_4^+-N uptake than NO_3^--N [67,68]. Therefore, there are research activities directed towards breeding sugarcane cultivars with enhanced capacity to use nitrate as well as undertaking agronomic measures that will reduce nitrification in soil [67]. Low nitrate content in shoots of sugarcane cultivars accompanied with low translocation rates of ^{15}N-nitrate to shoots has been reported and it indicates inefficiencies in the uptake and root-to-shoot transfer of nitrate [67]. Even though nitrate or assimilatory products of ammonium and amino acids act as regulatory signals in plants, there is negative feedback arising from endogenous nitrate

on transport systems and can be inferred from the whole plant or organ studies which show negative correlation between nitrate concentration and uptake rates [69,70]. For instance, nitrate concentration levels in cytosol of barley roots were found to be 4 mM whereas vacuolar nitrate concentrations increased from 4 to 75 mM when plants were supplied with 0.01 to 10 mM nitrate [71].

Experimental results have indicated that nitrate uptake is inhibited in N-replete sugarcane and this is correlated with the increasing nitrate content in roots [67]. The advantage of nitrate as a N source is the uncoupling of N supply and demand, while ammonium causes toxicity in cells hence the rapid assimilation and is limited by the carbon supply to roots [69]. It is therefore assumed that many nitrophile species will exhibit efficient use of nitrate through rapid transport and storage of nitrate which is considered an evolutionary advanced character in angiosperms [72]. Thus, N uptake in excess of demand and the resulting storage of nitrate occurs when excess ammonium and nitrate are supplied to sorghum and maize but not sugarcane and other related species. These findings suggest a broader spectrum of N use among the studied crops and wild species than previously recognized and question the assumed efficient use of nitrate in sugarcane crop systems.

The problems associated with plant utilization of synthetic N fertilizers use might be solved by the use of microbes that are capable of biological N_2 fixation (bio fertilizers) [73]. Diazotrophic bacteria of the genera Gluconacetobacter [74], Azospirillum [75], Burkholderia [76] and Herbaspirillum [77] have been isolated from intercellular spaces, roots and rhizosphere of sugarcane [78-80]. Nevertheless, there arises some inconsistent responses of crop cultivars and growth locations that might limit the success of 'bio fertilizers' based on diazotrophic and plant growth-promoting rhizobacteria [81]. However combining both technologies might limit losses of synthetic N to the environment leading to eutrophication of aquatic systems [82].

5. GREEN UTILIZATION OF SUGARCANE BAGASSE

5.1. Bioethanol Production

Large amount of bagasse is generated as a result of industrial processing of sugarcane. Bagasse is the residue obtained after juice extraction through milling of cane. It corresponds to about 25% of the total fresh weight of the sugarcane plant and it contains between 60 – 80% of carbohydrates [83]. The abundant chemical composition of sugarcane bagasse include cellulose (32 – 44%), hemicellulose (27 – 32%), lignin (19 – 24%), and small amounts of extractives and mineral salts [84,85]. The most economical and ecofriendly way of disposing this waste should be through enzymatic conversion of the lignocellulosic biomass to bioethanol, though most factories prefer discarding it as agricultural waste or burning it for energy supply [86,87].

The main obstacle in the generation of bioethanol from sugarcane bagasse is supposedly the close association and complexity of the carbohydrate–lignin complex in sugarcane bagasse. Many efforts have been made to overcome this problem and make the process economically feasible. For instance, the development of an efficient pre-treatment step and optimization of enzymatic cocktails for cell wall deconstruction have been investigated. It is

more environment-friendly to use enzymes in the bioconversion processes than using chemical processes. The use of enzymes ensures product specificity and minimizes wastes thus making the process more eco-friendly [88]. However, enzymatic hydrolysis requires biomass in small particle sizes and the removal of lignin with phenolic compounds which show more inhibition than non-phenolic compounds [89,90]; hence the need for bagasse-pretreatment prior to enzymatic hydrolysis reactions.

It is difficult to hydrolyze the cellulose present in pretreated lignocellulosic materials due to both enzyme- and substrate-related factors. Changes in cellulose porosity and surface area, accumulation of lignin, and changes on its crystallinity and degree of polymerization can be summarized as substrate-related factors [91,92]. End-product inhibition due to glucose and cellobiose accumulation [93,94], thermal denaturation of enzymes after long periods of mechanical agitation [95], and irreversible adsorption of enzymes onto lignin and/or lignin-carbohydrate complexes [96,97] are classified as enzyme related factors. Enzymatic hydrolysis of cellulose can be achieved through a mixture of microbial hydrolases composed of three different classes of enzymes: 1) endo-β-1,4-glucanases, 2) exo-β-1,4-glucanases or cellobiohydrolases, 3) β-1,4-glucosidases; otherwise called ‘‘the cellulose complex’’. In summary, the enzymatic hydrolysis reaction (by fungal strains like Trichoderma reesei) is achieved through all the three classes of hydrolases that act synergistically for the complete enzymatic hydrolysis of cellulosic substrates. 1) Cellulose reducing and non-reducing chain ends are formed by the action of endo-β-1,4-glucanases, 2) cellobiohydrolases act on these chain ends releasing mostly cellobiose, with cellobiohydrolases I working progressively from the reducing ends while cellobiohydrolases II works from the non-reducing ends, 3) β-1,4-glucosidases complete this process by converting cellobiose to glucose [98].

