BIOMASS AS A RENEWABLE SOURCE OF CHEMICALS FOR INDUSTRIAL APPLICATIONS

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Abstract

Worldwide demand for cleaner burning fuels and 'clean' chemicals has been increasing from the global issues of environmental concern. This lead to a greater utilization of renewable resources to replace the old and existing fossil based feedstock for liquid fuels and chemicals. The ability to re-grow harvested biomass and recapture the carbon emitted to the atmosphere through photosynthesis allows the possibility of carbon neutrality encouraged the use of biomass. Moreso, the unstable rise of oil prices, the negative effects of petroleum on the environment and the advantages of biomass towards sustainability of resources accelerated the development and utilization of unused biomass. This paper reviewed some of the potentials of biomass as a source of chemicals for industrial applications. Pyrolysis is considered to be one of the most employed technologies for the conversion of biomass into bio-oil, char and gases. The utilization of biomass for chemical manufacture can significantly eliminate the harmful effects of fossil based chemicals on the environment.

Keywords: Chemical, renewable resource, biomass, sustainability, environment, pyrolysis

1.0 Introduction

The use and modification of renewable resources today involved a series of important processes that has greatly influenced human activities. Their application can be found in energy sector, plastic, fertilizer, textile, pharmaceutical, paints and coating, food industries etc (James and Fabien 2008). As such, they became a vital research area for valued alternatives for fossil-based raw materials. Adequate utilization of crops and the use of waste to produce energy, chemicals and materials are generating a wide spread of interest globally. This growing interest in the replacement of fossil-based chemicals with bio-chemicals is as a result of the anticipated depletion of petroleum coupled with the increased public awareness on the effect of emission of greenhouse gases to global climate (James and Fabien 2008; Mir Naiman Ali et al.2011).

Biomass mainly refers to any organic matter derived from agricultural or forestry sector that is available on a recurring basis (sustainable). It comprises of C, H, O and N;-a composition similar to fossil feedstock which has C and H (James and Fabien 2008). As such similar products can be obtained from biomass with that of petroleum counterparts (Xu et al. 2008). Carbohydrates (which are the currently limited non-food uses for starch), cellulose and hemicelluloses are the largest renewable sources of carbon (James and Fabien 2008).

The application of new and advanced technologies in chemical processing such as fermentation provide new opportunities for the conversion of these enormous natural resources (biomass). Pyrolysis is considered to be one of the most employed technologies for the conversion of biomass into bio-oil, char and gases depending on the pyrolysis conditions. Bio-oil is a polar and high density oxygenated liquid that can be used as a fuel and for the production of chemicals (Yang et al. 2006; Senzor et al. 2006; Amin and Asmadi 2008; Misson et al. 2009; Khor et al. 2009; Razuan et al. 2010; Gou et al. 2011; Arami-Niya et al.2012). The advantages of using biomass rather than petroleum to manufacture chemicals include opportunities for less pollution, no net CO2 contribution to the atmosphere, more biodegradable and sustainable products and, in some cases, lower cost (Brigewater and Peacocke 2000; Xu et a.l 2008; Jin and Enomoto 2009; Sukiran et al. 2009; Rivilli et al. 2011; Melligan et al). It has been found that many biomass derived chemicals have economical advantages, particularly for some functionalized chemicals (Xu et al 2008).The most important driving factor which resulted in the gradual shift toward the use of renewable biomass resources for chemical manufacturing is the implementation of the bio-refinery concept (Brigewater and Peacocke 2000; Yanik et al 2007; James and Fabien 2008; Xu et al 2008; Abdullah et al 2010; Brigewater 2011).

A bio-refinery also integrates a variety of processing technologies when compared with petroleum refinery to produce multiple bio-products from various biomass sources. Such an approach will help maximize the value of the biomass and minimize no value by-products (James and Fabien 2008; Xu et al 2008; Gent 2009; Guo et al 2011; Himadri 2011). This paper reviewed some of the potentials of biomass as a source of chemicals for industrial applications as well as presenting a few examples of those chemicals and their application. It also highlighted some of the enormous benefits to be derived from biomass application against the petroleum based counterparts after critical environmental, safety and cost assessment.

