



RESEARCH ARTICLE

Exergetic Analysis of Bioethanol Production from Tunisian Waste Dates

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Abstract:**Objective:**

This study aims at contributing to the area of sustainable bioethanol production system development. The main objective of this study is to thermodynamically evaluate a bioethanol production process from waste dates.

Methods & Materials:

To this end, several chemical engineering assessment tools have been simultaneously applied. These tools simulate the bioethanol production process using the SuperPro software in order to determine all the materials and energy exchanges. An exergy analysis is also carried out, based on the first and second laws of thermodynamics, in order to locate thermodynamic imperfections in the process.

Results:

The results obtained show that approximately 60% of the exergy fed to the process is recovered in the useful products (bioethanol and exhausted pulp used as feedstuff). The overall exergy destroyed in the process considered is about 377 kW which represents 7% of the exergy reaching the process. The distillation section, the most energy-intensive stage, constitutes the main contributor of exergy destruction, followed by the fermentation reactor with contributions of 47% and 33%, respectively.

Keywords: Bioethanol, Waste dates, Thermodynamic analysis, Exergy, Distressing pressure, Greenhouse gas.

1. INTRODUCTION

Anthropogenic activities exert distressing pressure on natural resources. In fact, the high fossil fuel consumption is confronted with several problems, including the limitation of natural resources and greenhouse gas GHG emissions (CO₂, CH₄ and N₂O). This alarming situation is marked by global warming, loss of biodiversity and depletion of resources. Thus, the energy transition towards renewable energy seems an emergency in the last decades. Several sources of renewable energies have already been topics of research works such as wind, solar, hydraulic, geothermal, biomass, etc. Currently, biomass is becoming increasingly important in research of renewable energies field. It can be converted into high-energy products, mainly through thermo-chemical routes with or without chemical catalysts such as combustion, gasification and pyrolysis [1], and biochemical processes using enzymes and / or microorganisms such as

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anaerobic digestion for the production of biomethane [2], alcoholic fermentation for the production of bioethanol [3], *etc.* Bioethanol is considered as an important contributor to possible solutions to our sustainable fuel needs [4]. It burns cleaner than gasoline, producing less CO, CO₂ and NO_x emissions [5]. However, bioethanol derived from maize and sugar cane, classified as first-generation bioethanol, is facing an intense debate “food versus fuel” [6]. Therefore, in order to avoid competition with agro-food chains, it is necessary to use non-food material such as agricultural wastes in view of their abundance and their renewable characteristics.

Tunisia is considered to be one of the major dates producing countries in the world [7]. The production of dates is estimated to be about 195,000 tones in 2013 [8]. Approximately, 30% of the total production is generally discarded due to inadequate texture (too soft or too hard), fungal contamination, or insect infestation [9]. Date wastes are generally used as feed for livestock or rejected posing environmental problems. The use of this waste for the production of bioethanol could be a strategic solution for its abundance and high-sugar content. The date is composed of a flesh and a hard seed representing approximately (10-15%) of the total weight of the date [10]. The flesh is composed of sugar-rich food fiber about 72.8% (sucrose, glucose, and fructose), mineral salts (potassium, phosphorus, magnesium, calcium, *etc.*) and proteins [11]. Waste dates are considered a better non-edible alternative source for alcoholic fermentation [12]. For this reason, several studies have been conducted to produce bioethanol from waste dates. B. Louhichi *et al.* [13] carried out a synthesis study of bioethanol from three secondary varieties of dates (Kunta, Eguoua and Bouhatem) in the Gabes-Tunisia region. The alcoholic fermentation was investigated under sugar concentration near to 200 g L⁻¹ at 30°C and natural pH. The results obtained showed that all the varieties tested allow producing ethanol with a mass yield (mass of ethanol / initial mass of sugar) equal to 11%. S. Chniti *et al.* [14] evaluated the bioethanol production capacity of the three yeasts, *Saccharomyces cerevisiae*, *Zygosaccharomyces rouxii* and *Candida pelliculosa*, from waste dates. The best result is retained with the strain *S. cerevisiae* with an initial concentration of 174 g L⁻¹ and with 38% mass yield of ethanol.

Currently, exergy analysis is used to evaluate the performance of different systems and to improve their efficiencies [15]. The link between the exergy analysis and the sustainability shows that reduction of the loss of energy quality (exergy) leads to ensure sustainability of energy use [15]. Exergy analysis is based on both the first and second laws of thermodynamics able to locate the imperfections of a system and identifying their causes [16]. Exergy is a relevant tool in terms of energy efficiency, thus contributing significantly to improving energy efficiency and thus increasing environmental efficiency (evaluating our consumption and production lead to less pollution). From a thermodynamic point of view, exergy is defined as the maximum amount of work that can be produced by a flow of material, heat or work in interaction with a reference environment (characterized by temperature T and pressure P and a composition of reference state) [17]. Many recent bioethanol studies have focused on exergy analysis to assess the performance and sustainability of the bioethanol production process [16, 18 - 20].

