

Bio-ethanol Production from Spent Grain and its Various Applications: An Overview

J. T. Oladeji<sup>1\*</sup> • A. O. Alade<sup>2</sup> • S. A. Popoola<sup>3</sup> • A. D. Ogunsola<sup>4</sup>

<sup>1, 3, 4</sup> Department of Mechanical Engineering, Faculty of Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria <sup>2</sup>Department of Chemical Engineering, Faculty of Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria <u>jtoladeji@lautech.edu.ng</u>

**Abstract**: The challenge to find and develop alternative sources of energy so that our decreasing reserves of crude oil and other fossil fuels may be conserved is of concern. However, this energy source must not interfere nor compete with human means of survival. The brewery industries generate a large amount of waste with a spent grain (SG) being the major one, which is currently under-utilized and usually disposed off indiscriminately. This has raised environmental concern. However, spent grain is a rich source of lignocellulose, which can be converted through hydrolysis and fermentation to bio-ethanol and this can be used as pure or blended fuel for automobile and heating purposes. The aim of this article is to review the composition, applications and other uses of brewer's spent grain (SG). The full utilization of existing technology and the promise of new development were also examined in this review. Also reviewed were works of few researchers who had worked on brewer's spent grain. This study concluded that spent grain though a waste product can be used to generate energy in form of ethanol production and that the quantity of ethanol that can be produced from spent grains depends on the quantity of reducing sugar and residual starch content. The higher the reducing sugar and residual starch content the higher the quantity of ethanol that can be extracted. Thus, spent grain is a potential biomass for the production of bio-fuel particularly in developing nations.

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# 1. Introduction

The main raw materials for industrial ethanol production are corn and sugarcane and it is expected that there will be a limit to the supply of these raw materials in the nearest future. This is because; the use of these crops for production of ethanol competes directly with their use as food sources (Pokhrel et al., 2008). Non-food feed stocks rich in fermentable carbohydrates are therefore of interest, particularly spent grain (SG), which consists of residues remaining after starch extraction. They are low valued products and are currently processed as an animal feed or disposed of as wastes (Mussatto et al., 2006).

However, they are a rich source of lignocelluloses, which may be converted to fermentable sugars for the production of bio-ethanol and can be blended with petrol or used as a pure fuel in certain engines (examples are flexi vehicles which are not available at the moment in West Africa).The advantages of using spent grain (SG) as a raw material for ethanol production is that it is abundant and can be gotten at a little or no cost, which makes it relatively cheaper than those gotten from sugar or starch based feed stocks.

There is resurgence in the research of bio-fuels, which is not in response to a single driving force, but to four independent forces. These forces are the need to develop a domestic fuel, a renewable fuel, a fuel which does not add net carbon to the atmosphere and a fuel that does not compete with food. At this present age, there is a need for pollution reduction especially those from industrial activities. This has become a global concern and both developed and underdeveloped countries are trying to adapt to this by modifying their processes especially most large companies no longer consider residues as waste, but recycles it as a raw material for other processes (Duru et al., 2003).

To meet the increasing demand for alternative bio-fuels, other bio-ethanol sources, asides those used for food or requiring large changes in land act needs to be exploited. Waste lignocelluloses bio-ethanol



from food processing such as spent grains (SG) from breweries has been identified as a potential bio-mass source for bio-ethanol production by microorganisms; which represents renewable supplies of fermentable sugars. Therefore, the world will have a lesser problem if every nation can produce her fuel by the processing and fermentation of lignocellulose rich bio-mass (spent grain) as a potential source of sugar for fuel ethanol (Kim et al., 2004).

# 2. Brewer's Spent Grain (SG): A Bye-Product of the Brewing Industry:

Brewers' spent grains (SG) are a major product of the brewing process and is generated at a rate of up to 30% of the weight of the initial malt grist (Aliyu and Bala, 2011). SG generated worldwide has been estimated at around 30 billion kilograms per annum (Mussato, 2009; Olugbenga and Ibileke, 2011).

