

Syngas to Higher Alcohols Using Cu-Based Catalyst – A Simulation Approach

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Higher alcohols production from syngas through chemical route has gained attention over the last decade because of characteristics such as: short-time reaction, abundant and lower price feedstocks, the use of lignin (a biomass component that is hardly used) and the almost complete conversion of the initial feedstock. In this route, cleaned and reformed synthesis gas (syngas), formed of carbon monoxide (CO) and hydrogen (H₂) is catalytically converted into a mixture of alcohols that after purification can be used as fuel, solvent, or as feedstock for other processes. In this particular case study we use a Cu-based (Cu-O-ZnO-Zr-Fe-Mo-Th-Cs) catalyst, which consists of a modified methanol synthesis catalyst, so as to conceive, simulate, optimize, and analyze a small scale syngas-to-higher alcohols production plant (process capacity of 100 km³/h of pure syngas). We assume that the WGS (water-gas-shift) reaction reaches equilibrium conditions and the alcohols production follows the ASF (Anderson-Schulz-Flory) distribution. The main advantage shown by this catalyst is the absence of water production, since all the water is consumed by the WGS reaction, on the other hand, the same reaction produces CO₂ that can be recovered only coupling another process in order to produce more CO. The final product separation (methanol, ethanol, propanol, butanol and pentanol) is facilitated by the absence of water. After process design and optimization, an energy and yield analysis is discussed while pointing possible solutions and next steps regarding the sustainability of the process.

1. Introduction

Observing the large urban conglomerates is clear the necessity of cleaner energy sources that ally energy security, easiness of production and transportation and great adaptation to the technology nowadays used. Thus, the energy policies around the world that include: decrease of CO₂ emission related to transportation, the diversification of energy matrix, and the development of a long-term plan of substitution of fossil fuels, turn their focus to the liquid and renewable fuels. In this scenario, we can cite higher alcohols as a possible alternative to fossil fuels, being some of them, as ethanol, already largely used.

Looking for different possibilities of production of these higher alcohols and some opportunities generated by first and second generation biofuels production (as generation of lignocellulosic residues), the interest in improving a technology from the beginning of 20th century, the production of oxygenated compounds from synthesis gas (syngas) is gaining space.

Biomass and coal gasification generate the syngas, a mixture of mostly, carbon monoxide (CO) and hydrogen gas (H₂), known by its use on ammonia and hydrocarbons production (Fischer-Tropsch process). However, the direct catalytic conversion of synthesis gas to higher alcohols can be seen as a possible alternative for the production of synthetic fuels or additives (Subramani and Gangwal, 2008)

In this route, the initial feedstock is gasified to the synthesis gas, which is then reformed, cleaned, compressed, heated, and finally catalytically converted in a mixture of alcohols with high molecular weight, that after purification can be sold separately (Phillips, 2007). This process presents advantages as: short

reaction time, abundant and cheap feedstocks, the use of lignin (component hardly used), and an almost complete conversion of syngas (He and Zhang, 2011), having the capacity to, in the near future, exceed the production of biofuels through conventional processes (Saga et al., 2010).

The proposal of this work, different from the current literature, is to conceive, simulate, optimize and analyse a whole process that produces higher alcohols from syngas, from reaction to separation of final products, using for this purpose the commercial simulator ASPEN Plus v7.3. To develop the simulation we used the data of a modified methanol production catalyst (CuO-ZnO-Zr-Fe-Mo-Th-Cs) (Kulawska and Skrzypek, 2001), using Anderson-Schulz-Flory (ASF) distribution to predict the quantities of alcohols with a carbon number greater than 3. The unities necessary for the process were optimized using sensitivity analysis, making possible further analysis regarding the energy consumption and the generation of products of economic interest.

2. Simulation

The simulation was carried out using the commercial simulator ASPEN Plus v7.3. Due to the polar nature of the components generated by the catalyst, the NRTL (non-random-two-liquid) thermodynamic package was used to develop the simulation. The components H₂, CO and CO₂ were set as Henry components due to their proximity to ideality in the gas phase and almost non-existent interaction with the other components within the system in the liquid phase.

2.1 Reaction Kinetics

The kinetic data was obtained from the work of Kulawska and Skrzypek (2001), which used a catalyst with the composition of CuO (50-60 %), ZnO (25-30 %), ZrO₂ (7-14 %), Fe₂O₃ (1-4 %), MoO₃ (7-15 %), ThO₂ (1-3 %), Cs₂O (0.5-1.5 %). This catalyst can be considered a modified methanol synthesis catalyst due its composition, which is mainly constituted by CuO and ZnO.