2.0 Renewable Resources

Renewable resources are generally regarded as natural resources which are naturally replaced over a period of time (Simone 2002; John 2004). These resources are highly sustainable and cheap. They are parts of our natural environment and form our eco-system. In order to avoid exceeding the natural world's capacity to re-supply them, these resources must be adequately managed. Resources such as solar radiation, tides, winds and other natural elements as well as biomass are renewable resources of energy and chemicals are now called renewable resources while resources like gasoline, coal, natural gas, diesel, and other commodities derived from fossil fuels are non-renewable (Brown 2003).

2.1 Biomass Sources and Availability

Biomass is a renewable resource derived from agricultural or forestry sector which has been estimated to provide about 25% of global energy requirements (James and Fabien 2008; Briens et al 2008). In addition, biomass can also be the starting raw materials for a lot of valuable chemicals, pharmaceuticals and food additives. The applications of new and advanced technologies in chemical processing provide new opportunities for the conversion of these enormous natural resources (biomass).

Currently, the annual worldwide production of biomass is estimated to exceed 100 trillion kilograms (Brigewater 2011). In the United States alone, the 250 billion kilograms of wasted plant biomass produced each year far exceeds the current total consumption of 100 billion kilograms for organic chemicals, plastic resins, and fibers (Xu et al 2008). However, presently, only 5% of chemicals are derived from renewable resources (Xu et al 2008; Brigewater 2011).Unlike fossil fuels, a renewable resource can have a sustainable yield. Therefore, there is huge potential for bio-based chemicals to share markets with their fossil based counterparts. Figure 1.0 below gives some of the sources of biomass.

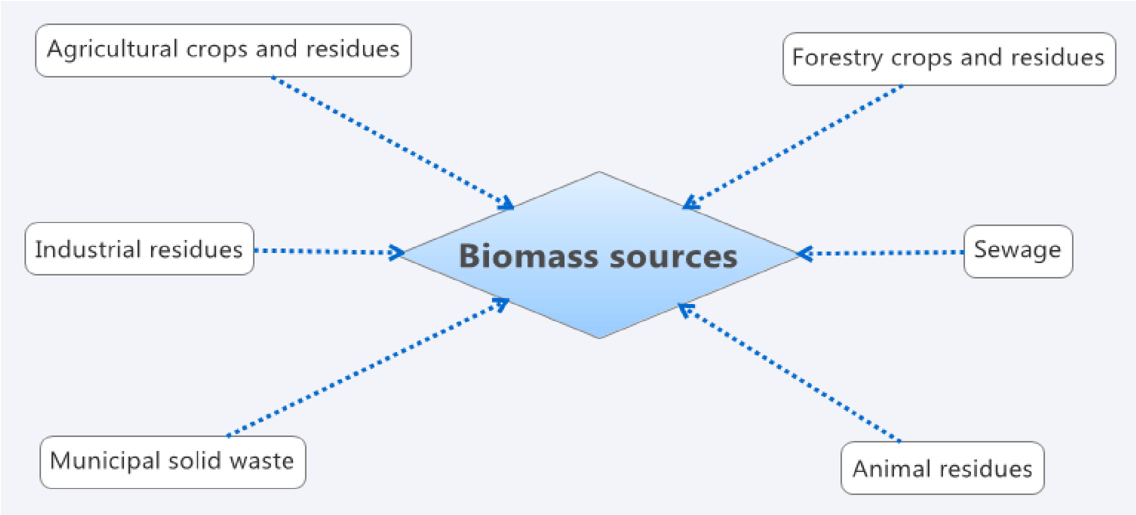

Figure 1.0: Sources of Biomass

2.2 Classification of Biomass

Carbohydrates are the most popular biomass feed stocks for commodity and specialty chemicals production. They by far, account for approximately 95% of the biomass produced annually (James and Fabien 2008; Xu et al 2008).They exists primarily in the form of polysaccharides, including starch and cellulose. Traditionally, starch has been used as a basic organic raw material by chemical industries. Many bulk chemicals and polymers can be produced by chemical modification or fermentation of starch and its monosaccharide derivative (D-glucose) (Xu et al 2008).

