Exergy efficiency of thermochemical syngas-to-ethanol production plants

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Abstract

This work presents exergy analyses applied in four different conceptual second-generation ethanol production processes through a thermochemical route using catalysts based on Molybdenum (P-1), Copper (P-2), and Rhodium (P-3 and P-4), aiming to assess their exergetic efficiencies. The results show that the conceptual processes have satisfactory exergy efficiencies in both cases, when compared among themselves and when compared with other processes reported in literature. The processes' efficiency for P-1, P-2, P-3 and P-4 were, respectively, 52.4%, 41.4%, 43.7% and 48.9%. The reactors were the sections in which exergy destruction was more significant, due to the exothermic reactions and mixing points (where streams with different temperatures were mixed). Such results show the potential of thermochemical ethanol production, besides opening the possibilities of process improvement.

Graphic abstract

Keywords Ethanol · Syngas · Thermochemical · Exergy

1 Introduction

Energy may be considered one of the main indicators of economic development for most countries [29]. Worldwide, the majority of the energy sources are conventional and non-renewable. The share of these resources in 2016 was about 57.6% from which 31.9% petroleum, 22.1% natural gas and, 27.1% coal. The local scenario in Brazil is similar to the global panorama. In 2019, around 53.9% of all fuel used in the country was of fossil origin [2]. Nevertheless, the increase in the prices of petroleum and the limitation of its supply have led to the exploration of

alternative energy sources, intending to improve energy security and energetic efficiency [29]. Due to the increasing global energetic demand, the improvements in the standards of living, and the fast depletion of the fossil fuel reserves, it is possible to anticipate that we will reach the complete scarcity of this resource or an unsustainable increase of its price in a near future. These problems may be aggravated by the environmental impact caused by such fuels, like global warming, climate change, acid rain and exhaustion of atmospheric ozone.

Therefore, the appropriate energy choices should be debated globally [3]. According to the Kyoto protocol,

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replacing fossil fuels for the utilization of hydrogen energy or biomass is essential for the sustainability of the planet. Thus, the use of biomass and other renewable sources to provide energy and chemicals is being put under scrutiny due to its potential as complement to the existing supplies and imposing a smaller environmental impact [27]. One of the forms to obtain energy from biomass is its conversion into biofuels. The use of biomass to produce biofuels and its utilization as transport fuel is an attractive option, considering that electricity and heat may also be generated through other renewable sources, like solar and wind power [31].

Biomass is generally considered a renewable source of energy and neutral in carbon emissions. Although, it also poses some disadvantages, such as limited availability in some countries and high logistic costs related to its low energetic density, making necessary the development of highly efficient conversion routes, so the use of biofuels can compete with fossil fuels.

Biofuel is defined as a fuel of biological and non-fossil origins, produced using biomass, sustainable, and that may be produced on an industrial scale from agricultural products such as sugarcane and corn, and a clean and renewable source of energy.

Biodiesel is an option for obtaining biofuels from biomass. For its production, the oil naturally produced by seeds of plants and algae is used. These oils are constituted almost exclusively of triacylglycerols (TAGs); They are similar to conventional fossil petroleum and may be transesterified into biodiesel. Another option to produce biofuels is bioethanol from starchy materials (corn kernels) or saccharose (sugarcane). Bioethanol has an important role worldwide, from the economic point of view and from the environmental point of view, which suggests a vast market potential for ethanol and its logistic and environmental advantages [27].

It is well known that saccharose and starchy materials, in general, may be used to produce first generation bioethanol. However, the use of food commodities as raw material for the production of biofuels is controversial, despite the beneficial mitigation of environmental problems caused by the substitution of fossil fuels by first-generation biofuels as source of energy. In response to that, the production of second-generation biofuels from agricultural and forestry residue (i.e. corn stover, sugarcane bagasse, and empty palm fruit bunch) has been object of global interest due to the abundance of sub utilized lignocellulosic residue materials [29]. One of the most applicable technologies for the conversion of non-edible biomass into second-generation biofuels is the process of gasification, followed by the Fischer-Tropsch synthesis. The synthesis gas (syngas) produced by the gasification of biomass may be converted into more useful forms of energy by the utilization

of metal-based catalysts (thermochemical process) or biocatalysts (thermochemical-biochemical process).

The thermochemical and the thermochemical-biochemical processes are currently the two main methods to produce second-generation ethanol through syngas processing. The production process of ethanol through thermochemical-biochemical route can be influenced by many factors as, for instance, the type of microorganism and the operation specifications of the bioreactor. Lately, this biochemical process is the most commonly utilized in lab-scale and preliminary analyses, showing itself promising, due to its high ethanol selectivity [21], high yield, smaller energetic costs, and fewer byproducts. Further, this process occurs under moderate conditions of temperature and pressure and does not require any pre-treatment of the syngas feed and the costs of catalysts acquisition are smaller when comparing to the thermochemical process [1]. The anaerobic organisms used as biocatalysts to produce biofuels may develop with CO and H₂/CO₂ (chemotropic reactions) and sources of carbon such as fructose, malate and glutamate [34]. It is well documented that many bacteria such as *Clostridium aceticum*, *Acetobacterium woodii*, *Clostridium ljungdahlii* and *Clostridium thermoaceticum* may effectively convert the components of syngas (i.e. CO, H₂ and CO₂) in acetate and ethanol, but, despite that, present low conversion of biomass into ethanol.

Despite the advantages mentioned above, there is still an increasing demand for innovative processing technologies and new energy conversion systems to respond to the financial and environmental questions associated with the production of biofuels. The thermochemical production process of bioethanol is presented as an alternative route. The conventional process of thermochemical bioethanol production starts at the pre-treatment and conversion of the biomass. In this context, the most efficient conversion method for the usage of biomass is gasification, in which partial oxidation converts it to syngas and condensable compounds.

