Optimizing the Exergetic Efficiency of a Pressurized Water Process for Bio Gas Cleaning

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A pressurized water process for bio gas cleaning is optimized by means of its exergetic efficiency. The exergy consumption of this process is a suitable measure as it weights electricity and steam consumption and considers the increase of physical and chemical exergy of the treated bio gas stream. In this paper the steps applied for modeling the process and for calculating the exergy of the streams are presented and an outlook on the optimal operation conditions is given.

1. Introduction

About 30 % of the gross electricity production (GEP) in Germany was generated from renewable sources in 2015 (Lentz et al 2016). While electricity from biomass is, with approximately 8 % of GEP, far behind the wind energy (approx. 15 % of GEP), it has the considerable advantage of being much easier to store. In fact, bio methane from bio gas is the only renewable energy source with a world scale storage facility - the European natural gas grid. However, only 8 % of the generated bio gas was upgraded to bio methane in Germany 2015 and thus used as green gas (Scheftelowitz et al. 2015). One reason for this relatively small figure is that the upgrading process requires capital and operational expenditures (CAPEX/OPEX) in an amount that allow an economically feasible operation only for larger plants. And up to now most of the plants operated in Germany are decentralized and of relative small size.

The advantage of decentralized bio gas production is that the transport ways of the biomass are kept short. Thus, it is important to have high efficient and low cost bio gas upgrade processes. One process that fits into these needs is the pressurized water process (Starr et al. 2012). A feature of this process is that it only requires water and no additional chemicals for the treatment of the bio gas. Consequently, the highest environmental impact of this process comes from the electricity consumption and the fresh water consumption (Ryckebosch et al. 2011).

2. Process Model

The evaluated process is a three-stage compression pressurized water process with an intermediate flash for methane recovery, an air stripper and a bio filter for hydrogen sulfide conversion. The process flowsheet is depicted in Figure 1.

2.1 Process Conditions

Composition and properties of the stream that is coming from the fermenter are given in Table 1. The air which is used for stripping is taken in at ambient conditions (25°C, 1.013 bar abs) and considered to be dry. Saturated steam of 1.1 bar abs is used for water make up. This should reflect the exergy requirements for providing water with sufficient purity. Cooling water is assumed to be available at ambient conditions, so that it has a physical exergy of zero. This means it is supplied with 25°C. Pressure drop in the heat exchangers is not considered.

Table 1: Feed conditions

Temperature	Pressure	Std. Volume Rate	N_2	O_2	CH_4	CO_2	H_2S	H_2O
40 °C	1.0 bar abs	300 m³/h	balance	-	60 mol%	36 mol%	300 mol ppm	3 mol %

To be fed to the natural gas grid the treated bio gas must have a methane concentration of at least 96 mol% and a hydrogen sulfide content of maximal 20 mol ppm.

With the reference values of the design variables shown in Table 2 these conditions are met. The table further more gives the bounds of these variables during the optimization.

Table 2: Design variables of the reference process with bounds for the optimization.

Name	Unit Op/Stream	Value	Unit	Lower Bound	Upper Bound
Intermediate Pressure	U 1	4	bar abs.	1.1	15
Absorber Pressure	U 4	9	bar abs.	U2	25
Gas Feed Temperature	U 5	30	°C	30	80
Liquid Feed Temperature	U18	30	°C	30	80
Stripping Air Flowrate	S 13	250	stdVm³/h	10	1000
Cycle Water Flowrate	U 14	85	stdLm³/h	5	500
Purge Ratio	U 11	1%	-	1%	10%
Intermediate Pressure 2	U 20	4	bar abs.	U1	20