However, there is a growing concern about the competition between industrial and food applications of starch which lead to the provision of newer technologies and processes for the conversion of lignocellulosics biomass into glucose and xylose using microbes and other biological systems for fuel and biochemical production. Lignocellulosic materials are composed mainly of cellulose, hemicellulose and lignin. Various conversion routes have been applied and utilized for the conversion of lignecellulosic materials to ethanol and chemicals after much pretreatment procedures for effective conversion. These include biological, thermal, and chemical conversion technologies (Brown 2003; Briens et al 2008; Xu et al 2008; Jin and Enomoto 2009; Akshat et al 2010; Mohammeda et al 2011). Oils and fats of vegetable and animal origin are important renewable raw materials for “green” lubricants, surfactants, and alkyd resins in many industrial and pharmaceutical applications. Different non-ionic surfactants have been produced by changing the length of the hydrophobic fatty acid moiety and the degree of polymerization of the hydrophilic part (Werpy and Petersen 2004; Xu et al 2008; Ahmad et al 2010). In addition, a variety of plants, including some flowers such as poppies and rosemary which provide drugs, fragrances and flavors, have been used as a source of fine and specialty chemicals (Zhang et al 2007; Xu et al 2008; Ioannidou et al 2009).

3.0 Biomass conversion routes and technologies

One way of minimizing the negative effects of wastes and maximizing the value of biomass is to convert biomass into a variety of chemicals, biomaterials and energy. The summary for the basic conversion routes or pathways of biomass into its subsequent chemical products are given in Figure 2.0 below:

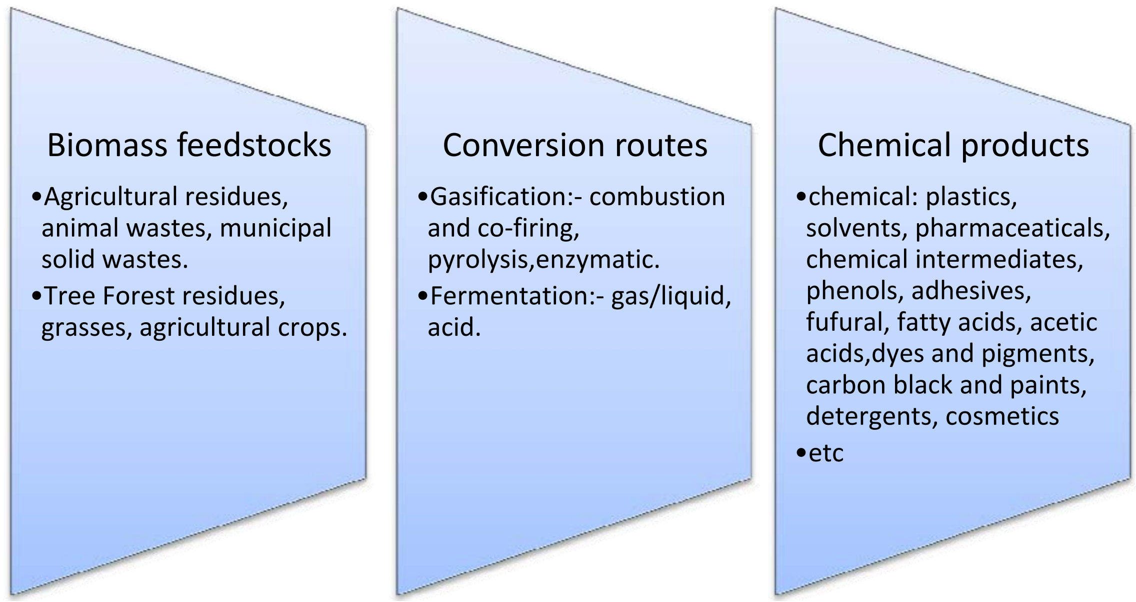

Figure 2.0: Summary of biomass conversion routes and corresponding chemical products. (modified from Bain 2004.)

