**Wine effluents valorization through a biorefinery scheme**

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Abstract

The wine industry produces a large amount of highly polluting wastewater; its inadequate disposal has become a social and environmental problem. At the same time, these effluents are characterized by having a high content of carbohydrates and alcohols; these compounds can be used in the generation of bioenergy, a priority to ensure energy sovereignty in Mexico. Current technology does not take advantage of the energy potential of this type of wastewater. Thus, the valorization of wine effluents is proposed through a biorefinery scheme that generates biofuels and value-added products. For this, the composition and pretreatment of the wastewater are determined, and the products of interest in the biorefinery are selected. A case study is defined, which process is designed and simulated into the Aspen Plus simulator. For comparative purposes, a conventional treatment scheme consisting of an anaerobic digester to produce methane gas is developed. As a result, the production of levulinic acid, sustainable aviation fuel, electrical energy, green diesel, naphtha, light gases, glycols, and bioethanol is obtained. In addition, the biorefinery reduces the Chemical Oxygen Demand (COD) of the effluent by 99.99% allowing it to generate water that meets the quality necessary for human use according to Official Mexican Standards (NOM-001-SEMARNAT-2021, NOM-127-SSA1-2021). On the other hand, the conventional treatment process, which is constituted by biodigester, has a COD reduction of 18.79%; this decrement is not enough to achieve national standards of water for human use. In conclusion, both the biorefinery and conventional treatment schemes are feasible technically. However, biorefinery can offer a wide variety of biofuels and value-added products, such as those aforementioned; in contrast to the conventional treatment process which only can produce methane. Besides, according to the COD reduction obtained for each process, the conventional procedure must be complemented with other operation units to reach the required level for Mexico authorities.

**Keywords**: Biorefinery, wine effluent, sustainable aviation fuel, simulation, valorization.

* 1. Introduction

The wine industry generates from 0.2 to 4 wastewater liters per liter produced. In México, 400,000 hectoliters of wine are manufactured annually. The main composition of this effluent includes glucose, ethanol, and lignocellulosic material, in smaller quantities, as well as some polyphenols, and carboxylic acids. The inadequate disposal of this type of wastewater may cause damage to ecosystems (Buitron et al. 2019).

There are several treatments to achieve discharge standards and recovery of value-added products from distillery wastewater; this kind of wastewater is similar to wine effluent due to its organic content (alcohol, glucose, carboxylic acids). Some treatments include physical-chemical methods (adsorption, coagulation, oxidation, ozonation, electrolysis, reverse osmosis, ultrafiltration, and nanofiltration), biological processes (aerobic and anaerobic), as well as a combination of them (Ratna S et al., 2021). For instance, Wagh et al. (2020) performed a reduction of 94.88 % Chemical Oxygen Demand (COD) by using electrocoagulation; Wilk et al. (2019) eliminated 62 % color in vinasse by employing *Lactobacillus* and *Pediococus*; in the field of bioenergy, Buitron et al. (2019) generated biogas from wine effluent by working with methanogenic microorganisms.

All the reported works related to the treatment of this wastewater involve the methods aforementioned. Indeed, Kopsahelis et al. (2018) proposed a biorefinery scheme to obtain polyphenols, tartaric salts, and ethanol from grape lees, which are represented by dead yeast, and whey. However, no one has employed the concept of biorefinery to valorize wine effluents, to obtain add-value products, and to produce a wide variety of biofuels, simultaneously. Therefore, the research aim is to valorize wine effluents through a biorefinery scheme to generate biofuels and value-added products.

* 1. Methodology

The second column of Table 1 shows the composition of the wine effluent considered as case study, which represents a possible scenario in Baja California State (the main wine producer in México). It is important to mention that solids are represented by cellulose (C6H10O5), hemicellulose (C5H8O4), lignin, and lees (dead yeast, CH1.83O0.56N0.17) (Wooley, et al. 1996).

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| **Table 1.- Comparison between feed stream for both schemes, treated water from biorefinery and digestor.** |
| **Parameter** | **Wine effluent** | **Treated water III (Biorefinery)** | **Treated water (Digestor)** |
| Mass flow (kg/h) | 10,000 | 4,922 | 8,959.76 |
| Water (% mass) | 71.76 | 100 | 77.94 |
| Ethanol (% mass) | 7.39 | 0 | 4.47 |
| Glucose (% mass) | 5.26 | 0 | 0.33 |
| Solid (% mass) | 15.59 | 0 | 6.96 |
| COD (PPM) | 210,052 | 29.42 | 206,105 |

Figure 1 represents the conceptual biorefinery. To simulate the process in Aspen Plus, it was used BK-10 (for DC-05 to DC-07), Peng-Robinson (for R-01 and R-02), and NRTL for the other equipment as thermodynamic models (Carlson, 1996). Besides, for all distillation columns, including the reactive ones, module Rad Frac is used. In the biorefinery scheme, solids are separated from wine effluent in CN-01. Inside RD-01, glucose reacts to form 5-Hydroxymethyl Furfural (5-HMF), Eq. (1), and then, 5-HMF is converted to levulinic acid and formic acid, Eq. (2) (Solis, et al. 2022). These products, coming from RD-01 bottom, are separated by DC-01 and DC-02.



