Bioethanol Production from Iraqi Date Palm Resources

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Abstract

The present work focuses on the most interested bioethanol production from Iraqi date palm resources (so called Zahde) as a sugar yield substrate using improved technology of hydrothermal extraction, fermentation and distillation. The extracted sugar liquid juices were converted into bioethanol by aerobic and anaerobic fermentation. Fermentation for bioethanol production consists of two operations, namely, biomass fermentation and bioethanol fermentation. The distillation consists of two stage columns rectification. The feasibility of this process has been improved by the construction of a well designed stainless steel pilot plant with 3 metric tons of bioethanol production per day of 96 vol.% purity. However, so many experiments have been carried out to optimize the productivity and the purity of bioethanol according to the design parameters. The pilot plant yield is 90 % based on the processes raw material with 96 vol.% bioethanol productivity of (300-330) liter per ton of date palm. The purity of bioethanol was tested using GC technology that indicated 96 vol.% purity of ethanol and 1.2 vol.% methanol at 25°C with not more than 450 ppm of contaminants. The optimum operating condition, equipment specification and the process flow diagram were extremely described in this paper.

KEYWORDS: Hydrothermal extraction, Saccharification, Fermentation, Distillation.

Introduction

Ethanol can be manufactured either synthetically from petrochemical raw materials or biologically though the fermentation of sugar. When pure ethanol is produced from glucose or some natural source by fermentation followed by distillation, the result is bioethanol. Bioethanol can be improved as a renewable fuel for vehicles in its absolute and pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Ehanol/bioethanol is alcohoic transparency liquid can be used as a raw material for alcohol derivative, chemical industry, paint base industry, pharmaceutical industry, a mixture of fuel for vehicles, given that the ethanol/bioethanol as a source of renewal energy to reduce the pollution of internal combustion engines. A grade 90-96% vol can be used in the industry, while ethanol/bio-grade that have 96-99.5% vol can be used as a mixture for basic industrial materials and pharmaceuticals. On a world level, bioethanol is the most used biofuel. It is produced from sugar-containing agricultural products such as sugar cane, corn, wheat, sugar beet, waste from sugar refineries, or sweet sorghum. The predominant technology for converting biomass to ethanol is fermentation, which is a mature biochemical technology.
S. Prasad et. al. (2007) outlined bioethanol production from sweet sorghum potential. Sweet sorghum is a crop with wider adaptation and grows rapidly and results in higher production of biomass as well. It has a four-month crop cycle which results in two crops per year as compared to only one in case of sugar cane. Sweet sorghum as an alternative energy source is a high biomass and sugar-yielding crop because it has a unique characteristic of high carbon assimilation and has a special ability to accumulate high levels of extractable.

M. K. Francis (2006) explained the production of bioethanol from sugar beets and wheat, in the European Union where almost 500,000 metric tons bioethanol capacity. Production grew 15.6% over the course of one year from 424,750 tons in 2004 and 491,040 tons in 2005. The review of bioethanol production studies the fact that wheat-based and sugar beet-based bioethanol production is viable options for the European Union, where the demand for biofuels in the EU is strong.

R., Caro and R. Hurter (2005) described the biorefinery using an electrolytic system includes a flow diagram of an ethanol fuel biorefinery that uses soda cooking to produce cellulose fiber and electrolysis to recover caustic soda, extract lignin, and produce hydrogen and methane gas as additional products. The example included in the diagram produces 12,000 gallon of ethanol and approximately 35 tons per day of cellulose pulp.

Da Silveira Dos Santos et. al. (2009) demonstrated bioethanol production from Sugarcane Bagasse by Zymomonas mobilis using Simultaneous Saccharification and Fermentation (SSF) Process. The researchers have noted that fermentation utilizing strains of Zymomonas mobilis and the use of simultaneous saccharification and fermentation (SSF) process has been proposed. Also statistical experimental design was used to optimize the conditions of SSF, evaluating solid content, enzymatic load, and cell concentration.

C.M. Drapcho (2008) et. al. illustrates the yeast Saccharomyces cerevisiae which is the universal organism for fuel bioethanol production using starch and sugar feedstocks. The sugars that are metabolizable by this organism include glucose, fructose, mannose, galactose, sucrose, maltose, and maltotriose. Bioethanol production by S. cerevisiae is carried out via the glycolytic pathway (also known as the Embden-Myerhof-Parnas or EMP pathway). In the simplest form, production of ethanol from glucose can be expressed by the following equation:

\[ \text{Glucose} \rightarrow 2 \text{ethanol} + 2 \text{carbon dioxide} + \text{energy} \]

Under ideal conditions, however, 90 to 95 percent of the theoretical yield can be achieved.