Therefore, for effective hydrolysis of sugarcane bagasse by enzymes, the following pretreatments of lignocellulosic materials are used: Steam explosion [99-101], Dilute acid hydrolysis [102], Alkaline pretreatment [102,103], Wet oxidation [104], Ammonia fiber expansion [105], Enzymatic pretreatment [106], Organosolvents [107] etc.

5.1.1. Alkaline Pretreatment

The alkaline pretreatment methods show less sugar degradation and furan derivatives formation [108] than thermal and acid pretreatment methods [109]. Alkaline pretreatment process may be improved through the application of ultrasound [110], as the ultrasonic treatment of aqueous media produces cavitation, which generates high temperature, pressure and extreme shear forces [111]. As such, the decomposition of water molecules into free radicals by cavitation will aid in breaking the linkages in lignin and xylan networks [112,113]. Ultrasonic energy combined with proper solvents allows destruction of the recalcitrant lignocellulosic structure, fractionation of biomass components, and then assists many thermochemical and biochemical reactions, with increased equilibrium yields of sugars, bio-ethanol and gas products by 10-300% [111]. Sonication promotes hydrolysis, esterification and transesterification in biodiesel synthesis, reduces reaction time by 50-80%, lowers reaction temperature and reduces the amounts of solvent and catalyst [111]. Pretreatment of bagasse with alkali/alkaline peroxide and ultrasound for the extraction of hemicellulose from sugarcane bagasse has been reported to yield 90 % hemicellulose and lignin removal [114]. More recently, the use of ultrasound assisted ammonia pretreatment method [115] and the use of ultrasound-assisted alkaline pretreatment of sugarcane bagasse for fermentable sugar production [116,117] have been reported. Under these technologies, the influence of

sugarcane bagasse particle size, liquid ammonia concentration, sonication time, temperature and liquid to solid ratio on cellulose recovery and delignification have been evaluated with maximum cellulose recovery and delignification observed at the optimum conditions of particle size 0.274 mm, sonication time 45 min, ammonia concentration 10%, liquid to solid ratio of 10 mL/g and temperature 80^{o}C.

Alkaline ethanolysis and sequential enzymatic hydrolysis for production of glucose and subsequent lactic acid has also been demonstrated using physico-chemical treatments, that is, ultrasonic bath and ultrasonic probe and compared to mechanical stirring [118]. The experimental results indicated the highest glucose yield with least contamination of xylose to be obtainable from acid ethanolysis fractionation of 5 N H_2SO_4 + 50%, v/v ethanol when stirred at 90 $^{\circ}$C for 4 h. The alkaline ethanolysis was accomplished with the release of high amount of both glucose and xylose, although it was not a favorable substrate for homofermentative lactic acid bacteria. An interesting one-step treatment of sugarcane bagasse with 80% acetic acid and 70% nitric acid mixture under sonication has also been reported to yield 43.0 - 43.6% of pure cellulose fraction which contain minor amounts of bound hemicelluloses (3.2 - 4.3%) and are relatively free of associated lignin (0.2 - 0.6%) [119].

5.1.2. Steam explosion

The process of bagasse pretreatment with steam explosion involves pretreatment of bagasse with saturated steam at 160–240^{o}C for about 20 to 30 min in the absence (autohydrolysis) or presence of an acid catalyst [94, 120-122]. The high pressure steaming results in partial hydrolysis of hemicelluloses and lignin to water-soluble monomers and oligomers while cellulose is modified partially from its crystallinity and degree of polymerization. This process improves cellulose susceptibility to solvation and enzymatic hydrolysis. However, this process sometimes generates biological inhibitors such as furan compounds and organic acids. Nonetheless, most of these inhibitors can be eliminated from the fibrous material by water washing [123, 124] although this detoxification step increases production cost due to energy consumption [125]. Another detoxification process can be through extraction of the steam treated material with boiling solvents in order to remove other inhibitory compounds such as phenolic acids [101,126]. Successful steam explosion pretreatment reproduction and alkaline delignification reactions for ethanol production from different varieties of natural sugarcane bagasse, pretreated bagasse and delignified pretreated bagasse have been documented [87].

5.1.3. Ammonia Fiber Expansion

The use of ammonia fiber expansion process as a pretreatment procedure for bagasse hydrolysis to bioethanol has been described. In this process, liquid ammonia is added to the biomass under moderate pressure (100 to 400 psi) and temperature (70 to 200°C) before rapidly releasing the pressure [105]. In particular, this process decrystallizes the cellulose, hydrolyses hemicellulose, removes and depolymerises lignin and increases the size and number of micropores in the cell wall, hence significantly increasing the rate of enzymatic hydrolysis [123]. It has been experimentally shown that the process can improve accessibility of cellulose and hemicelluloses during enzymatic hydrolysis by breaking down the ester linkages and other lignin carbohydrate complex bonds in bagasse [127]. Furthermore, maximum glucan conversion of the ammonia fiber expansion process pretreated bagasse and

cane leaf residue by cellulases is approximately 85%, and the supplementation with hemicellulases during enzymatic hydrolysis improves the xylan conversion to 95-98%.