Traditionally, these materials had either been discarded or sold as animal feed. However, these days, brewing industries are seeking to find addedvalue applications, which change traditional views of "waste" streams and reclassify them as "co-products". There has been a substantial amount of research published in recent years targeted at finding novel and more profitable or energy efficient use for SG.

Brewer's grains are a heterogeneous mixture of grain remnants from which the soluble and mast digestible components of malt have been extracted. SGs at source are typically 70-85% moisture (Aliyu and Bala, 2011). At these levels, spoilage due to mold growth, for example, can occur within five to seven days in warm climates. An efficient washing process will digest practically all of the starch in malt together with some protein fractions, as well as stabilizing many low molecular weight compounds and soluble gums. The remaining material is enriched in soluble lignin and cellulosic materials. However, the relatively high protein and carbohydrate contents of SG both augur well for its functional properties so long as adequate and cost-effective strategies for processing the material can be developed.

# **3.**Generation of SG in Brewing Operation:

Brewer's spent grain (SG) is the main byproduct of the brewing industry, representing approximately 85% of total by-products generated and it is rich in cellulose non-cellulosic polysaccharides and has a strong potential to be recycled (Aliyu and Bala, 2011). Spent grains are also the residue remaining after the extraction of wort. This lingo-cellulose rich biomass provides a source of sugar for bio-ethanol fermentations.

The composition of brewer's spent grain as described in the literature contains primarily grain husks and other residual compounds such as hemicelluloses, cellulose and lignin (Kanauchi, et al., 2001; Russ et al., 2005; Mussatto and Roberto, 2006; Mussatto et al, 2008a). All these contents make the spent grain a good feedstock for ethanol production.

Brewers' spent grain has high nutrients value (Tang, et al., 2009), and contain cellulose, hemicelluloses, lignin, and high protein content as shown in Table 1. The more distinct monosaccharide available in SG are xylose, glucose, and arabinose (Mussatto, 2009). However, the variation in its component percentage composition can be due to the variety of the grains used, harvest time, malting and mashing conditions, method of preservation and also the quality and type of adjuncts used during the process (Robertson, et al., 2010).

| Table | 1:  | Chemical    | composition     | of brewers' | spen |
|-------|-----|-------------|-----------------|-------------|------|
| grain | (SG | ) as report | ed in the liter | ature.      |      |

|                         | 17 1.    | <b>D</b> . | 14       | 16             |               | 771 1 1       |
|-------------------------|----------|------------|----------|----------------|---------------|---------------|
| Components              | Kanauchi | Russ et    | Mussatto | Mussatto       | Adeniran      | Khidzir       |
| (% dry weight)          | etal.    | al.        | and      | etal.          | etal.         | etal. (2010)  |
|                         | (2001)   | (2005)     | Roberto  | (2008a)        | (2008)        |               |
|                         |          |            | (2006)   |                |               |               |
| Cellulose               | 25.4     | 23-25      | 16.8     | $16.8 \pm 0.8$ | -             | -             |
|                         |          |            |          |                |               |               |
| Hemicelluloses          | -        | 30-35      | 28.4     | $28.4\pm2.0$   | -             | -             |
| T !!                    | 11.0     | 70.9       | 27.9     | 27.9 + 0.2     |               |               |
| Lignin                  | 11.9     | 7.0-8      | 27.8     | $27.8 \pm 0.3$ | -             | -             |
| Proteins                | 24       | 19-23      | 15.3     | -              | $2.4 \pm 0.2$ | $6.4 \pm 0.3$ |
| Ashes                   | 2.4      | 4-4.5      | 4.6      | $4.6 \pm 0.2$  | 7.9 ±0.1      | 2.3±0.8       |
|                         |          |            |          |                |               |               |
| Extractives             | -        | -          | 5.8      | -              | -             | -             |
| Others                  | 21.8     | -          | -        | $22.4\pm\!1.2$ | -             | -             |
| Carbohydrates           | -        | -          | -        | -              | 79.9±0.6      | -             |
| Crude fibre             | -        | -          | -        | -              | 3.3±0.1       | -             |
| Moisture                | -        | -          | -        | -              | 6.4±0.2       | -             |
| Linid                   | 10.6     | -          | -        | -              | -             | 2 5+0 1       |
| ырю                     | 10.0     |            |          |                |               | 2.5±0.1       |
| Acid detergent<br>fibre | -        | -          | -        | -              | -             | 23.3          |
| Total Carbon            | -        | -          | -        | -              | -             | 35.6±0.3      |
| Total Nitrogen<br>(%)   | -        | -          | -        | -              | -             | 1.025±0.05    |