During the gasification, the chemical energy of the biomass is converted into thermal energy and chemical energy in syngas. Compared to the biochemical route, the thermochemical route presents considerably faster rates of conversion of syngas attaining 62–83% conversion [29]. Aiming to optimize the process it is possible to regulate, among other factors, the temperature of the reaction, as well as alter type of catalyst or support. Despite the positive factors, the production of thermochemical ethanol still faces problems, such as low selectivity for ethanol during the conversion of syngas. Rhodium (Rh) catalysts, for example, are currently the most studied and used for lab-scale thermochemical synthesis of ethanol and are among the most selective to the

product [6, 31]. However, they still present low conversions of syngas, which affects the overall performance of the process. A lot of research effort is being applied into finding a catalyst that has high selectivity to the synthesis of ethanol, and high conversion of syngas. A way to achieve this is by developing a catalyst that presents high yields in all phases of the ethanol synthesis. It is worth noting that the hydrogenation reactions present in the conversion of syngas into ethanol are highly exothermic and favorable.

Spivey and Egbebi [27] conducted research related to obtaining and improving efficient catalysts. The results pointed that copper (Cu) and molybdenum (Mo) based catalysts usually have higher activity for ethanol in terms of conversion of carbon monoxide. Besides, these are relatively cheap and have high selectivity for hydrogenation reactions in the vapor phase. These reactions may be considered the most important ones in the production of thermochemical ethanol. In this context, Cu and Mo may be considered potential substitutes for the Rh as main catalysts for the production of thermochemical ethanol.

However, when compared to other Rh-based catalysts, these catalysts have low ethanol selectivity. This is because Cu and Mo-based catalysts have a mechanism for chain growth formation of higher alcohols, which suggests that these may be formed by successive condensation of lower alcohols. This mechanism is slow to condensate methanol and form ethanol and fast to condensate ethanol and form higher alcohols. This ends up consuming most of the ethanol produced, diminishing the selectivity of the process. Thus, a method that considers the energetic balance of the process may be used for assessing of the viability of using Cu or Mo catalysts in the production of bioethanol.

Measuring the efficiency or renewability of an energetic resource using methods that directly quantify energy is questionable because such methods are based on the first law of thermodynamics, which includes the principle of energy conservation.

The second law of thermodynamics may be considered using the exergy, which expresses, for all energy forms, the maximum shaft work that can be produced by a system or flux (matter, heat or dynamic energy) when these are taken reversibly to equilibrium with their environment [17].

Exergy analysis is a technique of thermodynamic analysis technique that allows comparing different processes and systems in a cohesive form. This is because it identifies the places and causes of thermodynamic losses, as well as the environmental impact in a clearer way than the energy analysis between thermodynamic indicators. In contrast with energy analysis, exergy analysis points out the quality of the available energy and the possibility to produce work from its surplus, making processes more efficient and sustainable. For this reason, it is verified that the exergy

analysis is the most powerful tool for the analysis of energy conversion systems because it allows the recognition of the causes and quantitative positions of thermodynamic imperfections [28].

Due to the exclusive conceptual characteristics of the exergy analysis, such methodology has been largely applied to analyze and optimize several energy systems such as thermoelectrical plants [7], vapor compression refrigeration systems [23], distillation columns [30], multi-crystalline solar photovoltaic systems [18], supercritical thermoelectric coal plants assisted by solar concentrator [23], active solar distillation systems integrated with solar ponds [22], cogeneration with LNG [11] and desalination plants [9].

Exergy analysis might identify the losses associated to various biofuel synthesis, to find and introduce improvement strategies. Furthermore, many research attempts were made to apply the exergy analysis in various ethanol production systems in the last decade. For example, Yang et al. [33] identified the renewability of the total production of corn ethanol in China using the cumulative exergetic method and considering the non-renewable resources used in the whole process, since the farm where the biomass was collected to the residue treatment. In another study, an energetic evaluation was applied in a sugar-ethanol integrated production plant, considering a cogeneration system, thus reducing the irreversibilities of the process [5]. Tan et al. [29] also compared the efficacy of second-generation ethanol and methyl ester from palm using the concept of exergy. Later, van der Heijden and Ptasinski [31] conducted the exergetic analysis of thermochemical ethanol production by indirect gasification of woody raw material processed through steam-blow and further catalytic conversion of the syngas produced in ethanol. Sohel and Jack [26] also applied the exergy analysis to assess the production of biofuels from lignocellulosic biomass using a new route, and exergetic analysis of the performance of an integrated production system of first and second-generation ethanol from sugarcane was carried out by Palacios-Bereche et al. [17].

There are also studies about the production of ethanol from syngas, focusing in the technical viability and kinetic modeling of the related process. For example, Najafpour and Younesi [15] used a single inorganic carbon source (i.e. carbon monoxide) to produce acetate and ethanol through fermentation process using *Clostridium ljungdahlii*. In a different study, Cotter et al. [4] aimed to improve the stability of the microorganism culture and improve the ethanol/acetate ratio using resting cells (not growing) of *C. ljungdahlii* for the fermentation of the syngas. Later, Hurst and Lewis [8] assessed the effects of constant CO partial pressure in the cellular growth, production of acetic acid and ethanol

production using *C. carboxivorans*. Maddipati et al. [10] studied the viability of substituting the yeast extract by corn steep liquor (a low-cost nutrient source) for the fermentation of syngas, to be later used in ethanol production, using *Clostridium esterpe*. In another study, Mustafiz et al. [14] tried to enrich the mixed anaerobic bacterial culture through the fermentation of syngas.