Using the Arrhenius approach (Eq.1), the authors obtained the kinetic parameters of methanol, ethanol and propanol formation. In this way, to obtain a more extended kinetic model we used the Anderson-Schulz-Flory (ASF) distribution to estimate the quantity of pentanol and butanol formed by the catalyst. In addition, using in the simulator a reactor in equilibrium, the kinetic data for the water-gas-shift reaction (WGS) was obtained using the model represented by Eq.2. According to the experimental data, almost all the water is consumed by the WGS reaction, the production of hydrocarbons is absent (only traces, not considered in this work) and the alcohols produced are linear considering the range of C1-C5.

$$r_{alcohol} = Ae^{(-E_a/RT)} P_{H_2}^x \quad (1)$$

$$r_{WGS} = Ae^{(-E_a/RT)} P_{CO}^x P_{H_2O}^y \quad (2)$$

Where: r →reaction rate, A →pre-exponential factor, E_a →activation energy, P_{H_2} →hydrogen partial pressure, x and y →reaction order of the respective component are denoted, respectively.

The reactions used in the simulation are represented by the equations (R1-R5) as follows, and their kinetic parameters (already converted to the units used in this work and the simulation) are shown in Table 1.



Table 1: Kinetic Parameters

| Reaction | E_a (J/mol) | A (mol/gcat/h/MPa ⁿ) | x (adm) | y (adm) |
|----------|------------------|-------------------------------------|------------|------------|
| R1 | 72190 | 59.40 | 2.00 | - |
| R2 | 81450 | 268.00 | 1.50 | - |
| R3 | 78100 | 48.30 | 1.50 | - |
| R4 | 59860 | 3.21 | 1.20 | - |
| R5 | 69410 | 25.00 | 0.82 | - |
| R6 | 20166 | 144.80 | -0.57 | 1.00 |

2.2 Process Layout

The process layout shown in Figure 1 comprises a compressor, a PFR reactor, a flash drum, the SEP-1 block (group of distillation columns responsible for the purification of alcohols) and the recycle section, which consists in a reactor operating in equilibrium to produce more syngas and a separator that purges exceeding oxygen from the system. The reactor feedstream (S-1005) is specified at 100 kmol/h of pure syngas, with a ratio between CO and H₂ of 1:2. After the reactor is placed, a flash drum, which recovers in its top stream the effluent raw material and most of CO₂, its bottom stream composed mostly by alcohols is then directed to the block SEP-1.

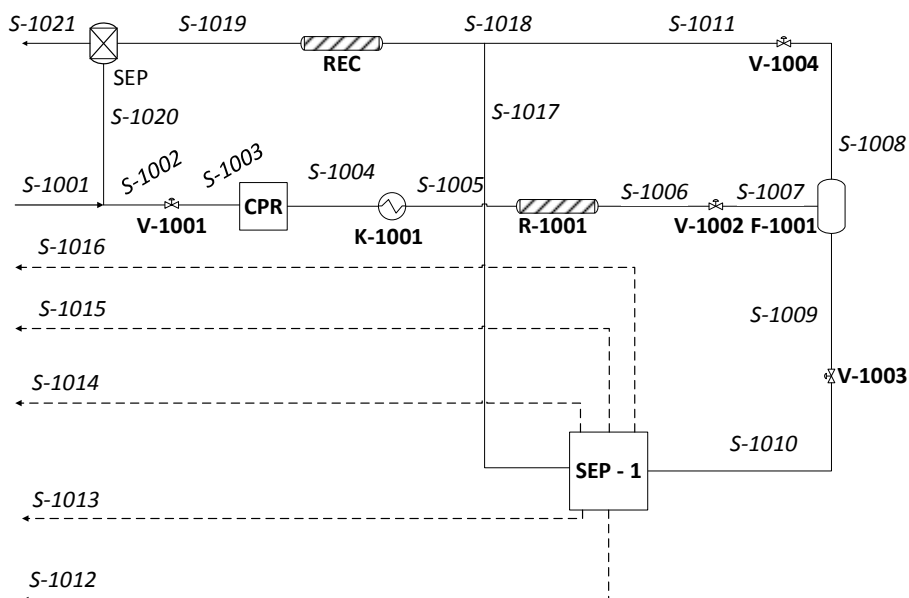


Figure 1: Process Flowchart

As can be seen in Figure 2, in the SEP-1 block, four distillation columns perform the alcohols purification. The direct order of separation was heuristically defined as being the energetically best for this separation. Thus, in the top streams of the columns (C-101 to C-104) are obtained, respectively, methanol, ethanol, propanol and butanol, and in the bottom stream of the last column (C-104), we have the heavier component, pentanol.