The biogas coming from the fermenter [1] is compressed in a first compressor unit (1) and then cooled down to a temperature 5 K above its dew point temperature in the heat exchanger (2). Stream [3] is then mixed with the stream [11] which mainly contains methane recovered from the rich water leaving the scrubber (6). The pressure of the gas mixture is increased to the scrubber pressure in the second (units (20) and (21)) and the third (units (4) and (5)) compression stage with an intermediate cooling down to 5 K above the dew point in heat exchanger (21). All compressors are modelled with an adiabatic efficiency of 50 %.
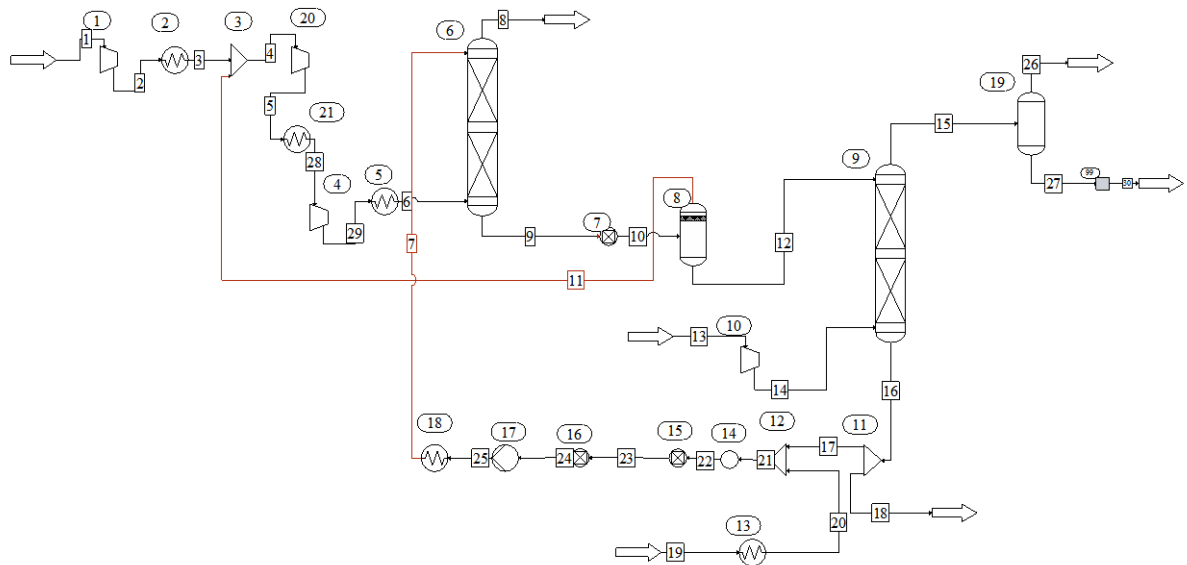

Figure 1: Pressurized Water Process modelled in CHEMCAD 7 (CC7)

The gas temperature at scrubber inlet is controlled with the heat exchanger (5). The regenerated and cooled scrubbing water [7] is entering the scrubber column (6) at the top. The scrubber is represented by 20 equilibrium stages with efficiencies as given in Section 1.3. The conditioned bio gas [8] is leaving the process from the top of the scrubber column. The rich water [8]/[9] is fed to a flash vessel (8) where methane is recovered due to a pressure reduction. However, depending on the pressure level of the first compressor, a certain amount of water, carbon dioxide, and hydrogen sulfide (stream [11]) is recycled together with the recovered methane to the inlet of the second compressor (20).

The remaining rich water [12] is given to the top of the stripper column (9) where a part of the absorbed gases is removed with air which is fed at the bottom of the column (stream [14]). Ambient air [13] is transported to the stripper column with a blower (10). The stripper (9) is operated at a slight overpressure of 100 mbar (g). This pressure is required to allow the vapor stream [15] to pass the bio-filter (19) before it is send to the stack. A part of the regenerated scrubbing water is purged in unit (11) to avoid an accumulation of components in the recycle stream. Make up water [20] is mixed to the regenerated water [17] to fill up water losses from the scrubber, the stripper, and the purge. Steam condensate is used as make-up water to guaranty a sufficient cycle water quality.

The water is brought back to scrubbing pressure with the recycle pump (17) modelled with an adiabatic efficiency of 70%. The inlet nozzle is assumed to be in a height of 5 meter above the pump. The heat exchanger (18) is used to control the inlet temperature of the scrubbing water.

Controller (7) is used to set the pressure of the flash vessel equal to the outlet pressure of the first compressor while the controllers (15) and (16) are used together with the stream reference (14) to adjust the balance of the plant. The exergy of all streams is calculated in the VBA unit operation (99) as described in Chapter 2.