The main objective of this study is to evaluate the energy performance of the bioethanol production process from waste dates *via* an exergy analysis. This analysis serves as a guide to improving efficiency by focusing on exergy destroyed during key stages of bioethanol production in order to identify areas of imperfection and to understand the sources of thermodynamics imperfections

2. MATERIALS AND METHODS

2.1. Characterization of Waste Dates

Waste dates, considered in this work, comes mainly from the two varieties of dates: ” Allig” and ” Deglet Nour” produced in the desert regions of southern Tunisia. These two Tunisian varieties constitute the large part of the production (about 195,000 tons in 2013 [8]). A significant fraction of production is lost during picking, packaging and storage [21]. The date is composed of soft, edible flesh and a hard seed, representing approximately (10-15%) of the total date weight [10]. The flesh consists of sugar-rich food fiber (sucrose, glucose, and fructose), mineral salts (potassium, phosphorus, magnesium, calcium, *etc.*) and proteins. Table 1 shows the average chemical composition of the dates considered [11]. These data are used subsequently to study bioethanol production process by alcoholic fermentation of waste dates.

Table 1. Chemical composition of date fleshes [11].

Component	Value
Dry matter (%)	73.1±0.8
Sugars ^(a)	72.8±0.27
Sucrose ^(a)	13.9±0.13
Glucose ^(a)	29.9±0.2
Fructose ^(a)	29.0±0.48
Total dietary fibre ^(a)	18.4±0.45
Insoluble dietary fibre ^(a)	11.7±0.22
Soluble dietary fibre ^(a)	6.68±0.23
Ash ^(a)	2.52±0.01
Potassium ^(b)	823±13.10
Phosphorus ^(b)	104±0.24
Magnésium ^(b)	44.1±0.97
Calcium ^(b)	63±1.00
Sodium ^(b)	10.1±1.6
iron ^(b)	2±0.21
Protein ^(a)	3.02±0.13

^(a) In % dry matter ^(b) In mg/100 g dry matter.

2.2. Simulation of the Process

The bioethanol production process from waste dates includes three main sections: (1) pretreatment, (2) fermentation and (3) purification. The purification section was adopted from a published article [22] dealing with the production of bioethanol from sugarcanes and blue agaves. To describe the process and calculate the material and energy exchanges, the bioethanol plant was simulated by SuperPro Designer[®] 8.5 (Intelligen, Inc.). The flowsheet is given in Fig. (1). The simulation results are subsequently used to compute all exergy forms exchanged in the process.

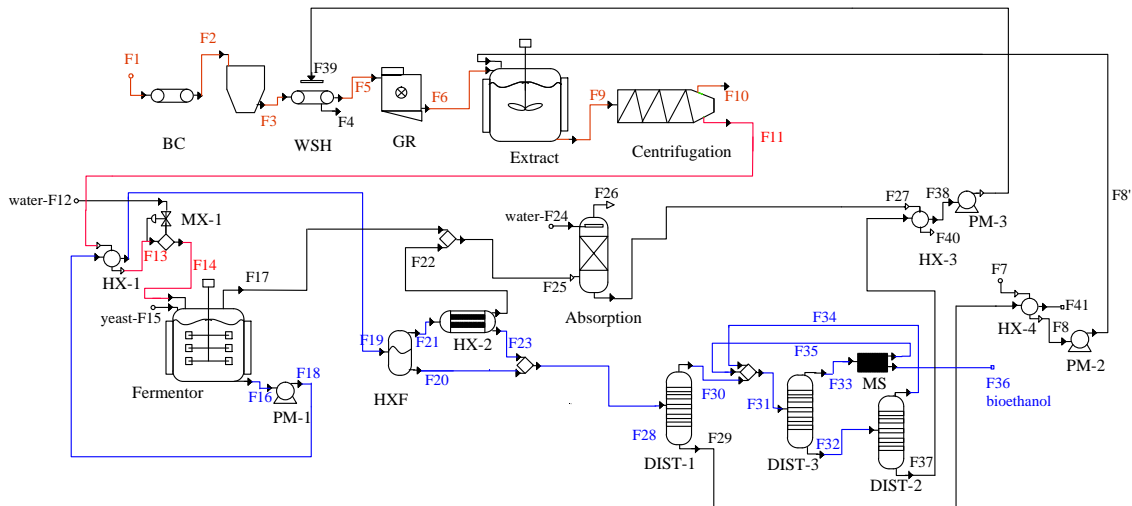


Fig. (1). Detailed flow diagram of bioethanol production process from waste dates.

2.2.1. Pretreatment

The pretreatment section is devoted for sugar extraction, using various equipments. A conveyor belt (BC) is used as a mechanical supplier to feed the process (F1). Dates are then washed (F5) and grinded (F6) to make them suitable for the sugar extraction stage respecting optimums conditions described in B.louhichi *et al.* [13]. To separate sugar-rich juice (F11) from the solid phase (F10), a following centrifugation operation is carried out. The exhausted pulp (F10) is considered a byproduct which it could be used as feed for livestock.

2.2.2. Fermentation

The operating conditions in the fermentor are fixed on the basis of results published by B. Loufichi *et al.* [13]. The reactions extents are closely related to the yeast strain retained for this study (*S.cerevisiae* FRCH strain [23, 24]). The main reactions involved in the fermentor are summarized in Table 2. An adjustable flow mixer (MX-1) is used to adjust the stream (F14) to the desirable concentration of sugars.

Table 2. Reactions involved in the production of bioethanol from date waste.

Reactions	Fraction converted to product	References
Glucose \rightarrow 2 Ethanol + 2CO ₂	92%	[23]
Fructose \rightarrow 2 Ethanol + 2CO ₂	76%	[23]
Sucrose + H ₂ O \rightarrow 4Ethanol + 4CO ₂	93%	[24]

2.2.3. Purification

The distillation section is dedicated to the recovery of bioethanol. For this purpose, three distillation columns (Dist-1, Dist-2 and Dist-3) followed by a molecular sieve (P-20, /MS) are used.

