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Viability of Municipal Solid Waste as a source for Bioenergy products production

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Abstract*— *Energy is an important requirement for population growth, technological progress and urbanisation. Worldwide energy demand has been projected to increase 5-fold by 2100. Fulfilment of these energy requirements cannot be solely reliant on fossil fuels, such as oil, coal and natural gas, on account of their adverse environmental impacts and concomitant depletion of natural resources. As a result multiple approaches for generating alternative energy are being explored globally.In this review paper, focused on the viability of waste especially MSW being a source for bioenergy products such as methane gas, bio-enzyme, biofuel and bio-fertiliser production. This review also focuses on the environmental impacts of MSW, the effect of MSW pre-treatments and properties (physical and chemical) on bioenergy products production.

Keywords*— *MSW; pre-treatment; MSW management; Solid State Fermentation (SSF); recycling;Biogas; Methane gas; Anaerobic digestion (AD); biofuel;ethanol; butanol and bio-fertiliser.

I. INTRODUCTION

Environmental impact of Municipal Solid Waste (MSW)

The earth's climate is changing, with temperatures rising since the beginning of the twentieth century partly due to an increase in atmospheric concentrations of greenhouse gases. Climate change has become a long term concern and as a result production of bio energy is considered to be one solution for solving environmental issues such as water, soil and air pollution, as well as decreasing reliance on fossil fuels.

There are many resources which are available for producing bio energy, such as agricultural crops and their waste, animal waste, food processing and MSW. These are considered as potential renewable and sustainable energy sources. Generally, MSWs are considered to be one of the most sustainable resources world-wide[1]. Additionally, MSW presents an environmental problem in relation to its disposal. Furthermore, MSW treatments play a critical role in producing bio-energy in the form of high quality gases; biofuels and fertilisers. Presently there are many available technologies applying for bio-energy production, such as Anaerobic Digestion (AD), incineration, Refuses Deprival Fuel (RDF) and fermentation for biofuel productions [2].

MSW is a complex waste material whose composition is heterogeneous in nature, within MSW some of the components are stable, while others degrade as a result of biological and chemical processes causing potential pollution problems [3]. Waste generation is becoming increasingly significantly (Fig 1.1) which is leading to increasing pollution problems. For this reason, Solid Wastes Management (SWM) is an important consideration in order to decrease the effect of pollution.

In most countries, solid waste landfill is the most common means of disposal. Landfill sites are unsightly, unsanitary, generally smelly, and attract animals and insects [4]. To overcome the problem of MSW, incineration is wildly applied; incineration produces a safe substrate called ash, which can be used for further applications[5, 6]. Unmanaged MSWs have various impacts on the environment and on human health. For instance, water may become polluted by leachate if the leachate enters surface and ground water before sufficient dilution. Presence of leachate in the water may lead to serious pollution which affects animal and human life[7]. Personal use of water polluted by MSW for bathing, food irrigation and drinking water can expose individuals to disease causing organisms and other contaminants [8].

In regards, atmospheric pollution, MSW have been shown to emit Green House Gases (GHG) during the decomposition of solid waste when present in the landfill [9]. Managing MSW can lead toa decrease in GHG emissions as shown in a study carried out in Europe (EU)

where overtime total annual net CO_2production decreased(Fig 1.2). In addition, the World Health Organization (WHO) estimates that around a quarter of diseases affecting human health occur due to prolonged exposure to environmental pollution [10].

Generally, bio-energy production has a negative impact on living organisms due to the increase in erosion, depletion of soil nutrients and soil quality. These problems are related to the cultivation of annual crops; a further impact is in the use of pesticides and fertilisers. These agriculture inputs can affect people's health by leaching residues into ground water [11].

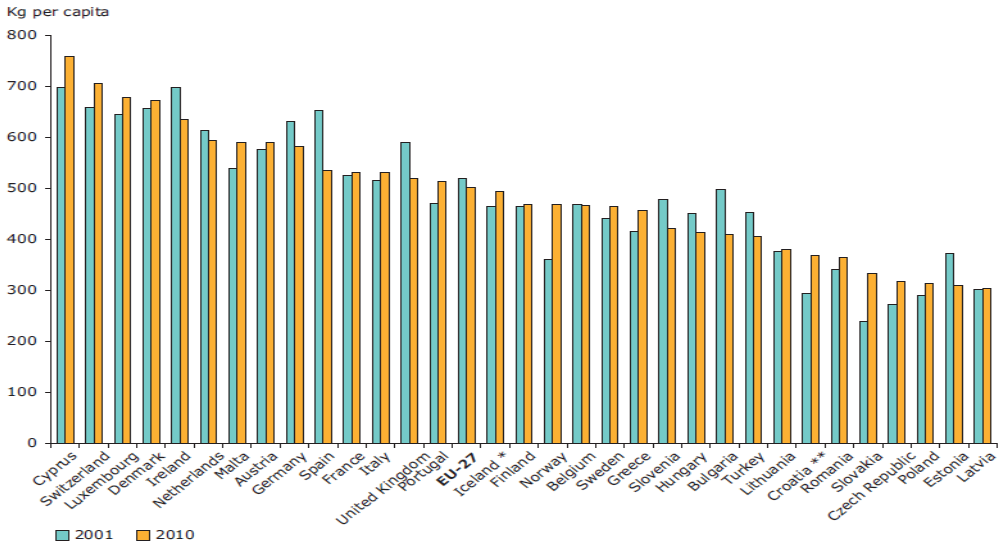

Fig.1.1 Municipal wastes generated per capita, 2001 and 2010[12, 13]

Note: (*) 2008 data used for 2010. (**) 2004 data used for 2001. According to Eurostat the comparability of the data over time is high. However, some breaks in the time series are documented, which can influence the comparability between countries and within a country. Generally, the quality of the data has improved during the period 2001–2010.

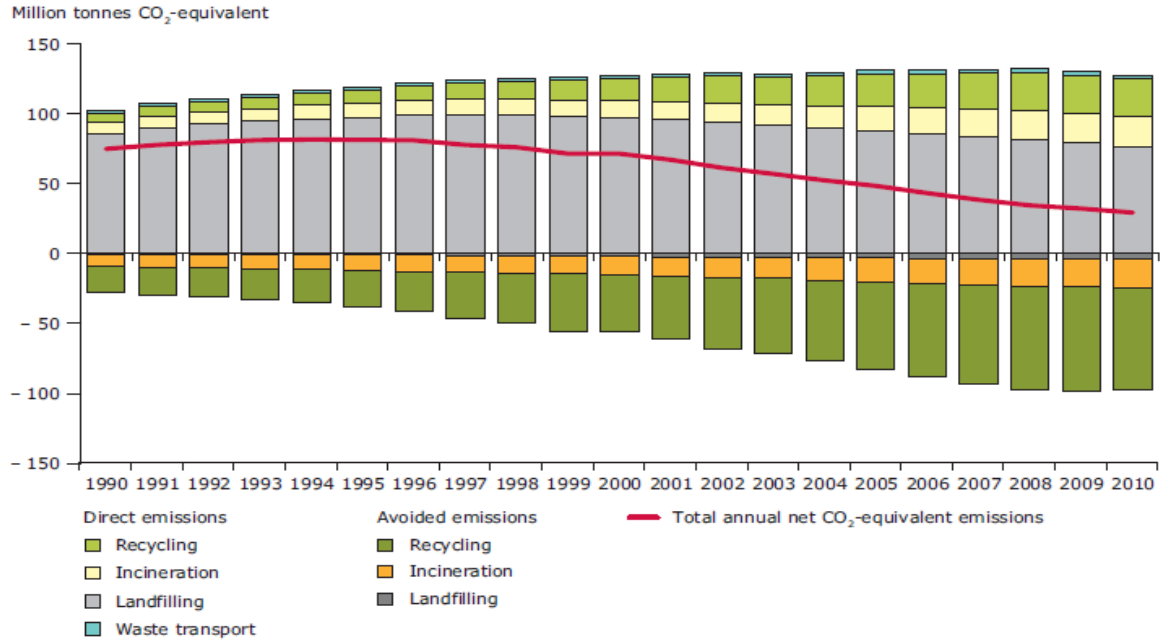

Fig.1.2 GHG emissions from municipal waste management in the EU, Switzerland and Norway[14]

Note: Excluding Cyprus due to lack of data. GHG emissions before 1995 are calculated based on backcasted waste data.

The concentration of CO_2 in the atmosphereis responsible for global worming hadby 2001 risen to 391ppm; an increase of about 6% compared to records forthe year 2000. Comparing GHG production, in particular CO_2, with the world total population, the 2010 world energy statistics [15] show that 44% of total CO_2 emission comes from 17% of the world total population (developed nations) while the remaining 83% of the world population (developing and least developed) contribute half of the total emissions [16](see Fig 1.3).

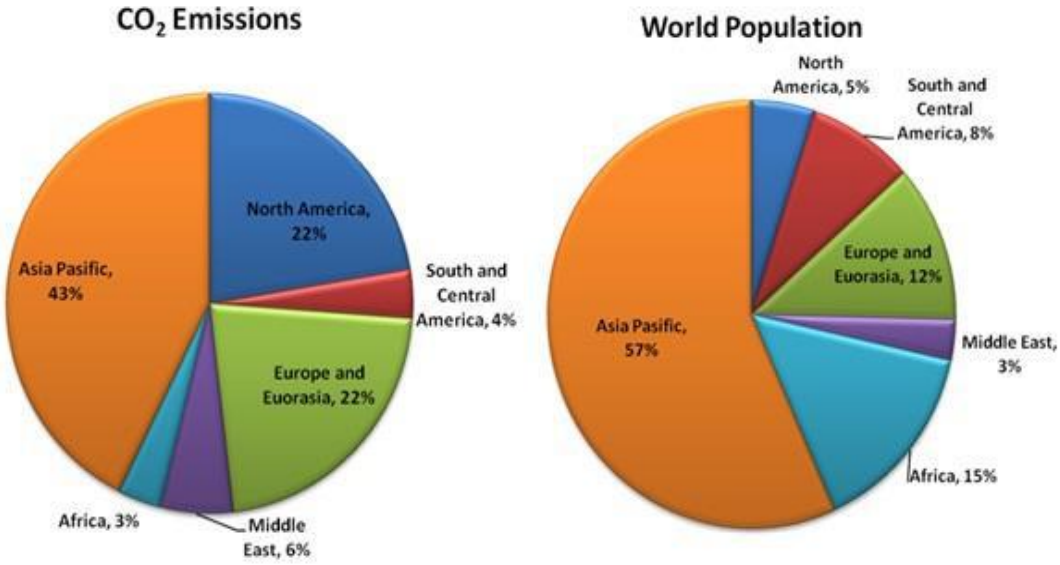

Fig.1.3 Comparison of World Population and CO_2 emission[17].

II. CURRENT AND FUTURE APPLICATIONS FOR MSW

Nowadays industrial chemical synthesis need to consider impacts including energy use, economic and effects on the environment. So any commercial products must be produced with minimum energy requirement. One way to satisfy the above constraints is by using a biochemical processes. These processes can be environmentally friendly, cost effective and carried out at ambient conditions [18]. Examples are methane or biofuel production [19] and bio-compost production from MSW [20].

2.1 Methane gas production by anaerobic digestion

AD is a process that has attracted increasing attention in both developing and developed countries as a promising approach for the conversion of organic waste into biogas. AD is a biological treatment method that relies on microbial activity to digest the waste [21]. It was originally used to manage the accumulation of organic wastes and/or for organic fertiliser production, but the emphasis is now shifting to renewable energy generation. These facilities generally treat organic materials which are abundant in their geographical locations. Consequently, waste from farm animals is the predominant feedstock for AD in China, India and North America, wastewater in North America, while MSW and industrial food processing wastes are utilised in Europe, [22, 23]. There were around 120 plants operating in Europe between 1998 and 2008, with a total operational capacity of around 4.6 million tonnes per annum, with the highest production in Germany Fig 2.1. The EU was the highest biogas producer in the world in 2012 and is predicted to maintain this position until 2022 (Fig 2.2.)