#### 4. Preservation Techniques of SG:

Several methods have been proposed to prolong brewer's spent grain (SG) storage time as a result of its high moisture content. Factory drying has been the most effective method of preserving SG. However, owing to the growing global concern over high energy cost, many breweries, especially those in the developing countries can no longer afford this practice (Ikurior, 1995).

The advantage of drying as a preservation method is that it reduces the product volume, and decreases the transport and storage costs. Many breweries have plants for SG processing using twostep drying technique, where the water content is first reduced to less than 60% by pressing, followed by drying to ensure the moisture content is below 10% (Santos et al., 2003). However, the traditional process for drying SG is based on the use of direct rotary-drum





driers. This procedure is considered to be energyintensive.

Bartolome' et al. (2002) studied the effects of SG preservation using freeze-drying, oven drying and freezing methods. Their findings showed that preservation by oven drying or freeze-drying reduces the volume of the product and does not alter its composition while freezing is inappropriate as it affects the composition of some sugars such as arabinose. But overall, freeze-drying is economically not feasible on the large scale; making the ovendrying to be the preferred method. Thin-layer drying using superheated steam was proposed by (Tang et al., 2005) as an alternative method. The circulation of superheated steam occurred in a closed-loop system; this reduces the energy wastage that occurs with hotair drving. Also, the exhaust steam produced from the evaporation of moisture from the SG can be used in other operations. Thus, the superheated steam method has several advantages including the reduction in the environmental impact, an improvement in drying efficiency, the elimination of fire or explosion risk, and a recovery of valuable volatile organic compounds. Another method is the use of membrane filter press. In this process, SG is mixed with water and filtered at a feed pressure of 3 to 5 bar, washed with hot water (65°C), membrane-filtered and vacuum-dried to reach moisture levels of between 20 and 30% (El-Shafey et al., 2004). Moreover, chemical preservatives such as lactic, formic, acetic, benzoic acid and potassium sorbate can effectively be used for preserving the quality and nutritional value of SG as reported by Al-Hadithi et al. (1985).

# 5. Previous Works on Bio-Ethanol Production from Spent Grain (SG):

White et al., (2008) studied bio-conversion of brewers spent grain to bio-ethanol and P. stipitis strain was selected based on its superior performance compared with several xylose-utilizing strains (Candida, Cryptococcus, Kluyveromyces, Pichia and Pachysolen species). The K. marxianus strain was also included as it showed excellent activity on glucose and also known to utilize xylose (Yablochkova, et al., 2003) and due to its high temperature tolerance (Hughes. et al., 1994).

Also, in preliminary experiments, this strain performed better than a distilling strain of S. cerevisiae on glucose synthetic media. Hydrolysate was prepared from 20% SG, pretreated with 0.16N HNO3, partially neutralized to pH 5-6 and digested with enzymes for 18 h, contained 27g/l glucose, 16.7g/l xylose and 11.9g/l arabinose. P. stipitis and K. marxianus produced 8.3 and 5.9g/l ethanol respectively from a hydrolysate containing 66.6 g RS/1.