2.2 Selection of the Thermodynamic Model

The process conditions range from a temperature of 20 °C to 80 °C in the absorber and up to 600 °C behind the compressors, considering the extreme compression ratio of 25:1, while the pressure of all process streams is within 1 bar abs and 25 bar abs. At these conditions nitrogen, oxygen, methane, and carbon dioxide are in a supercritical state (CO_2 above 31 °C). Solubilities of supercritical gas in water are commonly modelled with Henry's law.

However, to calculate consistent values for enthalpy and entropy in all phases which also reflect that at the phase equilibrium the Gibbs enthalpy of the mixture reaches a minimum this approach is not adequate (Schöneberger 2016). The phase equilibrium must be calculated with an iso-fugacity approach (eq. (2)) where the fugacity coefficient φ_i is calculated with the same equation of state which is used for the calculation of enthalpy and entropy.

Thus, an equation of state (EoS) is required which accurately predicts the solubility of the involved components in water and gives acceptable values for the liquid heat capacity and the heat of vaporization. To solve the first issue gE mixing rules have been introduced for EoS by Huron and Vidal (1979). Theses mixing rules have been further developed by Holderbaum and Gmehling (1991) to give the Predictive Soave Redlich Kwong EoS (PSRK) which makes use of the group contribution gE model UNIFAC. The problem of the bad values for liquid enthalpies was then tackled by the successor of PSRK, the Volume Translated Peng Robinson EoS (VTPR). For VTPR the Twu alpha function is introduced which contains three additional parameters that can be used to fit vapor pressures and liquid heat capacities simultaneously (Ahlers and Gmehling 2001).

With VTPR an accurate equation of state is available in a process simulation environment to consistently calculate physical and chemical exergies of streams in thermal separation processes or absorption processes respectively. The BIP matrix for the main-group interaction is 100% full when using the data from Schmid et al. (2012) and the Twu parameters of all involved components can be found in the Dortmund Data Bank (DDB).

In Figure 2 Henry coefficients from literature are compared with coefficients calculated by VTPR. The VTPR results are quite accurate and only for Oxygen a higher solubility is predicted compared to the data given by Perry et al. (1999). This fact is negligible here, as only a small amount of oxygen is present in the gas streams.
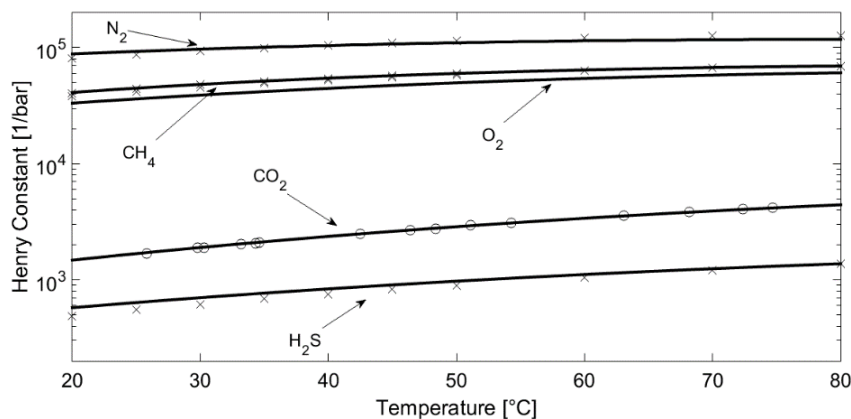

Figure 2: Comparison of the VTPR model (lines) with literature data from Perry (x-marks) and DDB (o-marks).

Carbon dioxide and hydrogen sulfide both dissociate in water. This can be taken into account by using an electrolyte model. However, the most commonly used electrolyte model, eNRTL from Chen and Evans (1986), is a g^E model and thus its application is followed by the same consistency problems regarding the exergy calculation as discussed above for Henrys law. Furthermore, as most g^E models it is not explicitly made to handle supercritical components.

