VALORIZATION OF DATE WASTE (HMIRA CULTIVAR) FOR THE PRODUCTION OF BIOALCOHOL AND BIOGAS

Abdelaziz Arroussi 1*, Ahmed Tahri 2, Oussama Kheirddine Nehar 3, Ahmed El-Amine Soulimani 2, Mohammed El-Amine Dahou 4

1Saharan Natural Resources Laboratory, University of Adrar, Faculty of Sciences and Technology, Adrar, Algeria
2Unit of Renewable Energy Research in the Saharan Environment, URERMs, Center for the Development of Renewable Energies, CDER, 01000, Adrar, Algeria
3Inorganic Chemistry and Environment Laboratory, University of Tlemcen, Tlemcen, Algeria
4Energy, Environment and Information Systems Laboratory, University of Adrar, Faculty of Sciences and Technology, Adrar, Algeria

Abstract
During the past years, bioethanol and biogas have a significantly development, they are fuels obtained from the fermentation of sugar plants and anaerobic digestion of organic compounds respectively. The major advantage of these biofuels is the reduction of gases Global Warming effect. In this work, two steps were performed: the first was the production of bioethanol from date waste by the fermentation. In the second stage, anaerobic digestion experiments are conducted in four digesters, each with a one litre capacity and a working volume of 600 mL. The digestion process takes place at 37°C for a duration of 45 days. To prepare the digesters, 10 g of volatile solids (VS) from the substrate are used. Alkaline pretreatment is employed with NaOH concentrations of 6%, 12%, and 18% (weight/weight, w/w) based on the substrate's volatile solids (VS). We obtained a yield of 360 mL of bioethanol of 93 ° per 1 kg of date waste. For the anaerobic digestion, the obtained results show that a 12% NaOH is the best concentration with a 1178 mL CH4/gVS.

Keywords: anaerobic digestion, bioethanol, biogas, date waste, fermentation, pretreatment.

1. INTRODUCTION
Today, due to the growing population, the demand for energy is increasing all over the world. Presently, the main source of source of energy is represented by non-renewable sources and fossil fuel such as natural gas, oil and coal. These are utilized for the generation of electricity and the production of other consumables (Ivančić Šantek et al., 2016). It has been proposed that these resources will run out quickly in the near future. Due to the excessive consumption of fossil fuels, especially in large urban areas, it has induced an increase in pollution due to the emission of greenhouse gases (GHGs). Therefore several countries are looking for new sources of energy as solution. Over the past decades, GHGs concentrations has increased considerably in the biosphere (Arroussi et al., 2019). Thus, many researchers are focused on finding other renewable sources of energy which can be environmentally friendly and could help reducing GHGs emissions.

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*Corresponding author, E-mail address: azizchimie01@gmail.com
Biogas is a renewable resource, resulting from anaerobic digestion of organic waste (effluents from agro-food industries, wastewater treatment plants sludge, animal waste, farmyard manure and slurry, fermentable fraction of household and green waste). This generally natural phenomenon can be controlled and optimized in digesters. It essential to assess appropriate technologies and/or techniques for efficient energy recovery. Anaerobic digestion is considered to be one of the best methods of dealing with the organic fraction of waste. These technologies assures the recovery of energy as biogas, which is a considered a clean fuel when compared to other traditional solid or liquid fuels (Valo et al., 2004; Mehrez et al., 2021).

Anaerobic digestion possesses both perks of waste treatment and generation of energy, such as, higher residence time and the inability of anaerobic organisms to completely consume all organics such as high lignin content waste and low solubility organic polymers in municipal solid waste (MSW) during the residence time due to the lower hydrolys rate (Sindhu et al., 2020). Because of its capability of decreasing waste quantity, significant calorific value biogas production and pathogens free final products, anaerobic digestion (AD) of solid organic waste seized much attention (Shanmugam et al., 2009). AD has many advantages over other treatment process, in regard to climate change (Riggle, 1998; Baldasano et al., 2000; Popp et al., 2011). Berndes et al. predicted that the potential global bio-energy supply will increase from less than 100 EJ/year to over 400 EJ/year by 2050 (Berndes et al., 2003).

