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Bioethanol production from date palm fruit waste fermentation using solar energy

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Every year, more than 236,807 tons, equivalent to 30% of date-palm fruits produced in Algeria, is lost during picking, storage, and commercialization processes. Gasification of this huge biomass can generate biogas such as bioethanol, biodiesel, gasoline and other useful substances. Bioethanol is becoming the main biofuel produced by chemical synthesis or anaerobic fermentation from biomass and is significant for industrial development, investment, and use. It is eco-friendly, moderately costly and cleaner than other gasses. Actually, due to modern biotechnologies, it is possible to valorise the common date-palm waste (CDPW) by bioconversion and to commercialize them in local and international markets in the form of new products with an acceptable added value such as bioethanol. CDPW is a renewable and sustainable resource of energy that is not greatly used in industries. The date is rich in biodegradable sugars, providing bioethanol after fermentation during 72 h at 30°C in the presence of *Saccharomyces cerevisiae* yeast and the distillation of date's juice obtained. In the first experience, a solar batch fermenter (SBF) of 50L capacity, and a butane gas distiller using a cocotte (cooker) of 30L capacity was designed and constructed. The bioconversion systems led to the production of 250 mL/kg of ethanol at 90° after distillation of the CDPW juice at 78°. This is in comparison to the theoretical ethanol directly produced from sugar by chemical synthesis process. The 33% efficiency that was obtained appeared satisfactory and it encouraged the great scaling development of bioethanol based on CDPW biomass and other raw materials abundant in Algeria Sahara.

Keywords: Algerian Sahara, bioethanol, dates-palms waste valorization, distillation, fermentation, solar energy, *Saccharomyces cerevisiae.*

INTRODUCTION

Energy produced and used are crucial elements for the development of countries and improvement on human activities (WEA, 2000). Electricity and heat generation from biomass is an efficient manner of energy conversion that is climate friendly. In Algeria, biomass potentially offers great promises with the bearing of 3,700,000 tons of oil equivalent (TOE) coming from forests and 1,330,000 TOE per year from agriculture and urban wastes (Hasni, 2006). A pre-review showed the feasibility of electricity production of 3-6MW from the discharge of Oued-Smar in Algiers (Himri et al., 2009). The removal of biogas by combustion is essential to protect the atmosphere from the undesirable emission of unburned methane contained in biogas. The increasingly use of biogas, particularly produced from landfills, has commenced with national pilot research projects initiated by Renewable Energy Development Center (CDER, http://portail.cder.dz), studying methane recovery from cull dates and fruits processing of by-products. This operation is followed by the successful experience carried out by Renewable Energy Research Unity in Sahara Medium (URERMS) located at Adrar Province in Southern Algeria. The project is considered as a first progressive step as regard biogas energy generation in the country.

Bioenergy, including bioethanol, biodiesel, and other substances is feasible and have economically become the future solution for energetic and ecologic issues. Amongst other biogases, bioethanol has higher burning effect €2.25/kWh and lower environmental effect (Sindhu et al., 2016). According to the Renewable Fuels Association (RFA), USA, Brazil, EU and China produced 50.3%, 25.5%, 4.5%, and 2% million gallons of ethanol in 2014 respectively (Sanchez and Cardona, 2008). Certainly, the countries with agronomic based economy are therefore appropriate for bioethanol generation (Mielenz, 2001). Governments around the world have actively promoted the identification, development and commercialization of technologies for the production of alternative biofuels within the last three decades. The operation includes the production of bioethanol, which captures the attention of many researchers, consumers and investors in the hopefulness of better fuel sustainability (Oh et al., 2010). The competition between food and fuel risks the equilibrium of the equation.