5.1.4. Enzymatic Pretreatment

Pretreatment of sugarcane bagasse can also be achieved using enzymes prior to the hydrolysis reactions in a similar manner as the bleaching process of wood pulp with ligninolytic enzymes [106]. This process is advantageous due to: i) the mild reaction conditions, ii) higher product yields and fewer side reactions, iii) less energy demand, iv) minimal corrosion and pressure build up in the reactors [128]. Naturally, lignin decomposition is primarily attributed to metabolism by organisms especially microorganisms such as white-rot [129]. White-rot produces several ligninolytic enzymes including laccases, manganese peroxidases and lignin peroxidases that catalyze one-electron oxidation of lignin units, producing aromatic radicals [130]. The microbial lignin degradation can be mainly attributed to secondary metabolism or to restricted availability of nitrogen, carbon, or sulphur and it is not degraded as sole carbon and energy sources, requiring additional co-substrates such as cellulose, hemicellulose or glucose [131]. Generally, most white-rot fungi preferentially attack lignin more readily than hemicellulose and cellulose [132,133]. Among these groups of fungi include the *Ceriporiopsis subvermispora*, *Phellimus pini*, *Phlebia* spp. and *Pleurotus* spp. However other White-rot fungi exhibit a pattern of simultaneous decay characterized by degradation of all cell wall components and in this group we have *Trametes versicolor, Heterobasidium annosum* and *Irpex lacteus* as examples [134]. This technique has recently been patented by Kumar et al., [135] where they claim a process for one step production of L-Lactic Acid from lignocellulosic biomass using thermophilic bacteria *Paenibacillus macerans* IIPSP3 (MTCC5569), which is not only capable of hydrolyzing cellulose to glucose but also further ferments it to L-Lactic Acid under aerobic conditions without any growth inhibition in the presence of lignin. The invention further provides a process which has less chances of contamination as the fermentation is carried out at higher temperatures and is economically attractive, since preferably no external enzyme loadings are required.

5.1.5. Wet Oxidation Pretreatment Method

Wet oxidation pretreatment method involves hydrothermal treatment which is the process of treating bagasse with water and air or oxygen at temperatures above 120ºC [136]. The two types of reactions that occur during wet oxidation include 1) a low-temperature hydrolytic reaction, 2) a high-temperature oxidative reaction [137]. It has been demonstrated experimentally that alkaline wet oxidation at 195ºC for 15 min yields a solid material with nearly 70% of cellulose, with a solubilization of approximately 93% of hemicelluloses and 50% of lignin, and an enzymatic cellulose convertibility of about 75% [137]. However, it should be noted that a significant part of the polysaccharides is lost, and the enzymatic convertibility of the pretreated material is poor.

5.1.6. Organosolvents

This pretreatment technology involves the use of an organic liquid and water, with or without the addition of a catalyst which can either be an acid or alkali. The mechanism involved in removal of lignin from lignocellulosic materials is the partial hydrolysis of lignin bonds to give a pulp rich in cellulose. Addition of a catalyst enhances the selectivity of the

solvent with respect to lignin with most of the hemicellulose sugars being reported to be solubilized by this process [138,139]. The advantages associated with this technique over the aqueous based processes include the recovery of lignin and polyoses from the liquor which is easily achieved through distillation [107]. Specifically, lignin is separated as a solid material while polyose fraction is obtained in aqueous solution. Nevertheless, pretreatment of sugarcane bagasse with organosolvents has some limitations such as i) the pretreated solids need to be washed with organic solvent to avoid the re-precipitation of the dissolved lignin and ii) the reactions occur at higher pressures hence not economically viable.

Mesa et al. experimentally showed that the combination of a dilute-acid pretreatment followed by organosolvent pretreatment (with NaOH) under optimized conditions of 60 min, at 195ºC and 30% v/v ethanol was efficient for the fractionation of sugarcane bagasse with the subsequent enzymatic hydrolysis yielding a residual solid material containing 67.3% (w/w) glucose [139].

Novo et al. reports a process of using glycerol- water mixtures to obtain a pulp with a residual lignin amount lower than 8% with delignification being close to 80 % and residual cellulose content higher than 80 % [107]. The use of glycerol here presents some advantages such as: 1) low solvent cost as the crude glycerol produced in the transesterification process for biodiesel production can be applied instead of pure glycerol, 2) the pretreatment can be performed under atmospheric pressure, decreasing the energy consumption, 3) due to its highly polar structure, glycerol can easily penetrate the bagasse tissue, providing an effective reaction medium for delignification. However, the high energy consumption for solvent recovery may decrease the attractiveness of using glycerol [140,141].

5.2. Lignin Production

Lignin extracts from sugarcane bagasse have been utilized as natural and potent substances for coating and preserving fresh fruits [142]. This property of lignin arises out of its inability to be degraded by most forms of biological means and the fact that lignin has antimicrobial and antifungal activities [143]. The best way of extracting lignin without interfering with its chemical composition is by soaking it in dilute (0.5% v/v) phosphoric acid for 4 h followed by steam explosion at 180^{o}C for 10 min prior to ethanol extraction as shown in Figure 2 [144].

5.3. Biohydrogen Production

Sugarcane bagasse has been utilized as a feedstock in biohydrogen production. Biohydrogen is produced biologically via biophotolysis, dark-fermentation and photo-fermentation of sugars such as glucose, fructose, galactose, arabinose, lactose and sucrose [145-148]. Rai et al. have integrated sugarcane bagasse in the dark-fermentation process by *Enterobacter aerogenes* and photo-fermentation by *Rhodopseudomonas* [149]. Sugarcane bagasse was hydrolyzed using sulphuric acid and the hydrolysate detoxified by passing it through adsorbent resin column to remove the inhibitory furfural before being subjected to dark-fermentation process.