The above conversion routes can be classified into either chemical/thermo-chemical or biological.

3.1 Thermo-chemical

Chemical conversions refer to processes which directly convert biomass to chemicals at high temperature and pressure and in the presence of a catalyst(Brigewater 2007). Some bulk chemicals, including levulinic acid and furfural, can be produced by treating biomass at high temperature for specific times in the presence of conventional mineral acid catalysts, such as hydrosulfuric, hydrochloric, and phosphoric acids (Brown 2003; James and Fabien 2008; Xu et al 2008; Jin and Enomoto 2009 ; Mohammeda et al 2011). However, low yield and significant volumes of side products, together with the use of corrosive chemicals, are challenging commercialization and environmental issues. A thermo-chemical process, generally referred to as gasification, partially oxidizes biomass into syngas, a fuel gas mixture consisting of hydrogen, carbon dioxide, nitrogen and carbon monoxide (Crocker and Crofheck 2006; Zhang et al 2007; Ioannidou et al 2009). The syngas can be converted to important chemical intermediates, including methanol, ammonia and oxy-alcohols (Crocker and Crofheck 2006; Xu et al 2008). However, this route is relatively slow and typically requires large, complicated and expensive equipment (Brigewater 2011).

Many efforts have been made to design innovative alternative pathways to effectively convert biomass to chemicals. The main area of focus is the catalysts efficiency through the improvement of size and shape of the catalysts. Advancement of efficient conversion processes have been reported as well (Xu et al 2008). Hydrothermal processing was the most promising for the conversion of biomass into acetic acid using supercritical water as a reaction medium. In addition, chemical conversions have been used to convert the chemical intermediates, which were produced from biological conversion, to final chemical products, including tetrahydrofuran and gamma-butyrolactone from 1, 4-diacids (succinic, fumaric, and malic), and 1,3-propanediolfrom 3- hydroxypropionic acid (Xu et al 2008 Jin and Enomoto 2009;).

3.2 Biological conversions

Biological conversions involve the utilization of biological enzymes or living organisms to catalyze the conversion of biomass into specialty and commodity chemicals. Overall, it is considered to be the most flexible method for conversion of biomass into industrial products (McMillan 2004). Biological conversions are not a new topic, but rather some commercial bulk chemicals, such as ethanol, lactic acid, citric acid and acetone-butanol, have been produced *via* yeast and bacterial fermentation processes (Xu et al 2008). Recently, there has been growing interest in utilization of biocatalysts to convert renewable resources into chemicals, due to high yield and selectivity, and fewer byproducts. However, because of the metabolic restriction in microorganisms, only a few bulk products currently are produced through fermentation (Xu et al 2008).Therefore, development of new technologies to broaden the product spectrum is necessary.

Genetic engineering has emerged as a powerful tool for genetic manipulation of multistep catalytic systems involved in cell metabolism (James and Fabien 2008; Xu et al 2008). Recombinant DNA technology is used to clone and manipulate gene encoding enzymes in organisms. Recombinant microorganisms, with altered sugar metabolism, are able to ferment sugar to some specialty chemicals, which cannot be produced by the corresponding original stain. Currently, efforts are continuing to identify, characterize, and even modify enzymes and living organisms and processes so they can better utilize renewable resources to produce structurally diverse and complex chemicals. High yield and selectivity, as wells as minimum waste streams, favor biological conversions as pathways to transform biomass to higher-value chemicals.