2.3. Basis of the Exergy Analysis

2.3.1. Different forms of Exergy

In this paper, three forms of exergy are considered: exergy associated with heat transfer, exergy associated with mechanical work and exergy associated with a steady stream of matter. The environmental temperature and pressure used in this work are respectively 298.15 K and 1 atm.

a. Exergy associated with heat and work transfer

The exergy associated with a heat flow is expressed as follows (Eq.1) [25].

$$Ex_Q = Q\left(1 - \frac{T_0}{T}\right) \quad (1)$$

Where T is the reference temperature (298.15 K), T is the temperature at which the heattransfer occurs, Q is amount of heat transferred.

- The exergy associated with the transfer of mechanical work (Eq.2).

$$Ex_W = W \quad (2)$$

b. *Exergy associated to material stream* This step consists in determining the exergy associated to material stream (Ex_M) that includes five terms, namely physical exergy (Ex_{phy}), chemical exergy (Ex_{chem}), the exergy of mixing (Ex_{mix}), the kinetic exergy (Ex_{kin}) and the potential exergy (Ex_{pot}). Only the chemical, physical and mixtures exergy are calculated in the present study. The variations of the kinetic and potential exergies are often neglected in the expression of matter [16, 18].

$$Ex_M = Ex_{phy} + Ex_{chem} + Ex_{mix} \quad (3)$$

The exergy associated with the material flow is computed accordingly to the methods described by A.P. Hinderink *et al.* [26] frequently adopted in research topics dealing with exergetic analysis [27, 28].

The physical exergy (Ex_{phy}) is the maximum amount of work that can be retrieved when a material flow is brought from its initial state (T, P) to the state of the defined environment by (T, P) by a process involving only a thermal interaction with the environment [25]. This component is given by A. P. Hinderink *et al.* [26] (Eq.4).

$$Ex_{phy} = \Delta_{actual\ state \rightarrow ref\ state} \left\{ D \left(x_l \left(\sum_{i=1}^n x_i H_i^l - T_0 \sum_{i=1}^n x_i S_i^l \right) + x_v \left(\sum_{i=1}^n x_i H_i^v - T_0 \sum_{i=1}^n x_i S_i^v \right) \right) \right\} \quad (4)$$

where n is the number of chemical species in a flow of material, D is the mass flow, x_l and x_v are the mass fraction of liquid and vapor, respectively, in the flow of material, x_i and y_i are respectively the mass fraction of species i in the liquid and vapor phases steam, H_i and S_i are respectively mass enthalpy and entropy of the pure component i. Indices l

and v refer respectively to the liquid and vapor phases.

-The chemical exergy (Ex_{chem}) is the maximum work that can be recovered when the substance under consideration is brought from the environment, defined by the parameters T and P , to the dead state by a process involving only heat transfer and material exchange with the environment (Kotas, 1995) [25]. The chemical exergy is given by [26] A.P. Hinderink and *et al.* (Eq.5).

$$Ex_{chem} = D \left(x_{0,l} \sum_{i=1}^n x_{0,i} \epsilon_{chem,i}^{0l} + x_{0,v} \sum_{i=1}^n y_{0,i} \epsilon_{chem,i}^{0v} \right) \quad (5)$$

Where $\epsilon_{chem,i}^{0l}$, $\epsilon_{chem,i}^{0v}$ are respectively the standard chemical exergy of the species (i) in liquid and vapor phase, determined from Kotas [25]. Chemical exergies process components are evaluated using the composition of the reference environment defined by Kotas [25]. The mixing exergy (Ex_{mix}) always has a negative value (Eq.6) [26].

$$Ex_{mel} = \Delta_{mix} H - T_0 \Delta_{mix} S \quad (6)$$

Where

$$\Delta_{mix} H = D \left(x_l \left(H^l - \sum_{i=1}^n x_i H_i^l \right) + x_v \left(H^v - \sum_{i=1}^n y_i H_i^v \right) \right) \quad (7)$$

$$\Delta_{mix} S = D \left(x_l \left(S^l - \sum_{i=1}^n x_i S_i^l \right) + x_v \left(S^v - \sum_{i=1}^n y_i S_i^v \right) \right) \quad (8)$$

2.3.2. Exergetic Evaluation

To establish an exergy balance, we consider an open system operating in steady state. This balance consists on coupling an enthalpic and entropic balance that highlighting the term of destroyed exergy ($Ex_{destroyed}$). The arrangement of material, enthalpy and entropy balances leads to Eq.(9) [25].

$$\sum_{in} D_{in} Ex_{M,in} - \sum_{out} D_{out} Ex_{M,out} + \sum_k Q_k \left(1 - \frac{T_0}{T_k} \right) + \sum_k W_k - T_0 S_{gen} = 0 \quad (9)$$

This expression, known as the exergy balance, includes four terms:

- 1: Specific exergy associated with matter ($Ex_M = Ex_{phy} + Ex_{chem} + Ex_{mix}$).
- 2: Exergy associated with heat transfer.
- 3: Exergy associated with mechanical work exchange.
- 4: Term corresponding to the creation of entropy due to the different irreversibility of the system, it is exergy destroyed.

With:

D_{in} : Mass flow of material at system inlet.

D_{out} : Mass flow of material at the system outlet.