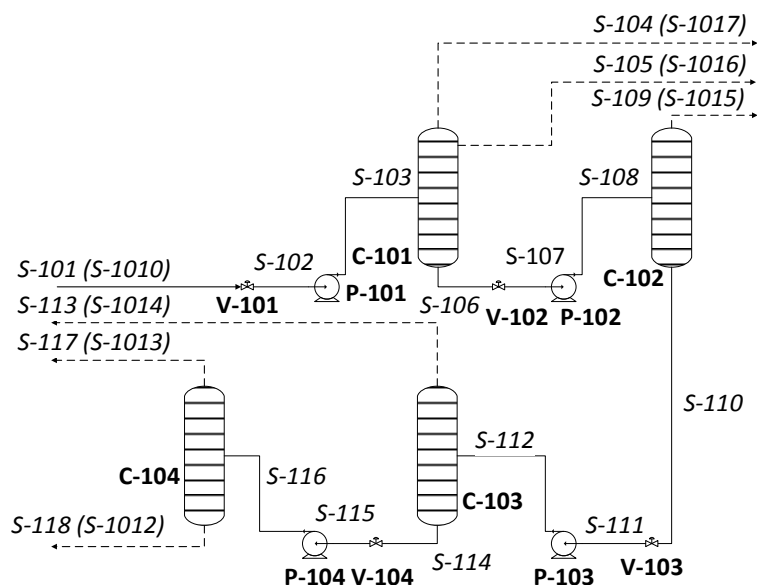


Figure 2: SEP-1 Flowchart

The downstream operations were arranged in a way to make possible the optimization, and thus, resulting in a recycle stream with most of the CO₂ of the system. The recycle section was built to calculate the amount of syngas that can be recovered from the process when the entire effluent stream is converted to syngas and reintroduced into the system. As an hypothetical operation, the stream S-1020 can be turned on and off without impact to de rest of the process, with the proper adjustment made by the stream S-1001, maintaining S-1005 at 100 kmol/h of syngas (1:2 CO:H₂)

3. Results and Discussion

3.1 Unit Operations

Compressor (CPR): determines the pressure of the feed stream (S-1003, sum of S-1001 and S-1020) to the reactor's operation pressure (100 bar).

Heat Exchanger (K-1001): receives the stream leaving the compressor at 361.93 °C and 100 bar and then reduces the temperature isobarically to the reactor operation temperature (349.85 °C).

Reactor (R-1001): its operational variables were defined by sensitivity analysis. As seen in Figure 3a and 3b, the best choice of reactor's operation regarding the mole ratio was 1:2 (CO:H₂), condition in which the best results for both, ethanol selectivity and conversion were obtained at the maximum pressure (100 bar). Considering the results obtained in figure 3c, the temperature was also maintained in its maximum (349.85 °C). The catalyst load was defined based on the figure 3d that shows that the maximum conversion for the system is attained at 3.750 kg of catalyst in the reactor.