The Algerian palm grove plays a pivotal role in the oasis ecosystem, primarily due to its significant production capacity, resulting in substantial waste generation during each season. Based on data provided by the Algerian Ministry of Agriculture, the national production in 1998 amounted to 387,313 tonnes, out of which 30 to 50% constituted waste and low-value dates, approximately 120,000 tonnes that hold potential for reclamation (Arroussi et al., 2022). Additionally, a considerable quantity of unused dates, potentially surpassing 30% of the total production, around 120,000 tonnes, remains available for recovery and processing.

The date waste is rich in fermentable sugars, comprising approximately 65% of the composition, rendering it an ideal substrate for the production of various high-value substances. Notably, among the products derived from this waste, ethyl alcohol holds significant importance as a strategic energy resource and a fundamental raw material utilized across numerous industries.

In addition, it is useful to point out that despite the importance of its phoenicultural potential, Algeria does not have any date processing industry. It should not be forgotten that for this industry to be economically viable, it is necessary to have a product that can be obtained in large quantities and at a relatively low price and common dates as well as waste meet this requirement perfectly (Kaidi et al., 2001).

The production of bioethanol from date waste in Algeria is feasible and very successful as it was studies by several researchers (Mehani et al., 2018). However the challenge of researchers is whether the waste of dates could be utilised using several processes. Our research focuses on the fermentation process to produce bioethanol, followed by the production of biogas by anaerobic digestion from the leftover date waste of the fermentation process.

2. MATERIALS AND METHODS
2.1. Fermentation
Vegetal matter
The Hmira date product (Figure 1) was chosen to facilitate the alcoholic fermentation due to its dominance and low market value in the Adrar region. The paste of this date (fermentate) was used...
as a substrate for anaerobic digestion in the goal of producing biogaz. The fermentation temperature was controlled by means of a water bath at the temperature of 37 ±2 °C; then, the biogas produced was gradually transferred into a vessel from where it passed to the measuring and filtering system.

**Figure 1. Hmira date waste**

**Alcoholic fermentation**

Dry yeast, Saccharomyces cerevisiae was chosen to carry the fermentation process as it’s known to be a superb ethanol producer. The apparatus used in this experiment shown in Figure 2.

**Figure 2. The bain-marie and the fermentation reactor**

**Preparation of dates mash**

After washing, the dates are soaked in hot water (90 to 95 °C) to ease pitting. The grinding of the pulps is carried out subsequently. The sugar-rich imbibition water will be used to dilute dates mash. The dates - thus treated - are then diluted to a concentration of 200 g of pulp per 0.8 L of water. The pH of the mash is adjusted with sulfuric acid (H₂SO₄, 1N) to be between 4.3 and 4.7. This acidic pH, favors the proliferation of yeasts and prohibits development of bacteria, (El-Hussieny et al., 2020).

**Fermentation process and distillation of alcohol**

After inoculation of the medium with the yeast Saccharomyces cerevisiae (1g/l), the bioreactor is immersed in a bain-marie at constant temperature of 30 ± 2°C. Fermentation is realized anaerobically for 72 hours. In order to follow the progress of the fermentation process, samples are taken every 24 hours to measure the acidity, glucose levels and alcohol ratio. (Ojeda et al., 2011).
After the fermentation stopped, the resulting date wine was subject to distillation (at 78°C) to obtain high alcohol concentration liquor which can be further purified by using molecular sieves.

**Determination of reducing sugars**
The reducing sugars are determined by titrimetry using Fehling's liquor. The principle of the method consists of reacting an excess of cupro-alkaline solution with the sugars. Subsequently, cuprous oxide is separated by decontamination, then treated with a solution of ferric sulphate (0.02N). The titration is carried out using a solution of potassium permanganate (0.015N). A table gives the correspondence between the poured volume of potassium permanganate and the mass of glucose (Audigie, 1978).

