

Simulation, Optimization and Analysis of a Syngas to Ethanol and other Oxygenates Production Plant Using a Rh-Based Catalyst

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Synthesis gas (syngas) is mostly known by its use on ammonia and hydrocarbons (Fischer-Tropsch process) production. However, a less explored route to produce chemical products, among them alcohols and other oxygenates, from syngas is gaining attention over the last few years. In this route, an initial feedstock as biomass is firstly gasified to synthesis gas, which is reformed, cleaned, compressed and finally catalytically converted in a mixture of alcohols and oxygenated products that after separation steps attain sufficient purity to be sold. In this case of study, the commercial simulator ASPEN Plus v7.3 is used to evaluate the application of a Rh-based (Rh-Mn-Li-Fe/SiO₂) catalyst in a small scale plant with processing capacity of 100 kmol/h of pure syngas. This plant, besides methane, water, and CO₂ produces 8 oxygenated products: methanol, ethanol, propanol, butanol, acetic acid, acetaldehyde, methyl and ethyl acetates, being necessary 9 further separation or concentration steps in order to obtain the products in their desired purity. The main goals of this work were to design and optimize a process so as to produce alcohols and other oxygenates using syngas as feedstock. After conceiving the process, an optimization was performed, which started by evaluating the reactor conversion/selectivity in order to produce more add-value products. Then, the downstream separation processes were optimized searching for less energy consumption and recovering as much as possible add-value products. Lastly, we aimed at possible solutions and improvements concerning sustainability, feedstock and energy integration, and utilities consumption.

1. Introduction

The search for alternative and sustainable fuels has increased in the last decade pushed by the great energy consumption of processing industry, the growing demand of energy-based comforts and mobility and the perspective of depletion of the world's petroleum reserves. Presently the focus of international policies regarding liquid and renewable fuels are associated with the search of sustainability and energy security. In this direction, we can cite the *Biofuels Directive* from the EU, which has as its main goal to achieve a minimum quota of 20 % consumption of renewable biofuels until 2020 and a mandatory quota to be attained by all EU members of 10 % of biofuels in transportation in the same year. In the same way, the USA approved the *Renewable Fuels Standard*, which has as one of its goals the reduction of 20 % of gas emissions related to the renewable fuels lifecycle (Kendall et al., 2009)

With such attention directed to renewable biofuels and their sustainability, the development and improving of biofuels production processes are needed. In this scenario, the use of synthesis gas (syngas) to produce biofuels (and other by-products) through thermochemical conversion can be seen as a possible process alternative regarding the improvement on biofuels production and feedstock usage.

In the thermochemical route, syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂), is produced by gasification of biomass or coal and then reformed, cleaned, compressed, heated and finally catalytically converted in a mixture of oxygenated products of high molecular weight. These products are then purified and can be sold separately as fuel, solvent or used as feedstock to other processes (Subramani and Gangwal, 2008).

In this work, the commercial simulator ASPEN Plus v7.3 is used to design, simulate and optimize the conversion of syngas to alcohols (methanol, ethanol, propanol and butanol) and oxygenated compounds (acetaldehyde, acetic acid, methyl and ethyl acetates) using a Rh-based (Rh-Mn-Li-Fe/SiO₂) catalyst (Yin et al. 2003). After simulation and optimization of the whole process, an energy and production analysis is proposed while pointing out the major products and the major energy consumers in the process, making possible to propose some solutions and further developments for the process.

2. Simulation

The simulation was carried out using the commercial simulator ASPEN Plus v7.3. The thermodynamic package NRTL (non-random-two-liquid) was chosen based on the polarity of the components involved in the process. In the operations involving acetic acid, the Hayden-O'Connell (NRTL-HOC package) model was used so as to calculate the non-idealities of the gas phase.