C. Xiros, C.Uolos (2009) explained the second generation process for biofuel production. They concluded that the profile enzymatic of the extracellular extract from F. oxysporum submerged cultures using brewer's spent grain (BG) and corn cob as the carbon source was proved efficient for a successful hydrolysis of BG. The fermentation study carried out using sugar mixtures simulating However, a considerable bioconversion yield was achieved (60% of the theoretical) making this bioprocess worthy of further investigation for a potential commercial application.

**Date Palm**

Iraq is a famous agriculture country in the crop of date palm, because there are so many types and shapes of this fruit, with a production capacity approach's 400,000 tons in 2010 (General Agency of Palm Tree/MOA Iraq-2010). Each piece of a date palm (Zahde) characterizes of a length which is more than its width and has a thin waxy cover coated the inner core, which is the valuable raw material, and has a single centered solid kernel. The weight of each piece is ranged between 5-15 gm with average weight of 7.9
gm and specific density of 1.08. The monosucrose content varies between 54-57 percent and disucrose is about 9.6 percent and the solid seed kernel weight percent is about 10 percent. The chemical composition of date palm is the monosucrose that comprises 70% of its weight. The monosucrose content is a mixture with 55% of glucose and 45% fructose. Other components are proteins, amino acids, pectin, starch, cellulose, tannin, fats, mineral salts and water. Date palm are fruit crop mature in summer and grows independently results in higher production of biomass as well. It has a year crop cycle and the total cultivated area of palm in Iraq are about 111989 hectares where each hectare usually contents 224-368 palm trees (Passat 1971) that’s make Iraq the best harvest country in the production of date palm crop in the world.

Process Sequence

Date palm were compiled as the best standard raw material for bioethanol production in Iraq for two reasons, firstly the produced juices are more purer than the other sources of sugar or starch, secondly the cost of dates palm juices production is commonly less expensive than the cost of other sources. Normally the acidity of dates palm juices has a natural pH of 3-4 which is already suitable for fermentation step.(Drapcho et. al. 2008)

1. Hydrothermal Extraction:
The dates palm processing included a several steps starting with washing and destaning (kernels separation), then digestion at a high temperature by exposure to direct steam at temperature range of 85°C to 100°C, which leads to the extraction of sugar and preparation of liquid juice containing mono and disucrose with concentration of 20-25% TSS. The Juice is filtered using filter press to separate cellulose fibers, then cooled and diluted to a concentration of 10-15% TSS.

2. Fermentation:
At the first operation, only biomass is produced by aerobic fermentation, while at the second with anaerobic fermentation both alcohol and biomass are produced, even though the latter is produced at a rate that is lower than that of the previous operation. If yeast or suitable bacteria are added to dates palm juices, the fermentation process occurs and bioethanol is created. The enzymes mixture present in the yeast act as a catalyst for the glucose (C_{6}H_{12}O_{6}) conversion process. In this process, the sugar compound is cleaved to form alcohol (C_{2}H_{5}OH) and carbon dioxide (CO_{2}). This conversion process can be described in extremely simplified form with the following equation:

\[ C_{6}H_{12}O_{6} + \text{yeast (Saccharomyces cerevisiae)} \rightarrow 2C_{2}H_{5}OH + 2 \text{CO}_{2} \]

The mechanism steps of this reaction are as follow (Passat 1971):

\[ C_{6}H_{12}O_{6} \rightarrow 2\text{CH}_{2}\text{OH},\text{CO},\text{CH}_{2}\text{OH} \text{ (dioxy acetone)} \]

\[ 2\text{CH}_{2}\text{OH},\text{CO},\text{CH}_{2}\text{OH} \rightarrow \text{CH}_{3},\text{CO},\text{COOH} \text{ (pyroracemic acid)} + 2\text{H}_{2} \]

\[ \text{CH}_{3},\text{CO},\text{COOH} \rightarrow \text{CH}_{3}\text{CHO} \text{ (acetaldehyde)} + 2\text{CO}_{2} \]

\[ \text{CH}_{3}\text{CHO} + \text{H}_{2} \rightarrow \text{CH}_{3}\text{CH}_{2}\text{OH} \text{ (Ethyl alcohol)} \]

The cell mass synthesis is achieved by the transformation of sugar to complex compounds that interfere within the cell composition, hence new generation of yeast is build up. Obviously, the Fungous grows by the division of single cell to two new cells and after a certain time the two cells are also divided to new four cells, so that yeast rapidly propagates within short periods (2.5 hr) from one generation to another generation. The chemical reaction that explain this mechanism is as follow:

\[ C_{6}H_{12}O_{6} \rightarrow \text{CH}_{3}\text{COCH(OH)}_{2} \text{ (pyroracemic acid aldehydlyrate)} \]
The last material creates another material called Alanin (Passat 1971). That is converted to protein material (polypeptide polymer) that participate in the synthesis of a new cell of yeast.