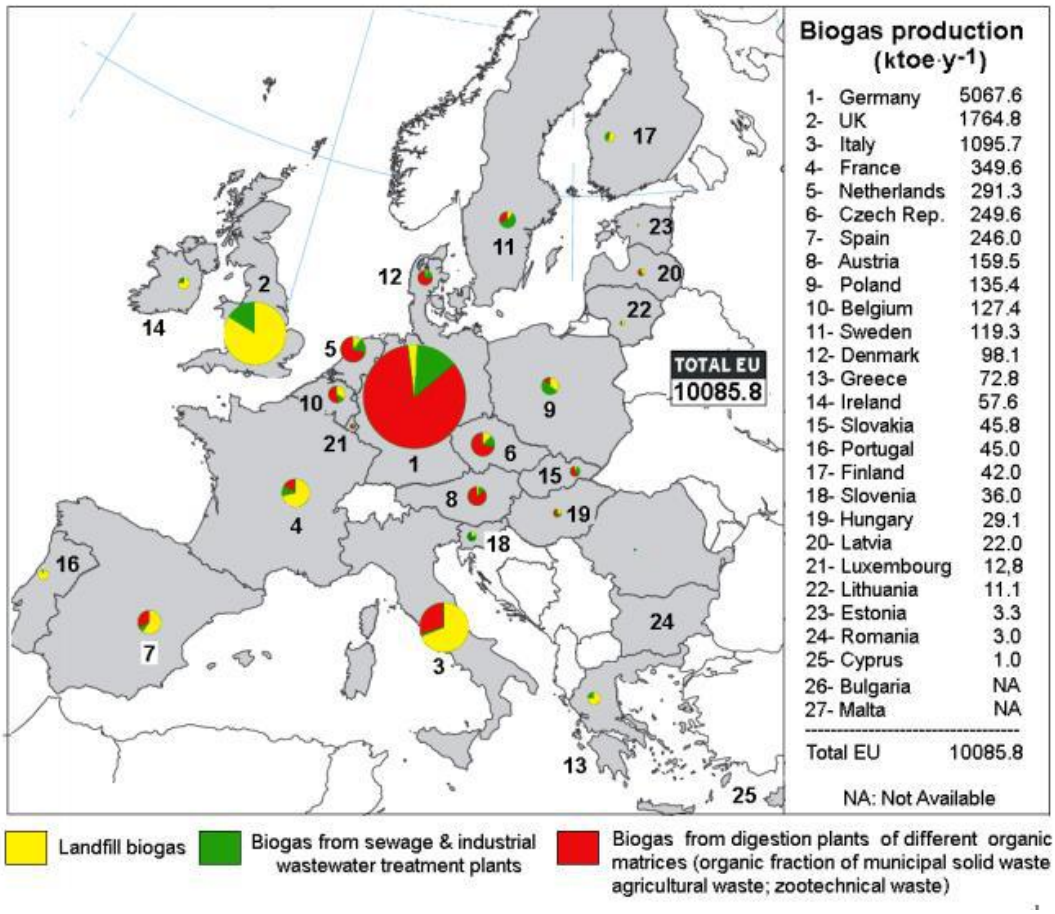

*Fig.2.1 Primary energy production of biogas in the European Union in 2011 (ktoe /y)***[24].**

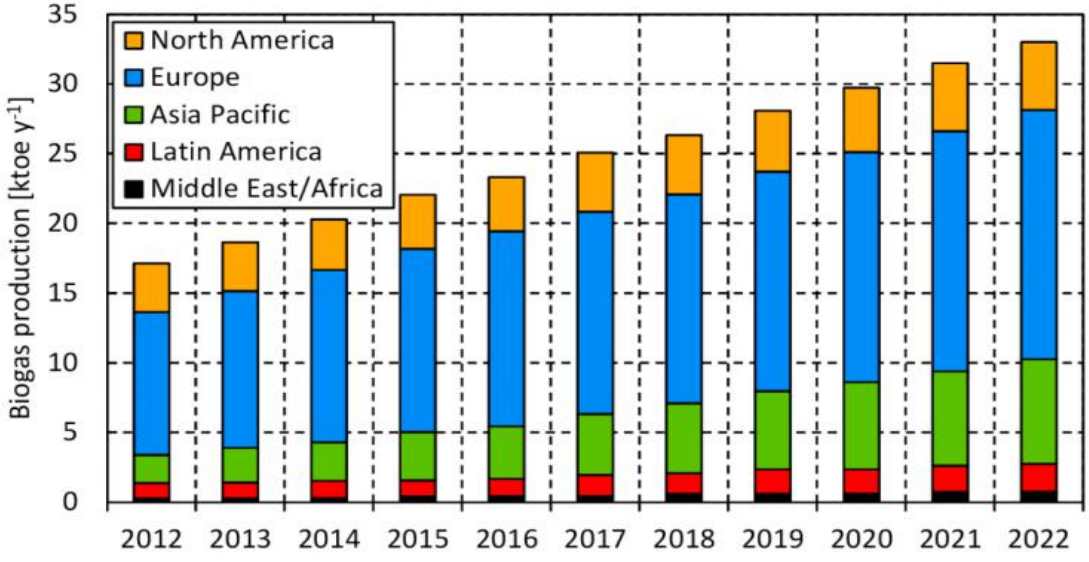

*Fig.2.2 Biogas production at 2012 and predicted trend to 2022 in different areas of the world***[25].**

Second generation biofuels

Bio-energy is energy which is derived from biomass, bioenergy production is an attractive, controllable and storable form of renewable energy [26]. Bio-energy can be generated by biological, chemical or physical processes. Energy ultimately derived from sunlight is stored as chemical bonds between carbon, hydrogen and oxygen atoms; these bonds can be broken down by digestion, combustion or decomposition releasing the stored energy [27].

Substrates require pre-treatment for biofuel production. The best and most effective pre-treatments are those that require no reduction in particle size, preserve the pentose (hemicellulose) fraction, avoid formation of possible inhibitors of hydrolytic enzymes and fermenting microorganisms, minimise energy use, have low running costs (operating costs, capital costs, and biomass costs), low catalyst cost, consume of little or no chemicals and which use cheap chemicals[28]. Pre-treating lignocellulosic material aims to produce a more reactive material than the original material; this process can produce soluble fermentable sugars [29].

Several methods have been introduced for pre-treatment of lignocellulosic material prior to enzymatic hydrolysis or digestion. These methods are classified into: physical pre-treatment, physio-chemical pre-treatments, chemical pre-treatments, and biological pre-treatments [30, 31].

Physical pre-treatments

Physical pre-treatments, includes size reduction such as chipping, shredding, grinding, and milling. These methods have been used to enhance the digestibility of lignocellulosic biomass [32]. Harvesting and preconditioning reduces lignocellulosic biomass from logs to coarse particle sizes of between10–50mm.Chipping reduces the biomass particle size to 10–30mm, however, the process reduces heat and mass transfer limitations. Grinding and milling can further reduce particle size to 0.2–2mm and these processes can start to have an impact on the crystallinity of cellulose.

Research has revealed that reducing biomass particle size below 40 mesh (0.4mm) has little effect on rates or biomass hydrolysis yields[33]. Reduction of particle size hasn't been studied widely in terms of hydrolysis [34], but some studies have shown that milling increases biogas, bioethanol and bio-hydrogen yields. Using milling will increase the cost of production, however, milling is viewed as being economically feasible [29]. **Thermal pre-treatments**are applied in order to solubilise hemicellulose, thereby improving rates of hydrolysis of lignocellulose material [35]. There are various thermal pre-treatment methods such as use of steam (~ 240°C and high pressure for a few minutes) [29], steam explosion (a rapid release in pressure which causes a disruption in the structure of the material) [29], liquid hot water treatment (where water is maintained as a liquid at high temperatures (160 to 230°C) and under high pressures (>5 MPa) [36-38].

As the temperature used in the hydrolysis increases above 150–180ºC, hemicellulose and lignin become solubilised [39]. There are two main components of hemicelluloses (xylan and gluco-mannans), the xylans are the least thermally stable when compared with gluco-mannans. If temperatures during pre-treatment exceed 180ºC, an exothermal reaction (probably solubilisation) of the hemicellulose begins [40], the thermal reactivity mainly depends on the composition of the lignocellulosic biomass and has an influence on the temperature at which this exothermal reaction begins [41].

Generally, during thermal processing, the hemicellulose portion of the plant cell wall becomes hydrolysed forming acids, presence of these acids catalyses the further hydrolysis of the hemicellulose [42]. Furthermore, thermal processes can cause an increase in the Crystallinity Index (CrI) of cellulose, though no increase was observed when the CrI was already high [43].

The thermal pre-treatments also produce phenolic compounds as a result of the solubilisation of lignin, these phenolic compounds have been shown to be toxic or inhibitory to the growth of bacterial, yeast and methanogens/archae[44]. Furthermore, if these phenolic compounds are not removed quickly they have been shown to re-condense as a precipitate onto the biomass [45]. Use of severe pre-treatment conditions enhances the condensation and precipitation of solubilised lignin compounds [46].

Steam pre-treatment is characterised by the use of a large vessel, steam at temperatures up to 240ºC and high pressure, moisture content of the biomass during pre-treatment with steam is an important factor, for example the higher the moisture content, the longer the optimum time required for steam pre-treatment [47]. Steam pre-treatment has been shown to solubilise a fraction of the hemicelluloses, this process is referred to as 'auto-cleave'. A common term used in steam pre-treatments is the so called 'severity factor' (log R0), which is a measure for the severity of the pre-treatment [29]. Steam-explosion is the most commonly used pre-treatment method, the process includes injecting high pressure saturated steam into a reactor, leading to the temperature rising to 160-260ºC. Pressure is suddenly reduced and the biomass undergoes an explosive decompression leading to the destruction of the

fibre structure, decreasing crystallinity of the cellulose, and increasing the surface area substrate [48].

Liquid Hot Water (LHW) biomass pre-treatment is a hydrothermal process, which does not require addition of chemicals, the process uses water under high pressure. This process has been shown to penetrate into the biomass, hydrate cellulose, and remove hemicellulose and part of the lignin, this makes the process cheap and more industrially relevant [49]. Use of hot water also reduces the requirement for reducing the size of the lignocellulosic prior to pre-treatment and produces lower amounts of neutralization residues. In this process, hemicellulosic carbohydrates are dissolved as liquid-soluble oligosaccharides and can be separated from insoluble cellulosic and lignin fractions [28]. This process increases enzyme accessibility by increasing surface area of the cellulose [50]. Pre-treatments with steam and LHW are both hydrothermal pre-treatments characterised by higher pentose recovery and lower formation of inhibitory components [51].

Mechanical pre-treatment (MPT)MPT is a process which includes waste sorting and homogenisation, and is followed by biological treatment [52]. This method is reliant depends on stressing the substrate cell wall without addition of any chemical substances [53, 54]. The MPT can break down the crystalline structure of cellulose; thus increasing the reactant surface area following fine milling (nano-milling) [48]. Other pre-treatments which use mechanical treatment are: High Pressure Homogenisation (HPH), stirred ball mills, and the jetting and colliding method [55, 56].