Furthermore, many studies and exergetic analyses to determine the efficiency of the processes or equipment applied in the production of ethanol were conducted in the last decade [13, 29, 31, 32]. However, the results reported in these studies show that there is an evident need for more research and development in this area because it could optimize the variables involved and innovate the existing processes [32].

Such studies reiterate that the application of exergetic analysis in a component, process, or sector can lead to a perspective of how to improve the sustainability of the activities that may compromise the system by reducing energy loss and identify the economic and energetic viability of the process. In other words, exergetic analysis enables us to specify the maximum performance of a system and the sources of irreversibility found in it. This allows for a perspective of possible improvements in the process in sectors where the irreversibility and the exergy losses occur, thus improving its efficiency and energetic yield.

That being said, to justify the production of thermochemical second-generation ethanol, more specifically, using Mo, Cu and Rh catalysts, the exergy analysis should confirm that the energy produced from the lignocellulosic biomass is bigger than the energy used in the production of ethanol [17].

The objective of this study is to assess the efficiency and viability of the conceptual processes developed by Miranda et al. [12]. These innovative conceptual processes utilize the most representative classes of catalysts, based on Mo, Cu and Rh, to convert biomass-based syngas into second-generation ethanol through the thermochemical route. The efficiency and viability are assessed using exergetic analysis and the results compared to the results obtained by different processing technologies, serving as groundwork for further technology developments and thermodynamic studies.

The present work is organized in Methodology, which brings a brief description of exergy and the assumptions made for the analysis application; Results and discussion, which presents the results obtained from the analysis, evidencing the exergy inputs and outputs in each stream of each process, as well as performing a comparison between the studied processes and the processes present in literature and; Conclusion, in which all the work was summarized highlighting the results, main findings and directions for future works.

2 Methodology

2.1 Definition of exergy

Any spontaneous changes in substances that occur in the natural environment will occur with the decrease of the exergy of such substances. That is the law of the exergy reduction in spontaneous processes, analogous to the law of the reduction of affinity in spontaneous processes. In contrast with energy, that is always conserved in any process due to the first law of thermodynamics, the exergy is exempted from the laws of conservation and affinity.

The exergy of a system is conventionally classified in two parts: physical exergy, associated with temperature (thermal exergy), pressure (pressure exergy, dynamic exergy) and concentration (mixture exergy) changes; and chemical exergy, associated with changes in the composition of substances. Therefore, exergy can be expressed as:

$$Ex = Ex_f + Ex_c + Ex_{cin} + Ex_{pot} \quad (1)$$

where Ex is the exergy of a system, Ex_f is the physical exergy of the system, Ex_c represents the chemical exergy present in the system, and Ex_{cin} and Ex_{pot} are related to the exergy associated with changes in the kinetic and potential energy of the substances present in the system. However, according to Rivero and Garfias [24], in closed systems, it is possible to disregard the last two terms because the exergy of a substance is function only to its physical and chemical components. According to Sato [25], it is possible to represent the terms of Eq. 1 through physicochemical properties of the components of a system.

For a system composed by mass streams (inputs and outputs), it is possible to represent Eq. 1 as:

$$\sum \left(1 - \frac{T_0}{T_k}\right) \cdot Q_k - \left(W - P_0 \frac{dV_{vc}}{dt}\right) + \sum m_e \cdot e_e - \sum m_s \cdot e_s - e_{des} = \frac{de_{vc}}{dt} \quad (2)$$

where T_0 and P_0 are the temperature and pressure of the reference environment, T_k , Q_k , W , m_e , m_s , e_e and e_s represent respectively the temperature and heat of component k , the work exerted in the system, entry and exit mass, and exergetic input and output. The term e_{des} represents the destruction of exergy, which occurs mainly in reactors and mixers.

Having quantified these terms, it is possible to determine the exergetic efficiency that is defined as the ratio between the production of useful energy and the consumption of exergy, or even the ratio between the exergetic input and output. Besides, the exergetic efficiency can be calculated as a function of the destruction of exergy. The exergetic efficiency characterizes the

performance of a system or component of the system from thermodynamic point of view. Such characterization is somewhat subjective, in a sense that it possesses various definitions in literature. These may be divided in two main groups:

- (a) If considering the exergetic balance as:

$$\sum e_e = \sum e_s + e_{des} + e_L \quad (3)$$

Where e_L characterizes the exergy losses. The exergetic efficiency may be defined as the ratio between the exergy that enters the system and the exergy that leaves the system, as evidenced by Eq. 4:

$$\varepsilon = \frac{\sum e_s}{\sum e_e} \quad (4)$$

- (b) The second group consists of formulating the exergy balance in terms of desired output or useful exergy, and necessary input or fuel exergy.

$$e_p = e_f - e_d - e_L \quad (5)$$

This way, the exergetic efficiency may be represented as in Eq. 6.

$$\varepsilon = \frac{e_p}{e_f} = 1 - \frac{E_d}{\sum e_e} \quad (6)$$

where e_p is the exergy associated with the product or desired output exergy, e_f is the fuel exergy and E_d is the sum of the exergy destroyed through irreversible processes (e_d) and the exergy lost in eventualities of the process (e_L). The second definition is beneficial because it enables the assessment of the exergetic efficiency, separating the products from the process. This way, it is possible to quantify the exergetic efficiency of the ethanol and all its byproducts or the

ethanol by itself, considering the byproducts as exergy losses. This approach was used in this study because it express how selective the process is for a product of interest which is one of the bottlenecks of the use of such catalysts in the production process of thermochemical ethanol. This way, it is possible to compare the processes studied with other processes described in the literature in terms of exergetic efficiency.

