Higher alcohol biofuels production from levulinic acid: Technical evaluation and energy integration

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Resumen

El alto consumo de combustibles fósiles conlleva al aumento de concentración de gases contaminantes y de efecto invernadero en la atmósfera. Alcoholes superiores como butanol y pentanol obtenidos a partir de biomasa lignocelulósica pueden usarse como biocombustibles en motores de encendido por compresión. En el presente trabajo se considera el proceso de producción de 2-butanol y 2-pentanol a partir de ácido levulínico obtenido a partir de la transformación de biomasa lignocelulósica. El objetivo ha sido diseñar conceptualmente un proceso a través de una ruta termoquímica técnicamente viable y energéticamente eficiente. Se realizó una simulación con Aspen Plus V14, usando UNIQUAC como modelo termodinámico, la cual permitió establecer características preliminares que tendría la planta de operaciones, sus condiciones de operación, los equipos necesarios y enfocándose en una mejora de la eficiencia energética en el proceso. La ruta de reacción seleccionada incluye reacciones de formación de gas de síntesis seguida del proceso de Fischer-Tropsch. Lo cual requiere el uso de diferentes equipos de reacción y separación. Entre estos equipos se ha integrado el calor requerido logrando un ahorro de energía de ca. 32%. Los resultados encontrados son el diseño conceptual de una planta de conversión de ácido levulínico que junto con la integración energética permiten producir con alto rendimiento y pureza los alcoholes 2-butanol y 2-pentanol con un ahorro de energía significativo.

Palabras clave—Simulación, bio-butanol, bio-pentanol, simulación, integración.

Abstract

The high consumption of fossil fuels increases the concentration of polluting and greenhouse gases in the atmosphere. Higher alcohols such as butanol and pentanol obtained from lignocellulosic biomass can be used as biofuels in compression-ignition engines. In the present work, the process for the production of 2-butanol and 2-pentanol from levulinic acid obtained from the transformation of lignocellulosic biomass is considered. The aim was to conceptually design a process through a technically feasible and energy-efficient thermochemical route. A simulation was carried out with Aspen Plus V14, using UNIQUAC as a thermodynamic model, which allowed to establish preliminary characteristics that the operations plant would have, its operating conditions, the necessary equipment and focusing on an improvement of energy efficiency in the process. The selected reaction path includes syngas formation reactions followed by the Fischer-Tropsch process. This requires the use of different reaction and separation equipment. The required heat has been integrated between these devices, achieving energy savings of ca. 32%. The results found are the conceptual design of a levulinic acid conversion plant that, together with energy integration, allows the production of 2-butanol and 2-pentanol alcohols with high yield and purity with significant energy savings.

Keywords— *Simulation, bio-butanol, bio-pentanol, simulation, integration.*

1. INTRODUCTION

Biofuels represent a cleaner alternative for ignition, compression engines, and heating equipment. Its use, however, must be evaluated from a sustainable point of view, i.e., considering social, environmental, and economic impacts. The development of biofuel projects represents an opportunity for technological and economic development in the energy sector. In Mexico there is a lack in this regard, so it is important to promote the design and construction of new biofuel production plants, for which technical-economic feasibility studies are required to help technologists and entrepreneurs make decisions.

In the last 15 years, significant research has been conducted worldwide on developing biofuels applied to internal combustion engines. Alcohols such as bio-butanol and bio-pentanol can be used as fuels in compression ignition engines [1,2]. Vehicles that use this type of engine are essential for agricultural operations, public transportation, handling of industrial equipment, and the transportation of multiple goods for society.

Alcohols are organic compounds of utmost importance in industry and daily life. Butanol is used as a solvent in different applications, including the automotive industry, cleaning, cosmetics, and metallurgy, among others. Pentane is also used as a solvent in polymers, cosmetics, dyes, paints, glues, and pharmaceutical industries, among other applications. When used as solvents, alcohol mixtures work perfectly, but they are required to have high purity for chemical syntheses or more selective extractions.

Current alcohol production processes focus on the biochemical route (fermentation) and the thermochemical route (gasification or pyrolysis). Despite their profitability, these processes are limited by multiple factors, of which the economic part stands out due to the high cost of process equipment, the availability of sustainable raw materials, and high energy consumption.