2.1 Reaction Kinetics

The reaction kinetics used in the simulation was obtained from Yin et al. (2003) that used the catalyst Rh-Mn-Li-Fe/SiO₂, a Rh-based catalyst capable of promoting the direct synthesis of ethanol (Subramani and Gangwal, 2008). The kinetic data for Arrhenius model (Eq. 1), was originally obtained for methane, methanol, ethanol, acetaldehyde (R1-R4) and a mixture of oxygenated compounds with 2 or more carbons (C₂₊) which counts with the ethanol and acetaldehyde parts. Therefore, to calculate the proportion between the other components (propanol, butanol, acetic acid, methyl and ethyl acetates), the data was recomputed subtracting continuously the ethanol and the acetaldehyde portion. Thus, the data was divided based on the reaction enthalpy (ΔH_R) of each reaction (R1-R9) obtaining the final proportion between the components reflected in the pre-exponential factor. The kinetic data is shown in Table 1 as follows.

$$r = Ae^{(-E_a/RT)} P_{H_2}^x P_{CO}^y \quad (1)$$

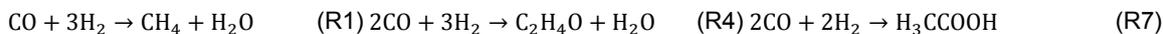


Table 1: Kinetic Parameters

Reaction	Ea (kJ/mol)	x (adm)	y (adm)	A (kmol/kg _{Rh} .h.kPa ^{x+y})	K (kmol/kg _{Rh} .h.kPa ^{x+y})
R1	126700.0	0.90	-0.76	2.33 x 10 ¹⁰	0.081
R2	89900.0	0.53	0.14	3.13 x 10 ⁵	0.003
R3	114839.7	1.39	0.23	1.68 x 10 ⁴	0.985
R4	114839.7	1.39	0.23	2.24 x 10 ⁴	2,553
R5	114839.7	1.39	0.23	1.04 x 10 ⁴	0.330
R6	114839.7	1.39	0.23	1.25 x 10 ⁴	0.476
R7	114839.7	1.39	0.23	2.24 x 10 ³	0.083
R8	70600.0	0.16	-0.10	1.48 x 10 ⁴	0.005
R9	156800.0	0.79	-0.60	2.35 x 10 ¹³	0.126

2.2 Process Layout

The process layout (Figure 1) is composed by a compressor, a PFR reactor, a flash drum, a gasification reactor and nine separation units, which are represented by general blocks for simplicity. The pure syngas enters in the system through the stream S-1001 at 1 bar and 25 °C is then mixed with the recycle stream (S-1009, 300 °C, 1 bar), compressed (in the CPR unit) and sent to the reactor (R-1001). Inside the reactor, the products are synthesized, in the effluent stream (S-1004) can be found methane, methanol, ethanol, propanol, butanol, acetaldehyde, acetic acid, methyl and ethyl esters and non-reacted syngas. The stream S-1005 enters the flash, which operates at 10 °C and 6.5 bar, at 304.8 °C and 3 bar. This stream is then split in two other streams, one containing mostly CH₄, CO and H₂ (S-1006) and the other (S-1011) the oxygenated compounds.