Autoclaving is a heat treatment, the autoclave is an instrument which uses relatively high temperatures, and pressure. This process has been applied previously to sterilise hospital wastes and some animal wastes [57].The process as applied on MSW is a relatively recent innovation and the commercial process is shown in Fig 2.3.

The main reasons for autoclaving unsorted MSW includes destroying bacteria, reducing the size of waste by 60%, reducing moisture content, removing recyclable materials from the waste stream and, finally, increasing the quality of recyclable metals (by stripping away label glue from food cans and heat shrink packaging). However, heat can have an adverse effect on some recyclable plastics, such as polyethylene terephthalate (PET) and high density polyethylene (HDPE) [58, 59].

The process consists of collecting waste from resources, followed by injecting unsorted MSW automatically into the autoclave [60]. To run any autoclaving method, some points need to be taken into consideration such as pressure (6.2 bar is maintained for between thirty and sixty minutes). Aeration can be supplied via a blower directed from the bottom through the material, and gasses are collected at the top in order to analyse them. Steam is injected at pressure and the temperature increased to 130^{o}C. This temperature is considered to be the optimal temperature for pre-treatment of total solids [61].

Chemical pre-treatments

There are many chemical substances which can be used for the pre-treatment of biomass such as oxidizing agents, alkali, acids and salt [62].Acid hydrolysis or pre-treatments, is one of the most common methods used for the pre-treatment of lignocellulosic biomass to attain higher sugar yields [63]. The main goal of this method is to solubilise the hemicellulosic fraction of the biomass, which increases the accessibility of the enzymes to the cellulosic fraction [64].

Either dilute or strong acid can be used for this type of pre-treatment to hydrolyse hemicellulose and solubilise or precipitate lignin [29]. Studies have shown that 0.5% H_2SO_4 is an optimal acid concentration for treatment of waste from vegetables and rice straw [65]. While, higher acid concentrations of up to 2.5 M are capable of separating lignin and other organic components [66, 67].

Weak acid hydrolysis (dilute acid treatment), the most efficient pre-treatment for lignocellulosic substrates with low lignin content is the use of dilute acid, which offers a good sugar recovery. The aim of this process is to remove hemicelluloses thus increasing porosity and as a result improving enzymatic digestibility [68]. Some disadvantages are the further degradation of hemicelluloses sugars which can be corrosive and degraded further to furfural and hydroxymethylfurfural (HMF), presence of these compounds can be inhibitory in microbial fermentations [35]. Indeed for some years dilute sulphuric acid has been added to biomass to manufacture furfural commercially [69]. The production process hydrolyses hemicelluloses to xylose which is then condensed into furfural, which is recovered by distillation [70].

Various dilute acids can be applied for pre-treating different lignocellulosic substances including sulphuric acid [71], nitric acid [72], hydrochloric acid [73], phosphoric acid [74], peracetic acid [75] and oxalic acid [76].

Among these, the most commonly applied is dilute sulphuric acid due to its availability, cost, safety and low environmental concerns [77]. Pre-treatment with sulphuric acid helps to achieve high yields of xylose from xylan[36].and increases the enzymatic digestibility of cellulose [78]. However, use of sulphuric acid produces

inhibitors such as furfural [79], dilute acid pre-treatments have also been found to be suitable for a wide range of feed stocks including softwood, hardwood, herbaceous crops, agricultural residues, waste paper and MSW [80].

However, use of dilute acid has some drawbacks such as corrosion, the need for neutralisation before the fermentation process, formation of degradation products and the acids or chemical price should be taken into consideration [81]. Dilute acid pre-treatments can increase the cellulose conversion by enzymes to sugar but doesn't fully remove lignin which precipitates on the cellulose surface and may inhibit the hydrolysis process [82]. To decrease the negative impact of lignin on the Enzyme Hydrolysis (EH) process, some studies have added surfactants such as Tween-80, dodecylbenzene sulfonic acid and polyethylene glycol 4000 (PEG, 4000), to acid pre-treated corn Stover biomass at 140–220°C.The presence of these surfactants enhances lignin removal and improves the digestibility of the cellulose by increasing the hydrophobicity of the biomass [83].

To further improve digestibility, dilute acid pre-treatments can be combined with other pre-treatments such as combining acid and alkaline pre-treatments (strong acid–strong alkali or weak acid–weak alkali), these combined pre-treatments have been shown to remove most of the non-cellulosic materials [84]. Generally there are two types of weak acid hydrolysis:

- High temperature and low-solids loading (T>160°C, 5-10% wt substrate concentration).
- Low temperature and high-solids loading (T≤160°C, 10-40% substrate concentration) [35].

Strong acid hydrolysis; Concentrated H_2SO_4 and HCl have been used for treating lignocellulosic substrate due to their ability to directly hydrolyse cellulose and thus not require any use of enzymes [85]. This method has some advantages such as high monomeric sugar yield and mild temperatures are required. However, drawbacks for this process are the corrosive nature of the acid and the need to recycle acid in order to lower costs, toxicity, and the requirement for expensive construction materials [86]. Some companies have commercialised the use of strong acids for microbial fermentation purposes [35].

Alkaline hydrolysis or pre-treatment, for alkaline pre-treatments, the most common chemicals used are calcium and sodium hydroxide for solubilising lignin [36]. Sodium hydroxide (NaOH) is mainly used because it is a safer chemical substance and can be recycled [87]. However, it is expensive and needs to be removed because of salt production [88]. This method has not been applied industrially [89]. Sodium hydroxide has received the greatest attention due to its outstanding delignification capacity which is essential to achieve high biomass digestibility [90]. The main goal of alkaline pre-treatment is to increase the internal surface area of the lignocellulosic material due to swelling induced by the alkali [89]. This method is more effective with low lignin containing biomass such as agricultural residues, herbaceous crops and hardwoods than on softwood which have a higher lignin content [91]. Furthermore, due to the low severity of the alkaline pre-treatment little sugar decomposition occurs and hemicellulose is retained in the biomass, the method can remove acetyl and various uronic acids which can lower enzyme accessibility [87]. However, use of strong alkali concentrations leads to dissolution, 'peeling' of end-groups, alkaline hydrolysis and decomposition of dissolved polysaccharides [92]. This peeling has advantages but could be at risk of degradation and loss of polysaccharides or carbon in the form of carbon dioxide. To prevent peeling, the temperature is kept low during the extraction process (room temperature or lower) [41]. Research has revealed that applying NaOH at room temperature for 24hr preserves most of the carbohydrates but caused substantial lignin degradation [81]. Research has shown that applying 121 °C autoclaving using NaOH as a pre-treatment on biomass was an impractical temperature, along with the use of pressure of 15 psi, for large scale industrial applications [93]. However, alkaline pre-treatment at room temperature seems to be the best pre-treatment method using caustic materials [94].

The advantages of alkaline pre-treatment are the use of lower temperatures, pressures and residence times when compared to other pre-treatment technologies [95]. Alkali pre-treatments also have lower running costs when using chemicals such as sodium hydroxide, ammonia, peroxide and lime [96]. While, alkaline pre-treatment drawbacks include that these types of pre-treatment have little impact on the solubilisation of cellulose and hemicelluloses [97] and conversion of alkali into irrecoverable salts during the pre-treatment [29].

The efficiency of this process for hydrolysing the organic fraction of MSW has been investigated by using 0.5 – 2M alkali (NaOH, $Ca(OH)_2$, NaOH-urea, Na_2CO_3) at 120-200°C. Use of alkali at these concentrations substantially facilitated saccharification and improved enzymatic hydrolysis [89]. Recent studies have shown that a combined acid/alkaline pre-treatment of lignocellulosic wastes was more efficient than acid or alkaline individually [98].

Alkaline treatment can also be separated into two types on the basis of the alkali employed. These include: Pre-treatment with calcium, sodium and potassium hydroxide

and pre-treatment with ammonia. Ammonia Fiber Explosion (AFEX) treats lignocellulosic biomass (40–50% moisture content) with pure liquid ammonia at mild temperatures (80–100°C) and high pressures (40–50atm) followed by explosive pressure release, pre-treatment helps to disrupt the fibre structure and increases the surface area. The advantage of this process is lower moisture content, lower formation of sugar degradation products and ability for ammonia to reduce lignin inhibitory effect on enzymatic hydrolysis. Disadvantages included costs due to recycling and treatment of chemicals [99].

The mechanism of alkaline hydrolysis depends on solvation and saphonication of intermolecular ester bonds crosslinking xylan hemicelluloses and other components such as lignin [85]. Solvation and saponification causes the removal of these cross-links and enhances the porosity of the lignocellulosic materials [100]. There are a number of important aspects of alkaline pre-treatment which cause low lignin removal and cellulose swelling; first is that the higher the monomeric hemicellulose fraction, the lower the total recovery of the hemicellulose [101], because the monomeric forms are easily degradable to other volatile compounds for example furfural, which leads to losses of digestible substrate for the ethanol process [102]; secondly, alkali extraction can also cause solubilisation, redistribution and condensation of lignin and modifications in the crystalline state of the cellulose; thirdly, alkaline pre-treatment changes the cellulose stricture to a form a denser and thermodynamically more stable form than the native cellulose [42].

Biological processing

The main biological method for the generation of fermentable sugars is through enzymatic hydrolysis usually after a hydrothermal or chemical pre-treatment. The enzymes are normally produced by microorganisms (fungi and bacteria) and the products of the hydrolysis are usually reducing sugars such as glucose. Cellulase enzymes are mainly used for the hydrolysis of lignocellulosic substrates [103].

The most common microorganisms able to produce hydrolytic enzymes are bacteria belonging to the *Clostridium, Cellulomonas, Bacillus, Thermomonospora, Ruminococcus, Bacteriodes, Erwinia, Acetovibrio, Microbispora,and Streptomyces*genera[104], and fungi such as *Sclerotiumrolfsii, Phanerochaetechrysosporium*and species of *Trichoderma, Aspergillus, Schizophyllum and Penicillium (*Sternberg, 1975;Duff and Murray, 1996). In the fungal kingdom, *Trichoderma* has been most extensively studied for cellulase production [105]. However, white rot fungi are thought to be the most efficient for lignin hemicellulose degradation in waste material [106]. White and soft rot fungi attack both cellulose and lignin, the fungi can degrade lignin using enzymes such as peroxidases and laccase, while brown rots mainly degrade cellulose [107].

Enzymes which participate in the hydrolysis of cellulose consist of three major groups: (1) endoglucanase (endo-1,4-glucanohydrolase) which have been shown to degrade low crystalline structures within the cellulose fibre, creating free chain ends; (2) exoglucanase or cellobio hydrolase(1,4-glucan cellobiohydrolase) which remove cellobiose unit from the free chain ends and (3) glucosidases which hydrolyse cellobiose to produce glucose [85]. While, for hydrolysing hemicelluloses, a number of enzymes such as glucuronidase, acetyl esterase, feruloyl esterase, xylanase, xylosidase, galacto mannanase and gluco mannanase are used[108]. The rate and degree of the EH is influenced by: mass transfer resistance, including surface film resistance around cellulose, bulk phase resistance and the resistance through the capillary pores of the cellulose particles [109]. Two major factors contribute to lower hydrolysis rates during EH. Firstly cellulose may be transformed into a less digestible form for enzyme during hydrolysis [110]. Secondly, the soluble products, including glucose and celluobiose, may have a profound inhibiting effect on the action of cellulosic enzymes[111].