Butanol and pentanol can be produced in a cleaner and more energy-efficient way from a renewable feedstock. In México there is a large amount of biomass waste that is currently wasted or used as firewood. In particular, lignocellulosic waste is abundant and represents an alternative for its conversion into intermediate chemical compounds.

Among these intermediates is levulinic acid, which is one of the most versatile biobased chemical building blocks as it can be used to manufacture a wide range of finished products that, so it can effectively cover many of the chemical product characteristics. and materials from petroleum [3]. Renewable levulinic acid therefore represents an opportunity for technological development of biofuels and other products that are commonly produced in petrochemical plants.

Due to their molecular weight, both biobutanol and biopentanol can be mixed better with gasoline than ethanol, and obtain similar yields due to the octane number[4].

The conversion of levulinic acid to alcohols has been previously studied [5,6]. These works are limited to establishing the experimental procedure or process without mentioning an energy integration.

The objective of this work is to study the technical-energetic viability of a production process of 2-butanol and 2-pentanol from levulinic acid. To do this, first the design of a levulinic acid conversion process is conceptually proposed and its simulation is carried out with Aspen Plus V14, using UNIQUAC as a thermodynamic model.

The simulation is carried out in 4 stages, starting with a first simulation of the equipment in steady state, followed by another stage in which auxiliary services and mass integration are added, through recycling. In a third stage, energy integration is carried out using the Pinch methodology, and finally the best process scheme is evaluated based on maximum energy savings.

Different scenarios have been evaluated with the objective of finding the optimal conditions that maximize the energy savings of the process. The scope of this work is to test the technical feasibility of a 2-butanol production process. and 2-pentanol from levulinic acid and improve its energy efficiency. The raw material is levulinic acid considering that it has previously produced from lignocellulosic biomass.

2. CONTENT

2.1. Alcohol production process from levulinic acid

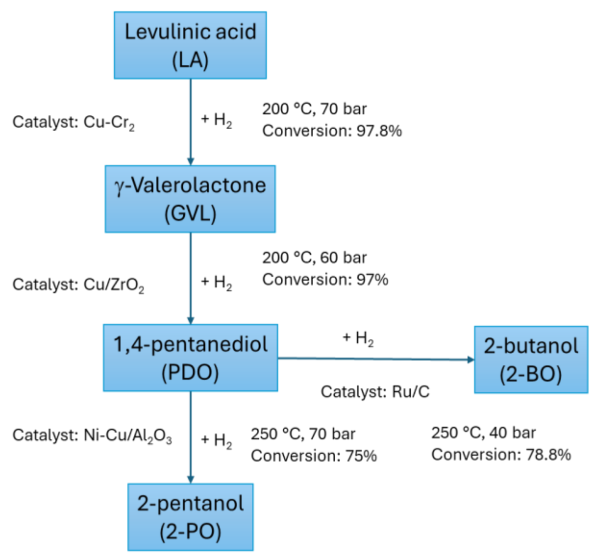
Levulinic acid can be converted to alcohols through a thermochemical process. This process is carried out through two main stages: the first stage involves the conversion of the raw material through gasification or pyrolysis processes into synthesis gas (mixture of carbon monoxide and hydrogen) or biogas (mixture of hydrogen, carbon dioxide carbon and methane). In the second stage, the synthesis gas or biogas is subjected to a Fischer-Tropsch synthesis process to produce alcohols.

The production of alcohols by this thermochemical conversion pathway presents some challenges, such as the need for specialized infrastructure for the processing of solid, liquid or gaseous materials, and the generation of solid and liquid waste. Additionally, some thermochemical conversion processes can be energy intensive and require high temperatures and pressures.

The conceptual design of the process is made following the "onion" model, in which the reactor is established as the center and starting point for the design of a chemical plant.

The chemical route to convert levulinic acid to butane and pentanol includes different chemical steps such as esterification and hydrogenation. Figure 1 shows these reaction stages, along with their operating conditions and the catalysts currently used.

Fig. 1. Chemical route for the conversion of levulinic acid into butanol and pentanol.



Adapted from References [7-10]

The products obtained are then separated in distillation columns to reach the desired purity. Both the reaction and the separation require heating or cooling for which heat exchangers are added. Finally, auxiliary services are considered. Effluent treatment has not been considered.