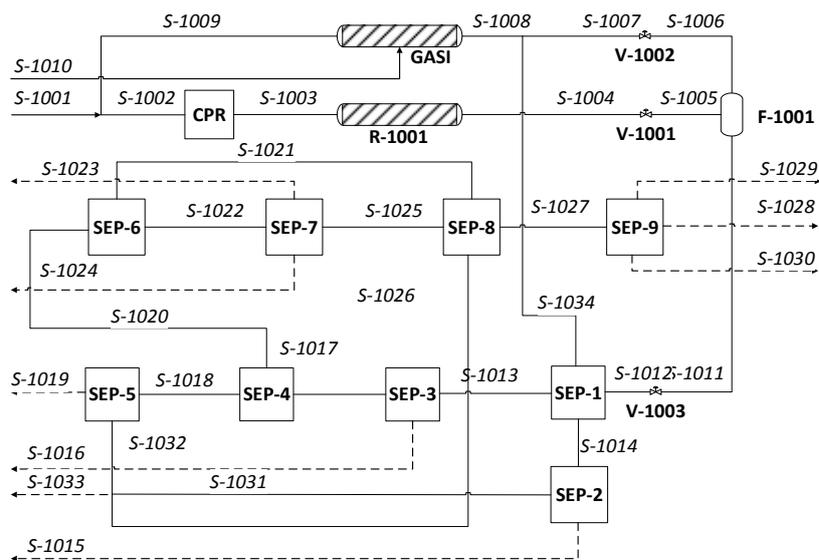


Figure 1: Process Layout

The bottom stream leaving the flash drum (S-1011) is directed to SEP-1 block (Figure 2a) in which the stream S-106 recovers the rest of syngas and methane that come from R-1001, and in the stream S-104 which contains 66,34 % w/w of the water entering the distillation column and 100 % w/w of the acetic acid. This stream is sent to SEP-2 (Figure 2b) while the stream S-105 with the mixture of other components is sent to the SEP-3 (Figure 2c). In SEP-2 the stream S-203 enters the distillation column with a mixture of water (90 % w/w) and acetic acid (10% w/w) and is separated in two streams S-204 (99.0 % w/w acetic acid) and S-205 (99.9 % w/w water). In the SEP-3 block, acetaldehyde at 99.7 % w/w (S-304) is recovered from the stream S-303 and the stream S-305 is then directed to SEP-4 (Figure 2d).