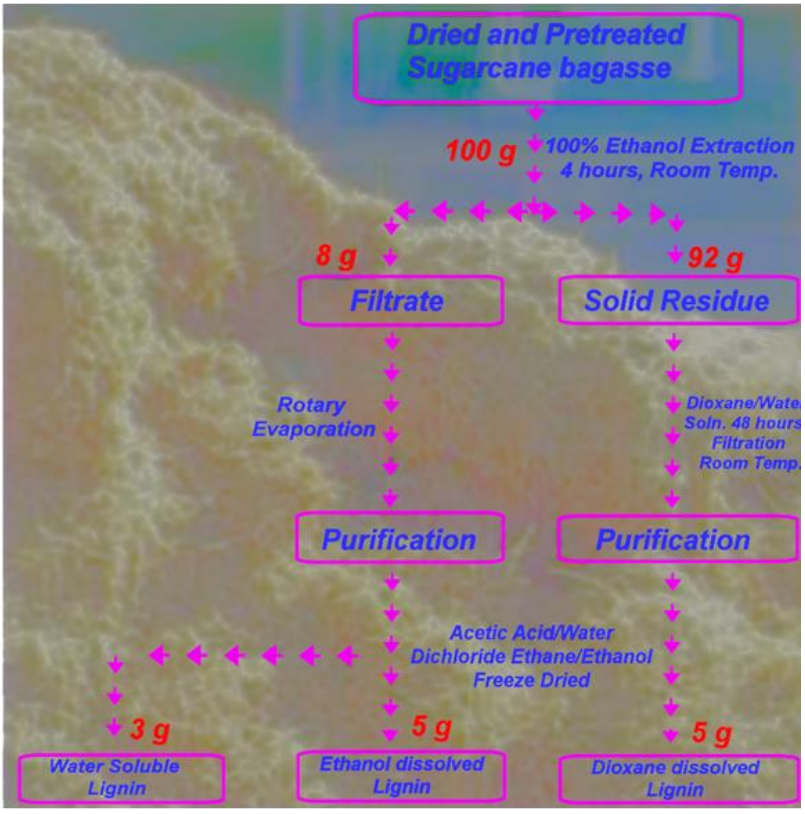

Figure 2. Lignin extraction from sugarcane bagasse [144].

The cellulosic residue from acid hydrolysis was hydrolyzed by the new isolate *Cellulomonas fimi* to release sugars for H_2 production by *E. aerogenes*, through simultaneous saccharification, filtration and fermentation. Optimum concentration for acid hydrolysis by H_2SO_4 was found to be 2% (v/v) for 60 min and cumulative H_2 production during dark-fermentation by *E. aerogenes* and simultaneous saccharification, filtration and fermentation was 1000 ml/L and 613 ml/L, respectively. Alternatively, bagasse can be substituted with molasses [150].

5.4. Hemicelluloses Production

There is emerging interest in the industrial use of hemicelluloses from sugarcane bagasse as water-soluble polymers that could see synthetic polymers being replaced [151]. Films and coatings made from hemicelluloses enjoy numerous applications in the food and medicinal industries such as active food packaging, wound dressings and drug capsules [152]. Banerjee *et al.* have demonstrated successful extraction of xylan-rich hemicellulose components from sugarcane bagasse by the use of pressurized hot-water extraction and alkaline peroxide method (Figure 3) [153]. The extracted hemicelluloses contained mainly arabinoxylans with varying substitutions and a classical structure with a backbone of β-(1→4)-linked xylosyl residues substituted with arabinose at C-2 and C-3 of the main chain. The main difference occurs in the distribution of branches along the xylan backbone.

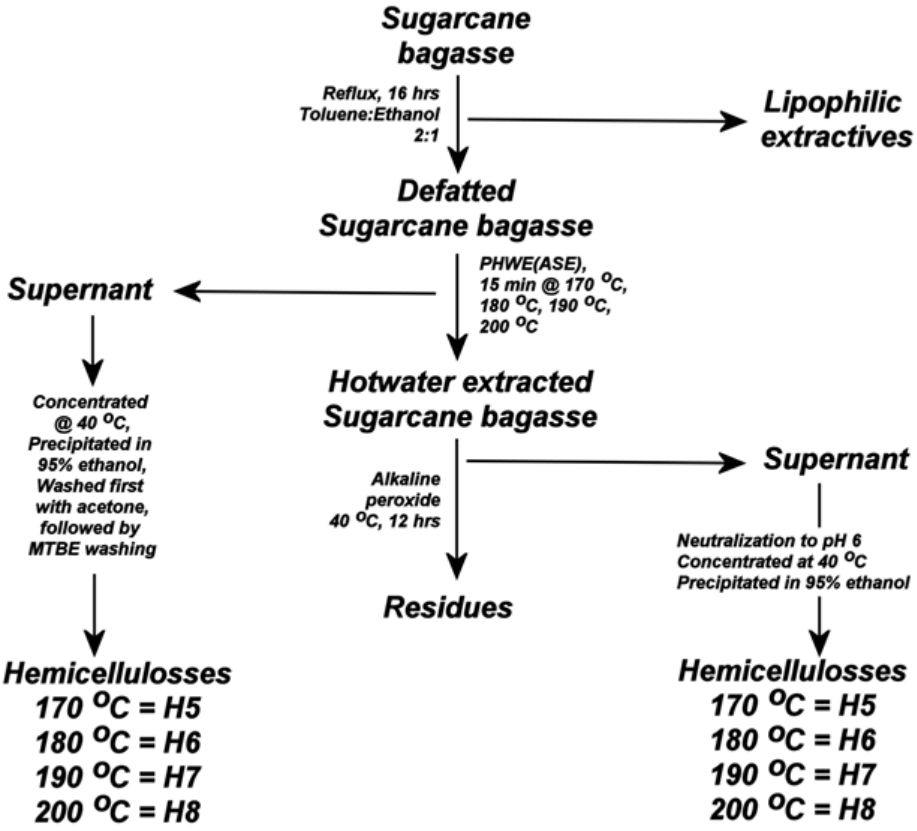

Figure 3. Scheme for the isolation of hemicelluloses by sequential extraction of sugarcane bagasse with pressurized hot water (PHWE) and alkaline peroxide [153].