Bioconversion process utilizes non-edible lignocellulose, starchy materials coming from agricultural and forestry biomass; and it is becoming the main solution to provide renewable eco-friendly and economical energy source. The characteristics and capabilities of bioethanol make it favorable to mix with gasoline (Balat et al., 2008). In addition, the need to satisfy the energy demand without environmental bearings and non-renewable fuels stock resulted from the fossil fuel, investing in research development in clean energy and sustainable development to which bioethanol is one of them (Krylova et al., 2008). Bioethanol prevents engine knocking and premature explosion due to its high octane index of 110. Moreover, higher octane index also provides wider flammability, higher heat vanishing and speed of flame (Lashinsky and Schwartz, 2006). Bioethanol has 35 to 40% lower energy content compared to gasoline, and 35% of higher oxygen content which makes the combustion cleaner and resulting in a lower emission of toxic substances (Li et al., 2008). Bioethanol helps to reduce CO_2 emission up to 80% compared to using gasoline, thus promoting a cleaner environment for the future (REN21, 2014). Chemically, bioethanol is less unsafe than gasoline and its higher flash point (13°C) gives better storage treatment ability and it is less flammable. The auto-ignition temperature is between 333 and 423°C and ethanol relatively require an elevated temperature than gasoline to be an auto-detonation; hence, ethanol vapor will be only combusted later than gasoline without a forced detonation (Shinsuke et al., 2005).

Many microorganisms (yeasts) can be used for transforming biomass into ethanol (Nigam, 2000). *S. cerevisiae* yeast can be used to produce ethanol of 48.8 mL/kg from pineapple cannery by-product and 120.7mL/kg from sorghum juice (Johansson et al., 2012). The augmented request of energy in homes, industries, transportation and agricultural sectors needs the rapid use of bioenergy options. Without exception, the founded biomass renewable energy is expected to progress from 50EJ/year in 2012 into more than 160EJ/year by 2050 (Kwiatkowski et al., 2006).The uncooked material and the energy request are the major cost factors in the bioethanol production (Vucurovic et al., 2012). Following the oil crisis of 1970, biofuels were perceived in many countries as a realistic solution to oil resources dependence problem. Moreover, the mixture usage with traditional fuels made it possible to consider the gain on the levels of vehicles pollutant emissions. The oil counterblows of 1986 and the too high maintenance and cost slowed down their development. To date, bioethanol is seen as the main biofuel for the future. It is subject to a significant industrial development around the world, and can be produced by chemical synthesis or fermentation (FAO Stat, 2015).

Algeria has several natural energy resources, including oil reserves of about 13.4 billion barrels, natural gas of 4502 billion m^3, and coal of 65 million tons. On the other hand, the date-palm grove areas have registered a significant expansion in Algeria, estimated at 69%, growing from 101,000 ha in the year 2000 to 169,361 ha in the year 2009 with a total of 18.7 million palm trees (Nakhla in Arabic word) scattered over around 1,000 farms, producing 789,357 tons of dates every year. Approximately 50% of these palms are currently in production (Elsanhoty et al., 2012). Algeria is a country situated in the sunbelt region of the earth where the solar radiation potential is over 8 billion MWh/year. Algeria has an important area of about 2.4 million km^2 and a feeble population density of 15.8 inhabitants/km^2 where the Sahara occupies more than 84% of the whole area. Algerian climate is maritime-north and semiarid to arid middle and south. Date-palm constitutes the principal axis of the oasis climate of the Sahara and found the basic agronomy structure of the inhabitants. These trees create the essential microclimate for all other cultivars of cereals