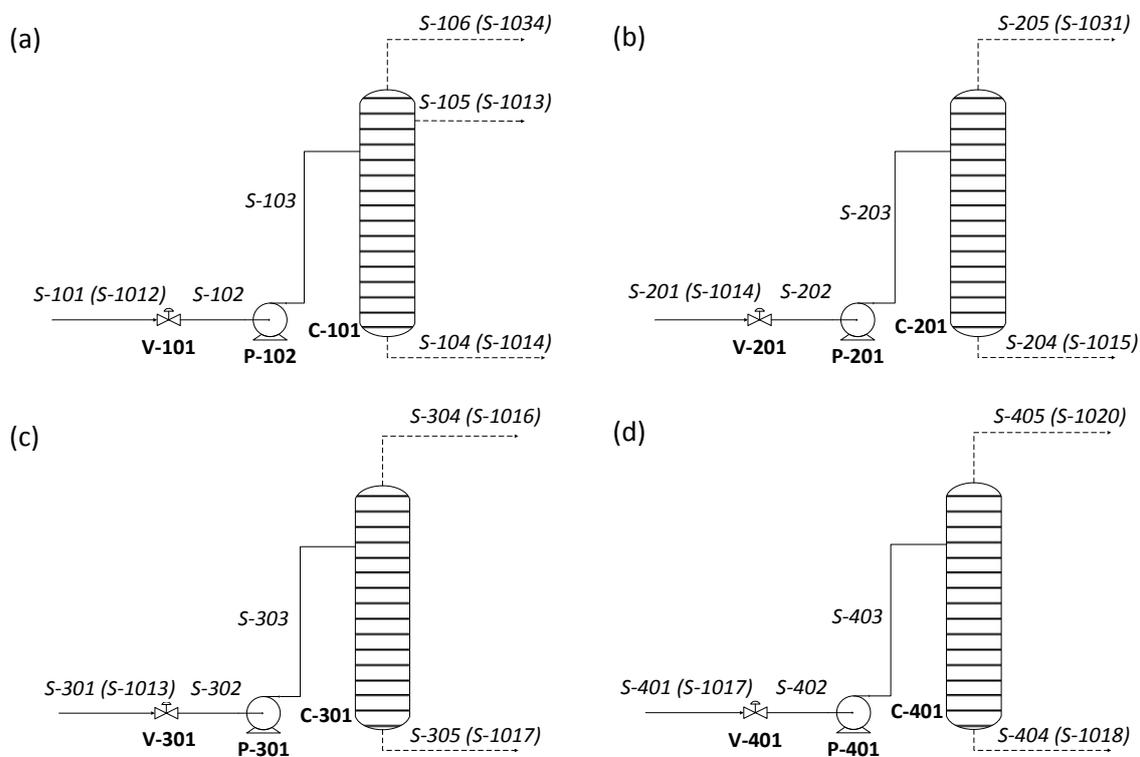


Figure 2: (a) SEP-1 layout; (b) SEP-2 layout; (c) SEP-3 layout; (d) SEP-4 layout

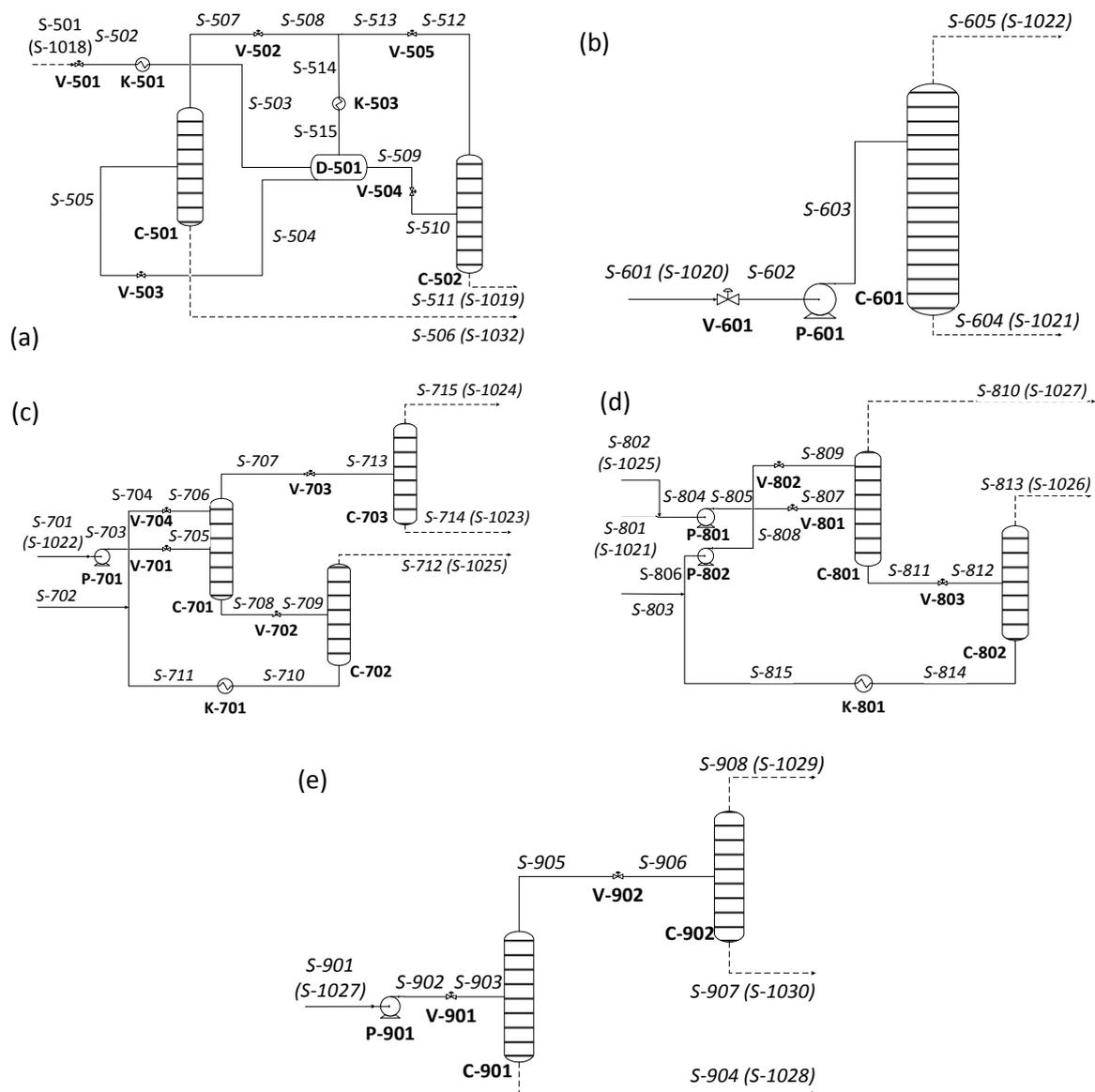


Figure 3: (a) SEP-5 layout; (b) SEP-6 layout; (c) SEP-7 layout; (d) SEP-8 layout; (e) SEP-9 layout

In the bottom stream of the distillation column C-401 (SEP-4) is recovered, a mixture of butanol (46 % w/w) and water (54 % w/w), while this stream (S-404) goes to SEP-5 block (Figure 3a), the stream containing methanol, ethanol, propanol, methyl and ethyl acetates (S-405) goes to SEP-6 (Figure 3b). To separate the heterogeneous azeotrope butanol-water, a special design is needed (Luyben, 2008). The mixture enters the block and first is directed to a decanter, which receives also the top streams of the two distillation columns (S-507 and S-512). The aqueous phase stream (S-504) goes to the distillation column C-501, which recovers the stream S-506 composed by approximately 100% w/w water. The organic phase of the decanter (S-509) with 84 % w/w butanol and 16 % water w/w is sent to the distillation column C-502 responsible for the recovery of stream S-511 with 99.3 % w/w butanol. SEP-6 separates the stream S-405 originated in block SEP-4 in two other streams: one containing the acetates plus water, ethanol and methanol (S-605), and the other one containing the rest of alcohols plus water (S-604). The first stream is directed to block SEP-7 (Figure 3c) and the second one to the block SEP-8 (Figure 3d). In SEP-7, using a solvent (Ethylene Glycol, EG) the entering mixture is dehydrated in the first column (C-701) generating the top stream (S-707), consisting in an acetate-rich stream and the bottom