The high cost of commercial “cellulose” cocktails is one of the largest obstacles to the economic bio-refinering of biomass which requires large amounts of enzyme [112]. There have been attempts to improve cellulase activity such as direct evaluation and rational design for each cellulase and the reconstitution of designer cellulosome or cellulase mixtures (cocktails) which have a direct activity on the substrate [113]. These improvements include basic studies on fungal physiology and chemistry, cellulase gene regulation and expression, recombinant enzymes, protein engineering of cellulase and development of cellulase enzyme cocktails [114]. The genome of *T. reesei* has revealed that this fungus contains fewer cellulases and hemicellulases than any other sequenced fungi despite being the best known commercial producer of cellulases [115]. Thus other fungal species may harbour more effective enzymes.

Factors affecting the enzymatic hydrolysis of cellulose including substrate condition (pre-treated and unpre-treated), environmental conditions (pH and temperature), and cellulase activity [85].

- **Substrate concentration** is one the main factors which affects the initial rate of enzymatic hydrolysis and yield. Increasing substrate

concentration has resulted in an increase in yield and hydrolysis reaction rates [116]. However, high substrate concentrations can cause substrate inhibition depending on the ratio of total substrate to total enzyme [117]. A 5%w/v substrate concentration achieved the highest rates of hydrolysis, further increase in the substrate concentration decelerated the rate of hydrolysis due to stirring difficulties and reduction in the aqueous mobile phase [118, 119]. Research has revealed that for MSW hydrolysis increased from 27% at 10 g/L to 53% at 50 g/L with a sugar yield of 385 mg sugar/g fibre[120].

- The **structural features** of the substrate including cellulose crystallinity, degree of cellulose polymerization, surface area, and content of lignin can all affect the susceptibility of cellulosic substrates to cellulases [85]. Pre-treatment of the substrate also influences cellulase enzyme activity (Fig 2.3). The substrate particle size has a significant effect on EH yields, the highest hydrolysis efficiency were observed for the particle size range of 150–300mm. Hydrolysis efficiency increased from 25 to 37% by increasing particle size. This was probably due to the grinding process which may change the surface chemistry or morphology of the fibres making them less accessible to the enzyme. Larger particle sizes above 300 mm resulted in a reduction in sugar yield, this effect can be explained by the longer diffusion of enzyme into the fibre particles suggesting that extensive milling is not needed for the conversion of the organic MSW concentrate [121]**.**
- **Environmental conditions;** increasing incubation temperature has been shown to increase the rate of initial hydrolysis, the maximum hydrolysis rate was observed at 50^{o}C[122]. This result could be attributed to the thermal inactivation of endoglucanase I and cellobiohydrolase I [123]. Studies investigating the effect of reaction time on the sugar yield during EH indicated that by increasing reaction time, sugar yields also increased. However, after 12 hr the hydrolysis rates became constant indicating that some inhibition may occur after that time [124]. The presence of reducing sugars as well as percentage hydrolysis rates decreased with prolonged time after the optimum. This effect may be due to the inhibition of the enzyme action by the accumulated of hydrolysis products [121].
- **Cellulase enzyme**, increasing enzyme dosage increased hydrolysis yields and rates; however, increasing enzyme dosage would also increase the cost of the process. Cellulose enzyme dosage varied from 7 to 33 FPU/g substrate, depending on the type and concentration of substrates [85]. Surfactants can be applied to decrease the irreversible adsorption of cellulase on cellulose but may also be partially responsible for deactivation [125]. Surfactants are also used to block lignin binding to the cellulose and thus enhance enzymatic saccharification of cellulose [126]. There are many surfactants that could be applied such as non-ionic Tween 20, 80 [127], polyoxyethylene glycol [128], Tween 81, Emulgen 147, amphoteric Anhitole 20BS, cationic Q-86W [129], sophorolipid, rhamnolipid, and bacitracin these surfactants are suitable for enhancing cellulose hydrolysis [85, 130]. In addition, the factors affecting activity of Cellulases include enzyme source and the concentration of enzyme. An effective concentration of enzyme for cellulose hydrolysis has been determined to be 10 to 60 FPU/gm of dry cellulose or glucan- glucanase- β- D-glucosidase ratio of 1-75-2IU (International Unit) [131].

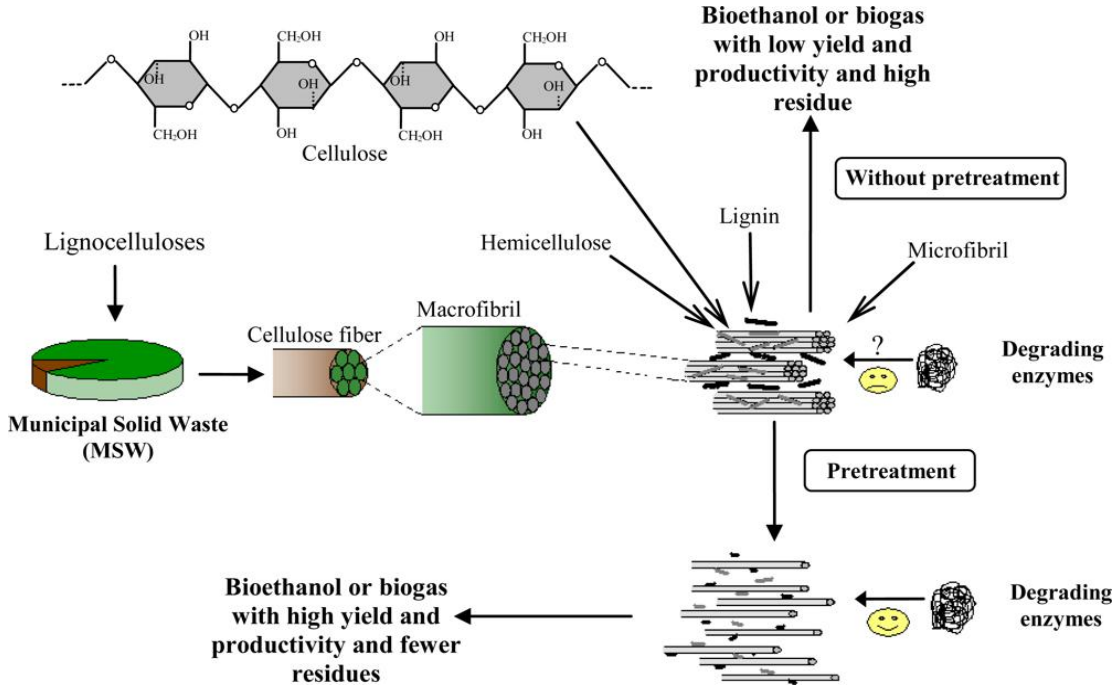

*Fig.2.3 Effect of pre-treatment of MSW on accessibility of degrading enzymes***[28]**

2.3 Biofuel and biochemical production from municipal solid wastes

Fuel production from lignocellulosic biomass, has been well researched, however, MSW has not been given as much attention for energy production when compared with other feed stocks [132]. Fuel production from MSW is a promising strategy for energy needs and effective management of MSW. European legislation aims to minimise landfill use in EU countries, and the amount of biodegradable MSW must be reduced by 65% by 2020 [133]. Studies have shown that up to 82.9 billion litres of waste paper-derived cellulosic ethanol could be produced worldwide, replacing 5.36% of gasoline consumption. The energy independence and security act mandated an increase of 36 billion gallons per year of renewable fuels to be blended into transportation fuels by 2022 [134].

The use of MSW as a biofuel feedstock is dependent on a number of factors which include regional reliability, characteristics of wastes, and compatibility with and efficiency of conversion technologies. Economic factors are cost of collection, transport, and waste conversion. Environmental performance including air and water emissions, greenhouse gases, and finally waste generation; all of these can affect costs and public acceptance [132].

Furthermore, the EPA has defined renewable fuel standards stating that advanced bio-fuels must be derived from feedstock's which meet the definition of renewable biomass. Therefore, MSW must be separated from plastic, rubber, metals and glass [132, 135]. There are many types of biofuel such as ethanol, methanol, bio-diesels which could be used as transportation fuels [134].

2.3.1 Ethanol production

Production of ethanol or ethyl alcohol has existed since the beginning of recorded history [136]. However, since the early 1980's the cost of ethanol production from lignocellulosic biomass was the main concern, at that time the cost was $ 0.95/litre (US $ 3.60/gallon) [137]. However, research has improved ethanol production yield through improved cellulase production, utilisation of a SSF rather than a SMF process, and advances in microorganisms to convert the xylose fraction, as a consequence much better yields and rates have been achieved[138].

The ethanol production process includes using lignocellulosic substrate such as wheat and corn [139]. However, corn is no longer used for ethanol production because of the wide planting for ethanol production which competes for use of arable land and thus threatens national food securities [140]. Lignocellulosic substrates can be used as alternative to corn options which are low in cost and have a high polysaccharide content [141]. Nowadays food wastes can be utilised as substrates for ethanol production, research carried out has shown that sweet potato can be converted into ethanol with a 80.23% yield [142].

A few studies has been applied for bioethanol production from MSW,[19] showed that using pre-treatment with dilute sulphuric acid followed by steam explosion did

increase the rate at which the maximum yield of glucose was formed. However, this pre-treatment did not give high yields for newspaper wastes.

Another study used selected biodegradable MSWfractions; these fractions were subjected to fifteen different pre-hydrolysis treatments to obtain the highest glucose yield for bio-ethanol production. Glucose yields were compared using a factorial experimental design. The highest glucose yield (72.80%) was obtained with a pre-hydrolysis treatment consisting of H_2SO_4 at 1% concentration, followed by steam treatment at 121°C, and enzymatic hydrolysis at 60 FPU/g substrate [143].

A study by Yan *et al*. (2012) using enzymatically hydrolysed food wastes showed that batch and fed batch hydrolysates, which contained reducing sugar concentrations of 131.41 and 194.43 g/L respectively, produced 62.93 and 90.72 g/L, ethanol following fermentation using *Saccharomyces cerevisiae* H058, for 48 hr.

There are three major stages involved in the conversion of lignocellulose to ethanol - pre-treatment, enzymatic hydrolysis and fermentation. This is followed by distillation to extract pure ethanol. The steps, or technologies, required for ethanol production are shown in Fig (2.4).

(1) Pre-treatment

Pre-treatments using physical, physicochemical, chemical and biological methods as mentionedpreviously,are an important step to make cellulose more accessible in the hydrolysis step. However, this is a costly step, accounting for approximately 33% of the total cost [144].

(2) Enzymatic hydrolysis

EH is the process used to convert polysaccharides into simple sugars, which can be fermented by bacteria or yeast [145].

In the second stage, the conversion of cellulose and hemicellulose can be expressed by the reaction of glucan (for hexoses) and xylan (for pentose) with water:

$$(C_6H_{10}O_5)n + nH_2O \rightarrow n\ C_6H_{12}O_6 \quad \text{.....(1)}$$

$$(C_5H_8O_4)n + nH_2O \rightarrow n\ C_5H_{10}O_5 \quad \text{.....(2)}$$

The maximum theoretical yield of hexoses and pentoses is 1.136kg and 1.111kg per kg of glucan and xylan, respectively [146].

(3) Fermentation

The fermentation reaction by yeast and bacteria of simple sugars produces bio-fuels such as ethanol or butanol, CO_2 is also produced during the fermentation process. The simplified reaction equation is: [146]

The conversion reaction for hexoses (C6) and pentose (C5) are as follows:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2CO_2 \quad \text{..... (3)}$$

$$3C_6H_{10}O_5 \rightarrow 5\ C_2H_5OH + 5CO_2 \quad \text{..... (4)}$$

The theoretical maximum yield of ethanol from hexoses and pentose is 0.511kg ethanol and 0.489 kg CO_2 per kg sugar, respectively [146].

Generally yeast such as *S. cerevisiae* are used for ethanol production, however, this yeast cannot metabolise xylose efficiently[147, 148].However, many bacteria and yeast are able to ferment xylose and other pentose sugars either naturally or following genetic manipulation[149, 150].