Figure 1.- Biorefinery scheme

Where CN= Centrifuge, RD= Reactive distillation column, DC= Distillation column, R= reactor, FT= Flash tank, MX= Mixer, Tb=Turbine, CD= condenser, P= Pump, CP= Compressor, HX= Heat exchanger.

DC-03 separates all formic acid traces and ethanol/water mixture, 1:1, for sending them to R-01; from the bottom, it obtains the first treated water stream (TW1). In R-01, ethanol dehydration occurs to get ethylene, Eq. (3). The ethylene coming from the DC-04 top reacts in R-02 to form alkenes (C2 to C20) by oligomerization; this is summarized by Eq. (4). After that, alkanes are developed by hydrogenation process in R-03, Eq. (5) (Romero et al., 2022). It is important to mention that the module employed in these reactors is R-Stoic. The H2 excess is recirculated by using FT-01 and the biofuels are separated by distillation arrangement DC-05, DC-06, and DC-07. The biofuels are defined as light gas (C2 to C4), naphtha (C5-C8), biojet fuel (C9-C16), and green diesel (C17-C20).

Water coming from the mixture of DC-04 bottom stream is separated by DC-08 to form treated water II (TW2). Treated water III (TW3) is constituted by the sum of TW1 and TW2. The remaining components are sent to DC-09. A mixture of ethanol/water, obtained from the DC-09 bottom, feeds RD-02; where bioethanol, propylene glycol, and dipropylene glycol are produced by using propylene oxide, Eq. (6) and Eq. (7). This process is known as bioethanol reactive dewatering (Guzmán et al., 2019). Finally, the thermal potential of glycols is taken advantage of by using the organic Rankine cycle.

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|  | (1) |
|  | (2) |
|  | (3) |
|  | (4) |
|  | (5) |
|  | (6) |
|  | (7) |

Figure 2 represents biogas production, which corresponds to the conventional treatment process. The wine effluent gets into BR-01 where polymers are hydrolyzed by enzymes. The reactions involved correspond to cellulose, hemicellulose, and dead yeast decomposition, Eq. (8-10) respectively; it is important to mention that lignin is inert in this stage. This operation unit is modeled by the R-Stoic module. In BR-02, it is carried out the steps involved in anaerobic digestion: amino acid degradation, Eq. (11), acidogenic, Eq. (12), acetogenic, Eq. (13), methanogenic, Eq. (14) (Rajendran et al., 2014); the lignin keeps inert. Once digestion has concluded, the mixture is sent to FT-01 for phase separation, where treated water is obtained from the flash tank bottom. The wet biogas is dried by FT-02.



Figure 2.- Conventional process. Anaerobic digestion

Where BR=Bioreactor, FT= Flash tank.

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|  | (8) |
|  | (9) |
|  | (10) |
|  | (11) |
|  | (12) |
|  | (13) |
|  | (14) |

For the biorefinery scheme and biogas process, a literature search is made for collecting the thermodynamic and chemical kinetic data, followed by the Aspen Plus V11 simulation. Once the processes have been modeled, parametric analysis is performed to adjust the manipulable variables by sensitivity analysis. Finally, both processes are evaluated and compared between themselves. The manipulable variables employed in parametric analysis are stage number, feed stage, reflux ratio, distillation rate, hold-up, reactive stages, reactant inlet flow, and pressure for reactive/conventional distillation columns (according to the case); temperature and pressure for flash tanks; finally, temperature and reactor volume for bioreactors.

To perform the evaluation and comparison, the next parameters are considered: COD, which is calculated by Aspen Plus, total heat duty, reactant conversion, and product yield. Eq. (15) and Eq. (16) show how conversion and product yield are defined.

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|  | (15) |
|  | (16) |

Where: cv =conversion, rin = reactant input to process (mol/h), rout = reactant output to process (mol/h), Yd = Yield, pms = desired product mass (kg), rms = reactant mass (kg).

* 1. Results

The product obtained, from anaerobic digestion, is 864.76 kg biogas/h, where 44.28 % mol is methane, 35.37 % mol is CO2 and 18.13 % mol is H2. About biorefinery, Table 2, summarizes all products. Although it might seem that digester get more biofuels, it is important to remember that the concentration of methane in gas is only 44.28 %mol; besides, this methane biogas has lower energy than those products obtained from biorefinery, because it has a longer carbon chain.