However, there are still problems with current biological conversions technologies. Sterilization, fermentation stirring, and separation of target products from aqueous systems with low production concentration entail high energy requirements (McMillan 2004). As such, considerable investment is required to make processes highly efficient and continuous (Xu et al 2008).This therefore, creates research opportunities in the development of new low cost biological conversions technologies to effectively transform biomass into chemicals.

In contrast, biological processing is usually very selective and produces a small number of discrete products in high yield using biological catalysts while thermo-chemical conversion often gives multiple and often complex products, in very short reaction times with inorganic catalysts often used to improve the product quality (Brigewater 2007; Brigewater 2011). Today, the role played by pyrolysis in any thermo-chemical conversion of biomass into energy and variety of chemicals is very vital in the sense that manipulation of any of the operating parameters such as, heating rate, temperature, residence time, etc will definitely altered the product distribution (Patel 2011).

3.3 Pyrolysis process overview

During pyrolysis which is one of the most promising thermo-chemical conversion routes, biomass is thermally converted to charcoal, oil and H_2-rich gases under an oxygen absence condition. The yields of end products of pyrolysis and the composition of gases are dependent on several variables such as temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration, as well as the extraneous addition of catalysts (Yang et al 2006; Pilon and Jean-Michel 2011).

Conventionally pyrolysis is a slow, irreversible, thermal decomposition process of biomass organic components. The slow pyrolysis process has traditionally been used for the production of charcoal. Fast and short residence time pyrolysis of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. The major advantage of fast pyrolysis process is that, it is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products (Yaman 2004).

In addition to the above conversion routes, some few commodity and fine chemicals can be extracted directly from biomass.. Arabinogalactan and quercerin dehydrate were isolated from larch wood (Lu et al 2008). Other numerous examples are available. Therefore direct extraction is a promising pathway for utilizing renewable resources, irrespective of scale. In general, from the economic point of view, the extraction of high-value added chemicals from biomass can be the most profitable, but the availability and variety of chemicals are limited.

4.0 Potential chemicals from biomass

Biomass can be exploited into a number of different ways to deliver valuable feedstock materials for industry. Current and potential future means of chemicals for the industries are reviewed by key plant metabolite sectors. These include (James and Fabien2008)

- Oil
- Carbohydrates- sugars, starch, cellulose. Hemi-cellulose
- Lignin

- Protein
- Waxes
- Secondary metabolites

Some identified potential top value added chemical compounds from different biomass sources are grouped and listed in Table 1 below:

Table 1: Some of the major common chemical compounds identified from different biomass sources (Jeno" 2001; Lobban 2006; Agbontalor 2007; Seon-Jin et al 2010; Guo et al 2011; Himadri 2011; Tsai et al. 2005)

1.Acids o Acetic acid, o Hydroxy benzoic , o Dodecanoic acid o Formic acid, o Propanoic acid, o Propionic acid, o Hexadecanoic acid, o 9,12-Octadecadienoic acid 2. Aldehydes o Acetaldehyde o Formaldehyde o Propanal,3-hydroxy3 3. Furans o Furan,2,5dimethyl, o 2-Furanmethanol, o 2H-pyran, 3,4-dihydro, o (3H)-furanone, 5, o 3-methyl 2-furanone	4.Sugars o α-d-Glucopyranose, o 1,4,:3,6-dianhydro o Arabinofuranose o 5-anhydro 5.Catechols o Hydroquinone o Benzene o 1,4-dihydroxy-Benzene, o Dihydroxy-meth	6.Phenol o Phenol,4-ethly, o 1,2-Benzenediol o Benzofuran, 2,3-dihydro, o 1,2-Benzenediol, 3-methyl o 1,2-Benzenediol, 3-methoxy, o Phenol, 4-ethyl-2-methoxy Phenol, 2,6-dimethoxy, o Benzaldehyde, 3-hydroxy-4-methoxy, o Phenol, 2-methoxy-4-(1-propenyl), o 2-methyl phenol, o 3-methyl phenol , o Cyclopropylcarbinol, o Vanillin, o Maltol , o Eugenol, o Guaiacyl acetone o Syringyl acetone