2.2. Simulation of the alcohol production process

Figure 2 shows the simulated scheme for the reaction stage, and Figure 3 shows the simulated scheme for the separation stage.

The type of reactor used in the simulation is the Rstoic, due to the lack of the kinetic models for the different reactions. The yields and conversions of each reaction have been taken from literature data from different sources [7-10]. As there is excess of hydrogen, it is recovered and then recirculated.

Fig. 2. Simulation of the reaction/recirculation stage

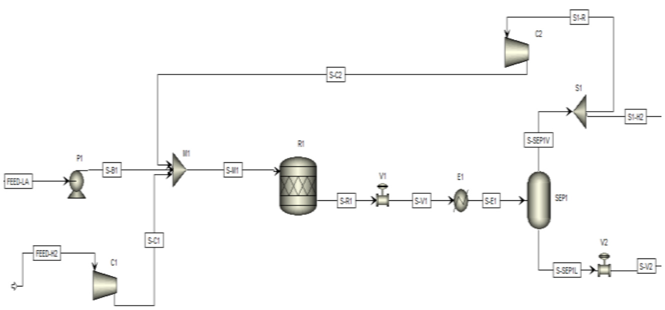
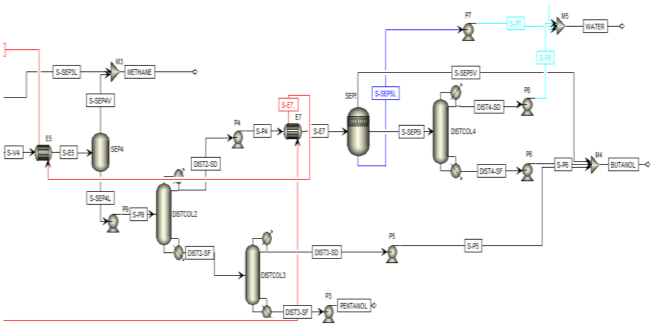


Fig. 3. Simulation of the separation stage



Equipment selection implies a good knowledge of the chemical engineering heuristic rules applied to the process.
The separation system consists of 4 distillation columns (RadFrac) and 4 separators (Flash), which fulfill the function of sequentially separating the different products obtained, ending in 4 streams: butane, pentanol, methane (the latter with a purity above 99%) and finally a stream of water to be treated (with a purity of 79.57%).

2.3. Energy integration

Figure 4 shows the grid diagram that includes the different exchangers added to the process. In this stage, the aim is to optimize the number of heat exchangers and auxiliary services. The auxiliary services added were heating oil, high and medium pressure steam, cooling water, electricity, and refrigerant.

The Aspen Energy Analyzer was used for energy integration, which includes the Pinch Analysis. The objective was to eliminate the large amount of expenses in auxiliary services, covering this energy need with 2-tube and shell heat exchangers, and making hot currents, which required cooling, meet with cold currents, which required heating, and thus seeking obtain the maximum allowable energy savings. See Figure 5.

Fig. 4. Heat exchanger network obtained from Pinch analysis

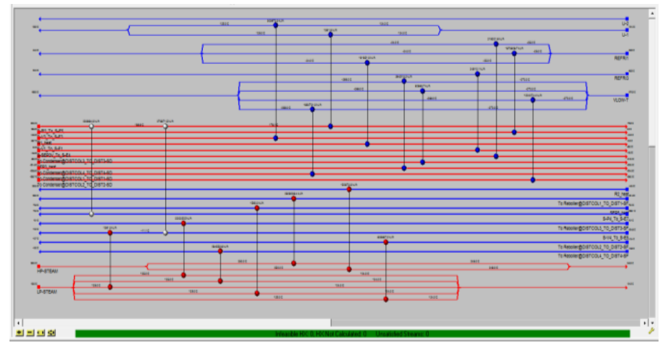
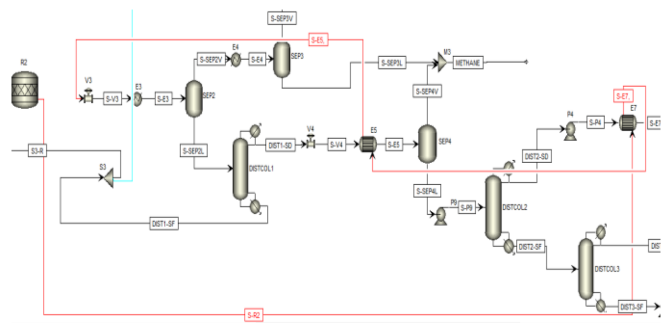


Fig. 5. Simulation including exchangers added by Pinch analysis



With this arrangement, a saving of 906.7 kW was obtained, which is equivalent to 32.62% energy savings. For a feedstock flowrate of 500 kg/h of levulinic acid, 224 kg/h of butanol and 71 kg/h of pentanol are obtained. Some values of the process streams are shown in Table 1.