Yohannan et al., (2010) worked on the conversion of SG from malted barley, sourced from malt whisky distillery and from an ale brewery spent grain to ethanol by acid/enzyme hydrolysis and the fermentation by K. marxianus and P. stipitis was examined. Dried and hammer milled SG (20% w/v) was hydrolysed with 0.16 N HNO3 by autoclaving at 121°C for 15 minutes after which the pH was adjusted to pH 5-6 by stepwise addition of 10 M NaOH and inoculated with P. stipitis or K. marxianus from 48 h cultures.

Fermentation by K. marxianus for 48 h produced 14.8 and 7.5 g/l ethanol from BSG and GSG hydrolysate respectively while fermentation by P. stipitis produces 13.3g/l and 9.1g/l for BSG and GSG respectively. The conversion of SG hydrolysates from brewer's malt and maize distiller's SG is compared. The highest ethanol yields were obtained for the brewing SG, with 14.8 and 13.3g/l produced by K. marxianus and P. stipitis fermentation, respectively.

This may be due to higher residual starch content of the BSG which would alter the glucose level of the SG hydrolysate, resulting in greater ethanol concentrations from fermentation of the brewer's SG compared to that from distiller's and also the differences in composition of the SGs which depends on the operational conditions used during mashing to extract the starch. The reduced ethanol yields in the study of White et al., 2008 may be due to the lower RS (reducing sugar) content of the hydrolysate. The hydrolysate had 66.6 g/l RS compared to 78 g/l for the BSG hydrolysate in the study of (Yohannan, et al., 2010).

Olugbenga, et al., (2011) also studied bioethanol production from brewers spent grain where the sample was hydrolysed with 1.25w/v H2SO4 in autoclave at 121°C for 17minutes and the pH of the sample was adjusted with 0.5 M NaOH, from 4.2 to 5.0 after this, the inoculums S. cerevisiae was added and the fermentation was carried out for 7 days. The alcohol content of the fermented mash after the seventh day was 1.9%. The result of this study shows that the rate of alcohol production through fermentation of industrial waste (spent grain) by baker's yeast (S. cerevisiae) increases with fermentation time. The finding of this work suggests that bio-ethanol can be produced from brewer's spent grain that has been pretreated with acid and in addition to this the quantity of bio-ethanol produced is directly proportion to the amount of total carbohydrate and reducing sugar available in the samples and inversely proportion to the fiber content of the sample.

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| Table 2: | Summary | of previous | works | by | various |
|----------|---------|-------------|-------|----|---------|
| authors. |         |             |       |    |         |

| Author    | Topic          | Inoculums   | Hydrolysis | Ethanol<br>Yield | Ethanol<br>Content |
|-----------|----------------|-------------|------------|------------------|--------------------|
|           |                |             |            | (g/l)            | (%)                |
| Olugbeng  | Bio-ethanol    | S.          | Acid       | NA               | 1.9                |
| a et al., | production     | Cerevisiae  | treated    |                  |                    |
| 2011      | from brewers   |             |            |                  |                    |
|           | spent grain    |             |            |                  |                    |
| Yohannan  | Brewer's spent | К.          | Acid/      | 14.8             | NA                 |
| et al.,   | grains (BSG) a | Marxianus   | enzyme     |                  |                    |
| 2010      | substrate for  |             |            | 13.3g/l          |                    |
|           | bio-ethanol    | P. Stipitis |            |                  |                    |
|           |                |             | 1/         |                  |                    |
|           | Maize          | K.          | Acid/      | 7.5g/l           |                    |
|           | distiller s    | Marxianus   | Enzyme     |                  |                    |
|           | spent grains   | D Stimitic  |            | $0.1 \sim 1$     |                    |
|           | (USU) a        | P. Supius   |            | 9.1g/1           |                    |
|           | bio-ethanol    |             |            |                  |                    |
| White et  | Bioconversion  | К           |            | 5 9 o/l          | NA                 |
| al. 2008  | of brewers     | Marxianus   |            | 5.591            | 1411               |
| ,         | spent grain to |             |            |                  |                    |
|           | bio-ethanol    | P. Stipitis |            | 8.3g/l           |                    |
| Erdelji,  | Bio-ethanol    | P.          | Acid       | NĂ               | 0.3                |
| 2007      | from brewers   | Tannophilus | hydrolysis |                  |                    |
|           | and distillers |             |            |                  |                    |
|           | spent grain    | P. Stipitis |            |                  | 0.15               |
|           |                |             |            |                  |                    |
|           |                | C. Tennuis  |            |                  | 0.008              |
|           |                |             |            |                  | 0                  |
|           |                | Cry.        |            |                  | 0                  |
|           |                | Albidus     |            |                  |                    |