All building block chemicals can further be converted to a wide spectrum of derivatives through chemical processes, such as reduction, oxidation, dehydration, hydrogenolysis and direct polymerization. Those chemicals can be used widely as solvents, fiber, antifreeze, and new polymers (such as polyesters, polyamides, and polyurethane) with better polymeric properties than those currently derived from petroleum (Zhang et al 2005; Lobban 2006; Agbontalor 2007; James and Fabien 2008; Xu et al 2008;). The products listed above represent only a small portion of the bio-chemicals made by different research groups around the world. Efforts to expand the spectrum of chemical derived from renewable resources are continuing.

4.1 Industrial application of biomass chemicals

The most widely known example of a bio-based chemical product is ethanol. Several generic categories of bio-based chemical products used falls within the following;- (Bain et al 2003; Bain 2004; Gent 2009):

- Carbohydrate polymers of natural origin
- Plant based fats and oils (and to a lesser extent of animal source)
- Terpene based materials
- Chemicals from carbohydrate containing materials
- Fermentation products from carbohydrate containing sources

Fermentation and enzymatic processes as well as direct extracted from plants (or aquatic biomass) are also employed for specialty chemicals production. Moreso, it has been shown that plants can be altered to produce molecules with functionalities and properties not present in existing compounds (e.g., chiral chemicals) (Brigewater 2003); Horvath and Anastas 2007; Gent 2009).

It is expected that advances in biotechnologies will have a vital role on the growth of the specialty chemicals market (Na-Ranong et al 2008; Leo 2010). Figure 3 gave a summary of some of industrial application of biomass chemicals.