Yeasts when utilised for ethanol production are required to be capable of fermenting all of the sugars present with high ethanol yields. Wild-type *S. cerevisiae* strains are unable to ferment pentose sugars; its capability for xylose utilization has been improved by intensive recent research. During the last fifteen years, research has been focused on finding xylose fermenting microorganisms and understanding the principles behind the utilisation of xylose [146]. *S. cerevisiae* has desirable characteristics such as efficient anaerobic sugar metabolism, toleration of inhibitory industrial substrates better than other microorganisms and ferments hexoses abundantly present in lignocellulosic hydrolysates, such as glucose, mannose and galactose with high yield and productivity [85].

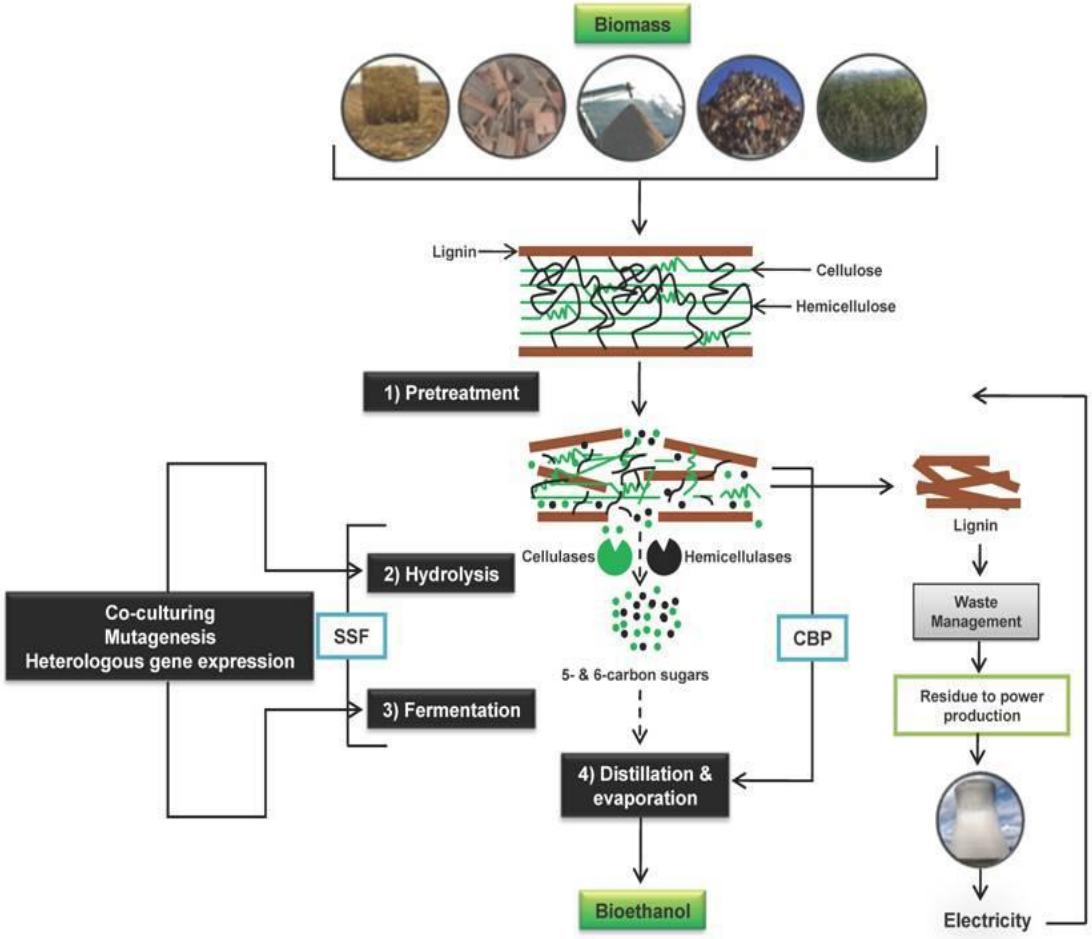

*Fig.2.4 Schematic for the conversion of lignocellulosic biomass to ethanol***[151]**

2.3.2 Butanol production

1-Butanol (butyl alcohol or n-butanol) is a four carbon straight chained alcohol with a molecular formula of C_4H_9OH (MW 74.12) and boiling point of 118°C [152]. Butanol is a good source of biofuel [153], because it has low vapour pressure, can be blended with either gasoline or diesel at any fraction [154]. Butanol has some advantages over ethanol as a fuel substitute, it has an energy content that is similar to gasoline, lower vapour pressure compared to ethanol and is safer during transport and when used in car engines[155].Butanol can also be used as an important chemical precursor for paints, polymers, plastics, solvents, plasticizers, butylamines, amino resins, butyl acetates production, et[152, 156]. Therefore, bio-butanol has the potential to substitute for both ethanol and bio-diesel in the biofuel market and is estimated to be worth $247 billion by 2020 [152].

For butanol chemical production of Oxo synthesis, Reppe synthesis, and crotonaldehyde hydrogenation are the three most important processes, most of these process rely on petroleum, however, butanol can be produced from biomass [157]. Butanol is currently manufactured from petroleum feedstock (Oxo process). While, Bio-butanol is produced via the Acetone Butanol Ethanol (ABE) fermentation process using renewable resources (biomass) and *Clostridium acetobutylicum* or *Clostridium beijerinckii*in anaerobic conditions) [154]. Conventional butanol fermentation is carried out by microorganisms in a two-stage batch process: an initial acidogenic stage followed by a solventogenic stage. This fermentation process is known as ABE production [158].

The microorganisms used for butanol, acetone, ethanol are production usually formed by *Clostridia* bacteria, these bacteria can degrade a number of toxic chemicals by producing chiral products which are difficult to make by chemical synthesis[159]

Currently butanol is produced from the fermentation of corn, cassava or molasses as substrates[160, 161]. Different types of biomass such as wheat straw[162, 163]rice straw [164], barley straw [165], corn stover[166], corn cob and fibres [167], palm kernel cake [168], cassava starch [169], pinewood and timothy grass [162], switch grass [170], have been used as substrates for ABE fermentation by numerous *Clostridium* strains [155]. MSW

has also been applied to reduce the cost for the biofuel market and has been shown to be more sustainable offering a lower carbon footprint and reduced GHG emissions [152]. Some studies have applied domestic organic waste (DOW) as a substrate for butanol production, using steam explosion and enzymatic hydrolysis for the washed and dried DOW produce using *Clostridium acetobutylicum* DSM 1731 produced 1.5 and *C. beijerinckii* B-592 0.9 g/L ABE and *Clostridium* LMD 84.48 1.9 g/L Isopropanol, Butanol, Ethanol (IBE) [171].

ABE fermentation is also used with domestic organic waste and *C. acetobutylocum* in a batch fermentation [171].Utilization of such waste materials improves the economy of butanol production [172].

2.3.3 Organic acid production from municipal solid waste

Organic acids are promising bio-energy products that could be produced using renewable carbon sources and microorganisms but are not currently produced at a large-scale processes. However, citric, lactic and succinic acids are three products at different stages of industrial development [173].

These acids are produced naturally by microorganisms, or are at least natural intermediates in major metabolic pathways. These acids are important for example succinic, fumaric and malic acid could replace the petroleum-derived commodity chemical maleic anhydride [174](Fig2.5).

To produce organic acids, various cheap substrates has been selected such as red lentil flour in India [175], kitchen waste in Japan [176], barley hydrolysates in the EU [177] and oat [178] or liquefied corn starch from cassava bagasse [179].

- **Citric acid**

Citric acid is widely use in the food and pharmaceutical industries. 70% of the food industry is dependent on citric acid followed by about 12% for the pharmaceutical industry and 18% for other applications [180]. Citric acid can be obtained by chemical synthesis by the filamentous fungus *Aspergillusniger*. In addition to fungi, yeast have been applied and developed as a microbial cell factory for citric acid [181]. *Yarrowialipolytica* is also used for the production of citric acid from carbon sources, such as glucose and sucrose [182].

Various agro-industrial residues such as apple pomace, coffee husk, wheat straw, pineapple waste, mixed fruit, maosmi waste, cassava bagasse, banana, sugar beet cosset and kiwi fruit peel have been investigated for their potential to be used as substrates [183].

Nowadays production of citric acid is approximately 1.6 million tons. There are many parameters that help to get highly efficient biotechnological production of citric acid such as “high substrate concentration, low and finite content of nitrogen and certain trace metals, thorough maintenance of high dissolved oxygen, and low pH”. Currently the production of citric acid is approximately 1.6 million tons (t) [184].

- **Lactic acid**

Lactic acid has been widely applied in the food, pharmaceutical, leather and textile industries and as a chemical feedstock. Currently, lactic acid is used as starting material to produce biodegradable polymers which are then used in medical, industrial and consumer products[185, 186]. The acid is produced by *Rhizopousoryzae* using SSF with sugarcane bagasse [187] or by *Lactobacillus paracasei* in solid-state conditions using sweet sorghum [188].

- **Succinic acid**

Currently, the succinic acid market is small at around 16,000 tons per year; this acid could replace petroleum derived maleic anhydride, which has a market volume of 213,000 tons/year. Deriving succinic acid from petroleum causes environmental pollution [189]. Microorganisms like *Escherichia coli* and filamentous fungi, including *Penicillium simplicissimum*, have been shown to naturally accumulate succinic acid [190].

- **Gluconic acid**

Gluconic acid is used widely in the food, pharmaceutical, cement, textile and chemical industries and is in high demand at 50,000–60,000 tons/annum. Gluconic acid is an oxidative product of the glucose industries[191, 192]. Solid state fermentation (SSF) and Sub merged Fermentation (SMF) have been used to produce gluconic acid using *A. niger*[193]. Various substrates have been used for gluconic acid production such as sugarcane molasses which have a high economic benefits in-terms of cost, by using SMF, many studies have applied SSF for gluconic production to reduce the cost [194].

- **Oxalic acid**

Oxalic acid and their salts can be used as a bleaching agent, in detergent formulation and as a metal polisher because of its capacity for reducing iron and other metals compounds [195]. Oxalic acid is also used as a mordant in dyeing processes. There are two ways to produce oxalic acid by either chemical or biotechnological processes, a chemical method uses formic acid salts (heating sodium

formate and treating the resulting oxides with sulphuric acid) or by carbohydrate oxidation by nitric acid [196]. Oxalic acid can be produced using biotechnological methods which include using microorganisms such as *Cyanobacteriae*[197], brown rot fungi [198] and other fungi, such as *Penicillium*[199], these organisms secrete oxalic acid at low concentrations. *A. niger* produces not only oxalic but also citric and gluconic acids according to the operating conditions [200]. Oxalic acid production efficiency depends on factors such as C- and N-source and the initial medium pH as well as the culture/broth pH during fermentation[201].