In a general way, the procedure adopted to determine the exergetic efficiency can be summarized by Fig. 1.

The exergy analysis is applicable if it is possible to obtain the data and variables of the analyzed process (temperature, pressure, enthalpy, entropy and the composition of mass streams). This type of data allows us to determine the chemical, thermal and dynamic exergies of each section. After quantifying each type of exergy present in the process using Eq. 2, Eq. 6 is applied to determine the exergy efficiency, thus obtaining a viability indicator of the process. In this context, one of the limiting factors in an exergy analysis is the choice of a reference environment that satisfies the process under analysis, noticing that different reference environments possess different standard exergies for compounds and elements, thus affecting the exergy efficiency and consequently the process viability.

2.2 Study cases

The data utilized for the exergetic analyses were taken from four simulations made by Miranda et al. [12]. The first process, named P-1 simulates a process that uses molybdenum as catalyst (K-Co-MoS₂/C), the process P-2 simulates a process that uses a copper-based catalyst (Cu/ZnO), while processes P-3 and P-4 use rhodium-based catalysts (respectively Rh-Mn-Li-Fe/Si₂O and Rh-La-Fe-V/Si₂O). All processes have different layouts, differing in the type of catalyst used as well as the disposition of its steps.

Fig. 1 Methodological representation of exergy analysis procedure

The cases were analyzed considering that the system operates at stationary state. With this assumption, Eq. 2 may be simplified as presented in Eq. 7.

$$\sum \left(1 - \frac{T_0}{T_k} \right) \cdot Q_k - W + \sum m_e \cdot e_e - \sum m_s \cdot e_s = e_{des} \quad (7)$$

Obtaining the exergy destruction, it is possible to calculate the exergetic efficiency of the processes using Eq. 6.

The information about the streams and their properties, as well as the flowcharts of the four analyzed processes, are available in Miranda et al. [12]

3 Results

Initially, we analyzed the process and the type of exergy consumed or generated in each step. We also determined the sections of possible exergetic destruction. From information regarding the composition of the streams involved in the process, we obtained the intensive and extensive variables necessary for the calculation.

For the determination of total exergy destruction, we made a balance according to Eq. 2. This way, the exergy destroyed in the process was determined by the difference between exergy inputs and outputs, being it chemical (matter), thermal (heat) or dynamic (pressure and separation). Thus, Eqs. (2) and (6) were applied to the processes

developed by Miranda et al. [12] to determine, respectively, the total exergy destruction and the exergy efficiency of each process. The values obtained for the exergy in each section of the referenced processes are shown in Tables 1, 2, 3 and 4.

With the exergy inputs and outputs it was possible to obtain the total exergy destruction in all study cases. It is important to notice that the asterisk symbol (*) represents a local exergy destruction, which was determined after calculation of exergetic inputs and outputs, as can be seen in Tables 1, 2, 3 and 4 the catalytic reactor was responsible for the majority of the exergy destroyed, corresponding to respectively to 66%, 82%, 78% and 75% from processes P-1 to P-4. Among the study cases, the process P-2 was the one that presented the largest percentage of exergy destruction. This happened mostly due to chemical irreversibilities, which mean a larger conversion of syngas to products. Such characteristics could impact positively on thermal and dynamic exergy results by reducing reagents recycle and consequently heat exchanging and pumping.

Besides, in all study cases, it can be noticed that, the chemical exergy inputs and outputs (matter in and out) represented the majority of the exergy, followed by dynamic exergy (separation units and compressors). Thermal exergy (heat exchangers) represented the smallest part of processes' exergy. Another important factor was that dynamic exergy from distillation columns was proportional to the mass flow input. This occurs because,

Table 1 Exergy quantification in each section of P-1 process

Process section	Exergy (kW)	Process section	Exergy (kW)
Reaction	4782.24	Preliminary Separation	135.64
Stream in (S-1001)	4988.03	Flash drum (F-1001)	121.08
Compressor (CPR-1001)	414.07	Distillation col. (C-1001)	14.56
Heat exchanger (H-1001)	370.90		
Reactor (R-1001)	-619.86*		
Reconditioning	-280.45		
RGWS	-219.67*	Heat exchanger (K-1002)	-13.93
GASI	-47.66*	Stream in	0.81
Purification	-4552.18		
SEP-1	-163.90	SEP-2	-4425.82
Distillation col. (C-101)	9.82	Distillation col. (C-201)	2.94
Distillation col. (C-102)	5.64	Stream out (S-1016)	-854.24
Heat exchanger (K-101)	-161.27	Stream out (S-1017)	-3574.52
Stream in (S-102)	0.68		
Stream out (S-1014)	-18.77		
Stream mixing	-47.75*		
Total Exergy In	5928.53	Total Exergy Destruction	934.94*
Total Exergy Out	4993.63	Ethanol Exergy out	848.85

Table 2 Exergy quantification in each section of P-2 process

Process section	Exergy (kW)	Process section	Exergy (kW)
Reaction	2702.39	Preliminary Separation	632.25
Stream in (S-1001)	3565.18	Flash drum (F-1001)	632.25
Compressors (CPR-1001)	496.97	Reconditioning	-229.74
Heat Exchanger (K-1001)	-45.69	REC	-224.36*
Reactor (R-1001)	-1314.07*	Stream out	-5.38
Purification	-3199.30		
SEP-1	-3199.30		
Dist. Column (C-101)	485.95	Stream out (S-1013)	-814.71
Dist. Column (C-102)	366.99	Stream out (S-1014)	-439.44
Dist. Column (C-103)	150.17	Stream out (S-1015)	-888.83
Dist. Column (C-104)	51.46	Stream out (S-1016)	-1520.41
Stream out (S-1012)	-590.48		
Stream mixing	-64.10*		
Total Exergy In	6272.49	Total Exergy Destruction	1602.53
Total Exergy Out	4669.96	Ethanol Exergy out	882.34

larger the flow, larger the quantity of exergy that will need be inserted in the system to make possible the effective separation of the products.