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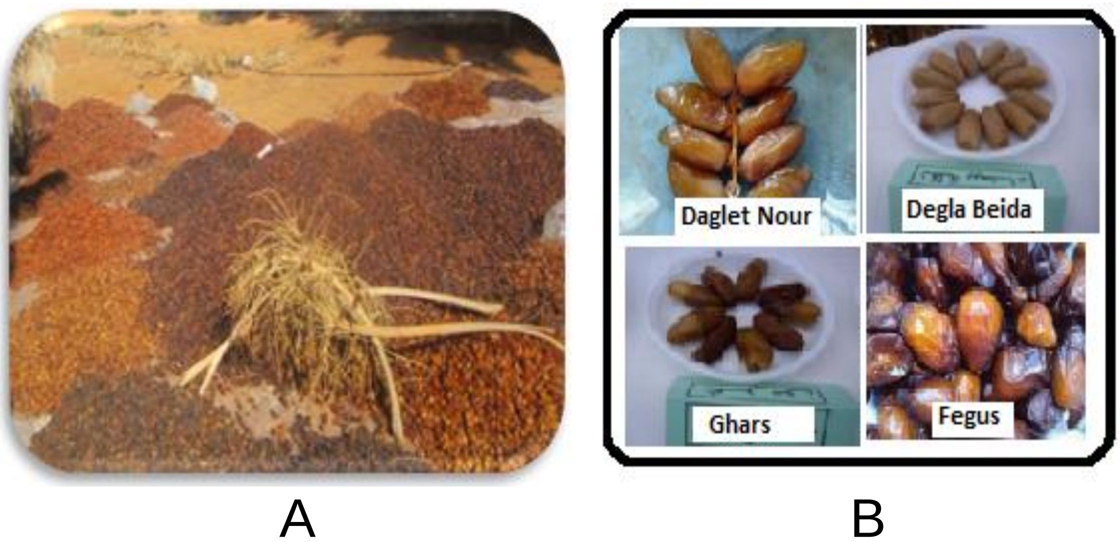

Figure 1. Some principal varieties of dates produced in Algerian Sahara. A, Dates of low quality; B, Dates of high quality.

and vegetables, provide materials, and burn biomass for building and warming. The top ten countries producing about 90.5% of the world's dates are Egypt, 17.2%; Saudi Arabia, 13.7%; Iran, 13%; United Arab Emirates, 9.8%; Pakistan, 9.6%; Algeria, 9%; Iraq, 7.2; Sudan, 5.4%; Oman, 3.5%; and Libya, 2% (FAO Stat., 2012). More than 236,8 tons equivalent to 30% of dates produced in Algeria are lost during picking, storage, commercialization and conditioning process, caused by the fungus, infestation by insects or simply due to their low quality, unconsumed by humans (Sofien et al., 2014). Only Adrar city region counted more than 3,000,000 of date-palm, playing an important ecological role, and offers great dates tonnage of 86,000/year. But in spite of this huge richness, these dates present a low commercial value (Figure 1a) compared to the high-class varieties of dates such as Deglet-Nour, Degla-Beida, Gears and Fergus (Figure 1b). Therefore, the CDPW are intended only for subsistence farming and animal feeds or barter exchange with foreigner countries, as in Mali, Niger, and others.

No processing industry was established in the Algerian Sahara areas to transform these huge harvests of (CDPW) into economic useful gain. Dates are generally a complete food value, rich in fermentable and biodegradable sugars, where energy reaches 2000 to 3000 Cal/kg, offering bioethanol, anaerobic fermentation, and distillation afterward. Their composition analyses showed that the Algerian Sahara dates varieties are very rich in reducing sugars, especially glucose and fructose of about 73 to 83% in dry basis (Acourene and Ammouche, 2012). Thus, making dates extract moderately suitable as feedstock for fermentation (Wei-Hao et al., 2016). For instance, we can produce ethanol after anaerobic fermentation by microorganisms such as *S. cerevisiae*. In addition to their sugars resource and moderately long conservation period, dates offer many other technological possibilities. They are seen as raw materials for the production of different metabolites, biopolymers, organic acids, antibiotic, amino acids, enzyme, bakery yeast, and also the butanol and hydrogen (Shahravy et al., 2012; Qureshi et al., 2012; Abd-Alla et al., 2012; Aditiya et al., 2016). The present work consists of the realization of an experimental solar batch fermenter prototype operating with the solar water heater, in order to reduce the energy consumed and to ensure anaerobic fermentation medium for the CDPW dates juice at 30%, and for producing a high quality and quantity of bioethanol at low cost after distillation.