**Alcohol content measuring**
The determination of alcohol content during fermentation was carried out by aerometry. The method consists in distilling the alcoholic juice, then measuring, at room temperature, the degree of the distillate using an alcoholmeter (graduated from 0 to 100°C) (Li et al., 2009).

**2.2. Anaerobic digestion**
The substrates used in this work for feeding digesters consist mainly of Himra date paste (Figure 3).

![Figure 3. Date paste before digestion](image)

**Anaerobic digestion apparatus**
The bioreactor is a batch-type which consists of a glass bottle with a capacity of 01 liter, with a double outlet stopper (figure 4); The first outlet is used for sampling; The second allows the biogas produced to escape, the bioreactor is hermetically sealed, to ensure anaerobiosis, the digestion temperature was fixed at 37°C using bain-marie (figure 2). The produced biogas was then transferred to the CO₂ measurement and elimination system.

*Corresponding author, E-mail address: azizchimie01@gmail.com*
Pretreatment
The pretreatment is carried out with three concentrations of sodium hydroxide (NaOH): 6%, 12% and 18% (w/W, based on volatile solid substrate (VS)). 0.6, 1.2 and 1.8 g of sodium hydroxide (NaOH) were dissolved in 100 mL of distilled water in glass flasks. To insure the complete dissolution of NaOH the flasks were shaken for 6 h at room temperature, stirring at 250 rpm. One VS of 10 g of crushed dry date paste is added to each flask and mixed evenly. This represents a liquid to solid ratio of 1 g VS: 10 mL of Sodium hydroxide solution. As a control, another flask was prepared in the same manner with the same Solid to liquid ratio. Eventually, the flasks were placed into the incubator at 37° C for 120 h continuously. Each experiment of alkaline pretreatment is repeated three times and averaged, at the end of the pretreatment we noticed that the dry date paste is successfully dissolved. The degradability of the substrate was deduced from measuring and comparing the pH and chemical oxygen demand (COD) analysis results at the start and the end of each experiment. (Djaafri et al., 2020).

The inoculum
The inoculum used in this research came from a digester (in operation for more than a month) contains cow dung from one of the farms near the town of Adrar.

Digestion experiment
Launch of three batch digesters with our substrates after pretreatment and inoculum. The ratio inoculum substrate (ISR) is 2:1 based on the VS content. with a substrate / inoculum ratio of 1/2 , and a control digester without pretreatment (Tahri et al., 2020). Each experiment is repeated three times and the result is the average of the three experiments, the initial characteristics of the substrates are presented in Table 01. These wastes were introduced into a one liter capacity digester. The digester is hermetically sealed to ensure anaerobiosis, then it is immersed in a water bath set at (37±0.1°C).
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Table 1. Characteristics of the substrates and of the inoculum before the launch of the experiment

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Unit</th>
<th>Inoculum</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>6.45</td>
<td>6.85</td>
</tr>
<tr>
<td>Dry matter rate (DM)</td>
<td>%</td>
<td>11.75</td>
<td>12.32</td>
</tr>
<tr>
<td>Organic matter rate (OM)</td>
<td>%</td>
<td>94.01</td>
<td>93.83</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>(mg/L)</td>
<td>21743.33</td>
<td>4865.33</td>
</tr>
</tbody>
</table>

Analysis and measurements

The pH was measured using a HANNA HI 8314 type pH meter, the determination of volatile fatty acids (VFA) and the complete alkalimetric title (TA) were monitored each week by the standard APHA method (Federation & Association, 2005). The level of dry matter, the rate of organic matter and the chemical oxygen demand (COD) were determined before and after each experiment by the same method, the COD analyzes are realised after centrifugation at 0.45 μm and filtration of the supernatant.