Summing exergy inputs and outputs of the process P-2 and P-3, shown in Tables 2 and 3, we obtained different results from the sections “Total exergy in” and “Total exergy out”. This is because both processes possess compression systems, named as *CPR* [12]. These systems are composed of a series of interleaved compressors and heat exchangers, this way, it was possible to obtain an exergy input for each compressor and an exergy output for each heat exchanger. Tables 2 and 3 present these compression systems as a single process, thus showing, the value of the exergy resultant from these systems.

The section “Stream mixing” of Tables 1, 2, 3 and 4 represents the destruction of thermal exergy caused by mixing two streams with different temperatures. As shown in Table 4, process P-4 presented the most relevant loss of thermal exergy due to the considerable difference in temperature between streams at the mixture points. An efficient way to avoid this kind of loss is by installing heat exchangers in those streams in order to minimize the temperature gap and make possible the utilization of this useful thermal energy in other section of the process.

In this context, Fig. 2 aims to make a qualitative analysis separating the kinds of exergy involved in the balances and to facilitate the comprehension of the types of exergy which influenced most processes’ efficiencies. As can be seen from this figure, the type of exergy which most influenced the balances is the chemical exergy, followed by the dynamic exergy and, finally by thermal exergy. On average,

94% of the exergy destruction occurred in the processes was from chemical origin, originated from the reactors, and from recovery section.

The dynamic exergy input varied from 16% to 43%. This happened because the case studies have different sub-products besides ethanol, being necessary the use of a different number of distillation columns for each process. Although P-3 has a larger number of distillation columns, process P-2 needs a larger exergy input to make it possible to effectively separate products and sub-products involved, which in this case, are mostly higher alcohols and hydrocarbons due the selectivity of the Cu-based catalyst.

From the Fig. 2c it is possible to notice that the chemical exergy destruction in process P-2 was around 90% larger than the other processes considered. This fact occurred due to the high influence of the WGS (Water-Gas-Shift) reaction inside the Cu-based reactor bed, which at high temperatures means a considerable amount of exergy is destroyed during the reaction. Figure 2b and Fig. 2c do not have data for dynamic exergy, considering that the output and the destruction of this kind of exergy were zero in all processes.

After quantification and analysis of all exergy inputs (Fig. 2a) and outputs (Fig. 2b), it was possible to determine the exergy efficiency of each process. Using Eq. 6, the value obtained for the exergetic efficiency for the process P-1 was 52.4%, considering only ethanol as a product, and 84.2% when considering hydrocarbons, methanol and higher alcohols. Further, the results for process P-2 were 41.4% when considering only ethanol as a product of the process and 74.5% when considering byproducts such as

Table 3 Exergy quantification in each section of P-3 process

Process section	Exergy (kW)	Process section	Exergy (kW)
Reaction	3046.47	Preliminary Separation	245.92
Stream in (S-1001)	3420.88	Flash drum (F-1001)	245.92
Compressors (CPR)	352.67		
Reactor (R-1001)	-727.08*		
Reconditioning	-133.26		
GASI	-133.86*	Stream in (S-1010)	0.63
Purification	-2780.89		
<i>SEP-1</i>	<i>110.29</i>	<i>SEP-7</i>	<i>-1852.28</i>
Dist. Column (C-101)	110.29	Dist. column (C-701)	43.39
<i>SEP-2</i>	<i>6.71</i>	Dist. column (C-702)	36.73
Dist. Column (C-201)	36.15	Dist. column (C-703)	6.65
Stream out (S-1015)	-29.44	Stream in (S-702)	12.34
<i>SEP-3</i>	<i>-636.93</i>	Stream out (S-1023)	-1054.49
Dist. Column (C-301)	72.67	Stream out (S-1024)	-896.90
Stream out (S-1016)	-709.60	<i>SEP-8</i>	<i>230.23</i>
<i>SEP-4</i>	<i>60.73</i>	Dist. column (C-801)	113.83
Dist. Column (C-401)	60.73	Dist. column (C-802)	85.12
<i>SEP-5</i>	<i>-337.67</i>	Stream in (S-803)	31.28
Dist. Column (C-501)	13.51	<i>SEP-9</i>	<i>-102.70</i>
Dist. Column (C-502)	27.22	Dist. column (C-901)	28.71
Stream out (S-1019)	-378.40	Dist. column (C-902)	23.15
<i>SEP-6</i>	<i>40.73</i>	Stream out (S-1028)	-117.76
Dist. Column (C-601)	40.73	Stream out (S-1029)	-33.12
		Stream out (S-1030)	-3.68
Stream mixing	-64.80*		
Total Exergy In	4605.76	Total Exergy Destruction	925.74
Total Exergy Out	3680.02	Ethanol Exergy out	693.32

hydrocarbons, methanol and higher alcohols. Process P-3 obtained exergetic efficiencies at 43.7% and 79.9% respectively, using the same consideration. Finally, the exergetic efficiencies obtained for P-4, using the same consideration, were 48.9% and 83.5% respectively, showing that process P-4 is more efficient than process P-3, due to its plant layout, despite both using rhodium-based catalysts inside the reactor of thermochemical ethanol synthesis.