The required energy for continuing the cell life of yeast is explained by the following reaction (Drapcho et al. 2008):

\[ C_6H_12O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 674 \text{ kcal (energy)} \]

In the present pilot plant, a controlled fermentation temperatures between 25-30°C were deduced using external well-designed heat exchangers so that the fermentation process can proceed successfully. The pH value should be fixed between 3-4. During this process, 90 to 95 percent of the TSS is converted to bioethanol and CO₂. The produced raw bioethanol from fermentors is approximately 10% to 14% by volume.

3. Distillation/Rectification:
The raw ethanol, which is obtained by fermentation, is distilled to approximately 75% by volume using direct live steam distillation column. During subsequent rectification, the distilled bioethanol is concentrated to about 96 vol% in the second distillation column with a reboiler.

Pilot Plant Set Up
The specification of equipment that explain the process technology for the production of 3 metric tons per day bioethanol from Iraqi dates palm (Zahde) involving:

1. Washers: They are metal mesh belt conveying machine supplied from sides with water spraying nozzles to clean the date palm from dust, dirt and the adhesive solid particles. The washers are fixed with a suitable inclined height with 0.3-0.5 m/s belt velocity.

2. Destaner: The date palm after washing passes to a destaning machine to separate the kernel from the core of date palm, at the same time slicing and chopping the date palm into paste. The destaner made of 304 stainless steel with 0.8 m diameter and 0.8 heights and equipped with a gear motor of 12 kW and a rotation speed of 100 rpm minimum.

3. Digestion Vessel: A cylindrical, bottom dished vessel made of 304 stainless steel with 1 m diameter and 1.25 m height combined with a sparger to feed live steam and water to extract sugar. Usually, digesters are equipped with a paddle and rotor connected to 7.5-10 kW gear motor. The rotation speed of the rotor exceeds 30 rpm. The working temperature is 85-100°C.

4. Filter Press: Hemicellulose and cellulose fiber continuously separated through the passes of the digested slurry via internal mainfolding filter press to produce clear juices with concentration of 20-25% TSS. The Multiunit filter press is a compact type with cloth filter media. The separated fibers usually washed with hot stream of water to assure total extraction of the residual sugar.

5. Dilution Tank: In dilution tank the juices passed to heat exchange and cooled to 25°C. Its concentration is brought to approximately 12° Brix equivalent to 12% TSS, a typical condition of fermentation. Dates palm juices have a natural pH of 3-4, which is suitable for fermentation. The tank is well agitated and baffled, with 10 m³ in size and 304 stainless steel construction, combined with external heat exchanger to control temperature.

6. Seed Vessel: Where the cell synthesis and the build up of new generation of yeast are taken place. The vessel is open type and its volume is 5% of the total volume of fermentors. Also the tank is 304 stainless steel made and equipped with agitator, purified air source and external heat exchanger to control its temperature between
25-30°C. The juices concentration is held stable and brought to approximately 10° Brix equivalent to 10% TSS during the yeast generation period.

7. **Fermentors**: The fermentation tanks are closed tanks, high bulky in volumes with 35 m³ size usually constructed of a polymer lined carbon steel or stainless steel. Commonly these fermentors are supplied with several control devices to maintain fixed solution temperature, CO₂ pressure, level, homogeneity etc. After fermentation period, the fermented solution passes to centrifugal separators to segregate the concentrated yeast that can be used again and recirculated back to new fermentors. The juices concentration is brought to approximately 12° Brix equivalent to 12% TSS at the starting and 0° Brix at the end of fermenting period.