Q_k : The quantity of heat exchanged by the system at a temperature T_k .

W_k : Non-thermal energy (mechanical, electrical ...) received by the system.

To compute the destroyed exergy, the detailed method is considered which provides the contribution of each equipment (*e.g.* distillation column) to the total exergy destroyed. More details about the calculations are provided in *supplementary materials*.

3. RESULTS AND INTERPERTATIONS

3.1. Process Design and Simulation

The simulation results show the thermal and mechanical powers exchanged at the various equipments (Table 3) and

the characteristics of the different material flows (flow, temperature, pressure, composition, enthalpy) (Table 4). The main operating conditions needed in the process simulation are retrieved from experimental study [13] to match as possible real operating unit and to get valuable results. The novelty of this work is the relevant application of waste dates in the field of bioethanol. However, conduct a rational comparative analysis between the studied system and real ones which involve the same transformations steps is a big challenge.

Table 3. Energy exchange in various equipments.

Equipment	Power consumed or delivered
Pitting machine	W= 12.50 kW
Belt conveying (P-1/BC)	W= 9.07 kW
Grinding (P-4/GR)	W=90.71 kW
Agitation (P-5/Extract) $R_{me}=90\%$	W=11.07 kW
Centrifugation (P-6)	W= 29.9 kW
Fermentor (P-9 /Ferment) Agitation $R_{me}=90\%$ Cooling	W=1.2 kW Q =11.96 kW (-)
Pumps: (P-10/PM-1) $R_{me}=70\%$ (P-10/PM-2) $R_{me}=70\%$ (P-10/PM-3) $R_{me}=70\%$	W=0.03 kW W=0.03 kW W= 2.80 W
Evaporator (P-11/HXF) $R_{th}=90\%$	Q=63.63 Kw
Condensation (P-12/HX-2) $R_{th}=90\%$	Q=3.38 kW (-)
Distillation (dist-1) Condenser Boiler	Qc=1058.22 kW (-) Qb=1094.59 kW
Distillation (dist-2) Condenser Boiler	Qc=119.9 kW (-) Qb=120.78 kW
Distillation (dist-3) Condenser Boiler	Qc=226.07 kW (-) Qb=249.3 kW

Table 4. Characteristics of material flows.

Flux	P (kPa)	T (K)	Mass Flow (kg/h)	H (kJ/kg)	S (kJ/kg.K)	Mass Composition (%)									
						Glucose	Fructose	Sucrose	H ₂ O	C ₂ H ₅ OH	CO ₂	Yeast	protein	Ash	Fibres
F1	100.00	298.15	1000.00	-7349.00	-6.14	29.00	29.00	14.00	5.00	0.00	0.00	0.00	3.00	2.00	18.00
F2	100.00	298.15	907.10	-7349.00	-6.14	29.00	29.00	14.00	5.00	0.00	0.00	0.00	3.00	2.00	18.00
F3	100.00	298.15	907.10	-7349.00	-6.14	29.00	29.00	14.00	5.00	0.00	0.00	0.00	3.00	2.00	18.00
F4	100.00	310.43	200.80	-15896.00	-9.13	0.00	0.00	0.00	99.80	0.20	0.00	0.00	0.00	0.00	0.00
F5	100.00	301.07	907.10	-7342.00	-6.12	29.00	29.00	14.00	5.00	0.00	0.00	0.00	3.00	2.00	18.00
F6	100.00	301.07	907.10	-7342.00	-6.12	29.00	29.00	14.00	5.00	0.00	0.00	0.00	3.00	2.00	18.00
F7	100.00	298.15	1800.00	-15972.00	-9.32	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F8	100.00	338.15	1800.00	-15791.00	-8.75	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F8'	150.00	338.16	1800.00	-15791.00	-8.75	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F9	100.00	333.21	2707.00	-12934.00	-7.77	9.72	9.72	4.70	68.20	0.00	0.00	0.00	1.00	0.67	6.03
F10	100.00	333.21	276.20	-8417.00	-6.21	2.58	2.58	1.24	18.00	0.00	0.00	0.00	9.90	6.60	59.12
F11	100.00	333.21	2431.00	-13444.00	-7.95	10.53	10.53	5.10	73.85	0.00	0.00	0.00	0.00	0.00	0.00
F12	100.00	298.15	216.90	-15972.00	-9.32	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F13	100.00	308.16	2431.00	-13545.00	-8.26	10.53	10.53	5.10	73.85	0.00	0.00	0.00	0.00	0.00	0.00
F14	100.00	307.21	2648.00	-13745.00	-8.35	9.67	9.67	4.67	76.00	0.00	0.00	0.00	0.00	0.00	0.00
F15	100.00	298.15	76.00	-6902.00	-6.02	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00
F16	100.00	303.15	2453.00	-14143.00	-8.67	0.83	2.50	0.25	81.77	11.54	0.00	3.10	0.00	0.00	0.00
F17	100.00	293.15	270.50	-8947.00	0.05	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00
F18	150.00	303.16	2453.00	-14143.00	-8.67	0.80	2.50	0.25	81.77	11.54	0.00	3.10	0.00	0.00	0.00
F19	150.00	326.42	2453.00	-14045.00	-8.36	0.80	2.50	0.25	81.77	11.54	0.00	3.10	0.00	0.00	0.00
F20	100.00	353.15	2399.00	-13838.00	-7.69	0.85	2.56	0.26	81.95	11.21	0.00	3.17	0.00	0.00	0.00

(Table 4) contd....