NA = Not available

# 6. Applications of Brewers Spent Grain (SG):

There are many applications of SG as highlighted in sections 6.1-6.2

### 6.1 Brewers Spent Grain as Animal Waste:

Brewers' grains have traditionally been used by farmers for feeding animals because of the presence of cellulose, hemicellulose and lignin, and also the amount of readily available substances such as sugars, protein content (circa 18% of dry matter) and amino acids which are of nutritional value helps in its usage as feed for ruminants (Bisaria et al., 1997).

But there are other numerous potential alternative uses, some now in place while others are still under development. The high amount of lingocellulosic matter in SG makes it indigestible to many animal species. The majority of SG used for animal feed is fed to ruminants (e.g., dairy cattle and pigs) which can cope with the high fiber content. Dairy cattle fed SG have been showed to increase milk production (Belibasakis and Tsirgogianni, 1996; Reinold, 1997; Sawadogo et al., 1989). SG can be used for this purpose either wet (70-85% moisture content) or dry (10-12% moisture content), the latter being more stable and cheaper to transport, but incurring additional drying costs. Animal feed prices fluctuate according to demand and represent a modest return.

The environmental implications of increased methane emissions from cows fed this hard to digest material can also be considered as having a negative environmental impact. The CO<sub>2</sub> emission of methane is approximately 21, which means that its impact as a greenhouse gas is approximately 21 times greater than that of carbon dioxide. Currently, the primary market for SG is dairy cattle feed, but as the SG provides protein, fiber, and energy, its consumption has also been investigated for a range of animals, including poultry, pigs and fish (Table 3). Kaur and Saxena (2004) evaluated SG as a replacement for rice bran in a fish diet, and observed that fish fed with a diet containing rice bran and 30% spent grain had a superior body weight gain when compared with fish fed with rice bran only. According to these authors, the better growth performance was due to the increased content of proteins and essential amino acids provided by the spent grain.

#### 6.2 SG in Biotechnological Processes:

Bio-ethanol can be produced from starch and sugar-based crops as well as lignocellulosic biomass. Most of the starch and sugar-based crop (sweet sorghum, maize starch, sugarcane, rice, wheat, sorghum, etc.), competes with human food production and also have high production prices makes its industrial production a little difficult. With the increase in demand for ethanol, the search for cheaper and more abundant substrate is underway and also the development of an efficient and less expensive technology so that there will be an increase in availability of ethanol at a cheaper rate (Alam et al., 2007, 2009).

The substantial hemicellulose and cellulose components of SG (approx. 55% of the material on a dry weight basis) consist of polymeric sugars. Cellulose is a polymer of glucose (C-6 sugar) whilst hemicelluloses contain C-5 sugars or pentose's such as xylose and arabinose. If these sugars could be liberated and fermented to generate bio-ethanol, each gallon of ethanol produced will save a gallon of oil. Such processes are still pre-competitive and require step changes in technology to bring them to market. However, second generation bio-fuel technologies are the subject of much current research and novel technologies developed will be applicable to SG, and even to the brewing process itself (Cook, 2011).

