

Thermodynamic Analysis, Energy Integration and Flowsheet Improvement of a Methanol Absorption Acid Gas Removal Process

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This paper analyses the thermodynamic performance and proposes different energy integration schemes for a methanol absorption based acid gas removal process, namely the Rectisol[®] process specifically designed for the selective removal of H₂S and CO₂ from coal derived syngas.

The study consists of three major tasks:

1. Calibrating the PC-SAFT equation of state for MEOH-CO₂-H₂S-H₂-CO mixtures at conditions relevant for the Rectisol[®] process.
2. Evaluating the thermodynamic performances and optimising the energy integration of the “Reference” scheme by means of “heat-cascade” based optimisation methodology.
3. Identifying attractive process modifications on the basis of Process Integration principles.

1. Introduction

Acid Gas Removal (AGR) processes play a significant role in coal gasification based plants which require the transformation of a dirty feedstock like coal into a cleaner synthesis gas suitable for the downstream energy conversion sections. For instance, the Fischer-Tropsch (FT) synthesis unit of a Coal To Liquids (CTL) plant imposes strict specifications on the removal of sulfur-based components from the syngas to be processed. Moreover, to make these facilities more attractive from the point of view of CO₂ emissions, it could be interesting to apply Carbon Capture and Storage (CCS), by separating also the CO₂ from the syngas and making it available as an almost pure liquid product ready for long-term storage.

Therefore, most coal gasification plants include an AGR section which can have a relevant impact on the overall performances from both a thermodynamic and economic point of view.

According to Bell et al. (2011), different options are envisaged to reach the prescribed removal of contaminants from the syngas. Anyway, so far only physical absorption processes, based on the different solubilities of the gaseous species of the syngas into a liquid solvent, have reached the maturity for large-scale commercial applications. Within this category, the Rectisol[®] is widely recognized to be one of the benchmark processes thanks to its deep cleaning capabilities compared to the other available technologies.

The Rectisol[®] concept entails a separation and a regeneration section where the H₂S and CO₂ of the raw syngas are respectively absorbed and desorbed by the solvent, a cooled methanol stream, separately or not according to the specific configuration. As Prelipceanu et al. (2007) and Kasper (2009) point out, the Rectisol[®] design and operative parameters can be tuned to deal with different purification goals and boundary conditions.

In this paper, we first select and calibrate the equation of state (EOS), then we identify and describe a “Reference” Rectisol[®] scheme for Coal to Fischer-Tropsch plants with CCS, afterwards we perform the thermal integration and the thermodynamic analysis of the “Reference” case, and finally we propose and evaluate the impact of some process and utilities modifications.

2. Selection and calibration of the Equation Of State

In the Rectisol[®] process, the physical absorption of CO₂, H₂S and other minor chemical compounds into methanol involves energy and mass transfers at pressures and temperatures close to the critical values for CO₂ and H₂S. Therefore, neither the liquid nor the vapour phase of such mixtures can be correctly modelled with the ideal behaviour.

For these reasons, it is necessary to adopt an equation of state capable of accurately modelling the main physical interactions between the different species within the vapour and liquid phases. This issue has already been tackled by Sun and Smith (2013) who select the PC-SAFT EOS and provide new calibration parameters for the binary pairs MEOH-CO₂ and MEOH-H₂S. However, (i) their model correction was limited to the reconciliation of the thermodynamic properties of the streams entering and exiting the absorption section of a specific Rectisol[®] plant, and (ii) they do not provide data for the binary pairs MEOH-CO and MEOH-H₂ as well as for the couple CO₂-H₂S which, instead, plays an important role in the CO₂ desorption column and in the MEOH regeneration section.

Our aim is to provide a set of calibrated binary interaction parameters that can cover the composition range and the whole operating temperature range of the Rectisol[®].

As in Sun and Smith (2013), we select the PC-SAFT thermodynamic model introduced by Gross and Sadowski (2001) because, being derived from statistical mechanics, it has a stronger physical foundation than cubic EOS. As a consequence, it should provide better estimates in the single phase regions. At the same time, as shown by Gross and Sadowski (2001), the PC-SAFT can be adjusted to predict the vapour-liquid equilibria of mixtures with slightly better accuracy than the Peng-Robinson cubic EOS simply by calibrating the binary interaction parameters.

The calibration was performed by means of the following steps:

- Identification of the temperatures and composition ranges of interest (the pressure range of the bubble and dew points is therefore a consequence of this choice)
- Collection of the vapour-liquid equilibria experimental data available from the literature
- Formulation of the EOS calibration as a non-linear constrained optimisation problem, where the objective function is the mean average error on the saturation pressure in absolute value (AAD%) as expressed by Eq(1), and the decision variables are the three coefficients (a_{ij} , b_{ij} and c_{ij}) which define the binary interaction parameters k_{ij} as a function of the temperature as proposed by Gross and Sadowski (2001) and reported in Eq (2):

$$AAD\% = \left| \frac{p - p_{ref}}{p_{ref}} \right| \%, \quad (1)$$

$$k_{ij} = a_{ij} + b_{ij} \frac{T_{ref}}{T} + c_{ij} \ln \left(\frac{T}{T_{ref}} \right). \quad (2)$$

The results of such optimisation are reported in Table 1, where the resulting accuracy is compared against that of the default parameters considered in Aspen Plus[®].

Table 1: Value of the binary interaction parameter for the most relevant binary mixtures involved in methanol based acid gas removal systems.