Aiming to establish a connection with recent developments, the results obtained with the chosen methodology were compared to works from different authors. Such comparison is shown in Table 5. It is possible to notice that the values for exergetic efficiency obtained in this work are similar to the values obtained by van der Heijden and Ptasinski [31] in their study regarding the production of thermochemical ethanol using molybdenum-based

catalysts. It is possible to observe that the sections with greater exergy losses in all processes are the points where streams of different temperatures are mixed, as well as the loss of thermal exergy in the reactor of thermochemical ethanol synthesis.

A way to increase the exergetic yield obtained would be to reduce the differences in temperature of the aforementioned streams with heat exchangers. An alternative is the reduction of the temperature in the synthesis reactor. However, this may result in a reduction in the conversion of syngas into ethanol. According to Pang et al. [19] and Ptasinski [20], the ideal temperatures for the conversion of syngas into ethanol utilizing rhodium and molybdenum catalysts is approximately 300°C. Thus, a system of heat exchangers could be implemented to adjust the temperature, aiming for maximum syngas into ethanol conversion.

Table 4 Exergy quantification in each section of P-4 process

Process section	Exergy (kW)	Process section	Exergy (kW)
Reaction	4061.96	Preliminary Separation	365.44
Stream in (S-1001)	4777.40	Flash drum (F-1001)	218.27
Compressors (CPR-1001)	337.68	Flash drum (F-1002)	147.17
Heat Exchanger (K-1001)	-313.21		
Reactor (R-1001)	-739.91		
Reconditioning	-234.81		
Heat Exchanger	-82.26	Stream in (S-1037)	0.75
GASI	-143.30		
Purification	-4114.77		
<i>SEP-1</i>	<i>-563.60</i>	Dist. column (C-1001)	95.24
Dist. Column (C-101)	90.63	Dist. column (C-1002)	35.00
Dist. Column (C-102)	62.37	Dist. column (C-1003)	12.73
Dist. Column (C-103)	53.39	Heat Exchanger (H-1001)	56.42
Dist. Column (C-104)	20.29	Decanter (D-1001)	31.21
Heat Exchanger (K-101)	-12.50	Stream out (S-1031)	-200.12
Stream in (S-103)	0.47	Stream out (S-1032)	1099.85
Stream out (S-1017)	-400.24	Stream out (S-1036)	-2312.54
Stream out (S-1019)	-66.71		
Stream out (S-1038)	-311.30		
Stream mixing	-87.82*		
Total Exergy In	5882.60	Total Exergy Destruction	971.03
Total Exergy Out	4911.57	Ethanol Exergy out	368.28

Another way to improve the exergetic efficiency would be adjusting number of compressors and heat exchangers. This way, the mass streams would not suffer harsh alterations of variables such as pressure and temperature.

The reactors were the largest sources of exergy destruction in the four processes analyzed, surpassing 65% share of exergy destruction in all cases, as can be seen in Table 6. This is due to the limited utilization of the energy from the exothermic reactions occurring inside the reactor, thus demonstrating the practical irreversibility of the synthesis of ethanol and higher alcohols.

Furthermore, van der Heijden and Ptasinski [31] suggest that Mo catalysts are among the best alternative catalysts to produce thermochemical ethanol, considering energy usage aspects. The results obtained in the present study indicate that the Cu catalyst obtained the smallest exergetic efficiency among the processes studied, however, this result alone is not enough to conclude if such catalyst is efficient or not. Exergy analysis is a useful tool to compare processes of the same category and data about the production process of thermochemical ethanol using copper catalysts are scarce in literature. However, the process presents a considerable exergy efficiency, presenting only 2.1% less efficiency than the process studied by van

der Heijden and Ptasinski [31] that uses rhodium as catalyst. This way, more studies regarding the use of copper as catalyst are needed in order to attest the viability of the process studied here.

It is possible to notice that efficiencies reached values above 70% due to the input of the process being syngas and not biomass. The energy losses during gasification of biomass are moderate when compared to the losses seen in the catalytical reactor. However, if the studied processes included the preparation and biomass gasification steps, such losses could be lessened by reducing the temperature of gasification [31], thus increasing the exergetic efficiency. According to Ptasinski [20], however, it still would not be larger than the value obtained in this study. Because with the high chemical exergy value of the biomass as input in the process, the amount of exergy destroyed in the gasification through heat dissipation, as well as the need for insertion of a cleaner or reformer of the syngas generated would result in a decrease of the exergetic efficiency of the process.

We point out that the difference between the exergy values obtained in the process studied by Velasquez et al. [32], Modaresi et al. [13] and Ortiz and Oliveira Jr. [16] and the present study may have occurred because

Fig. 2 Qualitative exergy analysis

the temperature and pressure conditions in fermentative reactors are milder than the ones needed in catalytical reactors, resulting in smaller thermal energy losses to the environment and thus increasing the global exergetic efficiency of the process. The biochemical route may be advantageous due to the absence of substrate loss related to chemical modifications and the use of moderate and non-corrosive physicochemical conditions (smaller reaction temperatures and pH), the degradation of lignocellulosic biomass using bio-catalysts is an irreversible complex process, and most of the exergy losses in a biochemical process occur in the bioreactor due to the irreversibilities of the fermentative process. These values state the efficiency of the process of biochemical ethanol but do not disprove the efficiency of the thermochemical process.

Then, aiming to quantify the amount of exergy per section in each process studied in this work, Fig. 3 is shown below, comparing the four processes studied here regarding output and exergy destruction amounts. Figure 3 is a perspective of the quantities of exergy in each step of the

process considering all the byproducts of the processes (P-1B, P-2B, P-3B and P-4B).