The composition of brewer's spent grain (SG) as described in reviewed literatures consist majorly grain husks and other residual compounds such as hemicelluloses, cellulose and lignin (Kanauchi et al., 2001; Russ et al., 2005; Mussatto and Roberto 2006; Mussatto et al., 2008a) and this makes it a good



feedstock for ethanol production. Current technology for the conversion of spent grain (SG) to ethanol requires chemical or enzymatic hydrolysis to produce majorly fermentable sugars, followed by microbial fermentation. Thus, large amounts of enzymes required for enzymatic conversion of cellulose to fermentable sugars impacts severely on the cost effectiveness of this technology.

However, Neurospora crassa and Fusarium oxysporum were found to have an exceptional ability to convert cellulose and hemicellulose directly to ethanol through the consecutive steps of hydrolysis of the polysaccharides and fermentation of the resulting oligosaccharides by secreting all the necessary enzyme systems (Xiros et al., 2008; Xiros and Christakopoulos, 2009). Both Xiros et al. (2008) and Xiros and Christakopoulos (2009) reported the ethanol yield of 74 and 109 g/kg of dry SG by N. crassa and F. oxysporum, respectively under micro aerobic conditions (0.01 vvm). Thus, brewer's spent grain can be used to generate a wide range of feedstock materials to supplement current bio-ethanol production from a starchy feedstock.

# 7. Economic Sustainability of Bio-Ethanol Produced from Spent Grain:

The economic sustainability of production of bio-ethanol is viewed from two perspectives as highlighted in sections 7.1-7.2

# 7.1 Profitability and Efficiency:

Before people can invest in bio-ethanol the issue of profitability most be well defined because it is the determining factor for its long term viability and before the issue of profitability comes into play, there should be marketability which determines economic profitability because producers will only be willing to invest in bio-fuel production if it is economically profitable.

The key factors that can affect the profitability of bio-ethanol include the alternative competitive uses of the feed stocks and the energy prices. Alternative uses of the feedstock aids decision making process of producers and if prices for bio-fuels fall below the prices of other possible end-products (food, feed, timber, etc.) it would be more profitable to cultivate these products than to derive fuel out of the feedstock. Accordingly, their prices determine the price floor for bio-fuels. To be profitable and also compete with fossil fuels, bio-ethanol production costs must be lower than the price of its oil equivalent. Therefore, oil prices set a price ceiling for the price of bio-fuels and if the cost exceeds this value, the bio-fuels will automatically be priced out of the market (Schmidhuber, 2007).

# 7.2 Competition with Food:

One of the major determining factors of the long-term economic feasibility of bio-fuels is its competition with food. According to FAO's definition, food security exists when "all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food which meets their dietary needs and food preferences for an active and healthy life" (FAO, 2003, p.29). When feed stocks used for food are also used for bio-ethanol, the food price increases and also the availability of food will be limited by the bio-fuel supply so far they compete for the same resources such as land, fertilizers, water. Therefore, bioethanol's potential competition with food should be considered when investing in bio-fuel; this issue is being tackled by making use of the second generation feed stocks.

The definition considers four dimensions; food availability, food access, food use and food stability. These dimensions are appraised next with regard to bio-energy production expansion. Food availability refers to having sufficient quantities of food of appropriate quality, supplied through domestic production or imports (including food aid). Regarding the impact of bio-fuels expansion of food availability it is important to point that the use of agricultural lands for bio-energy feedstock production is quite low relative to total agricultural land area

The other dimensions of food security are not expected to be significantly affected by the production of bio-fuels. Food access relates to individuals having adequate resources (entitlements) for acquiring appropriate foods for a nutritious diet. It depends on purchasing power of the population as well as the availability of adequate transport, storage and distribution infrastructure. Food access can be favored in contexts where bio-energy production stimulates the development of rural production system and increases household disposable income. On the other hand, food access can be negatively affected if biofuels development leads to significant food prices increases that reduce purchasing power among the population. Food utilization relates to how food is used through adequate diet, clean water, sanitation and health care to reach a state of nutritional wellbeing where all physiological needs are met. Food utilization brings out the importance of non-food inputs in food security; therefore, it is not expected to be meaningfully impacted by bio-fuels development.