stream (S-708) that consists of solvent, water and ethanol (the proportion in mass solvent:feed stream is 1:3). The acetate-rich mixture is directed to de column C-703 and separated in its two components methyl acetate 96.3 % w/w (S-715) and ethyl acetate 99.9 % w/w (S-714). The bottom stream of

C-701 goes to C-702, where the solvent is recovered at 99.9 % w/w in the bottom stream (S-710) and in the top stream is obtained a mixture of water, ethanol and methanol, directed to SEP-8. SEP-8 receives the streams containing alcohols (S-802 and S-801) originated from blocks SEP-6 and SEP-7. Using ethylene glycol in an extractive distillation (mass ratio of 2.35:1 related to the feed stream), the mixture water-alcohols is dehydrated in the first distillation column (C-801) which has as its top stream (S-810) a mixture of methanol, ethanol and propanol and as its bottom stream (S-811) the water-solvent. The solvent is then recovered in the bottom of the second column (S-814) and in the same column is obtained the stream S-813 composed by water 99.9 % w/w. From SEP-9 (Figure 3e), propanol (99.5 % w/w) in the first distillation column (C-901) and methanol (90 % w/w) and ethanol (99.4 % w/w) in the second distillation column (C-902) are obtained. It is important to notice (Figure 1) that the top stream of the flash drum passes through a reactor that generates pure syngas. This hypothetical operation calculates the amount of syngas that can be reintroduced to the system, being possible, for this reason turn the stream S-1009 "on" and "off" with no impact to the rest of the process by adjusting stream S-1001 to the reactor's feed stream composition and mass flow.

