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ABSTRACT

Alcoholic fermentations were performed, adapting the technology to exploit the residual thermal energy (hot water at 83–85 ◦C) of a cogeneration plant and to valorize agricultural wastes. Substrates were apple, kiwifruit, and peaches wastes; and corn threshing residue (CTR). Saccharomyces bayanus was chosen as starter yeast. The fruits, fresh or blanched, were mashed; CTR was gelatinized and liquefied by adding Liquozyme® SC DS (Novozymes, Dittingen, Switzerland); saccharification simultaneous to fermentation was carried out using the enzyme Spirizyme® Ultra (Novozymes, Dittingen, Switzerland). Lab-scale static fermentations were carried out at 28◦C and 35 ◦C, using raw fruits, blanched fruits and CTR, monitoring the ethanol production. The highest ethanol production was reached with CTR (10.22% (v/v) and among fruits with apple (8.71% (v/v)). Distillations at low temperatures and under vacuum, to exploit warm water from a cogeneration plant, were tested. Vacuum simple batch distillation by rotary evaporation at lab scale at 80 ◦C (heatingbath) and 200mbar or 400mbar allowed to recover93.35 %(v/v)and89.59%(v/v)of ethanol, respectively. These results support a fermentation process coupled to a cogeneration plant, fed with apple wastes and with CTR when apple wastes are not available, where hot water from cogeneration plant is used in blanching and distillation phases. The scale up in a pilot plant was also carried out. Ethanol, currently produced in India by the fermentation of sugarcane molasses, is an excellent biofuel and can be blended with petrol. Likewise, biodiesel which can be manufactured by the trans esterification of vegetable oil can be blended with diesel to reduce the consumption of diesel from petroleum. Ethanol and biodiesel are gaining acceptance worldwide as good substitutes for oil in the transportation sectors.

Keywords: bioethanol; fruits; corn threshing residue; fermentation; distillation

1. INTRODUCTION

India is the fifth largest primary energy consumer and fourth largest petroleum consumer in the world. Growing population and rapid socio-economic development has spurred an increase in energy consumption across all major sectors of the Indian economy. Given limited domestic energy resources, most energy requirements are met through imports. Provisional estimates indicate that India meets more than 76 percent of its petroleum demand through imports. Global depletion of energy supply due to the continuing over-utilization is being a major problem of the present and future world community. It is estimated that the fossil fuels will be running out by the next few decades therefore, attention has currently been dedicated to the conversion of biomass into fuel ethanol. Tremendous progress has been made technologically in the last few years in the area of biofuel production, fuelled by ever increasing price and shortage of fossil fuel. There are also concerns about global climate change and severe food shortage. Biomass is the least expensive and most globally available resource. Therefore, priority should be shifted towards utilizing biomass, leaving aside food for human consumption. New methodologies of fermentation and hydrolysis of biomass have become available, along with development of transgenic varieties amenable for biofuel production. Now is the time to look for new material sources of biofuels, which are naturally amenable to processing during extraction of biofuel, thus reducing costs drastically and substituting fossil fuels in all aspects. Biofuels are drawing increasing attention worldwide as substitutes for petroleum derived transportation fuels to help address energy cost, energy security and global warming concerns associated with liquid fossil fuels. Biofuels are going to play an extremely important role in meeting India's energy needs. The country's energy demand is expected to grow at an annual rate of 4.8 per cent over the next couple of decades. Most of the energy requirements are currently satisfied by fossil fuels – coal, petroleum-based products and natural gas. Domestic production of crude oil can only fulfil 25-30 per cent of national consumption Ethanol, currently produced in India by the fermentation of sugarcane molasses, is an excellent biofuel and can be blended with petrol. Likewise, biodiesel which can be manufactured by the trans esterification of vegetable oil can be blended with diesel to reduce the consumption of diesel from petroleum. Ethanol and biodiesel are gaining acceptance worldwide as good substitutes for oil in the transportation sector.