In order to judge the impact of the dissociation and the cross-effect of the HS- ions and the HCO3- ions (other ions occur only in very small amounts) on the vapor pressure of the electrolyte solution the gas phase compositions calculated with eNRTL are compared to those calculated by VTPR. For this purpose, the gas stream coming from the fermenter (see Table 1) is set into equilibrium with water at different temperatures and a pressure of 10 bar abs while the calculated gas phase composition is recorded. The results are shown in Figure 3.
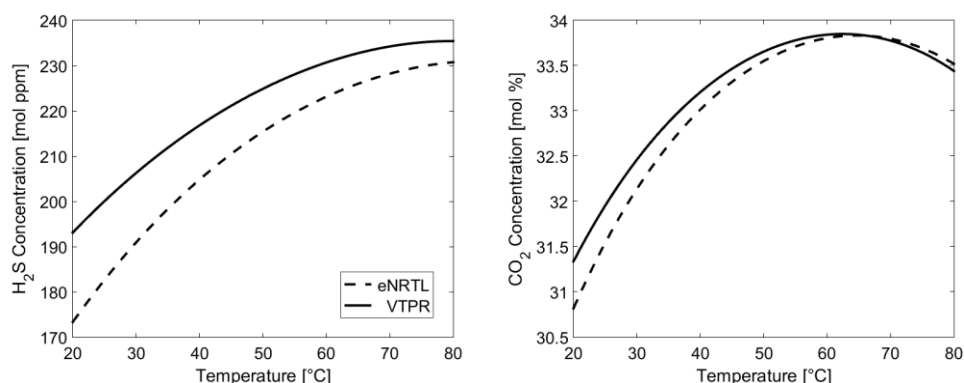

Figure 3: Impact of a) H_2S and b) CO_2 dissociation on vapor pressure of the electrolyte solution using eNRTL and VTPR models

There are considerable deviations of up to 0.5 mol % for CO2 and 20 mol ppm for H2S. The differences shrink with an increasing temperature. However, these deviations have to be accepted as there is currently no EoS available in a process simulation environment that has electrolyte capabilities. A summary of published models and current developments in this direction is given by Kontogeorgis and Folas (2010).

2.3 Modelling of the Separation Columns

The components of the bio gas stream are absorbed in water with different velocities. Therefore, it is not sufficient to model the separation columns with equilibrium stages. To judge the efficiency of absorption and desorption of the different components the columns are modelled with a mass transfer approach in a first step. For this rate based column model the diameter of the absorber is set to 0.8 m with 5 m height of 250Y Mellapack packing. The stripper is modelled with 1 m diameter and 10 m of the same packing. For the reference conditions these diameters refer to approximately 60% flooding. The resulting efficiency profiles are given in Figure 4.
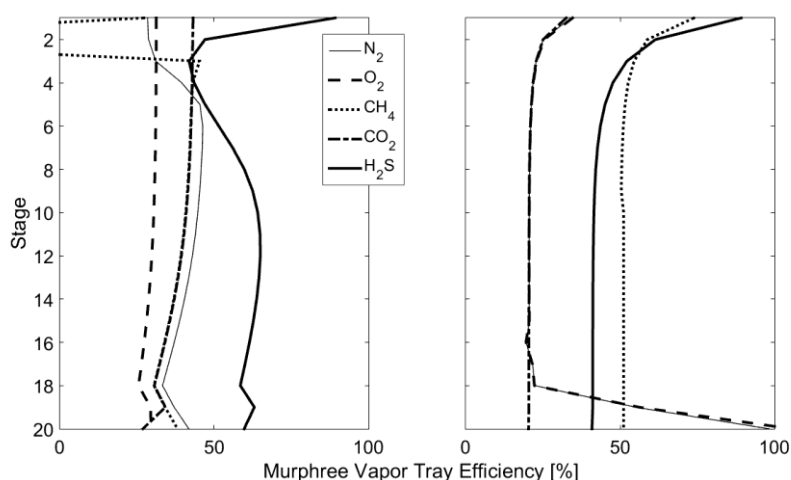

Figure 4: Efficiency profiles for the absorber (left) and the stripper (right) column.

Hydrogen sulfide is absorbed with the highest efficiency while methane is removed with the highest efficiency in the stripper.

Using the mass transfer model within an optimization procedure bears some problems because on the one hand the calculation takes more time than an equilibrium calculation and on the other hand columns can flood what leads to a non-converging flowsheet. Therefore, the Murphree efficiencies are extracted from the mass transfer calculation and used in an equilibrium stage model.

