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CELLULOSIC BIOETHANOL FROM SUNFLOWER SEED HULLS – A RENEWABLE ENERGY SOURCE

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ABSTRACT. The need for increased energy security as well as the concern over greenhouse gas emissions and depletion of fossil fuels requires sustainable alternatives to conventional sources. Biomass is a promising renewable alternative to fossil fuels. It is the world's fourth largest source of energy, following oil, coal and natural gas, and the raw material for biofuels. Bioethanol as a transportation fuel is attractive as it is more energy efficient than gasoline and produces less emissions. This paper presents an experiment undertaken to obtain bioethanol from sunflower seed shells. Sunflower seed husks represent a waste resulting from the extraction of cooking oil. Such waste has had limited and unimportant use. A rigorous technology for producing bioethanol from such a cheap resource could lead to valuable economic results and would help reduce pollution.

Key words: *Bioethanol, sunflower seed shells, sustainability*

INTRODUCTION

Growing demand for energy as well as the need to reducing GHG emissions requires sustainable alternatives to fossil fuels. Among alternatives, biofuels play an important role especially in transportation. Persistent high world oil prices in the last decade and the passage of the EPACT2005 in the USA and the Directive 2009/28/EC of the European Parliament have stimulated the use of bioethanol and biodiesel in the transportation sector (REN.21, 2011), (E.P. Directive, 2009). The following chart shows the global ethanol and biodiesel production between 2000 and 2010.

The expanding biofuel industry has recently raised important concerns, particularly regarding the sustainability of many first-generation biofuels, produced primarily from food crops such as corn, sugar cane and vegetable oils. Criticism has focused on the displacement of food-crops and adverse effects on the environment. Such criticism has raised interest to the potential of second-generation or advanced biofuels. These biofuels are obtained from feedstock, such as stems, leaves and husks or industry waste such as woodchips and pulp from food pressing (IEA, 2010).

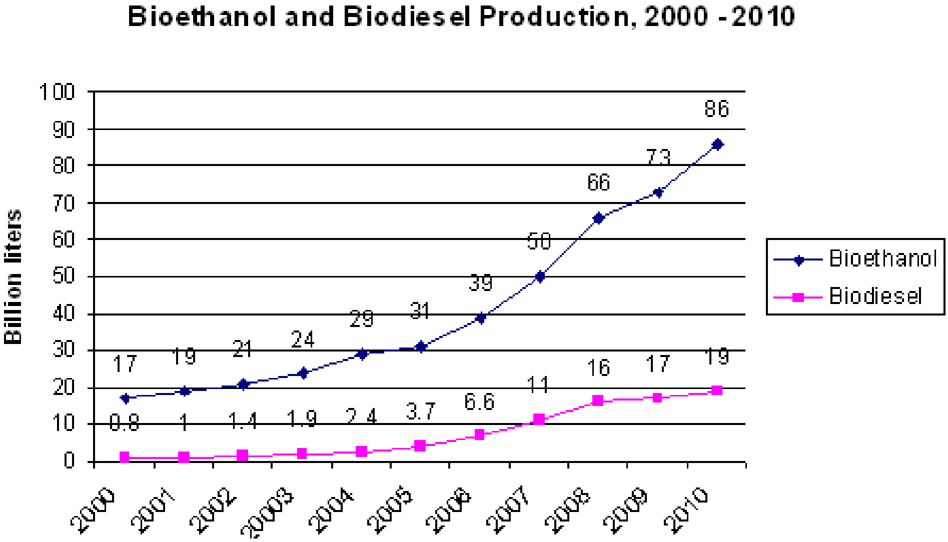

Fig. 1. *Ethanol and Biodiesel Production, 2000-2010 (Source: REN21, 2011)*

Bioethanol has multiple uses in several industries such as chemical, pharmaceutical, cosmetics and a small part is for human consumption. In transportation ethanol can be part of a fuel blend with gasoline or it can displace petroleum products. There are important advantages of using higher blend ratios of ethanol in gasoline such as reducing the reliance on imported oil and reduced greenhouse gas emissions. However, these advantages present special challenges, for example production concerns, including increased cost and limited production capability. Besides, engine factors and the corrosiveness nature of ethanol must also be assessed (Walner and McConnell, 2010).

Second-generation bioethanol can be produced from any raw material having a rich cellulosic content, sugars or starch, which can be easily converted into sugar. A study conducted by the Department of Wood Science at the University of British Columbia, Canada (Stephen, 2011), and also a report of the European Commission (2008) estimated that ethanol made from crop waste or wood chips will not be cost competitive with fuel made from corn until 2020 at the earliest. The need for pretreatment of the cellulose-rich raw materials and for more complex enzymes employed drives up production costs. In spite of these challenges, ethanol's potential seems to be enormous. For example, the United States could in theory replace all gasoline made from imported oil with ethanol. The industry's main objective is not as much to compete with first-generation ethanol, but rather with gasoline. The Italian company Gruppo Mossi & Ghisolfi began building the world's first commercial-scale cellulosic ethanol plant last year and expects it to become price competitive with gasoline this year (Stephen, 2011).

EXTRACTION OF BIOETHANOL FROM SUNFLOWER SEED HUSKS

At the INCDO-INOE 2000, Research Institute for Analytical Instrumentation, several methods for bioethanol production were studied, among them extraction of this fuel from sunflower seed husks. One of those projects is described in this chapter.

Materials

The feedstock was harvested from the sunflower oil plant's landfill. The sunflower seed husks represent the first valuable waste resulting from the sunflower oil production process following the shelling operation. The husks' content of the processed seeds can reach 22-27%. Seed hulls were considered an attractive lignocellulosic source for second generation ethanol production. Sunflower hulls have no special current use. They are used as cheap fuel in the steam boilers of the thermo-electric power station and in the seed dryer installations.