Fig. 1.1: world fuel ethanol scenario.

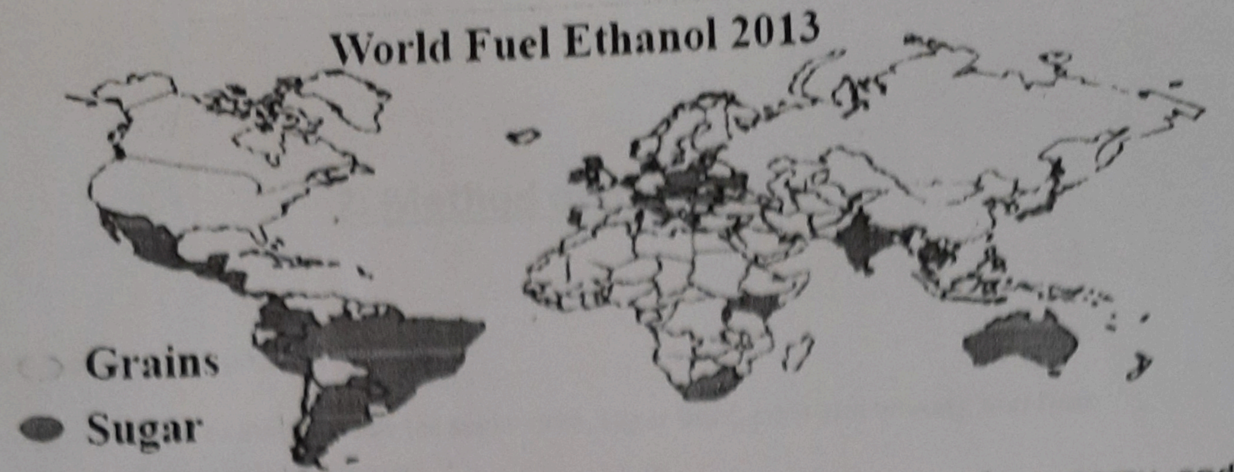


Figure 1: World fuel ethanol scenario (Source: Ministry of economy and Industry, Japan)

Fig.1.2: India first 2G- ethanol plant

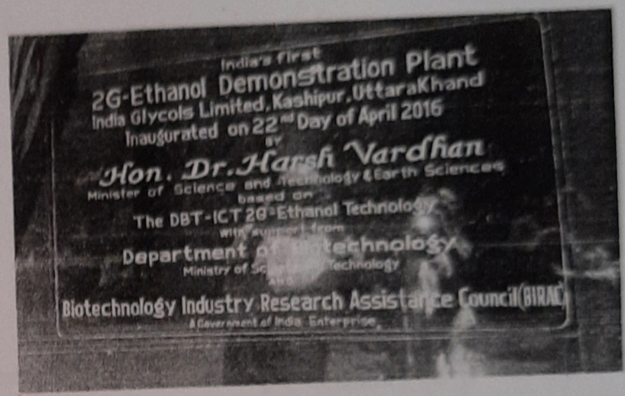
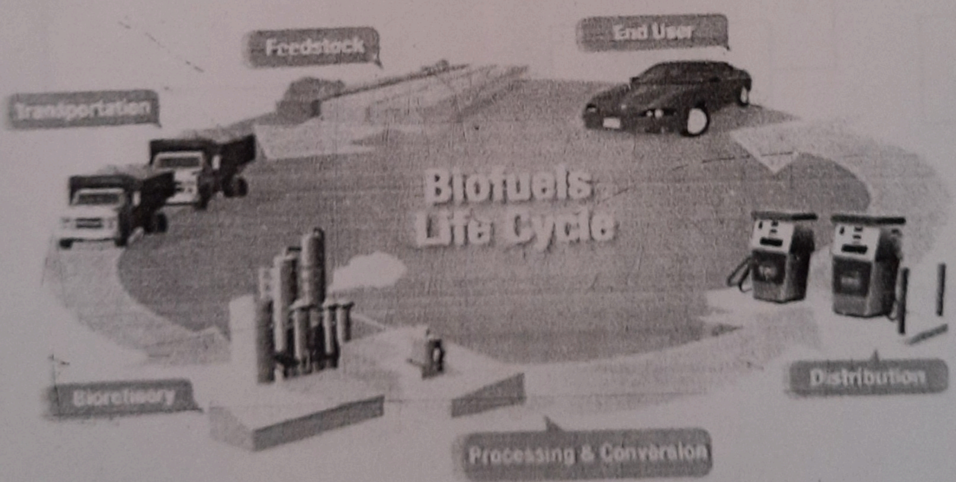