3. Results and Discussion

The results were obtained after an optimization carried out through sensitivity analysis. For the distillation columns the number of stages, the feed stage(s) and the mass reflux ratio were varied, for the flash drum were varied temperature and pressure, aiming to attain the specifications with less energy consumption in both cases. The reactor's feed stream is maintained at 100 kmol/h with a mole ratio of 1:2 CO:H₂. This ratio was also obtained through sensitivity analysis. As shown in Figure 4, the mole ratio within the possible range of operation in which the conversion and ethanol selectivity attain their maximum is 1:2. The reactor is operated at 304.8 °C and 30 bar, the catalyst load of 12 kg (Rhodium basis).

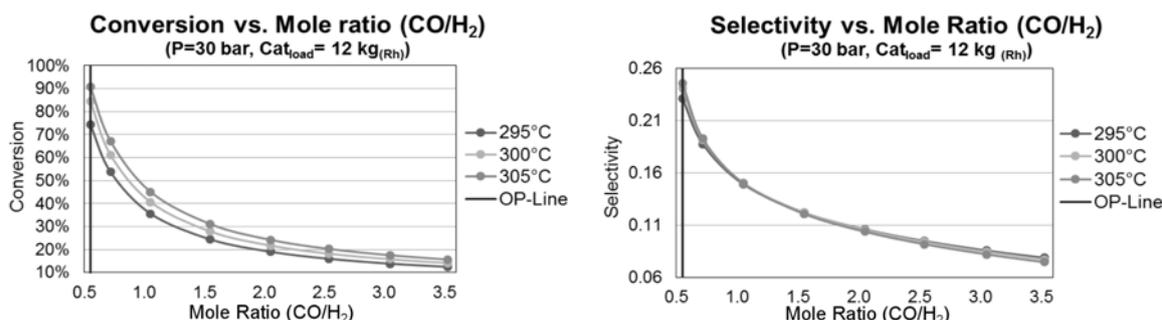


Figure 4: Reactor sensitivity analysis to mole ratio (a) Conversion (b) Ethanol selectivity

3.1 Products

In Figure 5 are shown the flow rate and the purity of the products obtained. As can be seen, ethanol is the major product of the process attaining 170.5 kg/h (99.4 % w/w) of production. Acetaldehyde and butanol are other products that can be highlighted with final mass flows of respectively 89.7 kg/h (99.8 % w/w) and 69.3 kg/h (99.3 % w/w). Regarding the recycle stream (S-1009), after receiving a stream basically composed by methane (148.9 kg/h), CO (87.5 kg/h) and traces of hydrogen, acetaldehyde and ethyl acetate and a stream composed by pure oxygen (S-1010, 151.7 kg/h), the reactor GASI converts all products to syngas at the rate of 401.3 kg/h at 1:1.56 mol (CO:H₂). The final production of water (S-1033) is 367.7 kg/h at 99.9 % w/w.

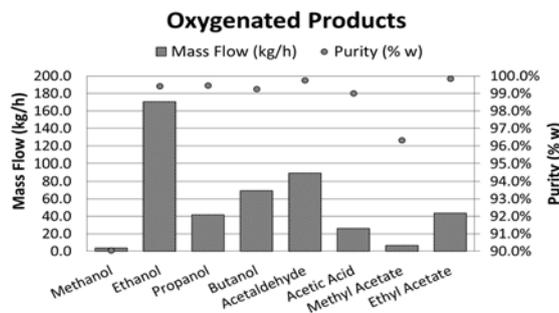


Figure 5: Products Mass Flow (kg/h) and Purity (w/w %)

3.2 Energy Consumption

Table 2 shows that there is a positive energy balance (1596.8 kW/h) between heated and cooled units. Due to the exothermic nature of the reactions involved in the process, the reactor has an impact almost equivalent to all heated units in the process and is responsible for more than 40 % of the consumption of cooling utilities. Among the heated units, the blocks with higher consumption are related with the high inlet flows (as SEP-1 and SEP-4) and complex separations as narrow boiling points (SEP-2/SEP-9) and azeotropes (as SEP-8).