Flux	P (kPa)	T (K)	Mass Flow (kg/h)	H (kJ/kg)	S (kJ/kg.K)	Mass Composition (%)									
						Glucose	Fructose	Sucrose	H ₂ O	C ₂ H ₅ OH	CO ₂	Yeast	protein	Ash	Fibres
						Mass	compositi on	(%)							
Flux	P (kPa)	T(K)	Mass Flow (kg/h)	H (kJ/kg)	S (kJ/kg.K)	Glucose	fructose	Sucrose	H ₂ O	C ₂ H ₅ OH	CO ₂	Yeast	protein	Ash	Fibres
F21	100.00	353.15	54.28	-12756.00	-7.01	0.00	0.00	0.00	73.92	26.08	0.00	0.00	0.00	0.00	0.00
F22	100.00	293.15	1.91	-12196.00	-8.44	0.00	0.00	0.00	62.97	37.03	0.00	0.00	0.00	0.00	0.00
F23	100.00	293.15	52.37	-13345.00	-8.70	0.00	0.00	0.00	74.32	25.68	0.00	0.00	0.00	0.00	0.00
F24	100.00	298.15	145.00	-15972.00	-9.32	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F25	100.00	293.15	272.40	-8956.00	0.04	0.00	0.00	0.00	0.44	0.26	99.30	0.00	0.00	0.00	0.00
F26	100.00	296.75	7.32	-9709.00	-1.84	0.00	0.00	0.00	16.44	9.66	73.87	0.00	0.00	0.00	0.00
F27	100.00	296.75	410.00	-11415.00	-3.21	0.00	0.00	0.00	35.36	0.00	64.64	0.00	0.00	0.00	0.00
F28	100.00	351.40	2452.00	-13813.00	-7.71	0.83	2.51	0.25	81.79	11.52	0.00	3.10	0.00	0.00	0.00
F29	100.00	373.15	1997.00	-14592.00	-7.58	1.02	3.08	0.31	90.37	1.41	0.00	3.81	0.00	0.00	0.00
F30	100.00	363.15	454.70	-8794.00	-3.66	0.00	0.00	0.00	44.10	55.90	0.00	0.00	0.00	0.00	0.00
F31	100.00	363.15	479.10	-8954.00	-3.77	0.00	0.00	0.00	45.40	54.60	0.00	0.00	0.00	0.00	0.00
F32	100.00	373.15	218.80	-14796.00	-6.94	0.00	0.00	0.00	96.41	3.59	0.00	0.00	0.00	0.00	0.00
F33	100.00	363.15	260.30	-5212.00	-4.49	0.00	0.00	0.00	2.50	97.50	0.00	0.00	0.00	0.00	0.00
F34	100.00	363.15	18.06	-10580.00	-4.90	0.00	0.00	0.00	58.59	41.41	0.00	0.00	0.00	0.00	0.00
F35	100.00	363.15	6.46	-15677.00	-8.43	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00
F36	100.00	363.15	253.80	-5006.00	-4.59	0.00	0.00	0.00	0.03	99.97	0.00	0.00	0.00	0.00	0.00
F37	100.00	373.15	200.80	-15586.00	-8.23	0.00	0.00	0.00	99.80	0.20	0.00	0.00	0.00	0.00	0.00
F38	100.00	316.87	200.80	-15867.00	-9.04	0.00	0.00	0.00	99.80	0.20	0.00	0.00	0.00	0.00	0.00
F39	150.00	316.87	200.80	-15867.00	-9.04	0.00	0.00	0.00	99.80	0.20	0.00	0.00	0.00	0.00	0.00
F40	100.00	325.70	410.00	-11277.00	-2.77	0.00	0.00	0.00	35.36	0.00	64.64	0.00	0.00	0.00	0.00
F41	100.00	334.94	1996.00	-14915.00	-8.47	1.02	3.07	0.31	90.37	1.41	0.00	3.81	0.00	0.00	0.00

3.2. Exergy Analysis Results

The different forms of exergy exchanged in the process (matter, work, heat) are gathered in Tables 5 and 6.

Table 5. Exergy associated with the exchange of work and heat at the equipment level.

Equipment	Power consumed or delivered	Associated exergy
Sugar Extractor (P-5/Extract) Agitation R _{me} =90%	W=11.07 kW	$Ex_w = 11.07 kW$
Fermentor (P-9 /Ferment) Agitation R _{me} =90% Cooling	W=1.20 kW Q=11.96 kW (-)	$Ex_w = 1.20 kW$ $Ex_Q = Q \left(1 - \frac{T_0}{T}\right) = 11.96 \times \left(1 - \frac{298.15}{303.15}\right) = 0.19 kW (-)$
Pumps (P-10/PM-1) R _{me} =70% (P-10/PM-2) R _{me} =70% (P-10/PM-3) R _{me} =70%	W=0.03 kW W=0.03 kW W= 0.003 kW	$Ex_w = 0.03 kW$ $Ex_w = 0.03 kW$ $Ex_w = 0.003 kW$
Evaporator (P-11/HXF)R _{th} =90%	Q=63.63 kW	$Ex_Q = Q \left(1 - \frac{T_0}{T}\right) = 63.63 \times \left(1 - \frac{298.15}{425.15}\right) = 19.00 kW$
Condensation (P-12/HX-2) R _{th} =90%	Q=3.38 kW (-)	$Ex_Q = Q \left(1 - \frac{T_0}{T}\right) = 3.38 \times \left(1 - \frac{298.15}{293.15}\right) = 0.06 kW (-)$
Distillation (dist-1) Condenser Boiler	Qc=1058.22 kW (-) Qb=1094.59 kW	$Ex_{Qc} = Q \left(1 - \frac{T_0}{T}\right) = 1058.22 \times \left(1 - \frac{298.15}{363.15}\right) = 189.05 kW (-)$ $Ex_{Qb} = Q \left(1 - \frac{T_0}{T}\right) = 1094.59 \times \left(1 - \frac{298.15}{425.15}\right) = 326.97 kW$

(Table 5) contd....