Fig.1.3: Biofuels Life Cycle



2. Method of production

Bioethanol can be produced from

(i) sugar or starch crops (as sugar cane, sugar beet, corn and wheat), and from
(ii) lignocellulosic biomass.

2.1:Different methods of bioethanol production have been practiced by researchers Biomass is converted to bioethanol by applying two reactions.

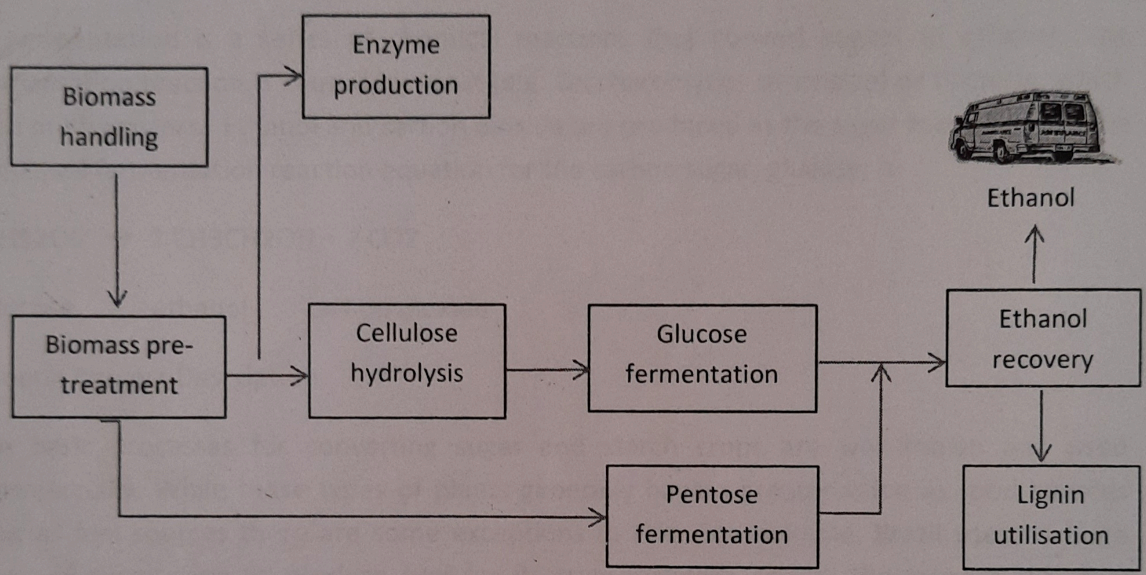


Fig2.1: Block Diagram of Ethanol production by biomass.

1. **Hydrolysis** is the chemical reaction that converts the complex polysaccharides in the raw feedstock to simple sugars. In the biomass-to-bioethanol process, acids and enzymes are used to catalyse this reaction.