5.5. Production of Adsorbent Materials

The use of biosorbent as efficient pollutant removal from industrial waste water and ground water has attracted much attention. Bagasse has been demonstrated to be an efficient biosorbent for heavy metals [154,155], manganese [156], hexavalent chromium [157], methylene blue and gentian violet [158], etherdiamine [159] etc.

The versatility of these benign environmental cleaning technique lies in the ability of bagasse to adsorb large amounts of the pollutant from aqueous media before its further processing techniques such as burning it in boilers to generate steam energy [160,161] and the resultant ash separated into individual industrial products. More so, the bagasse ash has recently found application in clay bricks formation by replacing natural clay for up to 20 wt.% [162] and in production of glass-ceramics with silicates as the major crystalline phases [163]. Furthermore, sugarcane bagasse can be modeled into nanomaterials in the form of long, straight, tubular structures with smooth walls and axially-uniform diameters, which is the characteristic of carbon nanotubes. These materials have typical lengths in the order of 50 nm and diameters in the range of 20 to 50 nm [164,165] and can be an alternative source of carbon nanotubes that have been reported as the best adsorbent materials [166].

5.6. Animal Feed

Besides its use for sugar production, sugarcane is a fodder resource increasingly used as a reserve for feeding ruminants during the dry season [167]. However, there arises a few environmental impacts such as release of CH_4 gas by animals fed on sugarcane forage even though it may be a more preferred way of disposing off the forage waste than burning it (in terms of CH_4 release to the environment). Ruminant CH_4 emission depends on the amount of organic matter fermented in the rumen and on the carbohydrate fermentation pattern [168]. Cell wall carbohydrate causes larger amounts of CH_4 emission than starch [169], although the effect of dietary soluble sugars on methane emission is not well known. According to a meta-analysis, fermentation of C_4 tropical grasses (grasses grown with a C_4 metabolism will result in higher CH_4 emission (10–17%) than that of C_3 temperate grasses [170]. Archimède et al. [168] used whole sugarcane plant forage with higher levels of total sugar, (300–500 g/kg DM, [171]) as compared to conventional C4 grass (26–122 g/kg DM, [172]) which is the most used tropical grass with lower total sugar, to study the amount of CH_4 gas released: DM = dry matter. They reported a higher CH_4 emission of Black belly rams consuming whole sugarcane forage compared with *Dichanthium* sp. hay.

6. GREEN UTILIZATION OF SUGARCANE MOLASSES

6.1. Antioxidants Dietary Source

Sugarcane by-products like molasses are long term dietary source of antioxidants and phytochemicals such as phenolics, flavonoids, triterpenoids, phytosterols etc. [173-175]. Phenolics and flavonoids extracted from fresh sugarcane and molasses show antioxidant, anti-inflammatory, antimutation and tyrosinase inhibitory capabilities in laboratory experiments [174,176]. Among other extraction technologies, supercritical carbon dioxide fluid extraction with piecewise distillation separation seems to offer the best results in obtaining antioxidants from sugarcane molasses [177]. The operating conditions for this method include: i) extraction pressure of 33.3 MPa, ii) temperature of 43.3 ^{o}C, iii) time of 86.7 min, iv) 90% ethanol content of sugarcane molasses, v) flow rate of CO_2 of 20 L/h. The advantages associated with the above method include its inability to extract high polar harmful compounds such as sylvite and sodium salt from the molasses [178]. Additionally, antioxidants from sugarcane molasses can be achieved through solvent extraction of steam exploded lignocellulosic biomass method [126]. Under this method, boiling solvent extraction shows higher solid and phenolic yields than room temperature extraction and solubilities of phenolics and sugars are higher in anhydrous ethanol and deionized water than in ethyl acetate under each individual extraction condition. Antioxidants can also be extracted from sugarcane bagasse. Mandelli et al. evaluated the enzymatic production of xylooligo-saccharides and antioxidant compounds from sugarcane bagasse using XynZ from Clostridium thermocellum, a naturally chimeric enzyme comprising activities of xylanase and feruloyl esterase along with a carbohydrate binding module [179].

6.2. Production of Alternative Energy

Sugarcane molasses have provided efficient raw materials for the production of agrochemicals such as butanol, lipids, acetate, butarate, ethanol, hydrogen gas etc. [150]. Of more environmental concern, is the use of sugarcane molasses as feed stocks for production of alternative energy sources to fossil fuels. Fossil fuels are non-renewable and may not be available for our children's children to use. For this reason, coupled with the increase in prices of petroleum based fuels, future depletion of worldwide petroleum reserves and environmental policies to reduce CO_2 emissions, have stimulated research towards the development of biotechnology to produce clean energy from renewable resources that are environmental-friendly [180-187].