Equipment	Power consumed or delivered	Associated exergy
Distillation (dist-2) Condenser Boiler	Qc=119.90 kW (-) Qb=120.78 kW	$Ex_{Qc} = Q \left(1 - \frac{T_0}{T} \right) = 119.90 \times \left(1 - \frac{298.15}{363.15} \right) = 21.46 \text{ kW} (-)$ $Ex_{Qb} = Q \left(1 - \frac{T_0}{T} \right) = 120.78 \times \left(1 - \frac{298.15}{425.15} \right) = 36.07 \text{ kW}$
Distillation (dist-3) Condenser Boiler	Qc=226.07 kW (-) Qb=249.30 kW	$Ex_{Qc} = Q \left(1 - \frac{T_0}{T} \right) = 226.07 \times \left(1 - \frac{298.15}{363.15} \right) = 40.42 \text{ kW} (-)$ $Ex_{Qb} = Q \left(1 - \frac{T_0}{T} \right) = 249.30 \times \left(1 - \frac{298.15}{425.15} \right) = 74.40 \text{ kW}$

Aspen Plus™ is employed in order to estimate the thermodynamic properties (enthalpy and entropy) of each stream. The hypothesis considered in this step is to assimilate all organic compounds that constitute date fleshes to dextrose (sugar predefined in AspenPlus database), thus dates are modulated as (95% dextrose and 5% water). To calculate the exergy associated to the stream material F1 (waste dates entering the system) we proceed as describe in the text.

$$Ex_M = Ex_{phy} + Ex_{chem} + Ex_{mix} ;$$

$Ex_{phy} = 0$ Because the flux is in environmental conditions (T=100 kPa, and T= 298.15 K).

$$Ex_{chem} = \left(x_{0,water} \varepsilon_{chem,water}^0 + x_{0,dextrose} \varepsilon_{chem,dextrose}^0 \right)$$

$$Ex_{chem} = (0.05 \times 173.33 + 16347.61 \times 0.95)$$

$$Ex_{chem} = 15538.89 \text{ kJ / kg}$$

Where

$\varepsilon_{chem,i}^0$ is the standard chemical exergy of the species (i) determined from Kotas [25].

$$Ex_{mél} = \Delta_{mix} H - T_0 \Delta_{mix} S$$

$$Ex_{mix} = \left(H - \sum_{i=1}^n x_i H_i \right) - T_0 \left(S - \sum_{i=1}^n y_i S_i \right)$$

$$Ex_{mix} = \left(H - (x_{water} H_{water} + x_{dextrose} H_{dextrose}) \right) - T_0 \left(S - y_{water} S_{water} + y_{dextrose} S_{dextrose} \right)$$

$$Ex_{mix} = \left(-7349.30 - (0.05 \times (-15972.07) + 0.95 \times (-6901.52)) \right)$$

$$-298.15 \left(-6.14 - (0.05 \times (-9.32) + 0.95 \times (-6.02)) \right)$$

$$Ex_{mix} = -8.81 \text{ kJ / kg}$$

$$Ex_{F1} = 1000 \times (Ex_{phy} + Ex_{chem} + Ex_{mix})$$

$$Ex_{F1} = 4313.91 \text{ kW}$$

Exergy associated to different streams are listed in Table 6.

Table 6. Exergy associated with flow matter.

Flux	Mass Flow(kg/h)	Ex _{phy} (kJ/kg)	Ex _{mix} (kJ/kg)	Ex _{chem} (kJ/kg)	Ex _M (kW)
F1	1000.00	0.00	-8.81	15538.90	4313.91
F2	907.10	0.00	-8.81	15538.90	3913.15
F3	907.10	0.00	-8.81	15538.90	3913.15
F4	200.80	1.11	-0.17	232.32	13.01

(Table 6) contd.....