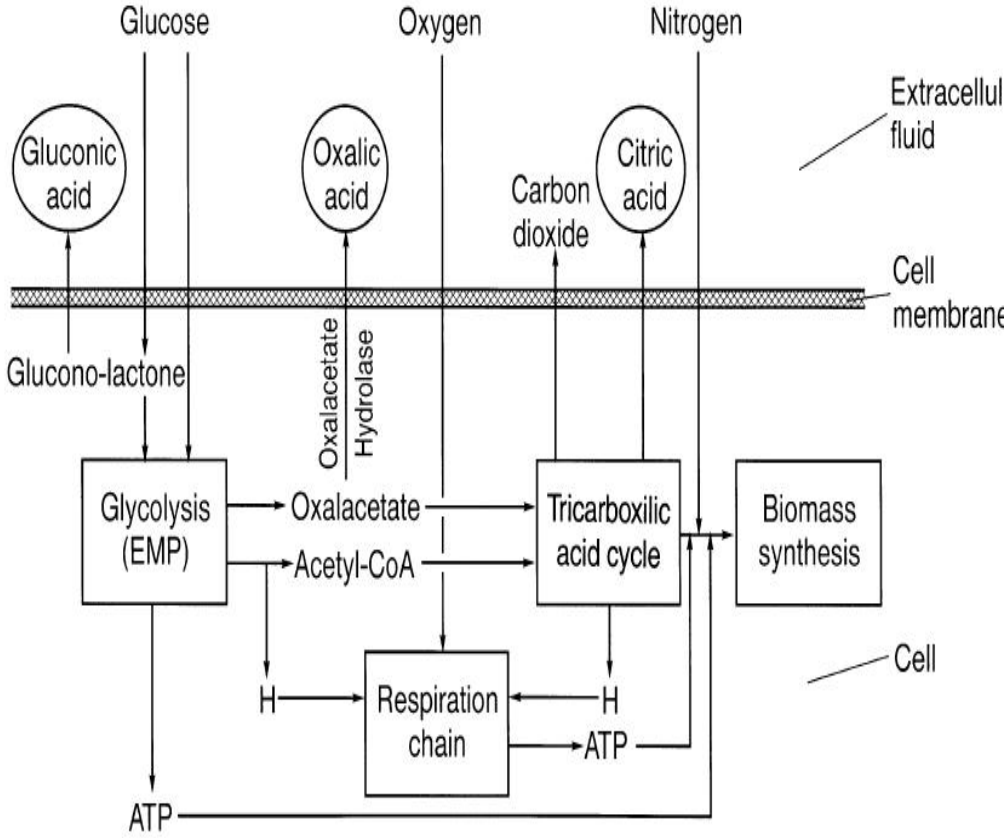

*Fig.2.5 Metabolic pathway for citric, gluconic and oxalic acid synthesis in A. niger***[196]**

2.4 Enzyme Production

2.4.1 Use of microorganisms for enzyme production from biomass and MSW

Solid state fermentation (SSF) is currently used for the production of various commercial enzymes [132]. These include those enzymes involved in the degradation of biomass. The substrates used in SSF can be classified into two categories: inert materials, which only act as an attachment for the microorganism and non-inert materials, which not only function as an attachment but also supply nutrients to the microorganism [202]. Several parameters need to be taken into consideration to insure a successful SSF process these include environmental parameters (temperature, pH, water content and activity) and the carbon source (biomass, substrate concentration, CO_2) [18].

pH plays an important role for cellulase production and the impact of initial pH of the culture medium has been extensively investigated. Research has revealed that the maximum cellulase activity from corn stover was obtained at pH 2 [203], at optimal temperature the optimal pH is 3-6 using fungi [204]. For SSF, it is difficult to monitor the pH and is normally not controlled during the SSF process and can only be adjusted at the beginning of the process [205]. It has been reported that in the first 4 days of SSF the initial pH drops and then increases after 8 days using rice straw [206]. The initial decrease in pH is due to the formation of organic acids and consumption of ammonium salt in the fermentation media[207].

Temperature, has an obvious effect on germination of spores [204]. The optimal temperature for *A. niger* growth is room temperature because this is similar to the natural habitat of the fungi, which is classified as a mesophilic microorganism [208].

Moisture is a crucial factor which affects metabolite production in SSF, because when the moisture level is low the solubility of nutrients decreases[209, 210]. However, high levels of water in the SSF media means that substrate particles will be surrounded by a thick layer of water, these particles stick together and limit the diffusion of air between the particles and the immediate surroundings [211]. The presence of water helps to swell the substrate and facilitates absorption of the nutrients from the substrates for growth and metabolic activities [212]. The nature of the substrate, porosity, specific surface area the requirements of microorganisms and the type of end product determines the optimal moisture conditions [213].

Inoculation size, for SSF inoculums preparation include spore suspension, mycelia disc, and mycelium suspension and pre-inoculated substrate [205]. Initially spores attach to the outer surface of the substrate particles and grow slowly, multiplying and penetrating into the substrate [214]. Optimal spore suspension concentration used in research is approximately 10^6 spore/mL[206, 215].

Incubation period has a significant role but maybe affected by several factors, such as the presence of different ratios of amorphous to crystalline cellulose [216]. The first signs of fungal growth were reported on day two of SSF for cellulase enzyme production and after 7 to 11 days the fungus completely colonised the substrate depending on the type of substrate used[217, 218]. During the colonisation phase of fungal growth, extracellulase enzyme was produced to degrade the lignocellulosic substrate into small particles, which helped fungal growth as a nutrient source [219].

Supplements - to increase cellulase activities some type of supplements such as carbon and nitrogen sources can be added to the substrate [220]. Generally cellulose in a lignocellulosic substrate acts as an essential carbon source, also fungal and cellulase production can be stimulated by nitrogen source, peptone can be used as a nitrogen source and is able to increase enzyme production, it's essential to have the proper combination of nitrogen source, lignocellulosic substrate and fungal strain for maximizing cellulase production [221]. Phosphorus, trace elements and other minerals can also be supplemented into the SSF media and play important roles, phosphorus helps the formation of phospholipid bilayers in the fungal cell membrane [222]. Addition of a surfactant such as Tween 80 and triton X-100 to the fermentation medium can help to improve the permeability of fungal cell membrane thus allowing the secretion of cellulase in a more rapid manner [223]. Some trace elements such as Zn^{2+}, Ni^{2+}, $Mn^{2+}$and Co^{2+}which serve as cofactors, may enhance cellulase enzyme production [224]. The presence of heavy metals could also interfere with energy supplying system for cellulase production for example cellulase of *P. chrysosporium* in liquid medium was inhibited in the presence of 50–150 ppm Cd^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+}. At 150–300 ppm Mn^{2+}or 300 ppm Cd^{2+} or Co^{2+}, no cellulase activity was detected[225, 226].

Particle size, the surface area plays an important role for microbial attachment, mass transfer of various nutrients and substrates and subsequent growth and product formation[227].

Type of lignocellulosic substrate, selecting a substrate that is able to support fungal growth, stimulates cellulase production and contains sufficient nutrients is particularly important. Selecting a substrate that enables the anchorage of fungi during fungal growth is also an important criterion before applying it for SSF [228]. In addition, there are many other approaches being taken to enhance cellulase production, such as genetic modification (mutagenesis, heterologous expression) of fungal strains and co-culture of different fungal strains [205].

2.4.2 Application of SSF using various biomass

SSF has been employed for the production of antibiotics, surfactants, biocides and enzymes [202], these products can be produced using bacteria, yeast and fungi. These microorganisms are capable of growth on solid substrates, among these microorganisms filamentous fungi have been commonly employed due to their physiological capabilities and hyphal mode of growth under conditions of low moisture [229]. Potential applications of SSF included:

I. Production of commercial products.

Industrial residues can be converted into valuable products, for example coffee (pulps and husks), soybeans, cassava husk and bagasse, sugarcane bagasse, sugar beet pulp, fruit wastes, palm tree wastes bio-converted into single cell protein, organic acids like citric and lactic acids, amino acids, pigments, antibiotics, mushrooms, bio-pesticides, gibberellic acid, flavour and aroma compounds[229].

II. Environmental control

The SSF process helps in the biodegradation of hazardous compounds, use of SSF has shown promise for the biological detoxification of industrial wastes and insecticides and for pest control in crops [202].

III. Food industry products

SSF has been used in the production of food additives or flavouring compounds [230], these compounds are produced via chemical synthesis or by extraction from natural materials [231]. Several microorganisms have the ability to produce aroma compounds from agro-industrial

wastes [232]. Some aroma compounds such as monoterpene alcohols and isoamyl acetate have been produced by *Kluyveromycesmarxianus* from cassava bagasse [233].

IV. Enzyme production

Several enzymes can be produce by SSF using lignocellulosic wastes [234], recent studies confirmed that SSF is the best system for producing enzymes and better than SMF with regards to yields obtained[235, 236]. Generally, the most common industrial enzymes produced using SSF are proteases, cellulase, ligninases, xylanases, pectinases, amylases, glucoamylases; also production of inulinases, phytases, tannases, phenolic acid esterases, microbial rennets, aryl-alcohol oxidases, oligosaccharide oxidases, tannin acyl hydrolase, a -L-arabinofuranosidase[202].

The most common enzyme produced is cellulase enzyme **"**Cellulases are a complex enzyme system, comprising endo-1,4-b -D-glucanase (EC-3.2.1.4), exo-1,4-b-glucanase (exocellobiohydrolase, EC-3.2.1.91) and b-D-glucosidase (b-D-glucoside glucanhydrolase, EC-3.2.1.21)"[202]. Cellulases are one of the largest groups in the structural classification of glycosyl hydrolyses, this classification is based on variability of catalytic domains and does not consider variability in cellulose binding domains[235, 236]. Cellulase is recorded as the third largest industrially produced enzyme, and is applied widely in cotton processing; paper recycling, juice extraction, detergents and as an animal feed additives. Cellulase is also commercially produced for saccharification of biomass[236, 237].

The enzyme is produced by various microorganisms (fungi and bacteria),including *Aspergillus* fungi [238]. Furthermore, the most investigated and genetically improved for fungi enzyme production are the *Trichoderma spp.*[239]. Generally, *Aspergillus* and *Trichoderma spp*. are well known efficient producers of cellulases [240] for example *T. reesei* produces 2 Cellobiohydrolase (CBH), 8(endo-B-1-4-glucanase (EG) and 7 B- glucosidase [241]. Commercially most enzymes are produced from these two strains of soft rot fungi, but *T. reesei* is not capable of producing substantial amounts of B-glucosidase, whilst *A. niger* produces a cellulose system lacking endo and exoglucanase[223].

In addition, the most important cellulolytic microbes which are able to produce cellulase obtain their energy primarily from carbohydrates and are unable to use lipids or proteins [235]. Fungi possess the ability to secret large amounts of extracellular protein; such strains are most suited for production of high levels of extracellular cellulase. The most commonly studied cellulolytic organisms is *T. reesei*[242].

SSF is gaining interest as a cost effective technology for cellulase enzyme production and bioconversion of lignocellulosic biomass using cellulolytic microorganisms. Comparing liquid culture with solid state culture for cellulase enzyme production, SSF has been shown to closely resemble the natural habitat of filamentous fungi, also enzyme titre produced from SSF is superior compared to the titre produced via SMF[243].

Advantages of SSF over SMF: SSF is a process which requires smaller amounts of water and therefore the cost of the process can be greatly reduced [244]; SSF has been shown to produce higher concentrations of enzymes; higher fermentation productivity and has a lower demand on the sterility of the equipment[245].Finally, the crude enzyme extracted from SSF can be applied directly to hydrolyse the lignocellulosic substrate [205]. Studies have reported a higher yield of cellulase from *T. reesei* using SSF compared with SMF processes [246]. Furthermore, some studies have proposed that SSF application could be a better technology for commercial production of cellulase with low cost, and by using naturally available cellulose sources [202].

2.4.3 Mechanisms of SSF for cellulase enzyme production

There has been extensive research on cellulase enzyme production [247]. For example the rate-limiting step for crystalline cellulose degradation has yet to be determined. It is not clear which segment of the cellulose fibrils cellulase binds to. A further unknown is how cellulosomes are able to efficiently catalyse the hydrolysis of cellulose and how free cellulose binding modules stimulate cellulase hydrolysis [248]. Finally, how mixtures of cellulases hydrolyse both crystalline and amorphous regions in bacterial cellulose, while most individual enzymes only seem to degrade amorphous regions [249].