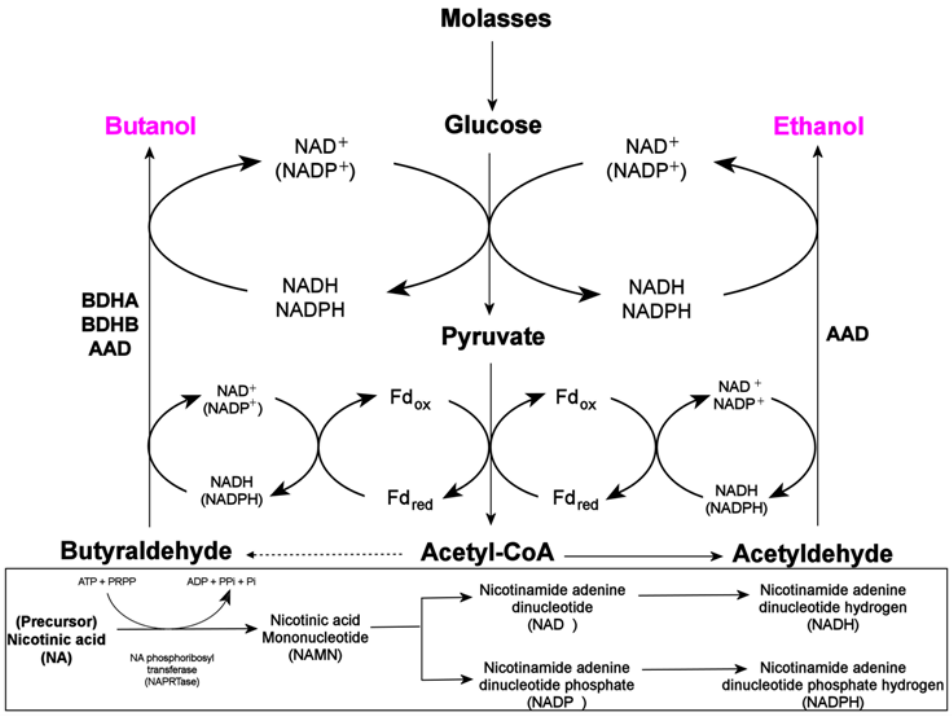

Figure 4. A summary of chemical processes in a butanol plant; showing relationships between alcohol synthesis and NADH/NADPH regenerations. The reducing cofactors (NADH/NADPH)-dependent enzymes are abbreviated as: AAD - alcohol/aldehyde dehydrogenase, BDHA - butanol dehydrogenaseI and BDHB - butanol dehydrogenase II [188].

The production of biochemicals from sugarcane molasses and bagasse are promising alternative energy sources and will continue to impact positively on the agro chemistry industry. Sugarcane molasses is an important organic waste due to its high sugar content (55%) and high volume of production. It is even more viscous and has higher total sugar content than beet molasses. The availability and cost of sugarcane molasses make it an attractive feedstock for use in many countries. The main contents of sugarcane molasses are shown in Table 2. The production of agrochemicals such as butanol and ethanol in large scale

from sugarcane molasses have been summarized in Figure 4. In these mechanisms, availability of reducing factors (e.g., NADH and NADPH) play important role in improving the efficacy of products conversion in cofactor-dependent production systems. Recently, Li et al. used nicotinic acid (NA), the precursor of NADH and NADPH, to supplement the growth medium of a wild-type *Clostridium* sp. strain BOH3 and achieved an increase in the levels of NADH and NADPH [188].

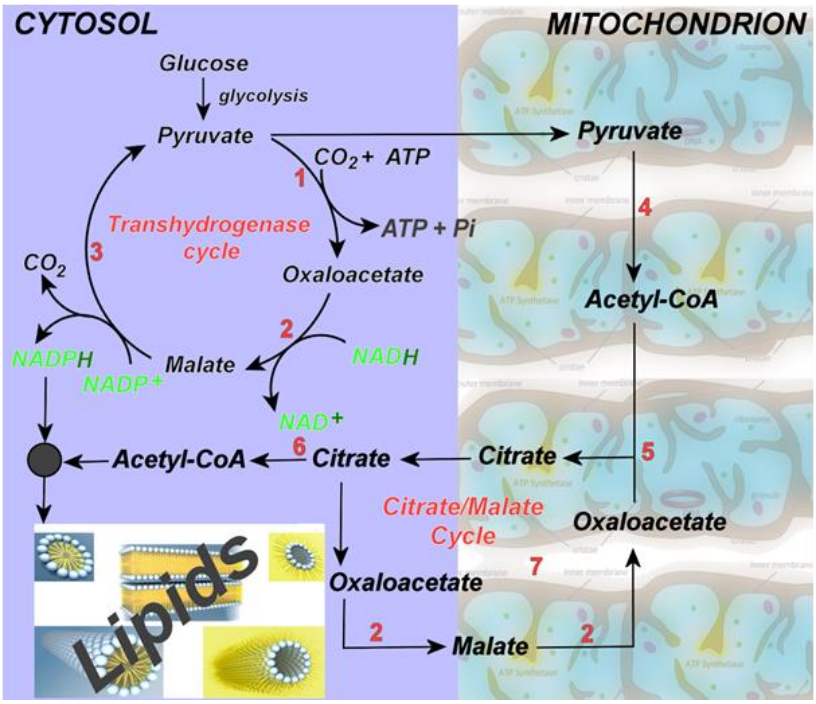

Figure 5. An overview of metabolic pathways involved in lipid biosynthesis by oleaginous fungi. The enzymes involved include: 1, pyruvate decarboxylase; 2, malate dehydrogenase; 3, malic enzyme; 4, pyruvate dehydrogenase; 5, citrate synthase; 6, ATP: citrate lyase; 7, citrate/malate transport [150].