MATERIALS AND METHODS

Raw material and microorganism

The mixture of the CDPW used in the study to produce bioethanol is composed essentially of Hchef, Kacien, and other varieties of date's scraps of the cattle food originated from Algerian Sahara (Figure 1a). The products are dried, kept in bags and stored at room's temperature. The microorganism *S. cerevisiae* used in the fermentation process of date's juice is provided by the industrial plant of bakery yeast production, coming from Oued-Semmar in Algeria.

Ethanol production medium

1. The CDPW (Figure 2a), were washed, plunged in a water bath, rubbed carefully, and rinsed with pure water to eliminate sand, pebbles, insects and remainder plants (Figure 2b).
2. The CDPW are petted to separate seeds from coasts (Figure 2c).
3. The CDPW substrates are ground and imbibed in hot water at 90

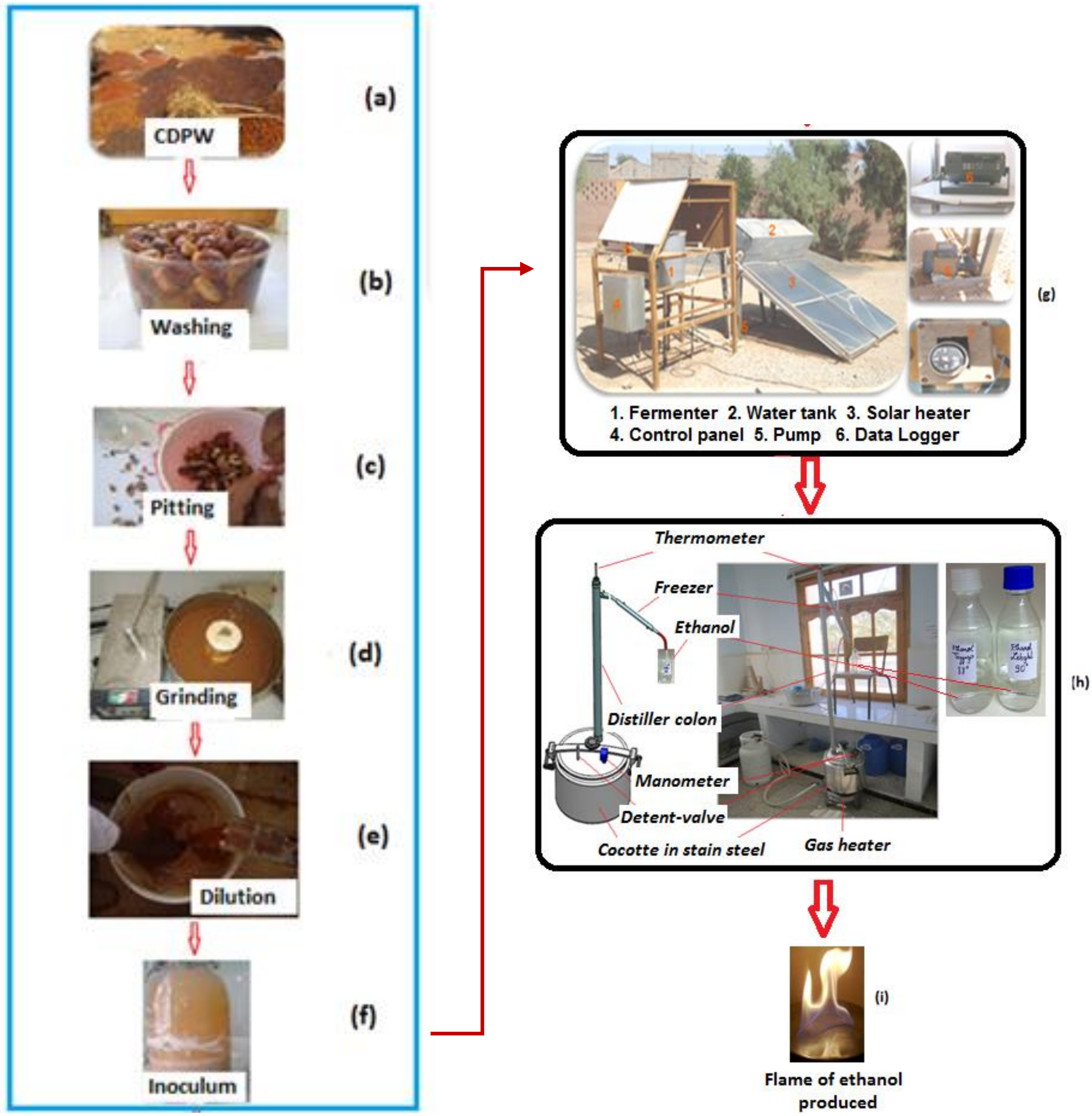

Figure 2. Bioethanol generation process.

to 95°C to facilitate sugars extraction (Figure 2d).

4. 200 g of CDPW was diluted into 800 ml of tap water, and simultaneously sulfuric acid was added and adjusted to ensure the pH between 4.3 and 4.7, for inhibiting the bacterial growth and favoriting overgrowth of the yeast (Figure 2e) (Wei-Hao et al., 2016). The fermentation medium is inoculated with 1g/L of *S. cerevisiae* and reactivated within 60 to 90min under an ambient temperature of 25 to 30°C in an aqueous solution in glucose with 12% V/V (Figure 2f).