8. **Distillation Column**: The raw bioethanol (10-14%), which obtained by fermentation, is distilled in this stage to approximately 75% by volume using distillation column. The distillation column is a cylindrical 304 stainless steel constructed with 50 cm diameter and 50 cm tray spacing contains 19 sieve trays that satisfy 12 m total column height including the upper vapor collection part and the lower liquid collection part. A vertical condenser with 110 tubes of ½” equipped with column. The heating medium is live steam of 3 kg/cm² gauge pressure. The operating conditions of the column are:

- Feed flowrate 20 l/min
- Product flowrate 2.8 l/min
- Reflux ratio 3
- Steam consumption 1 ton/hr
- Alcohol losses 1%
- Column temperature 80°C

9. **Rectification Column**: The hydrated bioethanol 75% by volume from the first distillation column is fed continuously to the second rectification column that is connected with a reboiler. The rectification column is a cylindrical 304 stainless steel constructed with 35 cm diameter and 30 cm tray spacing contains 29 sieve trays that satisfy 13 m total column height including the upper vapor collection part and the
lower liquid collection part. A vertical condenser with 98 tubes of $\frac{1}{2}''$ equipped with column. The heating medium is alcohol-water mixture produced by the equipped reboiler that works with steam of 1 kg/cm² gauge pressure. The operating conditions of the column are:

- Feed flowrate: 3 l/min
- Product flowrate: 2.1 l/min
- Reflux ratio: 4
- Steam consumption: 750 kg/hr
- Alcohol losses: 1%
- Column temperature: 78°C

**FIG.2 Process Flow Diagram for Distillation /Rectification Unit**

**Results And Discussion**

The designed pilot plant produces bioethanol in the rate of 3 metric tons/day with a productivity of more than 320 liter bioethanol of 96 vol.% volume percent measured at temperature 25°C per ton of Iraqi dates palm. This quantity of production has been considered economical and competitive compared with other agriculture starch or sugar sources that commonly used in other countries. Dates palm crop are used mostly for food and feed. However, because of their high sugar contents and availability dates palm are also good feedstocks for conversion to concentrated syrup that called Debis, bioethanol, bio-based products, and biofuels.

**Table 1 Properties of concentrated syrup extracted from Iraqi dates palm by Quantitative Chemical Analysis.**
Processing Temperature | Total Dissolved solid (Brix) | Total Sugar Percent | Purity % | Ash % | Proteins % |
---|---|---|---|---|---|
50°C | 65 | 51.1 | 78.5 | 1.56 | 1.56 |
80°C | 69.5 | 55.3 | 79.5 | 2.28 | 1.31 |
100°C | 73.5 | 59.1 | 80.3 | 1.95 | 1.20 |

Bioethanol pilot plant yield

The sucrose of dates palm juice is converted to glucose and fructose by the first enzyme (Anvertes) of Saccharomyces cerevisiae according to the reaction:

\[ C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \]

Sucrose Fructose Glucose

And the second enzyme (Zymase) convert the simple sucrose to ethyl alcohol and water according to the reaction:

\[ C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \]

Ethyl Alcohol

By subtraction, the overall reaction is:

\[ C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_2H_5OH + 4CO_2 \]

Table 1 indicate clearly that the total sugar percent at 100°C processing temperature reaches 59.1% per ton of dates palm concentrated syrup. Approximately each 1100 kg date palm produces 1000 kg concentrated syrup of 73.5 Brix equivalent to 59.1 % sucrose, so that the average sucrose percent is taken with good accuracy of 54 % per each ton of dates palm (Zahde).

The theoretical productivity of C\(_2\)H\(_5\)OH = 261.47 kg per ton dates palm.

The density \( \rho \) of 96 vol.% bioethanol at 25°C = 0.795 kg/l, where:

<table>
<thead>
<tr>
<th>( \rho ) at 25°C</th>
<th>vol%</th>
<th>wt%</th>
<th>mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.978</td>
<td>10</td>
<td>8.06</td>
<td>3.3</td>
</tr>
<tr>
<td>0.846</td>
<td>20</td>
<td>67.8</td>
<td>47.7</td>
</tr>
<tr>
<td>0.795</td>
<td>96</td>
<td>92.5</td>
<td>82.8</td>
</tr>
</tbody>
</table>

The theoretical productivity C\(_2\)H\(_5\)OH = 328.8 liter absolute per ton dates palm.

The average practical productivity of C\(_2\)H\(_5\)OH =310 liter of 96 vol.% per ton dates palm which is equivalent to 297 liter of 99.9 vol.% per ton dates palm