Finally, stability refers to the possibility that a population, household or individual has access to adequate food at all times. They should not risk losing access to food as a consequence of sudden shocks (e.g. an economic or climatic crisis) or cyclical events (e.g. seasonal food insecurity). The concept of stability can refer to both food availability and food access. Bio-fuels development can therefore affect the stability dimension of food security through the effects it can have on food availability if fuel uses of agricultural commodities prevail over food uses or production of other food-related agricultural goods is displaced to produce bio-fuel feed stocks. Bio-fuel development can also affect food stability through the effect on food access, negatively if it leads to significant food price increases that reduce purchasing power, or positively if it increases purchasing power among farmers and the general population in bio-fuels producing regions.

# 8. Bio-Refinery Concept – Looking into its Prospect:

A bio-refinery is a singular facility that produces multiple products from biomass and may be defined as a facility that converts biomass into fuels, chemicals, and power through integrated processes (Ragauskas et al., 2006a). Realff and Abbas (2004) also defined a bio-refinery as a process of converting renewable agricultural feed stocks to higher value added products for use as food, fuel feed, and fiber. Bio-refinery has been defined by International Energy Authority (IEA) as "the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bio-energy (biofuel, power, and/or heat)".

A way to improve the economy and also increase the net energy gain of the production of ethanol from lignocellulose would be to manufacture co-products and important chemicals during the process. In the petroleum industry about 5% of the total output from an ordinary refinery goes into chemical products, while the remaining 95% is used for energy and transportation fuels (Ragauskas et al., 2006b). In the case of breweries and corn ethanol production, an important co-product is spent grain (SG) and distiller's grain, which is used as cattle, fish, and pig feed (Wheals et al., 1999).

A major residual product of cellulosic ethanol from spent grain (SG) is lignin which can be burnt with other solids left after hydrolysis for the generation of heat and electricity (Wyman, 2003). In the cement context, a bio-refinery comprises integrated biomass conversion technologies to produce bio-ethanol and other useful and valuable commodities including energy. There is a wide range of valuable chemicals and materials that can be produced from lignocellulose bio-refinery which includes; cosmetics, nutraceuticals, bio-plastics, solvents, and herbicides. There is also a wide range of valuable products that can be produced from the lignocellulose-derived sugars by microbial conversion. Potential products include hydrogen, methane, propanol, acetone, butanol, butanediol,

succinic acid, itaconic acid, acetic acid, levulinic acid, butyraldehyde, ascorbic acid, adipic acid, propylene glycol, acrylic acid, acetaldehyde, sorbitol, glycerol, and malic acid (Kamm and Kamm, 2004; Wyman, 2003).

Another excellent product that can be derived from carbohydrates by microorganisms is lactic acid. Polymeric materials derived from lactic acid, for example polylactide, which is a very versatile thermoplastic, can replace some of the plastics made from petroleum. Polylactide is very popular in the food packaging industry because it is fully compostable and biodegradable and also used in the manufacture of films and fibers (Gruber, 2003). Other plastics, such as polyvinylacetate and polyethylene, can be produced with ethanol as the starting material.

The conversion of the ethanol must be done into ethene by chemical methods (Kamm and Kamm, 2004). An advantage with chemicals produced by microbial catalysis rather than by using petrochemical methods is that the products from the microorganisms are typically stereo and region-chemically pure. There is no need for expensive chiral catalysts and complex syntheses, which is the case in the production of many petrochemicals (Ragauskas et al., 2006b). Even if the major part of the biomass can be utilized in an efficient way in a bio-refinery, there will nevertheless probably be some waste products that are uneconomical to convert further to valuable chemicals or materials.