The chemical reactions and involved enzymes in starch hydrolysis (liquefaction) have been shown below:

$2\ nC6H12O11 + n\ H2O \rightarrow n\ C12H22O11$

Starch (ɑ-amylase) maltose

$C12H22O11 + H2O \rightarrow 2\ C6H12O6$

Maltose (glucoamylase) glucose

$C12H22O11 + H2O \rightarrow C6H12O6 + C6H12O6$

saccharose (invertase) glucose fructose

2. **Fermentation** is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast (e.g. Saccharomyces cerevisiae) or bacteria, which feed on the sugars. Ethanol and carbon dioxide are produced as the sugar is consumed. The simplified fermentation reaction equation for the carbon sugar, glucose, is:

$C6H12O6 \rightarrow 2\ CH3CH2OH + 2\ CO2$

glucose ethanol carbon dioxide

General Process Description:

The basic processes for converting sugar and starch crops are well-known and used commercially. While these types of plants generally have a greater value as food sources than as fuel sources there are some exceptions to this. For example, Brazil uses its huge crops of sugar cane to produce fuel for its transportation needs. The current U.S. fuel ethanol industry is based primarily on the starch in the kernels of feed corn, America's largest agricultural crop.

2.2:Steps description of ethanol production by biomass :

i. **Biomass Handling**. Biomass goes through a size reduction step to make it easier to handle and to make the ethanol production process more efficient. For example, agricultural residues go through a grinding process and wood goes through a chipping process to achieve a uniform particle size.

ii. **Biomass Pre-treatment**. In this step, the hemicellulose fraction of the biomass is broken down into simple sugars. A chemical reaction called hydrolysis occurs when dilute sulphuric acid is mixed with the biomass feedstock. In this hydrolysis reaction, the complex chains of sugars that make up the hemicellulose are broken, releasing simple sugars. The complex hemicellulose sugars are converted to a mix of soluble five-carbon sugars, xylose and arabinose, and soluble six-carbon sugars, mannose and galactose. A small portion of the cellulose is also converted to glucose in this step.

iii. **Enzyme Production**. The cellulose enzymes that are used to hydrolyse the cellulose fraction of the biomass are grown in this step. Alternatively the enzymes might be purchased from commercial enzyme companies.

iv. **Cellulose Hydrolysis**. In this step, the remaining cellulose is hydrolyzed to glucose. In this enzymatic hydrolysis reaction, cellulose enzymes are used to break the chains of sugars that make up the cellulose, releasing glucose. Cellulose hydrolysis is also called cellulose scarification because it produces sugars.

v. **Glucose Fermentation**. The glucose is converted to ethanol, through a process called fermentation. Fermentation is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast or bacteria, which feed on the sugars. As the sugars are consumed, ethanol and carbon dioxide are produced.

vi. **Pentose Fermentation**. The hemicellulose fraction of biomass is rich in five-carbon sugars, which are also called pentose's. Xylose is the most prevalent pentose released by the hemicellulose hydrolysis reaction. In this step, xylose is fermented using Zymomonas mobilis or other genetically engineered bacteria.

vii. **Ethanol Recovery**. The fermentation product from the glucose and pentose fermentation is called ethanol broth. In this step the ethanol is separated from the other components in the broth. A final dehydration step removes any remaining water from the ethanol.

viii. **Lignin Utilization**. Lignin and other by-products of the biomass-to-ethanol process can be used to produce the electricity required for the ethanol production process. Burning lignin actually creates more energy than needed and selling electricity may help the process economics.

Converting cellulosic biomass to ethanol is currently too expensive to be used on a commercial scale.

So researchers are working to improve the efficiency and economics of the ethanol production process by focusing their efforts on the two most challenging steps:

i. **Cellulose hydrolysis/enzymatic hydrolysis**. The crystalline structure of cellulose makes it difficult to hydrolyse to simple sugars, ready for fermentation. Researchers are developing enzymes that work together to efficiently break down cellulose.

ii. **Pentose fermentation**. While there are a variety of yeast and bacteria that will ferment six-carbon sugars, most cannot easily ferment five-carbon sugars, which limits ethanol production from cellulosic biomass. Researchers are using genetic engineering to design microorganisms that can efficiently ferment both five- and six-carbon sugars to ethanol at the same time.