It is possible to verify that the exergy destruction in case A is, in the worst scenario (P-2), stood below 16% of the total exergy of the system. Observing Fig. 3 it is possible to verify that processes P-1 and P-4 have smaller percentages of exergy destruction when compared to processes P-2 and P-3.

P-1 and P-4 use, respectively, molybdenum and rhodium-based catalysts, while P-2 and P-3 use respectively copper and rhodium. Figure 3 shows that the entry exergy conversion (in its majority syngas and heat) is larger in the process that uses molybdenum as catalyst (P-1A and B). This may be due to the contact surface of the Mo-based catalysts, which provide a larger generation of alcohols and smaller generation of hydrocarbons, which, in turn, have low energetic value [31]. Further, Fig. 3 shows that the molybdenum catalyst is more selective for ethanol than the other catalysts. This is evidenced by the smaller exergy loss in byproducts of process P-1B, which means a larger fraction of the feedstock syngas was converted into ethanol.

Table 5 Comparison of the exergetic efficiency values for the different production routes considering only bioethanol as a product

Bioethanol production method	Exergetic efficiency (%)	Reference
Ethanol from straw lignocellulosis	87.8	Modaressi et al. (2012)
Thermochemical ethanol from biomass gasification and catalytic synthesis using molybdenum catalyst	44.4	Van der Heijden and Ptasinski (2012)
Thermochemical ethanol from biomass gasification and catalytic synthesis using rhodium catalyst	43.5	Van der Heijden and Ptasinski (2012)
Fermentation of syrups using chemical and biochemical processes	77.8	Velásquez et al. (2012)
Bioethanol production from sugarcane bagasse	94.4	Ortiz and Oliveira (2014)
Thermochemical ethanol through conversion of syngas using molybdenum catalyst (P-1)	52.4 (84.2)*	Present Study
Thermochemical ethanol through conversion of syngas using copper catalyst (P-1)	41.4 (74.5)*	Present Study
Thermochemical ethanol through conversion of syngas using rhodium catalyst (P-1)	43.7 (79.9)*	Present Study
Thermochemical ethanol through conversion of syngas using rhodium catalyst (P-1)	48.9 (83.5)*	Present Study

*Values regarding the calculation of the exergetic efficiency considering all of the byproducts of the process such as hydrocarbons, higher and lower alcohols

Table 6 Reactor's exergy destruction

Process	Exergy destruction in reactor (MW)	% of Exergy destruction in the reactor
P-1	0.62	66.2
P-2	1.31	82.0
P-3	0.73	78.5
P-4	0.97	76.2

4 Conclusion

Based on the results obtained, it is possible to notice that despite the high values of exergetic efficiency of the process of production of thermochemical ethanol studied, these are smaller than what is obtained for the process of biochemical ethanol in other studies. This demonstrates that the fermentative processes for ethanol production are more efficient than thermochemical processes presented in this study. However, with the research and

Fig. 3 Exergy destruction and exergy output percentages

development of new materials as catalysts, supports, and promoters, this scenario could change, pointing to the need for more research regarding the production of thermochemical ethanol, as well as its exergetic efficiency and viability.

For the three classes of catalysts studied, the greater exergy losses (irreversibilities) occur in the ethanol synthesis reactor and in the point of joining streams with different temperatures. The exergy losses are moderate in the heat exchangers and separators, while the losses within compressors are smaller.

It is evident that the benefits from conducting an exergetic analysis in a system are reflected in the energetic yield. Because this tool can identify units that destroy exergy (equipment, streams, reactors, mixers), being a starting point for the design of an energy-efficient integration network that optimizes the whole process.

Thus, with the results obtained, it is possible to conclude that the production processes of thermochemical ethanol using catalysts based in Rh, Cu and Mo present high exergetic efficiency, which may be adopted as an indicator of viability of the process. Among these, process P-1 presents a satisfactory viability, being able to compete with the process proposed by van der Heijden and Ptasinski [31] due to a larger conversion of syngas and larger generation of products. It is also able to compete with the process proposed by Velasquez et al. [32] due to the greater selectivity for ethanol. This way, the exergy analysis has shown to be useful for determining the steps where exergy is lost and pointing out the necessity of the application of an energy integration in these steps. It aims at a process optimization, thus obtaining greater exergetic efficiency and consequently greater viability for the process, as well as assessing the most efficient process among the processes studied.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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References