The volumes of biogas and methane were monitored by the displaced liquid method, with a saturated NaCl solution (10g/L, pH = 2) in order to reduce the dissolution of CO2 as much as possible; CO2 removal using a 3M NaOH solution. (Methanogenic potential test or BMP) (Tahri et al., 2019).

![Figure 5. Diagram of the system for measuring the volume of biogas and CH4 produced. (Methanogenic potential test or BMP).](http://www.natsci.upit.ro)

In this scientific investigation, the determination of biogas and methane volume was conducted using the bio-methane potential (BMP) test, illustrated in Figure 5. The measurement of biogas production (4) was carried out employing the method of liquid displacement in an inverted graduated cylinder (2) containing a saturated solution (NaCl 10 g/L, pH = 2) (3). This step was taken to minimize the dissolution of CO2. Subsequently, the quantified biogas was directed (5) into a NaOH solution (3M/L) (6) to eliminate CO2 from the mixture. The resulting gas was then identified as pure methane (7) and quantified using the same method (Tahri et al., 2019).

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3. RESULTS AND DISCUSSIONS
3.1. Alcoholic fermentation of dates waste
Characterization of the substrate

The main physicochemical characteristics of the substrate used in this study are presented in table 2.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dates waste (Hmira)</th>
</tr>
</thead>
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<tr>
<td>Dry matter (%)</td>
<td>92.00</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>97.36</td>
</tr>
</tbody>
</table>

The fermentation process was monitored for 72 hours and the results are compiled in table 3, which shows that the alcohol produced increases during the last 48 hours of the fermentation where a significant consumption of the sugar is observed after 72 hours of the process. The total glucose level is greatly reduced over the course of the process, dropping from 13.8% at the start of the fermentation process to just 3% after 72 hours. The fermentation duration for date paste varies between 36 and 72 hours under similar conditions. Glucose was not used up completely due to the suspension of yeast growth caused by the accumulation of fatty acids. It was noticed a remarkable decrease in the density during fermentation which can be explained by the transformation of glucose into alcohol and the loss of mass in the form of CO2. After distillation and rectification, we obtained a yield which corresponds to 250 liters of alcohol/tonne of date waste. The ethanol produced is characterized by volatility, flammability, clarity and pungent odor. (Singh et al., 2016).

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>pH</th>
<th>Density (g/cm³)</th>
<th>Ashes (g)</th>
<th>Glucose (mg/mL)</th>
<th>Alcoholic Degree (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>4.5</td>
<td>1.08</td>
<td>0.07</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>4.13</td>
<td>1.05</td>
<td>0.06</td>
<td>15.77</td>
<td>7</td>
</tr>
<tr>
<td>48</td>
<td>3.95</td>
<td>1.03</td>
<td>0.05</td>
<td>8.40</td>
<td>16</td>
</tr>
<tr>
<td>72</td>
<td>3.86</td>
<td>1.02</td>
<td>0.04</td>
<td>2.63</td>
<td>23</td>
</tr>
</tbody>
</table>

Regarding the flammability of bioalcohol after distillation, illustrated by the photo in Figure 6.
3.2. Anaerobic digestion of date paste:

The pH
The optimum pH value for a good progress of anaerobic digestion is in the vicinity of neutrality with a pH between 6.5 and 7.5 (Lahbab et al., 2021).

Figure 7 shows the evolution of pH in the digestion media. We noticed the increase of acidity of the medium in the three digesters during the first ten days, which is explained by the degradation by the degradation of substrate and the formation and accumulations of fatty acids (Djaafri et al., 2020). Then the pH started to increase going towards neutrality, which could be explained by the transformation of fatty acids into methane. After the fifteenth day we notice the stability of pH between 7 and 7.5 (optimum value for anaerobic digestion). This stability is caused by the decrease of volatile fatty acids concentration and the depletion of organic matter in the media (Djaafri et al., 2019).
Figure 7. Medium's pH evolution during anaerobic digestion

Volatile fatty acids (VFA) and volatile organic acid and buffer capacity (TAC) ratio

Figure 8 showed that with the three concentrations and control sample the VFA / TA ratio begins near 1 in the first two days and begins to increase until exceeding 2 which is explained by the presence of the significant amounts of accumulated VFA, their accumulation influences negatively on the course of the anaerobic digestion (Kaidi et al., 2020).