5. The batch fermenter (Figure 2g) was designed and installed to operate efficiently by using solar water heater with the aim to reduce the cost of the bioethanol generation process. The fermenter was realized within the South Society of Metallic Construction (ECOMES, 2015), located at Adrar. The fermenter consisted of a tank of 50 L, built in double walls in galvanized stain steel and thermally insulated by fiberglass wool of 5 cm thickness. The heat exchanger is placed between the two walls of the tank. The lid of the tank is quite tight and contains a hole for evacuation of gasses and a second hole is

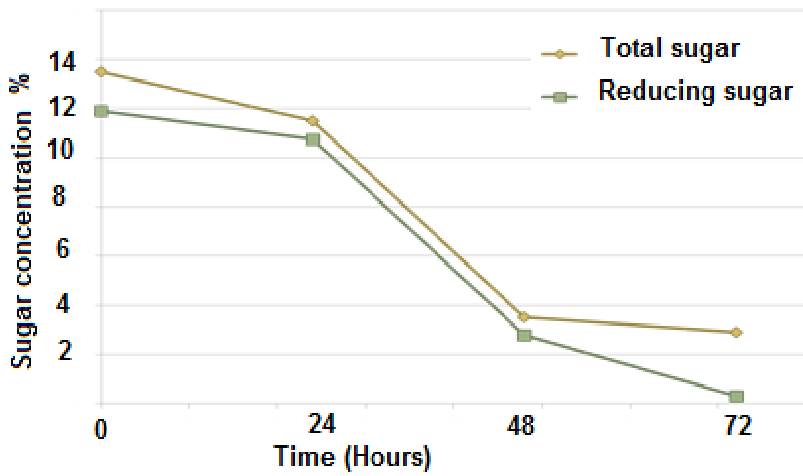

Figure 3. Sugars consumed during fermentation.

provided with a copper pipe. This was done in the middle of the tank and contained a thermostat for adjusting the substrate temperature close to 30°C. The fermenter is equipped with a manual agitator shaft and connected to a temperature data logger model Fluke 2635A with an internal memory card (Figure 2g). The batch fermenter is heated by water solar heater owned by the CDPW.