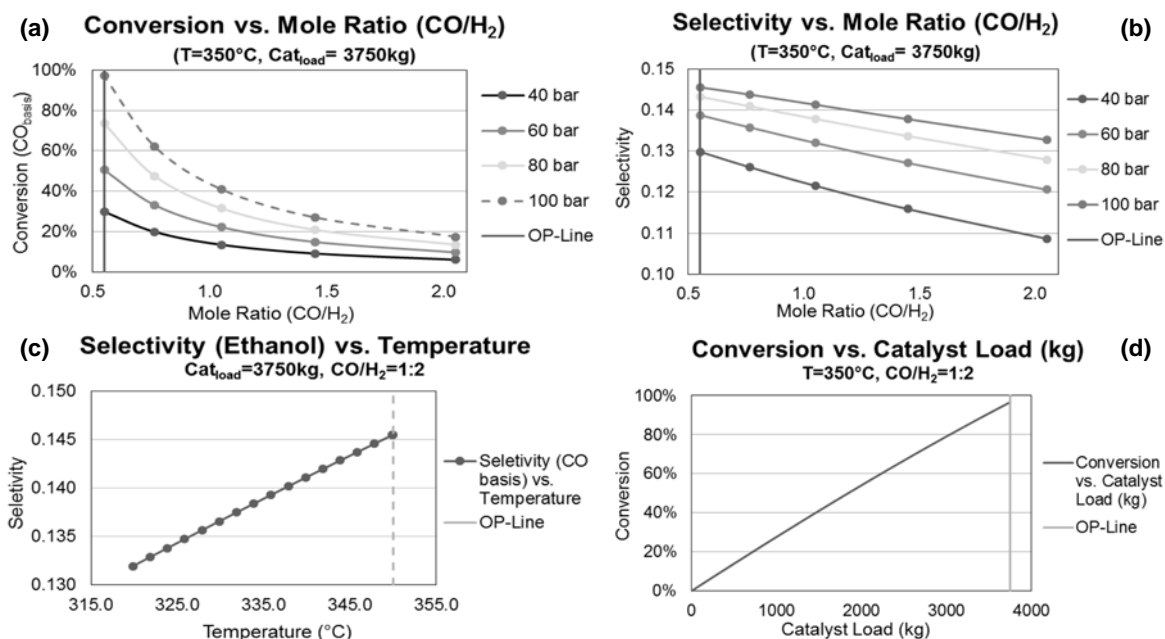


Figure 3: Reactor Sensitivity Analysis, (a) conversion sensitivity to mole ratio, (b) selectivity sensitivity to mole ratio, (c) selectivity sensitivity to temperature, (d) conversion sensitivity to catalyst load

Flash drum (F-1001): operates at 10 °C and 23 bar. These operation conditions were obtained by sensitivity analysis, in which the main goal was to recover the maximum amount of non-reacted syngas and CO₂ coming from the reactor stream (S-1006/S-1007) in the top stream (S-1008) and the higher amount of alcohols in the bottom stream (S-1009). Using this procedure was possible to recover 99.4 w/w% (98.91 methanol, 99.76 ethanol, 99.88 propanol, 99.95 butanol and 99.99 w/w% pentanol) of the alcohols and 95.2 w/w% (99.75 CO, 99.89 H₂ and 94.24 w/w% CO₂) of effluent gases.

Recycle section (RGWS/SEP): emulates a process attached to the system, which takes the effluent gas stream and reconditions it into pure syngas. The reactor is set to operate adiabatically and to produce a stream with only CO, H₂ and O₂ (this last one added as effect of the atom balance). The separator purges the exceeding oxygen from the process and reintroduces the syngas produced into the system through the stream S-1020. This operation is responsible for the reintroduction of 373.66 kg/h of syngas into the process with a ratio of 1:2.87 (CO:H₂). Adjusting the stream S-1001 was possible to obtain the mole flow rate of 100 kmol/h and 1:2 (CO:H₂) at the reactor's entrance (S-1005).

SEP-1: as shown in section 2.2 and Figure 2, the SEP-1 is a sequence of four distillation columns. The configuration of each column was obtained by varying the stage number, the feed stage and the mass reflux ratio aiming to reduce the energy consumption from reboilers and at the same time attaining the minimum concentration of 99 % of the desired products. The mass flow rates of the top streams were defined based on the mass flow of the desired products fed to the column. The results are given in Table 2.

Table 2: Columns configuration (SEP-1)

| Characteristic | C-101 | C-102 | C-103 | C-104 |
|---|---------|---------|---------|---------|
| Number of Stages | 50 | 40 | 39 | 39 |
| Position of Feed Stage | 28 | 20 | 20 | 22 |
| Mass Reflux Ratio | 2.5 | 2.2 | 2.8 | 2 |
| Top _{vapor} Mass Flow (kg/h) | 25.23 | - | - | - |
| Top _{liquid} Mass Flow (kg/h) | 246.07 | 108.00 | 47.50 | 81.73 |
| Bottom Mass Flow (kg/h) | 293.93 | 185.93 | 138.43 | 56.70 |
| Product _(TOP) Recovery | 99.00 % | 99.90 % | 99.90 % | 99.91 % |
| Product _(TOP) Concentration | 99.06 % | 99.74 % | 99.58 % | 99.85 % |
| Product _(BOTTOM) Recovery | - | - | - | 99.84 % |
| Product _(BOTTOM) Concentration | - | - | - | 99.86 % |

Table 2 shows that the separation of methanol in the first column can be considered the most difficult and sensitive operation in this sequence. Due the presence of CO₂ in the feedstream, a vapour stream was required in this column for an adequate separation. In this stream, part of the methanol that should be recovered, is continuously stripped with the CO₂, this fact resulted in a recovery of 99 % (the minimum accepted in the optimization) and with a purity of 99.06 % in weight. The elevated number of stages and reflux ratio of minimum 2 can be pointed as an effect of the narrow boiling points and the low relative volatility between the components in each separation.

3.2 Production

The mass flow of higher alcohols (C₂-C₅) obtained was 293.93 kg/h, such produced amount exceeds methanol production (246.07 kg/h). However, methanol selectivity is still high considering the focus of the process, the production of higher alcohols and mostly ethanol (108.00 kg/h).