3. Exergy Analysis

As stated by Ryckebosch et al. (2011) the highest environmental impact of the pressurized water process comes from its electricity consumption and its fresh water consumption. Both can be evaluated simultaneously by applying an exergy analysis. The exergetic benefit of the process is then the raise of exergy from the fermenter gas to the product gas with natural gas quality. The gas raises in physical exergy because of the compression and in chemical exergy because of its increasing Methane content. The exergetic efficiency of the process here is defined as the exergy of its product (stream 8) divided by all exergy inputs, which are the electricity consumptions of the pump and the compressors, the fermenter gas (stream 1), the air (stream 13), and the make-up steam (stream 19).

3.1 Calculation of the Stream Exergies

Physical and chemical exergy of the process steams are considered while the streams exergy is defined as the sum of both. The physical exergy rate $\dot{E}^{Ph}$ of a stream can be calculated with Eq(1), where $\dot{H}$ is the enthalpy rate, $\dot{S}$ is the entropy rate, v is the vapor fraction, x is the liquid phase composition and y is the vapour phase composition. The index 0 refers to the ambient conditions.

$$\dot{E}^{Ph} = \dot{H}(T,P,v,x,y) - \dot{H}(T_0,P_0,v_0,x_0,y_0) - T_0\big[\dot{S}(T,P,v,x,y) - \dot{S}(T_0,P_0,v_0,x_0,y_0)\big] \tag{1}$$

Eq(1) already suggests that flash calculations have to be performed at ambient conditions. This is done for all the streams in the VBA unit operation (99).

A reference environment is required to calculate the chemical exergy of a stream. The chemical exergy is then the work that theoretically can be extracted from an isothermal and isobaric reaction chamber where the stream components are converted at ambient conditions to components which exist in the environment and expanded (or compressed) to the related environment concentration, see e.g. Bejan et al. (1995).

In this work the environment defined by Diederichsen (1991) is used. However, the tabulated values for chemical exergies of the specific components e_i^{Ch} referring to this environment cannot be directly copied as Diederichsen used a different reference state for the entropy. The recalculated values which use the reference state for entropy in CHEMCAD are given in Table 3.

Table 3: Specific chemical exergies of the components recalculated with the CHEMCAD reference entropy.

Component i	N_2	O_2	CH_4	CO_2	H_2S	$H_2O(g)$	$H_2O(l)$
e_i^{Ch} [kJ/mol]	0.743	4.967	824.098	16.109	732.767	8.577	0.017

Neglecting heat of mixing and non-ideal entropy of mixing leads to Eq(2) for the calculation of the specific chemical exergy of one phase of a stream. Eq(2) shows the calculation for the liquid phase.

$$e^{Ch} = \sum_{i=1}^{Num.\ of\ comp.} x_{0,i} e_i^{Ch} + RT_0\, x_{0,i} ln(x_{0,i}) \tag{2}$$

The specific chemical exergies of both phases are weighted with respect to the vapor fraction at ambient conditions v_0 and multiplied with the overall flow rate to give the chemical exergy rate $\dot{E}^{Ch}$.

3.2 Results for the Reference Process

The reference process conditions lead to an exergetic efficiency of 87.2 %. The constraints are more than fulfilled with a Methane concentration of 96.9 mol% and a Hydrogen Sulfide content of less than 1 mol ppm. Furthermore, only two of the three available compression stages have been utilized. This gives space for optimization as presented in the next chapter.

4. Process Optimization

The maximization of the exergetic efficiency of the process leads to a nonlinear constraint optimization problem with eight design variables. Different approaches can be followed now to solve this problem. A

comparison of suitable approaches for flowsheet optimization with and without external tools can be found in Schöneberger and Fricke (2017). Students from all over the world are called to submit their solution to the problem in the Process Simulation Cup 2016 (PSC 2016). The final winner was determined in February 2017. A detailed analysis of the so determined optimum is given at the conference. However, some trends can be pointed out so far:

- A small purge ratio leads to lower exergy losses and thus to a higher efficiency
- The cycle rate, the absorber pressure and the air flow rate are highly coupled regarding their effect on the product purity
- The compressor duty of the intermediate compression stages can be minimized almost independently

5. Conclusions

A considerable amount of modeling work and the application of model simplifications are required before an optimization of the exergetic efficiency of a process is possible. However, once the work is done the optimization delivers not only better operation conditions but also improves the operational background of the process and reveals the dependencies of the design variables, the constraints, and the objective function.

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