Table 1. Process stream operating variables.

Stream	FEED-H_2	FEED-LA	S-B1	S-C1	S-M1	S-E1	S1-R
Temperature (°C)	25	25	36.0857	335.138	129.93	10	10
Pressure (bar)	1.013	1.013	100	100	100	80	80
Mass flow (kg/hr)	9	500	500	9	511.427	511.427	2.42687
Enthalpy (kW)	4.4645e-16	-825.171	-821.109	40.3825	-780.627	-909.939	-0.1526

Stream	H2-1	S-V1	DIST1-SD	DIS1-SF	S1-H2	S-SEP1L	S-SEP1V
Temperature (°C)	10	139.742	-224.298	182.013	10	10	10
Pressure (bar)	1	80	9	10.3	80	80	80
Mass flow (kg/hr)	0.12773	511.427	420	1302.89	0.12773	508.872	2.5546
Enthalpy (kW)	-0.00803	-864.98	-886.035	-5048.05	-0.00803	-909.778	-0.1606

Stream	FEED2-H2	BUTANOL	METHANE	PENTANOL	S-E5,	S-E7	S-E7,
Temperature (°C)	25	-9.57086	-165.011	-0.26781	178.012	70	189.431
Pressure (bar)	1.01325	1	1	1	26	1	27
Mass flow (kg/hr)	34	224.003	54.4617	70.9692	1791.46	215	1791.46
Enthalpy (kW)	$1.745e^{-14}$	-296.261	-83.6295	-83.6877	-5680.41	-529.999	-5603.11

Table 2. shows the specifications for the distillation columns. More details can be requested from the author's email.

Table 2. Design specifications for distillation columns

Specifications	DISTCOL1	DISTCOL2	DISTCOL3
Number of stages	14	15	16
Capacitor type	Total	Total	Total
Distillate flow (kg/hr)	420	215	123
reflux ratio	1.2	1.1	1.4
Feeding stage	En la etapa 9	En la etapa 8	En la etapa 8
Pressure in stage 1 / condenser (bar)	9	0.001	0.001
Pressure drop for each stage in the rest of the column (bar)	0.1	-	-
Distillate temperature (°C)	-224.298	-236.194	-13.5185
Condenser thermal load (kW)	-517.417	-278.965	-60.8997
Reboiler thermal load (kW)	724.732	232.191	61.1501
Bottom temperature (°C)	182.013	-10.7178	-0.420282

Table 2. Continued

Specifications	DISTCOL4
Number of stages	16
Capacitor type	Total
Distillate flow (kg/hr)	50
reflux ratio	2
Feeding stage	En la etapa 8
Pressure in stage 1 / condenser (bar)	0.001
Pressure drop for each stage in the rest of the column (bar)	-
Distillate temperature (°C)	-221.957
Condenser thermal load (kW)	-101.254
Reboiler thermal load (kW)	79.0425
Bottom temperature (°C)	-13.5422

3. CONCLUSIONS AND RECOMMENDATIONS

The production of alcohols by thermochemical route offers a promising alternative compared to the production of alcohols by petrochemical route and might be a viable option for the sustainable production of biofuels and renewable chemicals in the future.

Due to the multiple reaction and separation equipment in the process of converting levulinic acid into butane and pentanol, energy integration constitutes a fundamental step in its synthesis and plant design. The application of this methodology demonstrates that it is feasible to reduce energy consumption by 32% at the conceptual design level, which would result in a more energy-efficient process, probably with less environmental impact and more economically viable.

As future work, we are working on the economic analysis of the process, based on greater production at an industrial level, considering the price of raw materials, products and auxiliary services along with the appropriate sizing of the equipment.

3.1 General observations

The author declares that he has no conflicts of interest for the publication of this work.

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