Besides wheat straw, other cheap materials, such as banana peel, rice straw, corn cob residue, rice husk, wheat straw, banana fruit stalk, and coconut coir pith are all being used for cellulase production[250, 251] (Table 2.1).

Table.2.1 Applying various Substrates and Microorganisms for cellulase enzyme production

Substrate	Microorganism	Yield	Reference
Rice barn and corn straw	*Trichoderma reesei*	Cellulase18.5 IU/mL	[252]
Egg shell waste	*Neurosporacrassa*	Cellulase 2.30U/mL	[253]
Water hyacinth	*Trichoderma reesei SEMCC-3.217*	Cellulase 13.4 FPIU/g dry solid	[254]
Xylose industry	*Trichoderma reesei ZU-02.*	Cellulase (158 IFPU/g)	[255]
Vinegar industry	*Trichoderma koningii AS3.4262*	Cellulase 6.90 IU/g of substrate dry matter (SDM)	[256]
Wheat bran	*Trichoderma reesei*	Cellulase 2.63 U/ mL	[257]
Sugar cane bagasse	*Trichoderma reesei NEEL 11460*	Cellulase 154.58U/gds	[258]
Sweet potato	*Bacillus sp*	Amylase and cellulase 28 U/mL	[259]
Oil palm in the form of empty fruit bunches	*Trichoderma harzianum T2008*	Cellulase 8.2 U/gm	[260]
Saw dust and bagass	*Aspergillus niger*	Cellulase Sawdust gave the best result with an enzyme activity value of 0.0846 IU/mL while bagasse gave 0.0682 IU/mL	[261]
Rice bran	*Trichoderma reeseii QM9414 and T. reesei MCG77*	Cellulases 1.1635 U/g	[262]
Rice straw	*Acremoniumcellulolyticus*	Cellulases and hemicellulases DBMc, 10.8 FPU/mL and WDMc, 10.4 FPU/mL	[263]
Cocoa (Theobroma cacao) meal	*Aspergellus niger*	Cellulase 14.18 U/mL and xylanase11.86 U/mL	[264]
Banana waste	*Bacillus subtilis (CBTK 106),*	CellulaeThe optimal ®lter paper activity (FP Ase) of 2.8 IUgdsÿ1, CMCase activity of 9.6 IUgdsÿ1 and cellobiase activity of 4.5 IUgdsÿ	[265]

2.5 Composting and fertiliser

2.5.1 Compost and fertiliser production from municipal solid waste

Waste contain various levels of metals, some of them are discharged directly or indirectly in to the environment, which can cause serious environmental pollution, and threaten life [266, 267]. These metals are classified into the following three categories: toxic metals (such as Hg, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, As^{3-}, Co^{2+},Sn, etc.), precious metals (such as Pd^{2+}, Pt, Ag^{+}, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) [266].

In recent years, leaching which is used to remove metals from aqueous solution has been carried out using methods such as chemical precipitation, ion exchange, electrochemical treatment membrane technologies, adsorption on activated carbon etc[268].

The major advantages of bio-sorption over other methods include low cost, high efficiency, minimisation of chemical and biological sludge, no additional nutrient requirement, regeneration of bio-sorbent, and possibility of metal recovery [269]. The bioleaching process has many advantages: economically, the process is cheap and simple to operate, has lower energy requirement; environmentally, the process is environmentally friendly because there are no by-products e.g. gaseous pollutants are produced in bio-hydrometallurgy [270]. In addition, bioleaching has potential for the environmental clean-up of mining sites, treatment of mineral industrial waste products, detoxification of sewage sludge and for the remediation of soils and sediments contaminated with heavy metals [271, 272].

Microbial bioleaching is based on the natural ability of microorganisms to transform solid compounds to a soluble and extractable form. This may involve enzymatic oxidation or reduction of the solid compound, or an attack on the solid compound by metabolic products [273].

Bioleaching has been defined as the interaction between metals and microorganisms, which leads to solubilisation of metals in a solid form. Additionally, the term "bio-oxidation" is also used [274]. In addition, leaching can be direct (i.e., physical contact between microorganisms and solid material) or indirect (e.g., bacterial oxidation of Fe^{2+} to Fe^{3+} which catalyses metal solubilisation as an electron carrier) [275].

Various microorganisms can be applied for bioleaching processes such as autotrophic bacteria, heterotrophic bacteria, and fungi. Fungi belonging to the *Aspergillus* and *Penicillium*genus have been the most extensively studied [271],marine algae (eg*Sargassumnatans)*, yeast (eg. *S. cerevisiae*) have also been studied. Fungi are able to solubilise metal compounds by excreting acid, mainly in the form of organic acids, using heterotrophic fungi results in a faster leaching process and with a shorter lag phase; for example by using MSW fly ash as the substrate *Aspergillus thiooxidans* required 1-3 months, while *A. niger* only requires 2-3 weeks to complete the leaching process [276]. Addition of organic acids helps to increase the solubility of metal ions at non-acidic pH values by chelating, in addition, complexation between metal ions and organic acid anions may reduce their toxicity [271].

Fungi can withstand a much wider pH range, typically from 2 to 7, media composition and leaching environment[195, 271].

The organic acids are produced by fungi in complexes with metal ions and enhance metal solubilisation, these complexes help to reduce the toxicity of heavy metal ions to the fungi, and thus the fungi are fairly resistant to heavy metals [195]. Microorganisms are able to mobilize these metals by various reactions[277].

Currently, *S. cerevisiae* is also used for heavy metal bioremediation, yeast bioleaching strains are affected by many factors such as pH, redox potential, presence of anions and soluble organic compounds [278]. *S. cerevisiae* has advantages for bioremediation as the yeast is a mediocre bio-sorbent, easily cultivated at large scale, has a high yield of biomass, can be easily manipulated genetically and the complete genomic sequence is available [279]. In addition, research has shown that *S. cerevisiae* has the ability to remove toxic metals by accumulating metals in an external layer of the cell wall [280].

Due to ash being rich with nitrogen, phosphorous and potassium which are the main nutrients for plant growth, these MSW leachates could be used as a replacement for commercial fertilisers. In addition, application of lime or alkali substance can reduce soil acidity. However, the heavy metals present in MSW ash are toxic for plants and animals, removing metals makes it more applicable in the agriculture field [281]. One study has shown that MSW fly ash, bottom ash and combined ash can influence plant growth in a positive manner. Growth of alfalfa and Swiss chard in ash-amended soils was similar to that in soils amended with phosphorous and potassium fertiliser, indicating that MSW ash can supply essential nutrients for plant growth[6].

2.5.2 Mechanisms of Bioleaching

In the environment, heavy metals are present at low concentrations in the soil; however, these metals can be toxic at higher level such as zinc and copper, while others like aluminium and lead are only known for their toxicity. Soil acidity helps to dissolve metal containing minerals and increases uptake by plants, which causes metal toxicity as the plasma membrane of root cells is often damaged by exposure to toxic metals, resulting in leakage of cellular solutes. However, there are some plants called edaphic ecotypes which can tolerate the presence of heavy metals in the soil [282].

Nowadays, there are many causes increasing the concentration of heavy metals in the environment [283]. The composting process has been defined as the biological decomposition of organic matter by adverse population of microbes under controlled aerobic condition to form stable humus –like end products [284].

Fungi can tolerate metals using two mechanisms: firstly, extracellular (chelation and cell-wall binding) sequestration, this step avoids metal entry into the cell

[285]. The second mechanism is the intracellular physical sequestration of metal either by binding to proteins or other ligands preventing damage to cellular targets. In this mechanism metal transport proteins may be involved in metal tolerance, either by extruding toxic metal ions from the cytosol out of the cell or by allowing metal sequestration into the vascular compartment[286, 287](Fig 2.6).

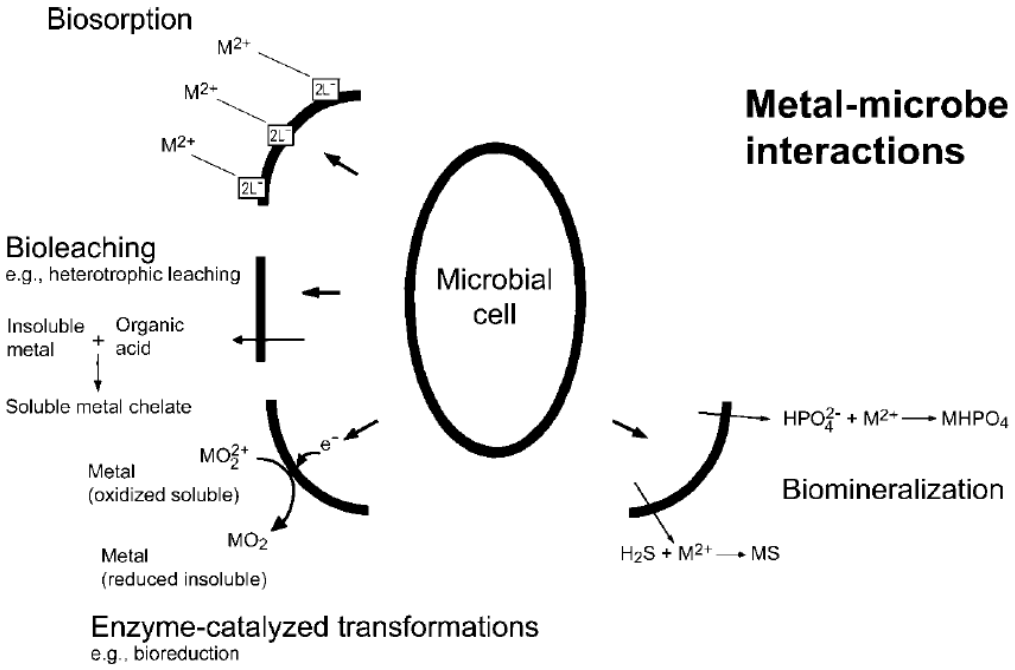

Fig.2.6 Mechanism of metal-microbe interactions that can be harnessed for bioremediation application **[288].**

The ability of microorganisms (bacteria and fungi) to mobilize and leach metals from solid materials is based mainly on three principles [277]:

I. Redoxolysis (oxidation and reduction reactions)

Divided into direct and indirect mechanisms: **direct mechanism**: metals are solubilised through enzymatic reaction, through physical contact between the leaching materials and microorganisms. Leaching a metal from a solid structure may occur through oxidation or reduction reactions. This involves the transfer of electrons either from the solid structure to an electron acceptor like O_2 called oxidation or the injection of electrons into the solid structure from an electron donor like H_2termed reduction [289].

Direct bacterial leaching can be described according to the following reaction:

$$MeS + 2\,O_2 \xrightarrow{\text{bacteria}} MeSO_4$$

In the above, MeS is the metal sulphide [290], direct leaching benefits the autotrophs, because they conserve energy during the process [291].

Indirect redox mechanism causes oxidation of ions originating from the microbial oxidation of ferrous iron (Fe^{2+}) compounds, which helps to dissolve metals from the solid chemically. Ferric iron is an oxidising agent [277]. Redoxolysis of fungal bioleaching is a reduction of ferric iron and manganese, mediated by oxalic acid in an acidic environment [195]. Indirect leaching of metal sulphides can be described by the following reactions [273]:

$$2\,Fe^{2+} + 2\,H^{+} + \tfrac{1}{2}\,O_2 \xrightarrow{\text{bacteria}} 2\,Fe^{3+} + H_2O$$

$$2\,Fe^{3+} + MeS \xrightarrow{\text{abiological}} Me^{2+} + S + 2\,Fe^{2+}$$

$$S + H_2O + 3/2\,O_2 \xrightarrow{\text{bacteria}} H_2SO_4$$

II. Acidolysis (the formation of organic or inorganic acids)

In acidolysis, organic acids are formed by bacterial metabolism resulting in organic acidolysis, complex and chelate formation (e.g. production of citric acid or gluconic acid by *A. niger* or *P. simplicissimum*, and sulphuric acid by *A. ferrooxidans* and *A. thiooxidans*) [292]. The acidolysis mechanism is solubilization of heavy metals by

bio-produced acids, this step plays the most important role in bioleaching process [293].