The thermochemical conversion processes: A different approach to bioethanol production from lignocellulosic biomass is represented by the thermochemical path, which consists of biomass gasification followed by catalysed reaction or fermentation.

2.3:Three main steps characterize of the first method .

1. Biomass gasification, in which syngas is produced from solid biomass. Gasification is the thermochemical conversion of biomass at high temperature (~ 800 °C), in the presence of an oxidizing agent (as air, steam or oxygen), into a low calorific value raw gas, steam and tar.

2. Syngas transformation, where gas composition is adjusted by catalytic synthesis processes.

3. Separation of products (bioethanol) Bioethanol Production from Agricultural Waste Biomass as a Renewable Bioenergy Resource in Biomaterials.

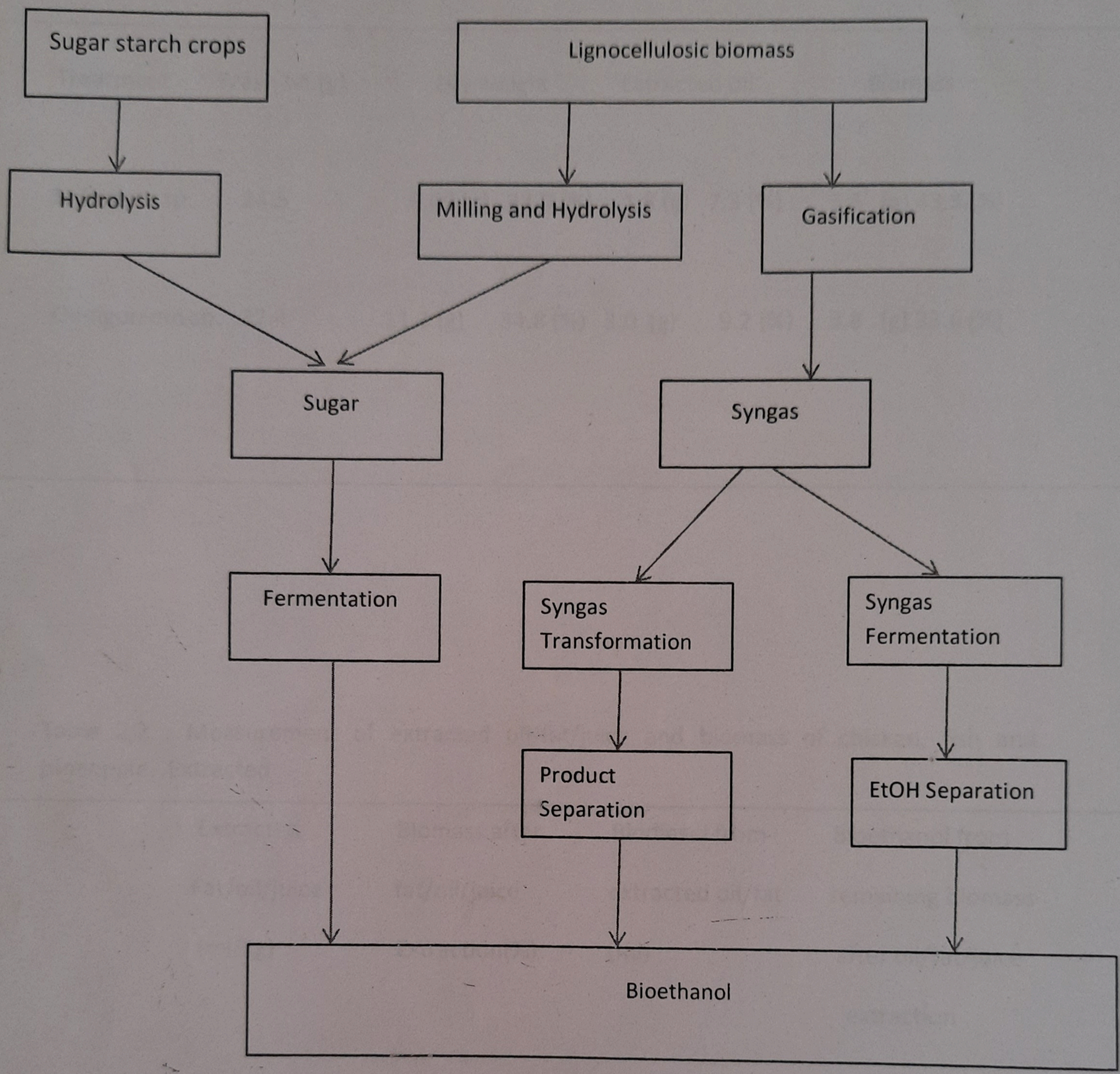


Fig2.2. Main pathways for bioethanol production.

Table 2.1. Measurement of fresh and dry weight, extracted oil and biomass of algae. [Petri dish size was same. Diameter was 7.5 and height 1 cm]

Treatment	Fresh wt (g)	Dry weight	Extracted oil	Biomass
Spirogyra sp.	24.5	8.09 (g) 33.0 (%)	1.8 (g) 7.3 (%)	3.5 (g) 43.3 (%)
Oedigonium sp.	32.4	11.3 (g) 34.8 (%)	3.0 (g) 9.2 (%)	3.8 (g) 33.6 (%)

Table 2.2 . Measurement of extracted oil/fat/juice and biomass of chicken, fish and pineapple. Extracted

	Extracted Fat/oil/juice (ml/kg)	Biomass after fat/oil/juice Extraction(%)	Biodiesel from extracted oil/fat (ml)	Bioethanol from remaining biomass after oil/fat/juice extraction
Chicken	170	60%	153	In process
Fish	100	80%	88	In process
Pineapple	500	50%	In process	In process

3. RESULT ANSD DISCUSSION