6. The water solar heater is inclined at Adrar latitude (27.88°N and 0.28°O) and oriented North-South to capture the optimum of solar energy incident during the year. The hot water is stored in a tank of 200 L and its circulation is ensured by a hydraulic pump controlled by a thermostat. Experimentation is performed during the cold season of the year, the first week of January 2015. During the fermentation process, the density sugars consumed, pH and the alcohol degree of the CDPW juice are controlled. The glucose evolution was controlled using Dubois method given in Michel-DuBois et al. (1956). Reducing sugars (RS) and total sugars (TS) are assessed by titration using a spectrometer UV. Saccharose content was estimated as the form:

Saccharose (%) = (TS – 0.95RS) % (1)

7. The pH was measured by a digital pH-meter model Mettler Toledo methods (ISO11289, 1993 and AOAC, 98, 1.12) and the date's juice temperature during the alcoholic fermentation was recorded using thermocouples K type connected to the data logger. After 72 h of alcoholic fermentation, the substrate juice to extract the bioethanol was used to filter. At the beginning of the distillation process (Figure 2h), the degree of alcohol is measured every 30min, and once the process is slowed, the alcohol is recorded every one hour. The process is stopped when the degree of alcohol became very weak. The distillation temperature was kept at about 78°C.

RESULTS AND DISCUSSION

The microorganism *S. cerevisiae* has an optional anaerobic breathing on the alcoholic bioconversion process. In anaerobic phase, the glucose is transformed into the ethanol by fermentation effect. During the first 48h of transformation, the process is active, especially between 24 and 48 h. However, the alcohol produced is increased throughout the last 48h of the process and an important degradation of the sugar is noticed after 72 h (Figure 3). The total glucose rate is strongly decreased during the time from 13.8% at the beginning of the fermentation process to 3% after 72 h. The period of the fermentation process of date's juice varied between 36 and 72 h under similar conditions. The glucose is not consumed completely due to the cessation of yeast growth caused by the accumulation of toxic substances (fatty acids), especially the octane and decane in CDPW juice (Figure 3), (Benziouches, 2011; El-Okaidi, 1987). Also, the density of the CDPW juice decreased significantly during the fermentation process from 1.07 to 1.0107 g/cm^3, which was caused by the transformation of sugar into bioethanol and the loss of mass under CO2 form (Figure 4). The continuous diminution of the refractive index indicated the increase of the light speed through the date caused by the decrease of the dates density. The total solvable solids in the date's juice were measured by a handheld refractometer for viniculture, using a refractometer, Atago model NAR-3T (°Bx), corresponding approximately to the total sugar concentration in (g/L). After distillation of the CDPW juice, a significant specific production of the bioethanol reached 250 mL/kg of dates at 90° was obtained, representing a bioconversion efficiency of 33% relatively to the theoretical sucrose transformation in the alcohol described using the following chemical synthesis equation:

$C_6H_{12}O_6$ + *S. cerevisiae* → $2C_2H_5OH + 2CO_2$ + Energy (2)

Where, 76 g/kg glucose produces 25 mL alcohol + x(g) of carbon dioxide if it is fermented by the yeast. Finally, the vibration sign of the biofuel produced is identified using the Infra-Red Spectra, showing different vibrations bands characterized by the