As mentioned above, residual materials, such as lignin, can be burned to generate power, but another possibility would be thermo chemical conversion of the residues to syngas. The produced syngas can then be used for the production of methanol, ammonia and Fisher-Tropsch hydrocarbons (Ragauskas et al., 2006b). Studies have shown that a cellulosic refinery plant that combines the production of fuels, chemicals and power can generate these products with a lower cost than if just one of them is produced (Wyman, 2003). Another possibility is to transform the pulp mills of today into bio-refineries (Ragauskas et al., 2006a). In essence, the bio-ethanol/ bio-refinery concept is to make the most of the whole bio-mass, rather than just a component of it, using chemicals and biotechnologies in a sustainable manner that reduces waste and saves energy. The concept of "zero emissions" in bio-refinery has been discussed by (Gravitis, 2007).

In addition to ensuring the quality of bioethanol processes, quality parameters of the end product are also important. In the US, the American Society for Testing and Material Testing (ASTM) approves analytical specifications for bio-ethanol transportation fuel performance quality (Davis, 2009).



This includes the key parameters to be measured, their units of measurement and their influence on quality. For example, pH and water elimination are important parameters for internal combustion engines. The Renewable Fuel Association (RFA) recommends minimum testing frequencies and method for bioethanol to ensure product quality and consistency and to meet ASTM standards.

The production and the use of bio-fuels such as bio-ethanol at the expense of fossil fuels contribute in a meaningful way to reduce GHG emissions. This is because the bio-massfeed stocks employed fixed carbon dioxide photo-synthetically during their growth and this leads to significant reduction in carbon dioxide equivalent GHG emissions compared to oil and gas combustion. Importantly in this context, the combustion of road transport fuel is currently responsible for around 20% of GHG emissions. As it is now clear with scientific evidence that "emissions from economic activity are causing changes to the earth's climate" (Stern, 2007). The US Environmental Protection Agency (EPA) has stated that relative to gasoline, utilization of corn ethanol reduces GHG emission by at least 20% but significantly cellulosic ethanol, especially from spent grain usage reduces emission far in excess of 60% (RFA).

Additional environmental and health benefits of bio-ethanol include: Removal of toxic methyl tertiary-butyl ether (MTBE) as a gasoline oxygenate (especially in the US). Ethanol as an oxygenate reduces harmful exhaust pipe emissions due to complete fuel combustion (ethanol contains 35% oxygen). Toxic and carcinogenic gasoline additives (e.g. lead, benzene is replaced by ethanol), and Ethanol is readily bio-degradable.

First generation bio-ethanol is faced with severe economic and environmental constraints, including contribution to higher food prices (by competing with food crops), production is not cost effective (without government subsidies), limited GHG reduction benefits, dubious sustainability criteria, potential negative impact on bio-diversity, and competition for scarce water resources.

The following represents the most important ethical challenges raised by increasing future bioethanol production, economics (affordability), food to fuel (changes in agricultural land use), genetic engineering (empowerment of GM. feed stocks), local environment (localization/ building of new biorefineries: demands on fresh water), and bio-business (potential monopolization of bio-resources or patents).

# 9. Conclusion

The full utilization of existing technology and the promise of new developments will make the

production of ethanol fuel easier and more economical in the near future. However, as fossil fuel supplies dwindle, it will become increasingly important to utilize every shred of available material and waste in the production of energy. Aside from the large scale production of bio-fuel, self-contained, automatic appliances that could turn all sorts of waste material into useable fuel would be an important development. Electric vehicles and small, regional hydro-electric plants would also help as would full utilization of solar, geothermal, and other energy alternatives. It is of paramount importance to know that the energy problem will not solve itself unless pro-active measures are taken.

# **Corresponding Author:**

J. T. Oladeji, Ph.D.

Department of Mechanical Engineering, Faculty of Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria. E-mail: jtoladeji@lautech.edu.ng

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