Biomass yield: Biomass (after oil extraction) was higher in Spirogyra sp. than Oedigonium sp. (Table 2.1). Fig. 2.2 showed extracted algal biomass. Fish biomass was higher (80%) than chicken (60%) and pineapple biomass (50%) [Table 2.2]. Biodiesel production was higher (153 ml/kg) in chicken fat than in fish fat/oil (88 ml/kg). Pineapple, chicken and fish biomass are preserved for bioethanol production. (Table 2.2) showed extracted chicken, fish and pineapple biomass which will be used for bioethanol production using bioreactor.

Biomass or agricultural residues consist of the polymers cellulose, hemicellulose, pectin, protein, and lignin. Of the carbohydrate monomers, xylose is second-most abundant after glucose in most plant cell walls [Because the raw material cost is > 50% of the overall cost of the ethanol process, fermentation of xylose is needed to improve the yield and lower the production cost of ethanol since many biomasses and agricultural wastes contain xylose, in the order of 10–40% of the total carbohydrate mass. Fermentation of both xylose and glucose is therefore crucial to reduce the costs of ethanol production from lignocellulosic raw materials.

4. CONCLUSION

Several aspects of the production of bioethanol from fruit wastes using the residual heat from chilling water of a cogeneration plant make this process highly suitable for its environmental sustainability. In fact, an alternative to disposal of residual biomasses with high carbon load vaporizes them, transforming agricultural wastes in co-products; the use of hot chilling water of a cogeneration plant allows to reduce the energy consumption needed for distillation, contemporarily reducing the environmental impact due to heat dispersal from the cogeneration plant; bioethanol, that can be used as a biofuel, is a renewable energy source. Among the tested fruits, apple showed the best performances. The possibility to feed the fermentation plant with CTR when fruit wastes are unavailable guarantees functionality throughout the whole year and the economical sustainability of the plant.

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