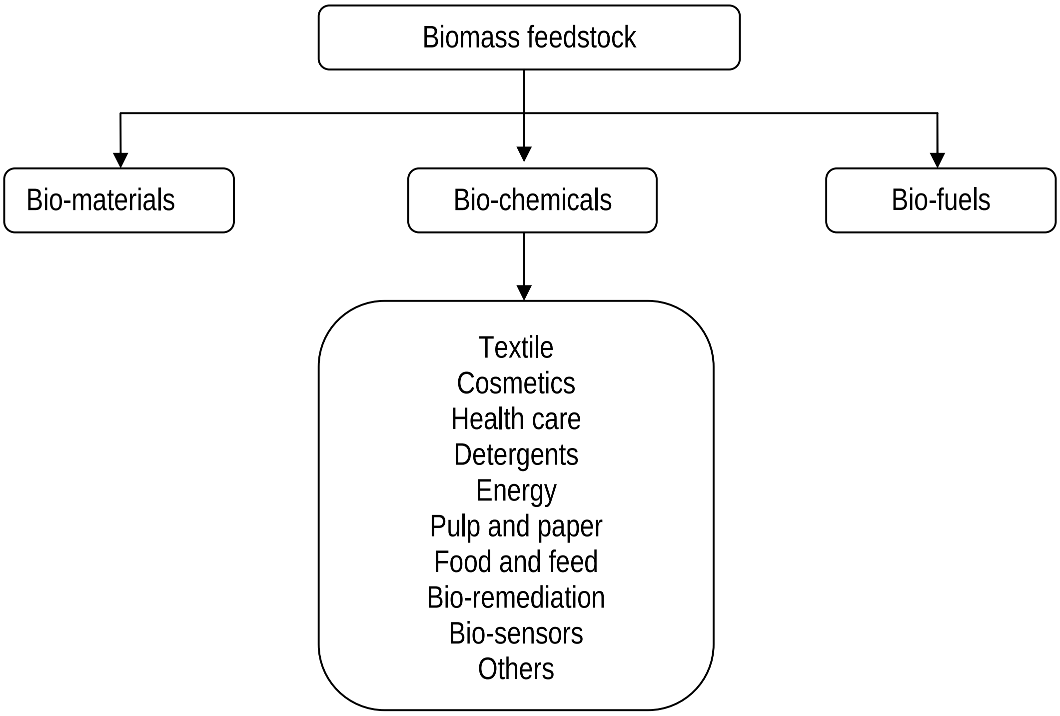

Figure 3.0: Industrial application of biomass chemicals

5.0 Economic and environmental benefits of biomass chemicals

The move towards the use of biomass as an alternative source for chemical production is gaining a wide attention due to some of the following reasons and advantages:-

Economical reasons:	**Political reasons:**
a. Economical advantages: • cheaper raw materials b. Technical advantages: • more simple processing, • better products	c. Security of supply: • fossil feedstock limited, • biomass seems unlimited d. Climate change: • biomass considered as CO_2 neutral

The use of bio-based renewable resources holds great potential value for industries in many sectors, including energy, organic chemicals, polymers, fabrics and health-care products.

5.1 Economic benefits of biomass chemicals

In general, a bio-based economy offers many benefits and opportunities (Zhang et al 2005; Ahmad et al 2010):

- new areas of economic growth and development for the many regions that have plentiful biomass resources;
- creation of new innovative business sectors and entrepreneurial skills;
- improved energy security by reducing dependence on non-renewable resources;
- enhance economic and environmental linkages between the agricultural sector and a more prosperous and sustainable industrial sector;
- job creation and rural development.

5.2 Environmental benefits of biomass chemicals

The global climate change agenda is a promising new platform whereby renewable technologies can receive support to gain new markets. In this context, bio-based chemicals are attractive alternative to help reduce fossil-based chemicals use. The need for renewable chemicals alternatives to mitigate climate change, the possibility to produce biomass resources on a sustainable basis, the opportunity to address rural socio-economic problems are some of the factors that make these technological options particularly interesting in many countries. Besides being renewable, the continues utilization of biomass for chemicals production can bring about other environmental benefits including the recovery of degraded land, reduction of soil erosion, and protection of watersheds. In essence, bio-based chemical offers a lot of benefits such as;-

- a reduction of greenhouse gas emissions;
- an improvement in health by reducing exposure to harmful substances through substitution of natural bio-based materials for chemical and synthetic materials;

However there are considerable technical, economic and logistical obstacles to the intensified use of renewable resources in the chemical industry: These include; (Gent 2009)

- Innovative biomass conversion methods and synthesis processes for chemical products are still at the development stage. Reliable forecasts from the idea through to the marketability of plant strategies and products are not possible at present.

- There is considerable uncertainty about the expected product costs and hence about profitability and competitiveness. Biomass resources represent the biggest cost factor. How this cost item will develop is impossible to estimate. The cost of investment in innovative processes (e.g. bio-refineries) can only be estimated within broad limits.

There is still considerable need for research. Process optimization, improved efficiency and the development of new enzyme systems and new sustainable synthesis processes are necessary in order to achieve economic viability.

6.0 Conclusion

The unstable rise of oil prices and the negative effects of petroleum on the environment have encouraged the search for new resources and techniques for chemical production. The advantages of renewable resources towards sustainability of resources and low cost accelerated the development and utilization of abundant unused biomass for chemical production. The biochemical compositions are similar to that of fossil feedstock and as such render biomass a promising raw material for chemical production. Advancement in technology such as bio-refineries, generic engineering and catalysis, assures greater development of chemicals from biomass. In the near future, bio-chemicals will share markets with fossil-based and ultimately replaced them since they are safe and environmental friendly. The utilization of biomass for chemical manufacture can significantly reduce or eliminate the harmful effects of fossil based chemicals on the environment and also provide a way of minimizing the negative effects of wastes on the environment.

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