The chemical composition of sunflower seed hulls is shown in the following table:

Table 1. *Chemical Composition of sunflower seed hulls*

Substance	**Content (%)**
Carbon	50-51
Hydrogen	5-6
Oxygen and nitrogen	45
Sulfur	0,1%

The sunflower hulls' calorific value is low, only 3500-4000 cal/kg being supplied through burning. Resulting ashes represent 1-1,2 %, but it contains a large amount of potassium salts (10-12%), which harms the furnace refractory masonry.

The presented facts show that bioethanol's production would represent a superior utilization of materials from an economic point of view and it would reduce expenses incurred in sunflower oil production.

Method

The process involves the diluted acid prehydrolysis in upstream lignocellulosic biomass (LCB) accompanied by enzymatic saccharification of residual cellulose and co-fermentation of glucose and xylose by-products of the process.

Bioconversion of sunflower seed hulls

Bioconversion of the dry material into ethanol takes place in four stages (Figure 2): pretreatment, hydrolysis, fermentation and formation of ethanol from glucose, and finally, distillation of ethanol.

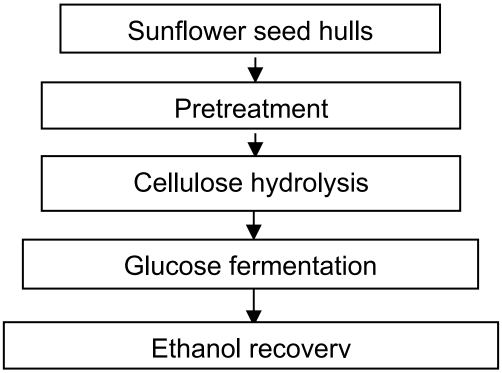

Fig. 2. *Stages of bioethanol production from sunflower hulls*

Pretreatment of sunflower hulls

The mixtures of hulls and water were homogenized at the desired proportion (8 kg/kg dry/solid) and the mixture was introduced in a pressurized reactor (Parr Instrument) at 180, 200 and 220 °C for 5 and 10 min. The pretreated material was separated by filtration into solid and liquid phases.

Analytical methods

The moisture content of raw material was determined by the weight loss after drying (105°C, 12 h). Determination of ash in sunflower shells was expressed as the percentage of residue remaining after dry oxidation of raw material at 590°C. Extractives were analyzed by using a one-step extraction process which included ethanol as an extractive solvent.

The chemical content of sunflower shells was determined through a process similar with the one developed by a team of Japanese researchers (Teramoto et al., 2008). The composition of cellulose and hemicellulose was determined as holo-cellulose content by treating the sunflower shells with $NaClO_2$ in acetic acid solution.

RESULTS

Pretreatment is the most important of the four stages since the lingo cellulosic structure breaks during this stage. A large number of physical, physicochemical and biological research studies (Zhu and Pan, 2010) on this topic have been undertaken. Various methods have been developed that convert lignocellulosic biomass material into its components using solvents and imposing long duration of the process (Senila et al., 2011). The liquid hot water method used only water at high temperature and pressure. The major advantages of this method are that few chemicals are used and the hemi-cellulose is recovered as oligosaccharide and monosaccharide soluble in liquid which can be separated from insoluble fractions (cellulose and lignin). Hydronium ions from water act as a catalyst for hydrolysis of hemicellulose (Okur and Saracoglu, 2006).

The content of sunflower seed hulls was determined and is show in Table 2.

Table 2. *Cellulosic content of sunflower seed hulls*

Composition	**%**
Holocellulose	56.47
Cellulose	27.43
Hemicellulose	29.04
Lignin	24.23
Ash	3
Extractibles	9

Glucose formation took place during pretreatment. Hemicellulose was separated through self-hydrolysis, in the liquid fraction while cellulose and lignin remained in the solid fraction. Hemicellulose is a mixture of pentoses (arabinose and xylose) and hexoses (glucose, mannose and galactose). Determinations showed that the content of holocellulose (cellulose and hemicellulose) is 57%. The high holocellulose content suggests that sunflower seed hulls are a potential feedstock for bioethanol production.

A large number of research studies have shown that lignin extraction before hydrolysis improves hydrolysis yield. One of the most used methods for complete lignin removing is the delignification (Saxena et al., 2009). Hydrolysis of cellulose into glucose and fermentation into bioethanol represent the second step of bioethanol production from sunflower seed hulls.

CONCLUSIONS

The study demonstrated that sunflower hulls, a cheap but valuable source of biomass, can be used for ethanol production. We should emphasize the environmental issues, such as the processing of agricultural waste as well as the benefits gained by replacing fossil fuels with bioethanol. This fuel contains 34,8 % oxygen in its molecule, which leads to complete combustion. Emissions of greenhouse gases are greatly reduced compared to other bio-fuels and 80 % lower than those generated by fossil fuels.

Other projects using sunflower seed hulls as feedstock have used different methods such as hydrolyis with Trichoderma reesei C-30 cellulase (Sharma et al., 2004), steam explosion in pretreatment stage (Vaithanomsat, 2009), or fermentation of sunflower seed hull hydrolysate to ethanol by Pichia stipitis (Okur and Saracoglu, 2007). Pretreated deseeded sunflower heads also represent a cheap and valuable raw material for bioethanol production (Thippareddy and Agrawal, 2008).

Against any criticism, forecasts regarding the development of biofuels are optimistic. It was forecasted that the lowest market price of ethanol would decline to $0,69/ gallon by 2020 from an average of $0,88 / gallon in 2010 (Stoeglehner and Narodoslawsky, 2009).

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