Table 1 compares the quality of water. The water produced from the digestor still having a COD value elevated, unlike biorefinery. Table 3 shows the values for those parameters selected to perform the comparison. In this sense, the digestor Ydtreated-water is better than the biorefinery one; however, it does not achieve with limits in Mexican Law about COD. On the other side, although the anaerobic digestor has employed solids to generate more quantity of biofuels, biorefinery can get better Ydbiofuels without using those solids. Finally, 93 % of energy employed for biorefinery comes from the energy contained in RD-01; it is important to highlight that heat integration is not considered. Indeed, the application of heat integration tools could reduce the heat duty for the refinery.

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| **Table 2.- Biorefinery products** |
| **Product** | **Mass flow (kg/h)** |
| Propylene glycol / dipropylene glycol | 47.66 |
| Levulinic Acid | 221.57 |
| Bioethanol | 4.56 |
| Formic Acid | 96.4 |
| Light Gas (C1-C4) | 86.32 |
| Naphtha (C5-C7) | 73.03 |
| Sustainable aviation fuel (C8-C16) | 103.83 |
| Green diesel (C17-C20) | 26.03 |

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| **Table 3.- Process comparison** |
| **Parameter** | **Biorefinery** | **Digestion** |
| Heat duty (kW) | 64,829.44 | 519.45 |
| cvglucose | 65.7 % | 94.32 % |
| cvethanol | 65.08 % | 37.59 % |
| cvsolids | 0 % | 58.96 % |
| Ydbiofuels | 2.94 % | 2.71% |
| Ydadd-value mol | 2.68 % | 0% |
| YdTreated-water | 49.22 % | 89.6% |

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* 1. Conclusions

In this research, the technical feasibility of obtaining biofuels is presented and confirmed, such as light gases, naphtha, sustainable aviation fuel, green diesel, and bioethanol through the simulation of a biorefinery for the processing of wine effluents. Additionally, the technical feasibility of the production of value-added molecules such as levulinic acid and glycols is verified. With the proposed scheme, it is feasible to obtain water with the quality required for human use according to the COD reduction achieved (99.98%) and the Official Mexican Standards (NOM-001-SEMARNAT-2021 and NOM-127-SSA1- 2021). Finally, even though this biorefinery presents a promising alternative to substitute the conventional process (anaerobic digestion), further investigations are needed such as mass/heat integration and economic aspects.

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* 1. References

G. Buitrón, F. Martínez, & F. Ojeda, 2019, Biogas production from a highly organic loaded winery effluent through a two-stage process, BioEnergy Research, 12, 714-721.

E. Carlson, 1996, Don't gamble with physical properties for simulations, Chemical engineering progress, 92(10), 35-46.

C. Guzmán, A. Castro, & F. Nápoles, 2019, Economic and environmental comparison of bioethanol dehydration processes via simulation: reactive distillation, reactor–separator process and azeotropic distillation, Clean Technologies and Environmental Policy, 21, 2061-2071.

N. Kopsahelis, C. Dimou, A. Papadaki, E. Xenopoulos, M. Kyraleou, & S. Kallithraka, 2018, Refining of wine lees and cheese whey for the production of microbial oil, polyphenol-rich extracts and value-added co-products, J Chem Technol Biotechnol, 93.

G. Romero, C. Gutiérrez, F. Gómez, & S. Hernández, 2022, Synthesis and intensification of a biorefinery to produce renewable aviation fuel, biofuels, bioenergy, and chemical products from Jatropha Curcas fruit, IET Renewable Power Generation, 16(14), 2988-3008.

K. Rajendran, H. Kankanala, M. Lundin, & M Taherzadeh, 2014, A novel process simulation model (PSM) for anaerobic digestion using Aspen Plus. Bioresource Technology, 168, 7-13.

S. Ratna, S. Rastogi, & R. Kumar, 2021, Current trends for distillery wastewater management and its emerging applications for sustainable environment, Journal of Environmental Management, 290, 112544.

J. Solis, H. Alcocer, E. Sanchez, & J. Segovia, 2022, Innovative reactive distillation process for levulinic acid production and purification, Chemical Engineering Research and Design, 183, 28-40.

M. Wagh, P. Nemade, P. Jadhav, 2020, Continuous electrocoagulation process for the distillery spent wash using Al electrodes, Techno-Societal, 41–49.

M. Wilk, M. Krzywonos, D. Borowiak, P. Seruga, 2019, Decolourization of sugar beet molasses vinasse by lactic acid bacteria-the effect of yeast extract dosage, J. Environ, 28, 385–392.

R. Wooley, & V. Putsche, 1996, Development of an ASPEN PLUS physical property database for biofuels components (No. NREL/TP-425-20685), National Renewable Energy Lab. (NREL), Golden, CO (United States).