Plant yield = 297/328.8 = 90 %

Juices and Bioethanol Analysis

A part of the juice is normally used for sugar syrup, which is a high-value food product, and can be used for bioethanol production as well. The solid residue or cellulose fiber from the extraction step, which is referred to as bagasse, is converted to animal's foodstuff. The cooling typically includes two stages. In the first stage the hot dates palm solution is cooled through a heat exchanger in counter-current flow to 60°C. In the second stage the solution is further cooled to 30°C using water as a diluent and coolant. The processing temperature in the digestor is so important to dictate the total amount of the dissolved solid that contains the total dissolved sugar and measured by the Brix. The Brix is a crude measure of sugar contents of a molasses or juices product. By definition it is a measure of the sugar content of a liquid if all the dissolved and suspended solids in the liquid were evaluated as sugar. The produced bioethanol from Iraqi dates palm is pure transparency alcoholic liquid with 96 vol.% that is the eutectic composition. The concentration of chemical constituents ( not more than 450 ppm) in the produced bioethanol differs periodically from time to time depends on the fermentation conditions especially the temperature parameter and the type and property.
of date palm, commonly this variation does not affect the global purity and properties of bioethanol. Gas chromatography tests indicate a purity of 92.5 wt % that equivalent to 96 vol.% of ethanol and about 1 wt% methanol at 25°C with not more than 450 ppm of the undesired constituents such as fossil oil, acetic acid, acetaldehyde, ethyl acetate, furfural, tannis, ester etc as indicated in table-2 and fig.3.

Table 2 average constituents concentration of various distilled bioethanol from Iraqi Dates Palm.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Concentration mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil oil</td>
<td>193</td>
</tr>
<tr>
<td>Total acids</td>
<td>36</td>
</tr>
<tr>
<td>Esters</td>
<td>18</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>3.2</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.45</td>
</tr>
<tr>
<td>Tannins</td>
<td>25</td>
</tr>
</tbody>
</table>

1 Determination is made with Gas Chromatography Technique.
2 as acetic acid
3 as ethyle acetate
4 as acetaldehyde

Bioethanol Productivity

In terms of the productivity, it was found that the bioethanol production is extremely feasible with 300-330 liter (310 liter average) of 96 vol%. percent bioethanol per 1 ton dates palm and this quantity is competitive compared with the production from wheat based or sugar beet. In terms of the value of the by-products from bioethanol production, it seems that the released CO₂ gas as by product can utilized the same quantity of bioethanol which explain the economical profits and benefits of this process. In terms of processing costs (considering labor, energy, and factory operation), there are no additional costs for dates palm processing compared with other processes, but
adversely some other sources processing are a bit more expensive than dates palm bioethanol. The data gathered in this study shows that bioethanol production from dates palm can offer prices that are emulative with conventional ethanols. In addition to other sources of fuel available in Iraq, the dates palm resources are an important potential feedstock for bioethanol production due to the importance of this biofuel as a source of a renewable energy and to save environment by reduce pollution.

**Conclusion**

This study considered the production technology of 3 metric tons per day bioethanol including hydrothermal pretreatment, fermentation, distillation and development of cheap and valuable bioethanol supply system by the processing of agricultural Iraqi date palm resources (so called zahde). Realization of this energy system will enable stable supply of cheap liquid fuel from local biomass. The degree of complexity and feasibility of biomass conversion to bioethanol depends on the nature of the feedstock. Date palm resources usually contain a mixture with 55% of glucose and 45% fructose. The conversion process implies the hydroextraction of date palm juices followed by aerobic biomass, and anaerobic bioethanol fermentation of glucose and sucrose with most preferred substrates among the sugars metabolized by Saccharomyces cerevisiae. The results presented in this study are based on number of experiments and input parameters of the pilot plant, which can significantly influence the bioethanol properties. The pilot plant yield is 90 % based on the processes raw material with 96 vol.% bioethanol productivity of (300-330) liter per ton of date palm. The GC tested bioethanol from Iraqi date palm exhibits a purer ethanol of 96 vol.% and 1.2 vol.% methanol with not more than 450 ppm of contaminants. The suggested procedure gives a productive and economic process that can be scaled up and converted to industrial scale.

**Future Work**

The finance program utilization of improved bioethanol from Iraqi date palm for industrial uses or biofuel grade that can be applied successfully by the low prices of bioethanol , and also the low prices of date palm raw material.

**References**


General Agency of Date Palm/ Ministry of Agriculture-Iraq report-2010/http://www.moaqer.com

Kenji Yamaji et al "Production of Low-Cost Bioethanol to be a Rival to Fossil Fuel" Japan Society of Energy and Resources, Osaka, Japan, March 2006.

Mary Kate Francis "The Economics of Bioethanol Production in the EU" USDA Foreign Agricultural Service, GAIN Report Number: E36081 (2006).

Rafael Vaisman "Bioethanol production in rural Angola" Bridges Trade BioRes Review, Volume 4 Number 1 March 2010.

S. Prasad, Anoop Singh, N. Jain, and H. C. Joshi "Ethanol Production from Sweet Sorghum Syrup for Utilization as Automotive Fuel in India" Division of Environmental Science, Indian Agriculture Research Institute, New Delhi-110012, India, April 4, 2007.