Flux	Mass Flow(kg/h)	Ex _{phy} (kJ/kg)	Ex _{mi} (kJ/kg)	Ex _{chem} (kJ/kg)	Ex _M (kW)
F5	907.10	0.04	-8.81	15538.90	3913.16
F6	907.10	0.04	-8.81	15538.90	3913.16
F7	1800.00	0.00	0.00	173.33	86.67
F8	1800.00	11.16	0.00	173.33	92.25
F8'	1800.00	11.22	0.00	173.33	92.28
F9	2707.00	7.50	-5.00	5316.75	3999.78
F10	276.2.00	5.54	-10.81	13436.24	1030.45
F11	2431.00	7.70	-4.52	4404.10	2976.14
F12	216.90	0.00	0.00	173.33	10.44
F13	2431.00	0.65	-4.58	4404.10	2971.34
F14	2648.00	0.54	-4.38	4055.16	2979.97
F15	76.00	0.00	0.00	16347.61	345.12
F16	2453.00	0.18	-8.33	4658.66	3168.81
F17	270.50	0.05	0.00	457.73	34.40
F18	2453.00	0.18	-8.33	4658.66	3168.81
F19	2453.00	5.40	-8.33	4658.66	3172.36
F20	2399.00	30.83	-53.12	4613.67	3059.64
F21	54.28	47.61	-16.34	7934.57	120.11
F22	1.91	0.17	-16.34	11093.86	5.88
F23	52.37	0.17	-16.34	7746.63	112.46
F24	145.00	0.00	0.00	173.33	6.98
F25	272.40	0.05	-4.32	534.87	40.15
F26	7.32	0.02	-21.57	3250.11	6.56
F27	410.00	0.01	-4.18	360.23	40.55
F28	2452.00	45.87	-8.33	4711.15	3234.39
F29	1997.00	65.40	-4.95	1950.88	1115.73
F30	454.70	203.01	-54.39	16919.13	2155.75
F31	479.10	197.67	-53.12	16529.64	2219.06
F32	218.80	124.38	-7.06	1329.06	87.91
F33	260.30	144.23	-12.91	29071.26	2111.51
F34	18.06	146.73	-40.23	12577.87	63.63
F35	6.46	28.19	0.00	173.33	0.36
F36	253.80	165.49	-0.30	29792.42	2112.01
F37	200.80	41.83	-0.39	237.15	15.54
F38	200.80	2.55	-0.16	232.32	13.09
F39	200.80	2.60	-0.17	232.32	13.09
F40	410.00	2.50	-15.37	374.72	41.21
F41	1996.00	9.13	-2.37	1917.24	1066.75

We display in Table 7 the outcomes of exergy balance carried on the main components of the process. More details about the calculations of exergy balance are provided in supplementary materials.

Table 7. The results of the exergy balance for each process element.

Equipment	Exergie In (kW)	Exergie Out (kW)	Exergie Destroyed (kW)	%of Total Destroyed Exergy
washing	3926.24	3926.17	0.07	0.02
Extractor	4016.51	3999.78	16.73	4.43
Fermentor	3326.29	3203.21	123.01	32.58
Absorption	47.13	47.11	0.02	0.01
Pump PM-1	3168.84	3168.81	0.03	0.01
Pump PM-2	92.28	92.28	0.00	0.00
Pump PM-3	13.09	13.09	0.00	0.00
Evaporator HXF	3191.36	3179.75	11.61	3.08
Exchanger HX-1	6144.95	6143.7	1.25	0.33

(Table 7) contd....

Equipment	Exergie In (kW)	Exergie Out (kW)	Exergie Destroyed (kW)	%of Total Destroyed Exergy
Condensation HX-2	120.11	118.34	1.83	0.48
Exchanger HX-3	56.09	54.30	1.79	0.47
Exchanger HX-4	1202.40	1159.00	43.40	11.50
Dist-1	3561.36	3460.53	100.83	26.71
Dist-2	123.98	100.63	23.35	6.18
Dist-3	2293.46	2239.83	53.62	14.20
Total	31284.09	30906.53	377.54	100.00

The distillation section has the most exergy destruction (Fig. 2) of 177.8 kW about 47% of the total exergy destruction in the bioethanol production process. According to the fractionating principles, reducing the reflux ratio, ie increasing the number of stages, could lead to a substantial reduction in the irreversibility of the column [29]. Heat exchangers (condenser and reboiler) are also a source of irreversibility in the distillation column due to the considerable temperature differences between the hot and cold streams. To see in details, the distribution of the exergy destroyed through the various distillation columns, the contribution of each column to the exergy destroyed is shown in Fig. (3). It is clear that the first distillation column “Dist-1” “constitutes the most zone of thermodynamic imperfection of the process. It contributes to more than half of the destroyed exergy of the distillation columns and thus accounts for 26.71% of the total exergy destruction from the process. The fermentation process contributes about 33% of the exergy destruction of the system. Its inefficiency is mainly caused by the creation of entropies during biochemical reactions and the dissipation of heat due to the exothermic nature of the reactions [30]. The heat exchanger (HX-4) is the third contributor to the exergy destruction with about 11.5% of the exergy destroyed this is due to the temperature difference between the hot and cold flow which is around 35° C. Finally, the extraction tank also contributes to the exergy destroyed about (4.43% of the total exergy destroyed) which can be at the origin of concentration gradient during perpetual diffusion of sugars from the concentrated zones to the diluted zones. The method conducted to compute the exergy destroyed is a detailed one *i.e.*, we focus on the exergy destroyed in each equipment to figure out its contribution to the thermodynamic imperfections. While the total exergy that entering the system is:

$$Ex_{in} = Ex_{F1} + Ex_{F7} + Ex_{F12} + Ex_{F15} + Ex_{F24} + \sum Ex_Q + \sum Ex_W$$

$$Ex_{in} = 5231.88 \text{ kW}$$

where

$Ex_{F1}, Ex_{F7}, Ex_{F12}, Ex_{F15}, Ex_{F24}$ are exergy associated to material streams F1, F7, F12, F15, F24 respectively. $\sum Ex_Q, \sum Ex_w$ are exergy associated with heat flow and mechanical work provided to the main steps of the system. Thus the overall exergy destruction (377.54 kW) represents 7.21% of the exergy entering the system.