1. Aghbashlo M, Tabatabaei M, S, H S, Younesi H, Najafpour G (2016) Performance analysis of a continuous bioreactor for ethanol and acetate synthesis from syngas via *Clostridium ljungdahlii* using exergy concept. *Clean Technol Environ Policy* 18(3):853–865
2. Albuquerque FA, Arriel NHC, Beltrão NE, Lucena E (2019) Monthly bulletin (Boletim Mensal). Technical report, Ministry of Mining and Energy (Min-istério de Minas e Energia)
3. Berthiaume R, Bouchard C, Rosen MA (2001) Exergetic evaluation of the renewability of a biofuel. *Exergy Int J* 1(4):256–268
4. Cotter JL, Chinn MS, Grunen AM (2009) Ethanol and acetate production by *Clostridium ljungdhlii* and *Clostridium autoethanogenum* using resting cells. *Bioprocess Biosyst Eng* 32(3):369–380
5. Ensinas AV, Modesto M, Nebra SA, Serra L (2009) Reduction of irreversibility generation in sugar and ethanol production from sugarcane. *Energy* 34(5):680–688
6. Hedayati A, Le Corre O, Lacarrière B, Llorca J (2015) Exergetic study of catalytic steam reforming of bio-ethanol over Pd-Rh/CeO₂ with hydrogen purification in a membrane reactor. *Int J Hydrogen Energy* 40(8):3574–3581
7. Hou D, Shao S, Zhang Y, Liu SL, Chen Y, Zhang SS (2012) Exergy analysis of thermal power plant using modeling approach. *Clean Technol Environ Policy* 14(5):805–813
8. Hurst KM, Lewis RS (2010) Carbon monoxide partial pressure effects on the metabolic process of syngas fermentation. *Biochem Eng J* 48(2):159–165
9. Janalizadeh H, Manesh MHK, Amidpour M (2015) Exergoeconomic and exergoenvironmental evaluation of integration of desalinations with a total site utility system. *Clean Technol Environ Policy* 17(1):103–117
10. Maddipati P, Atiyeh HK, Bellmer DD, Huhnke RL (2011) Ethanol production from syngas by *Clostridium* strain P11 using corn steep liquor as a nutrient replacement to yeast extract. *Biore-sour Technol* 102(11):6494–6501
11. Manesh MHK, Navid P, Blanco-Marigorta AM (2013) New procedure for optimal design and evaluation of cogeneration system based on advanced exergoeconomic and exergoenvironmental analyses. *Energy* 59:314–333
12. Miranda JCC, Ponce GHSF, Arellano-Garcia H, Maciel Filho R, Wolf Maciel MR (2020) Process design and evaluation of syngas-to-ethanol conversion plants. *J Clean Prod* 269:122078
13. Modaresi A, Kravanja P, Friedl A (2012) Pinch and exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw. *Appl Therm Eng* 43:20–28
14. Mustafiz A, Gosh A, Tripathi A, Kaur C, Canguly AK, Bhavesh NS, Tripathi JK, Pareek A, Sopory SK, Singla-Pareek SL (2014) A unique Ni²⁺—dependent and methylglyoxal—inducible rice Glyoxalase I possesses a single active site and functions in abiotic stress response. *Plant J* 78(6):951–963
15. Najafpour G, Younesi H (2006) Ethanol and acetate synthesis from waste gas using batch culture of *Clostridium ljungdhlii*. *Enzyme Microb Technol* 38:1–2
16. Ortiz PS, Oliveira S Jr (2014) Exergy analysis of pretreatment process of bioethanol production based on sugarcane bagasse. *Energy* 76:130–138
17. Palacios-Bereche R, Mosqueira-Salazar KJ, Modesto M, Ensinas AV, Nebra SA, Serra LM, Lozano MA (2013) Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane. *Energy* 62:46–61
18. Pandey AK, Tyagi VV, Tyagi SK (2013) Exergetic analysis and parametric study of multi-crystalline solar photovoltaic system at a typical climatic zone. *Clean Technol Environ Policy* 15(2):333–343

19. Pang J, Zheng M, Zhang T (2019) Advances in catalysis, volume 64, chapter Chapter Two—synthesis of ethanol and its catalytic conversion, pp 89–191. Elsevier
20. Ptasinski KJ (2016) Efficiency of biomass energy: an exergy approach to biofuels, power, and biorefineries. Wiley
21. Ragauskas AJ, Williams CK, Britovsek G, Cairney J, Eckert CA, Frederick WJ Jr, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T (2006) The path forward for biofuels and biomaterials. *Science* 311:484–489
22. Ranjan KR, Kaushik SC (2014) Exergy analysis of the active solar distillation systems integrated with solar ponds. *Clean Technol Environ Policy* 16(5):791–805
23. Reddy VS, Kaushik SC, Tyagi, SK (2014) Exergetic analysis and economic evaluation of central tower receiver solar thermal power plant. *Int J Energy Res* 38(10):1288–1303
24. Rivero R, Garfias M (2006) Standard chemical exergy of elements updated. *Energy* 31(15):3310–3326
25. Sato N (2004) Chemical Energy and Exergy: an introduction to chemical thermodynamics for engineers. Elsevier
26. Sohel MI, Jack MW (2012) Thermodynamic analysis of a high-yield biochemical process for biofuel production. *Bioresour Technol* 124:406–412
27. Spivey JJ, Egbebi A (2007) Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chem Soc Rev* 36(9):1514–1528
28. Szargut J (1980) International progress in second law analysis. *Energy* 5(8–9):709–718
29. Tan HT, Lee KT, Mohamed AR (2010) Second-generation bio-ethanol (sgb) from Malaysian palm empty fruit bunch: energy and exergy analyses. *Bioresour Technol* 101(14):5719–5727
30. Tarighaleslami AH, Omidkhah MR, Ghannadzadeh A, Hesas RH (2012) Thermodynamic evaluation of distillation columns using exergy loss profiles: a case study on the crude oil atmospheric distillation column. *Clean Technol Environ Policy* 14(3):381–387
31. van der Heijden H, Ptasinski KJ (2012) Exergy analysis of thermochemical ethanol production via biomass gasification and catalytic synthesis. *Energy* 46(1):200–210
32. Velasquez HI, Ruiz AA, de Oliveira Jr S (2010) Análisis energético y exergético del proceso de obtención de etanol a partir de la fruta del banano. *Revista Facultad de Ingeniería Universidad de Antioquia* 51:87–96
33. Yang Q, Chen B, Ji X, He YF (2009) Exergetic evaluation of corn-ethanol production in China. *Commun Nonlinear Sci Numer Simul* 14(5):2450–2461
34. Younesi H, Najafpour G, Mohamed AR (2005) Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium. *Clostridium ljungdahlii*. *Biochem Eng J* 27(2):110–119

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