Table 2. Selected major constituents of Sugarcane Molasses [150]

Constituent	Mg/g
Total Sugars	388
Total Proteins	29
Total nitrogen	4.6
Sodium	0.85
Potassium	24.34
Calcium	5.3
Magnesium	1.9
Phosphorus	0.78
pH	5.5

The use of lipids from single-cell oil microorganisms to produce biodiesel has been noted to increase its production and is of low ecosystem impact [189]. Microorganisms such as oleaginous yeasts and fungi have also been considered as potential oil sources for biodiesel production because they accumulate large amounts of lipids. Among these microorganisms, *Epicoccum purpurascens* [190], *Mortierella isabelina* [191] etc [192] have attracted special attention.

The generation of lipid by fermentative oleaginous fungi is accompanied by the formation of organic acids as metabolic products [193] that accumulate leading to a sharp drop in culture pH and subsequent inhibition of fungal growth. However, Baggy et al. utilizes this drawback by filtering the spent media and using it for H_2 gas production in the second step [150]. The first stage involves the isolation of oleaginous fungi: *Alternaria alternata*, *Cladosporium cladosporioides*, *Epicoccum nigrum*, *Fusarium oxysporum*, *Aspergillus parasiticus* and *Emericella nidulans var. lata* from the culture media after biosynthesis of lipids as shown in Figure 5. The isolated dry fungal biomass is then esterified to produce biodiesel. In the second stage, the spent medium of fungal culture is used as the fermentation medium for hydrogen production by *Clostridium acetobutylicum* (ATCC 824) as shown in Figure 6.

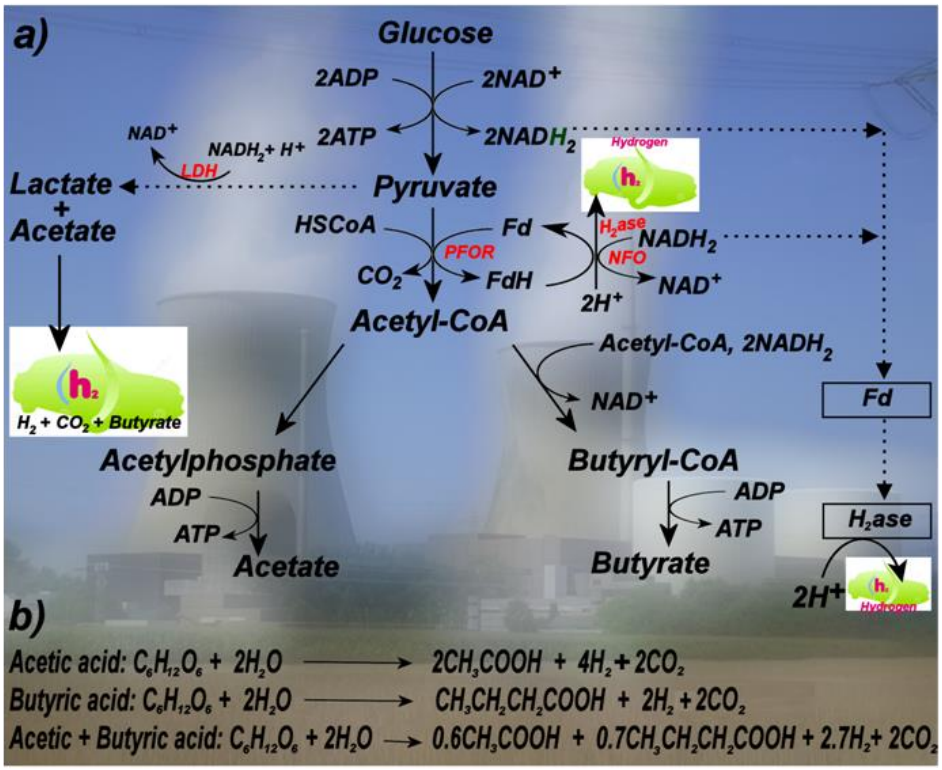

Figure 6. a). An overview of the metabolic pathways of glucose fermentation for biohydrogen production by *Clostridium acetobutylicum* and b). Stoichiometric relations between glucose and the products formed during carbohydrate fermentation. Dashed lines indicate hypothetical pathways. Enzymes: PFOR, Pyruvate ferredoxin oxidoreductase; LDH, Lactate dehydrogenase; NFO, NADH: ferredoxin oxidoreductase; H_2ase, Hydrogenase [150].