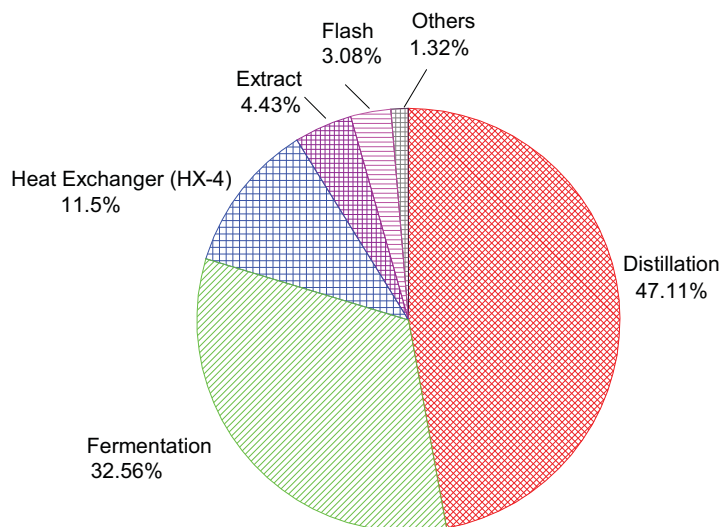


Fig. (2). Distribution of exergy destroyed in bioethanol process.

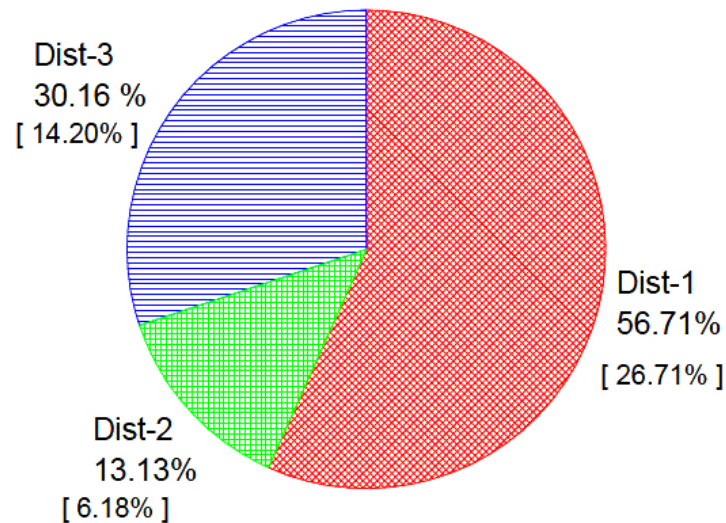


Fig. (3). Contribution of each column distillation to the total exergy destroyed associated to the the distillation section [% to the total exergy destruction].

Furthermore to calculate the exergetic efficiency of the process we adopt the rational exergy efficiency which is the ratio of exergy content of useful products to the total exergy input [27]. The useful products leaving the system are bioethanol (F36) and exhausted pulp used as feed for animal (F10), exergetic efficiency is computed as below

$$\eta = \frac{Ex_{F36} + Ex_{F11}}{Ex_{in}}$$

$$\eta = \frac{1030.45 + 2112.01}{5231.88} = 60.06\%$$

To the best of our knowledge exergetic analysis of bioethanol production from waste dates has not yet been carried out to measure the thermodynamic performance of such system which constitutes the novelty of this work. Exergy analysis can deal with any systems of different features and is powerful in qualitative analysis for any elements of a system. Furthermore, the exergy analysis can indicate the major cause of imperfections of a system. However, the lack of a formal procedure in using the results from an exergy analysis is one of its limitations. Therefore, the combination of two relevant methods the pinch and exergy analysis constitutes a rational basis for process modifications. Pinch or exergy analysis alone cannot fulfill the task for effective process modification, since they have their own intrinsic advantages and disadvantages. The power of pinch analysis (which is not the purpose of this work) is in showing the main features of a system on simple diagrams. Therefore, the proper combination of these two methods can brought significant benefits for process modifications, since it is essential to display the system information graphically to visualize its performance and quantitatively identify major directions for improvement [31].

CONCLUSION

The main objective of this study is to provide an exergetic investigation of bioethanol production system from waste dates. Several chemical engineering assessment tools have been simultaneously applied. The main outcomes of this research can be summarized in these points: - Approximately 60% of the exergy fed to the process is recovered in the useful product (bioethanol and feedstuff).

About 7% of the exergy reaching the process is destroyed due to the imperfections of the thermodynamic transformations.

The overall exergy destruction in the process is about 377.54 kW.

The greatest loss of exergy is localized in the distillation section; this is due to the mixture of the streams with unbalanced compositions and the differences in temperatures in the stages of the column.

The fermentation reactor occupies the second place in term of exergy destruction with a contribution of 33%

followed by the exchanger (HX-4) 11.5%. This paper could be used as a support tools for the implantation of industrial process for bioethanol production from waste dates.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

NOMENCLATURE

Notation

D	=	total mass flow rate
Ex	=	Exergy
H	=	mass enthalpy
LHV	=	lower Heating Value
n	=	number of chemical species in the material stream
P	=	Pressure
Q	=	heat transferred
S	=	mass entropy
T	=	Temperature

Subscripts

M	=	material stream
mix	=	mixing part
Q	=	heat transfer
phy	=	physical part
W	=	mechanical work
chem	=	chemical part
0	=	reference conditions

Superscripts

l	=	liquid phase
v	=	vapor phase
0	=	pure component properties at standard conditions at T, P

Greek letters

ϵ	=	mass standard chemical exergy
η	=	Efficiency

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