Table 2: Energy Consumption by Equipment

Equipment	Heated Units		Equipment	Cooled Units	
	Energy (kW/h)	% Consumption		Energy (kW/h)	% Consumption
SEP-1	252.89	17.1 %	R-1001	-1305.1	42.4 %
SEP-2	217.44	14.7 %	F-1001	-534.0	17.3 %
SEP-3	94.86	6.4 %	SEP-1	-224.7	7.3 %
SEP-4	255.63	17.3 %	SEP-2	-216.8	7.0 %
SEP-5	25.15	1.7 %	SEP-3	-35.0	1.1 %
C-501 (Reb.)	10.43	0.7 %	SEP-4	-255.1	8.3 %
C-502 (Reb.)	14.72	1.0 %	SEP-5	-25.9	0.8 %
SEP-6	46.73	3.2 %	D-501	-19.0	0.6 %
SEP-7	68.03	4.6 %	K-501	-3.8	0.1 %
C-701 (Reb.)	24.72	1.7 %	K-502	-3.1	0.1 %
C-702 (Reb.)	28.09	1.9 %	SEP-6	-46.2	1.5 %
C-703 (Reb.)	15.22	1.0 %	SEP-7	-68.3	2.2 %
SEP-8	177.81	12.0 %	C-701 (Cond.)	-9.7	0.3%
C-801 (Reb.)	115.04	7.8 %	C-702 (Cond.)	-11.5	0.4 %
C-802 (Reb.)	62.77	4.2 %	C-703 (Cond.)	-15.3	0.5 %
SEP-9	189.64	12.8 %	K-701	-31.8	1.0 %
C-901 (Reb.)	127.97	8.6 %	SEP-8	-177.2	5.8 %
C-902 (Reb.)	61.68	4.2 %	C-801 (Cond.)	-58.6	1.9 %
CPR-1001	153.73	10.4 %	C-802 (Cond.)	-40.7	1.3 %
Total	1481.92	100.0 %	K-801	-77.9	2.5 %
			SEP-9	-190.3	6.2 %
			C-901 (Cond.)	-128.6	4.2 %
			C-902 (Cond.)	-61.6	2.0 %
			Total	-3078.7	100.0 %

4. Conclusions

The use of the catalyst Rh-Mn-Li-Fe/SiO₂ results in a process with series of complex separations and a total production of 451 kg/h) of oxygenated products. With the proper energy integration, the positive net energy balance (1596.8 kW/h) can be used to reduce energy consumption making the process feasible and profitable. The use of syngas from different sources makes the process a sustainable alternative to the liquid fuels market and an option for process integration with first and second-generation ethanol production processes.

Acknowledgments

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References

- Kendall, A., Chang, B., Sharpe, B., 2009, Accounting for time-dependent effects in biofuel life cycle greenhouse gas emission calculations, *Environmental Science & Technology*, 43(19), 7142-7147.
- Subramani, V. and Gangwal, S.K., 2008, A review on recent literature to search an efficient catalytic process for the conversion of syngas to ethanol, *Energy and Fuels*, 22(2), 814-839.
- Yin, H., Ding, Y., Luo, H., He, D., Chen, W., Ao, Z. Lin, Liwu, 2003, A Kinetic Study of Selective Hydrogenation of Carbon Monoxide to C₂ Oxygenates on Rh-Mn-Li-Fe/SiO₂ catalyst, *Journal of Natural Gas Chemistry*, 12, 233-236.
- Luyben, W.L., 2008, Control of the Heterogeneous Azeotropic n-Butanol/Water Distillation System, *Energy & Fuels*, 22, 4249-4258.