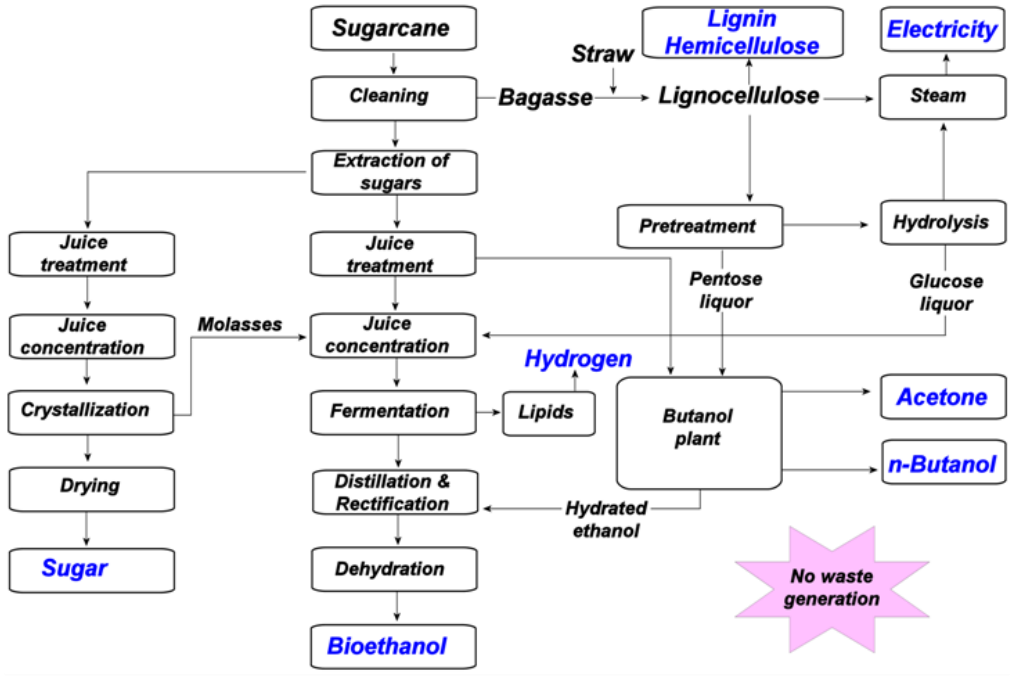

Figure 7. Summary of mechanisms involved in ensuring negligible waste generation from sugarcane processing.

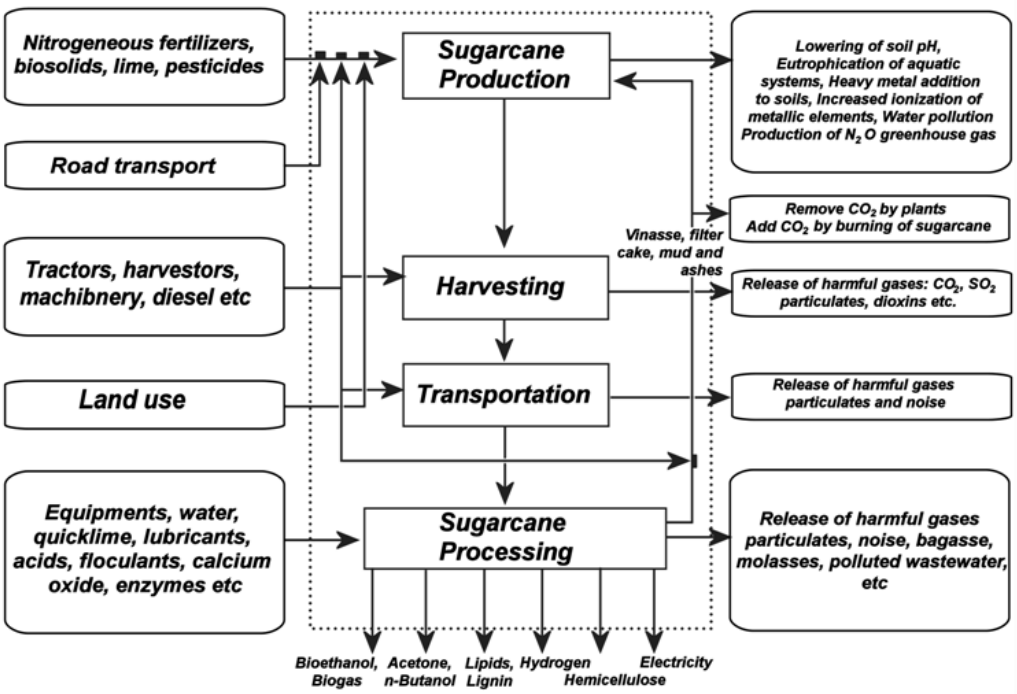

Figure 8. Summary of environmental impacts of sugarcane production and processing.

The maximum total H_2 yield is obtained with the spent medium of *E. nigrum and A. alternata*. These results demonstrated the possibility of interlinking the biodiesel production technology by fungi with hydrogen production by *C. acetobutylicum* ATCC 824 in order to exploit the residual sugars in the spent media and therefore increase the economic feasibility of biofuel production from molasses.

CONCLUSION

In summary, a flow chart (Figure 7) is used to show the no waste generation policy from sugarcane production and processing, and another flow chart (Figure 8) to show the environmental impacts arising out of sugarcane production and processing. To insure sustainable sugarcane production and processing, there is need to include the following strategies in management:

1. It is important to realize that sugarcane is an important plant that helps in sequestration of carbon dioxide; a greenhouse gas.
2. In order to manage soil acidification that arises out of nitrogenous fertilizer use in sugarcane production, the use of 650 kg/ha or 965 kg/ha of $CaCO_3$ to neutralize acid generated by 180 kg/ha of urea or diammonium phosphate respectively is recommended. Alternatively, use of basic nitrate fertilizers such as $Ca(NO_3)_2$ is advised.
3. In order to avoid contamination of aquatic systems within sugarcane plantation zones, use of pesticides according to label recommendations is paramount. In addition, correct weather forecast accompanied with precise timings in pesticide and fertilizer application will greatly reduce aquatic contamination due to surface runoffs and wash offs. Furthermore, region/site specific fertilizer requirement is significantly important both economically and for aquatic health protection.
4. Sugarcane bagasse is economically important in industrial production of bioethanol, biohydrogen, lignin, hemicelluloses and activated carbon and as effective pollutant adsorbents.
5. Sugarcane forage can be used as an effective fodder resource for feeding ruminants during dry seasons.
6. Sugarcane molasses are effective in production of antioxidants, butanol, lipids, acetate, butyrate, ethanol, hydrogen etc.

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