After one week of the experiment the direction of the curve begins to decline. After two weeks begins to stabilize between 1 and 0.5 Until the end of the experiment in the three digesters, which indicates the good progress of the anaerobic digestion process. (Porselvam et al., 2017).

Figure 8. VFA/TA progress over time during the anaerobic digestion
Cumulative Biogas and cumulative methane

According to figure 9, the maximum biogas volume at the end of the experiment of the 18% and 6% concentrations is 3100 mL and 3500 mL respectively, while for the 12% concentration the volume reached 8400 mL of biogas at the end of the experiment. This volume recorded with the last concentration could be explained by the good progress of the anaerobic digestion and a good adjustment of the medium (Adavski et al., 2018). In all cases, the quantity of biogas produced is greater than the quantity produced in the control reactor, which is estimated at 2900 mL.

![Figure 9. Biogas accumulation over time](image)

Figure 10 shows that in the case of the 18% concentration the maximum volume of methane is 1800 mL and for the 6% digester the maximum volume of methane is 2000 mL. However, the two volumes are small compared to the volume recorded in the 12% digester, which is 5000 mL; this is due to the good progress of the anaerobic digestion in the latter and a good consumption of organic matter in all the three reactors, the quantity of methane produced is greater than the quantity produced in the control reactor, which is estimated at 1650 mL. (Sunyoto et al., 2017).
From the results compiled in table 3 the COD of substrate of the concentration 12% (12434.8 mg / L) is more important than the CODs of the first day anaerobic digestion with 6% and 18%, and at the end of the experience there is a greater reduction in COD with the 12% concentration of the order of 5000 mg/l explained by the good progress of the anaerobic digestion. While a less significant reduction in COD is recorded with the concentrations 6% and 18% of the order of 1000 and 2000 mg/l respectively, this could be explained by an obstruction of the anaerobic digestion process inside the digester (Salem et al., 2018). However, the slightest change in COD value was recorded was of the control sample (without pretreatment).

Organic load degradation rates showed that the degradation is greater with the 12% concentration digester, which is 42.76%, compared with the other concentrations 6% and 18% with rates of 28.46 % and 40.69 % respectively. These results suggest that the 12% concentration is the most suitable medium for methanization and the anaerobic digestion, while the low degradation rate was recorded in the control sample process has proven the efficiency of the pretreatment.
4. CONCLUSIONS

In this study we studied the potential usage of the Hmira date verity from the Adrar region southwest of Algeria, in the production of alcohol and also the production of biogas after undergoing a pretreatment. Thanks to the chemical composition and richness in minerals and trace elements of Hmira date, its mash has shown a good raw alcohol productivity. The quantities of the alcohol obtained after 72 hours of fermentation and 1 hour and 20 minutes of distillation are satisfactory in comparison with other works on other types of waste. The anaerobic digestion of the fermentate resulting from the fermentation of date waste after undergoing a pretreatment with deferent concentrations of NaOH (6%, 12%, 18%) showed that with the concentration of 12% of NaOH we recorded the highest volume of biogas (8400 mL) and also the highest volume of methane (5000 mL), and a good reduction of the chemical oxygen demand from 12434.8 mg/L -7352.94 mg/L), and better organic matter consumption of around 42.76% compared to the other proportions studied. For that, we recommend a concentration of 12% of NaOH for a pre-treatment of the waste of the dates, for a good progress of the anaerobic digestion and an optimum energy exploitation of the substrate.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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*Corresponding author. E-mail address: azizchimiei01@gmail.com
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