Mineral solubilisation occurs simultaneously in the presence of ligands under acidic conditions. A kinetic model of the coordination chemistry of mineral solubilisation has been developed which explains the dissolution of oxides by protonation of the mineral surface and the surface concentration of suitable complex forming such as oxalate, malonate, citrate and succinate [292]. The protons and the oxygen combine with water and the metal is therefore detached from the surface [195].

$$MeO + 2\,H^{+} \longrightarrow Me^{2+} + H_2O$$

In the above, MeO is the metal oxide.

Protons are obtained from the acids produced, and the maximum amount available determines the amount of metal oxides solubilized. This process is usually fast and it is the most important mechanism for fungal bioleaching. In the above, MeO is the metal oxide [294].

III. Complexolysis (the excretion of complexing agents)

The third mechanism including extraction of metals by complexing agents, to form soluble metal complexes, organic acids can leach metals through complexation. Complexolysis is a slower mechanism when compared with acidolysis, metal dissolution depends on the complexing capacity of molecules and bonds in the solid particles, so if the bond between metal ions and ligands are stronger than the lattice bonds between metal ions with solid particles, the metal will be successfully leached out from the solid particles [291]. Additionally, the complexation of heavy metals can reduce metal toxicity to the fungi when high concentrations of metals are present [271].

IV. Bioaccumulation

Bioaccumulation is another important mechanism or process in fungal bioleaching. in this process the mycelium functions as a "sink" for the metal ions and causes continuous solubilisation of the metals by the accumulation of metal ions from the leaching solution through active metabolic reactions and passive adsorption, this continuous solubilisation upsets the equilibrium between the solid and dissolved metal. In addition, the fungal cell wall contains many different functional groups (e.g. hydroxyl, amine, carboxyl, phosphate and sulphydryl groups), which are able to bind metal ions to a greater or lesser extent [295].

2.5.3 Factors Influencing Bioleaching

The effectiveness of leaching depends largely on the efficiency of the microorganisms, chemical and mineralogical composition of the material to be leached and leaching conditions. The maximum metal extraction can be achieved only when optimum conditions are employed [296].

Nutrient Culture Media - Effective microbial growth, biosynthesis of new cells and metabolism requires nutrients in order obtain to get maximal growth some selective nutrients help in the production of the necessary metabolites for bioleaching. The presence of ammonium, phosphate and magnesium salts have been shown to increase growth rates; inorganic iron and sulphur compounds are required for chemo-litho-autotrophs [296]. For leaching metals some nutrients help to increase the production of organic acids and scavenge metals [297]. Research has revealed that potassium deficiency increased oxalic acid production significantly by tree seedlings colonised by the fungus *Paxillus involutus*, while Mg^{2+} deficiency increased oxalate production in both mycorrhizal and non-mycorrhizal tree seedlings in the same experiment [298]. Furthermore, carbon source plays an important role in the determination of quality and quantity of organic acid production [186].

Microbial type: There's a diverse range of mechanisms that microbes can adopt in bioleaching processes because of difference in their metabolic activities. These differences can be intra- or inter-species, depending on other factors such as exposure to high levels of heavy metals. For example, *Aspergillus* and*Penicillium* have mutants that can withstand heavy metals and a genetic adaptation (mutation) [186]. Aerobic and anaerobic microorganisms are both involved in many biohydrometallurgical processes; these microorganisms require adequate oxygen or CO_2 to get their optimum growth and activity. Aeration, shaking or stirring are some of the common methods employed in the laboratory to supply oxygen or CO_2 to the microbes because of insufficient oxygen or CO_2 cause slow microbial growth as a result there is a decrease in the metals leaching rate [271].

pH and temperature: Optimal microorganism growth is pH dependent as is solubilisation of metals. It is known that a low pH is the most favourable condition for metal solubilisation[299].Temperature plays a role in a bioleaching process, an optimal temperature should be maintained according to the optimal microbial growth condition. Mesophilic microbes grow at temperatures of

28-35°C, while thermopiles grow at temperatures above 50°C [271, 296].

Metal Resistance of Microorganisms: Leaching metals from the substrate is accompanied by an increase in metal concentration in the leachate. Generally heavy metals exhibit toxic effects due to four factors: (1) the blocking of functional groups of biologically important molecules, (ii) the displacement and /or substitution of essential metal ions from biomolecules and functional cellular units, (iii) the induction of conformational changes of polymers, and (iv) the influence on membrane integrity and transport processes [300]. In addition, highly toxic metals in a substrate could inhibit microbial growth, and thus decreases the bioleaching rate and efficiency [301]. A high content of carbonate in the solid residue, increases the pH of the leaching solution and influences microbial growth on substrates such as fly ash [290].

Particle Size, decreasing particle size leads to an increase in surface area resulting in an increase in the contact area between the leaching agents and the solid particles; as a result there is an increase in the leaching yield. Research has revealed that the highest solubilisation rate occurs with a particle size of a few tens of microns [271]. The solid liquid ratio's used is another factor. Increasing the solid mass causes an increase in the amount of a toxic metals in the leaching environment thus, an optimum pulp density must be determined for the bioleaching process [271, 296]

Bioleaching Period, bioleaching requires a longer period to leach metals when compared with chemical leaching i.e., *Thiobacilli* is a slow growing bacterium that may require a few weeks to complete the bioleaching process. Fungi generally show a shorter lag phase and hence may bioleach at a faster rate [293].

Physicochemical factors,other physical factors include shaking, and aeration. Most of these remaining factors are interconnected [186].

2.5.4 Fertiliser or compost production from MSW

MSW is composed largely of kitchen and yard waste; these wastes have been composted by many municipalities [302]. The composting process converts organic waste material into a low cost product, that is suitable for agriculture [303]. For compost production, many factors have to be taken into the consideration such as economic and environment, municipal landfill capacity; costs associated with land filling and transportation of materials; adoption of legislation to protect the environment; decreasing the use of commercial fertilisers; increasing the capacity for household waste recycling and improved quality of compost products [304].

The main advantages of compost production are: reduction in volume of the wastes, kill pathogens, prevents germination of weeds in agricultural fields, and destroys malodorous compounds [305]. There is rising interest in organic composter production from MSW for agricultural use due to positive effects on biological, physical, and chemical soil properties(Iglesias-Jiménez and Alvarez, 1993; Hargreaves*et al*., 2008).

Physical soil properties,the primary benefits of MSW compost is that it has a high content of organic matter and low bulk density [306]. MSW compost contains a humic acid to fulvic acid ratio of 3.55 [307]. MSW compost has some other advantages such as increasing soil organic matter; increasing soil C/N ratio; [308]; the compost has a higher water holding capacity than the soil; it improves soil structure [306]; and increases aggregate stability [309].

Biological soil properties soil quality is determined by soil microbiological properties [310]. Addition of MSW compost to the soil increases N, C and S immediately and for up to one month, while for P, biomass requires five months [311]. Other advantages of adding compost are an increase in soil microbial biomass and soil respiration (an index of general metabolic activity of soil microorganisms) [312]. Another measure of soil microbial health is the activity of soil enzymes involved in the transformation of the principal nutrients [313]. Research has shown that trace metals have an effect on the biological activity in a soil after being applied with compost derived from MSW, due to the high level of trace metals, this effects depends on the time of application, their concentration, and soil characteristics [313]. To study the effects of MSW compost on soil biology should include metal analysis [310].

Chemical properties

pHApplying MSW helps to increase soil pH and has been highlighted as a major advantage. This increase in soil pH is due to the mineralization of carbon and the subsequent production of OH ions by ligand exchange as well as the introduction of basic cations, such as K^+, Ca^{2+}, and Mg^{2+}[314].

Electrical conductivity EC and salt effects, increasing salt content has a negative effect on soil which effects plant growth, the EC of the soil solution relates to the dissolved solutes content and salt content in the soil. Agricultural soils EC levels range from 0 to 4 dS/m, while MSW composts range from 3.69 to 7.49 dS/m [315]. Applying MSW compost at rates ranging from 40 to 120 Mg/ha has led to an increase in the EC content of soil EC [308].

Nutrients (N,P, and K),differences in leaching rate or availability for plants depends on the feedstock and

compost maturity (Ring and Warman, 2000). MSW compost contains nitrogen which could become available for the plant, the availability of N in MSW compost has been estimated at 10% in the first year after application with some reports of N release in the second year after application(Zhang*et al.*, 2006; Hargreaves*et al.*, 2008). Some other study reported N in MSW compostcould be available 6 months after application [316]. While, for P from MSW compost requires three consecutive years [317]. Studies have reported 10-50% P in MSW being available during both the first and second years after application [306].

Phosphorus and nitrogen content in MSW compost are not regulated by the Canadian Council of Ministers of the Environment (CCME) or the United States EPA (USEPA, 2000; CCME, 2005)

Potassium is another important mineral for plant growth and was found to be increased even when low amounts of MSW derived compost was applied around 36–48% of total K in the MSW compost was found to be available to the plant [306]. The total concentration macronutrient and metals that has been found in MSW composts is shown in Fig 2.7.

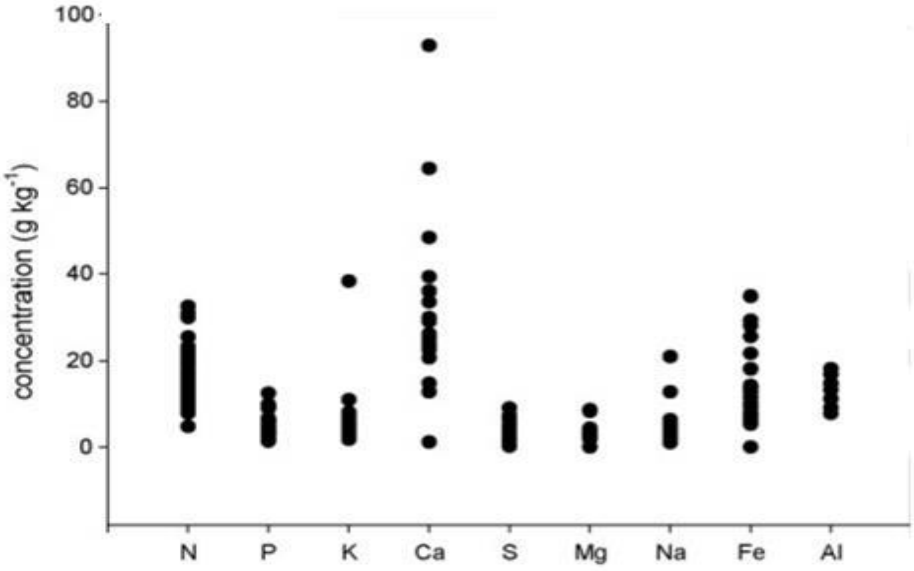

*Fig.2.7 Total concentrations of the macronutrients and metals present in MSW compost***[318]**

III. CONCLUSION

From the literature is clear that wastes especially municipal solid wastes can be used as a sustainable resource for bioenergy products such as biogas, biofuel, bioenzyme and biofertaliser. Generally, pre-treatment methods showed a significant increasing at bioenergy products,previous paper shown viability of MSW in bioenergy production published by[319-321].

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