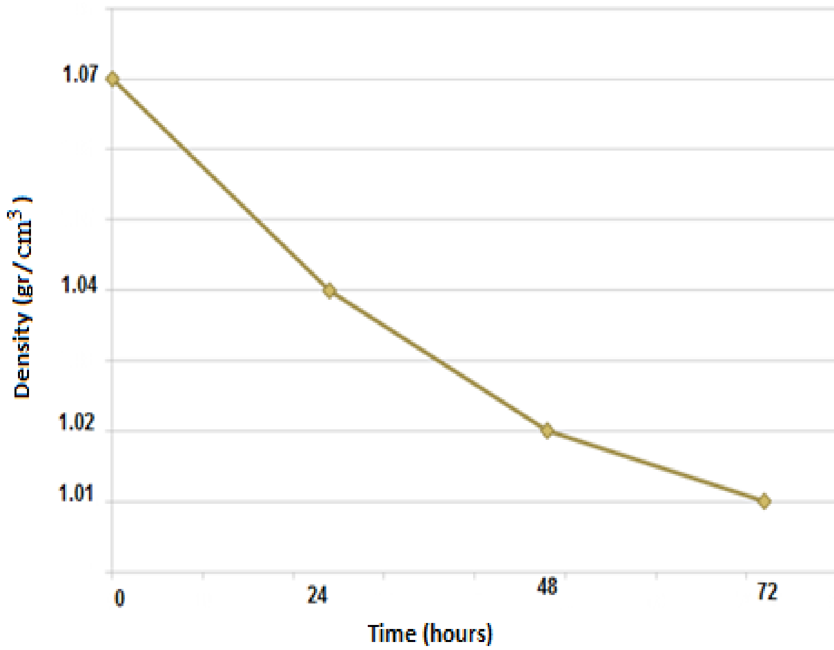

Figure 4. Density of (CDPW) juice during fermentation.

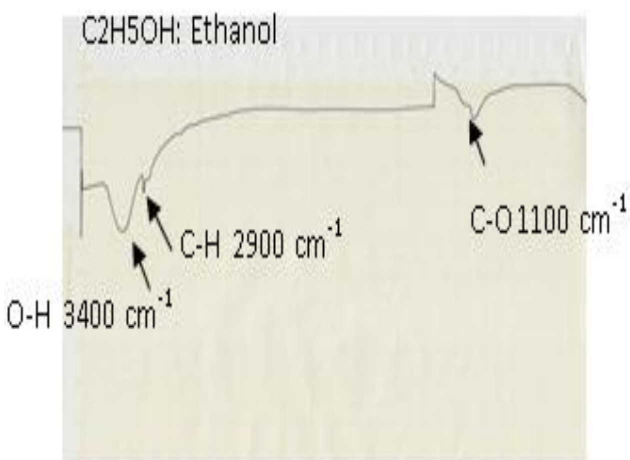

Figure 5. Vibration sign of the ethanol produced.

following wave numbers 2990, 3300 and 2990 cm^{-1}, corresponding to the molecules group C-H, O-H and C-O respectively (Figure 5).

Conclusion

The current study shows that the CDPW must constitute a favorable medium for *S. cerevisiae* growth, due to its sugar content and it is becoming an attractive raw material. It is intended to produce the bioethanol by using the solar batch fermenter at relatively moderate cost, especially in Sunbelt region of Algerian Sahara, without a negative effect on human. The CDPW distilled juice produced the highest ethanol concentration of about 90°, with an acceptable productivity of 250 or 3.47 mL/kg/h, assessing a scale efficiency of 33%. Compared to the theoretical ethanol efficiency obtained from a chemical reaction using the same sugar quantity which is 50%. The present results obtained is a strong encouragement to continue Research-Development in this renewable energy field. Therefore, It is necessary to start the construction of semi-pilot and pilot fermenters and investigate new methods, microorganism, and materials by-product to improve the quantity of ethanol produced and to reduce energy consumption during the bioethanol process transformation, for decreasing the cost of the final product. The quantity of 213,000 tons/year of CDPW and 1.8 $MWh/m^2/day$ of solar radiation appeared relatively sufficient for 40,000,000 inhabitants to develop an important biofuel industry in Algerian Sahara. Nevertheless, it is necessary to validate this purpose on bioethanol pilot installations in order to demonstrate the relevance of the proposed valorization before any transposition on an industrial scaling. Any main factor support for CDPW research and biotechnology development depend on the priority and emphasis of the national government to endorse the founding date-palms based agro-food and biofuel industry as well as local and international market to boost local economy.

Conflict of Interests

The authors have not declared any conflict of interests.

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