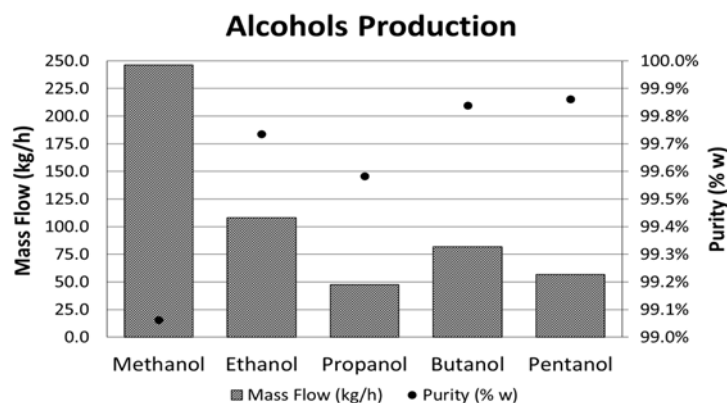


Figure 4: Alcohols Mass Flow (kg/h) and Purity (w/w)

Aiming a minimum recovery of 99.9 % of the desired products ethanol, propanol, butanol and pentanol were obtained in each column at high purity (in weight) of: 99.74 %, 99.58 %, 99.85 % and 99.86 %, respectively. These high concentrations were obtained due to the recovery restrictions (99.9 %w of the product in the feed stream) and can be pointed as a positive characteristic of the process considering the introduction of impurities (as carbon deposits in the catalyst) and the introduction of these alcohols in specific markets that require high purity reagents or solvents.

3.3 Energy Consumption

All the reactions involved in the process are exothermic. Beginning from this, is possible to imagine a positive energy balance within the whole process. To ensure this, Table 3 shows a net energy consumption of -1545.95 kW/h which means that this energy needs to be withdrawn from the process by the proper utilities. Due the exothermicity of all reactions involved in the process, the reactor is the operation in which more energy is withdrawn among the cooled units, being responsible for more than 40 % of the consumption of these.

Table 3: Energy consumption by Equipment

| Cooled Units | | | Heated Units | | |
|---------------|---------------|---------------|--------------|---------------|---------------|
| Equipment | Energy (kW/h) | % Consumption | Equipment | Energy (kW/h) | % Consumption |
| R-1001 | -909.35 | 40.18 % | SEP-1 | 520.73 | 72.58 % |
| F-1001 | -395.27 | 17.46 % | C-101 (Reb.) | 365.39 | 50.93 % |
| SEP-1 | -475.02 | 20.99 % | C-102 (Reb.) | 79.91 | 11.14 % |
| C-101 (Cond.) | -319.46 | 14.11 % | C-103 (Reb.) | 35.48 | 4.95 % |
| C-102 (Cond.) | -79.91 | 3.53 % | C-104 (Reb.) | 39.95 | 5.57 % |
| C-103 (Cond.) | -34.71 | 1.53 % | CPR - 1001 | 196.71 | 27.42 % |
| C-104 (Cond.) | -39.67 | 1.75 % | | | |
| K-1001 | -9.99 | 0.44 % | | | |
| Total | -2,263.39 | 100.00 % | Total | 717.44 | 100.00 % |

The separation (SEP-1) has an important role in both sides of utilities consumption, being the second greater consumer of cooling utilities (20.99 %) and the first one regarding heating utilities (72.58 %). Due the operation requirements and conditions of the stream S-1007, the flash drum requires that -395.27 kW/h be continuously withdrawn from the process. The syngas from stream S-1001 is entering the process at 25 °C and 1 bar, and the recycle stream S-1020 at 250 °C and 1 bar. These two streams are mixed and form S-1002, at 121.9 °C and 1 bar. Stressing out that the stream S-1002 needs to enter the reactor at 349.85 °C and 100 bar it is necessary to carry out a compression of such stream, which is made by the compressor CPR-1001 consuming 196.71 kW/h.

4. Conclusions

The process using the Cu-based catalyst has proven to be feasible in a small-scale plant and promising for a further large-scale test. Its main advantages are the absence of water in the reactor's exiting stream, facilitating the separations in both flash drum and SEP-1 and the representative production of only alcohols. On the other hand, due the consumption of water by the WGS reaction, CO₂ is formed and needs to be reconditioned and reintroduced to the process as CO. Methanol selectivity can be seen as a problem as well, consuming great part of the syngas introduced in the process. However, the initial kinetic studies do not count with the possibility of homologation reaction or condensation reaction, what shall be considered in further studies. Due the exothermicity of the reactions considered, the net energy consumption has a positive value, this fact opens the possibility of energy integration along the process or with other processes.

Acknowledgments

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