Component i	MEOH	MEOH	MEOH	MEOH	CO ₂	CO ₂	CO ₂
Component j	CO ₂	H ₂ S	H ₂	CO	H ₂ S	H ₂	CO
Number of exp data avail.	81	36	39	14	45	46	21
Temperature range, K	213-288	248-298	243-298	298-323	223-298	220-270	223-263
a_{ij}	-0.0039	0.0022	-0.0642	-0.0321	-0.0055	0.0371	0.0012
b_{ij}	0.0216	-0.0228	-0.2374	0.0603	0.0821	-0.5063	-0.0339
c_{ij}	0.0392	-0.1233	-0.546	-0.1097	0.1437	-0.2855	0.1094
T_{ref} , K	298.15	298.15	298.15	298.15	298.15	298.15	298.15
AAD NEW%	6.1	6.6	3.8	3.8	1.7	9.6	3.1
AAD DEFAULT ASPEN%	12.6	8.8	29.9	18.3	16.6	54.3	14.6

3. Definition and analysis of the Reference case

The "Reference" case selected for benchmarking the Rectisol[®] process is adapted from the scheme described in the original patent of Ranke and Weiss (1982), and reported also in Preliceanu et al. (2007) and Kasper (2009), with some modifications introduced to meet the CO₂ product specifications.

3.1 Assumptions and specifications

We consider the raw syngas generated by a GE total quench gasifier (NETL, 2010) operating at 40 bar and 1573 K, fed with Illinois #6 coal, and conditioned within a sour water gas shift reactor in order to obtain an H₂/CO molar ratio of 2. Such syngas composition is known to maximize the production yield of liquid fuels in a Cobalt based FT reactor.

In this study we assume that the raw syngas enters the acid gas absorption section already dried, being the water previously removed by a small fraction of methanol, and then regenerated in a dedicated separation column. The sweet syngas is delivered at 30 bar and should contain less than 50 ppbv of H₂S in order to comply with the tolerance of the Fischer-Tropsch catalyst. The target CO₂ capture level (CCL%) is 98%. The CO₂-rich stream is made available as a separate product at 150 bar and 298 K and it should contain more than 97 % (molar basis) of CO₂ and less than 100 ppmv of H₂S in order to meet the tight Enhanced Oil Recovery specifications. The H₂S fraction contained in the H₂S-rich stream sent to Claus should be higher than 20 % (molar basis) in order to ensure a proper operation of the downstream air-fired Claus unit.

3.2 Description of the Reference case

The flowsheet of the CO₂ capture process (Figure 1) can be conceptually divided into three sections: acid gas absorption, CO₂ desorption and methanol regeneration. The main operating conditions are set according to Ranke and Weiss (1982) and to Prelipceanu et al. (2007) with some modifications. The raw syngas (A1) is compressed up to the absorption pressure, here set to 60 bar, cooled down to 253 K and then sent to the absorber column. The absorber is a tray column ideally divided in two sections, the CO₂-absorber and the H₂S-absorber. The regenerated cold methanol (A2) enters the CO₂-absorber at 223 K from the top and removes the CO₂ contained in the sulfur-free syngas stream rising from the bottom of the column. The CO₂-absorber presents a side cooler, in order to remove part of the CO₂ absorption heat from the down-flowing liquid stream. The CO₂-loaded methanol is then split in two fractions: a 50 % is drawn-off and sent to the CO₂-desorption section (A4), whereas the remaining 50 % flows down throughout the H₂S-absorber section. This second methanol stream removes the H₂S from the raw syngas.

The two liquid methanol streams (A4 and A5) loaded with acid gases are then sent to the CO₂-desorption section, after being flashed for recovering the co-absorbed fractions of CO and H₂ (A6 and A7). Such section comprises two columns: a desorption column at 6 bar in which 90 % of the CO₂-loaded methanol (B1) is flashed to release an almost pure vapour stream of CO₂ at 239 K, and a desorption column at 2.7 bar equipped with a reboiler in which the remaining CO₂ is released at 223 K. The methanol stream richer in H₂S (B2) is pre-heated to 283 K and introduced in the lower part of the CO₂-desorption column to recover its CO₂ content. The liquid leaving the column (B3) still contains a relevant amount of CO₂ and is therefore partly vaporized in a sequence of two flashes. The vapour streams (B4 and B5) released by the flash drums are then recycled to the bottom of the column. The liquid (B6) leaving the second flash at 2 bar is sent to the desorption column operating at lower pressure in order to vaporise the remaining CO₂ dissolved with the methanol. In the standard Rectisol[®] (Ranke and Weiss, 1982), the CO₂ removal is performed by means of N₂ stripping. However, this configuration would generate a vapour stream of CO₂ (B9) diluted with N₂ which would not reach the specifications prescribed on the composition. For this reason, in the "Reference" scheme simulated in this study the stripper is replaced by a reboiled column operating at 2.7 bar. The lower part of the column is fed at the top with liquid (B6) containing both CO₂ and almost all the H₂S to be sent to the Claus, and produces two streams: a liquid stream (B10) at 259 K rich in methanol with an H₂S to CO₂ ratio suitable for the Claus and a reboiled vapour stream mainly composed of CO₂ and H₂S. The latter reaches the upper part of the column where it is washed by the remaining 10% fraction of the CO₂-loaded methanol (B8) in order to release a CO₂ stream with less than 100 ppmv of H₂S. The methanol to be regenerated (B10) is then fed to the top of the regeneration column operating at 1.2 bar and equipped with a top condenser and a bottom reboiler. The vapour distillate (C1) is sent to the Claus unit, whereas the liquid bottom (C2) consists of practically pure methanol at 343 K ready to be cooled down and recirculated.

The clean syngas (A3) leaving the absorption section at 228 K provides cooling and mechanical power through an expander placed between two heaters.

The vapour streams leaving the CO₂-desorption section (B7 and B9) are compressed first by a five-stage intercooled compressor up to 80 bar, then by a pump up to the delivery pressure of 150 bar. The compressed CO₂ is then cooled down to 298 K by means of cooling water.

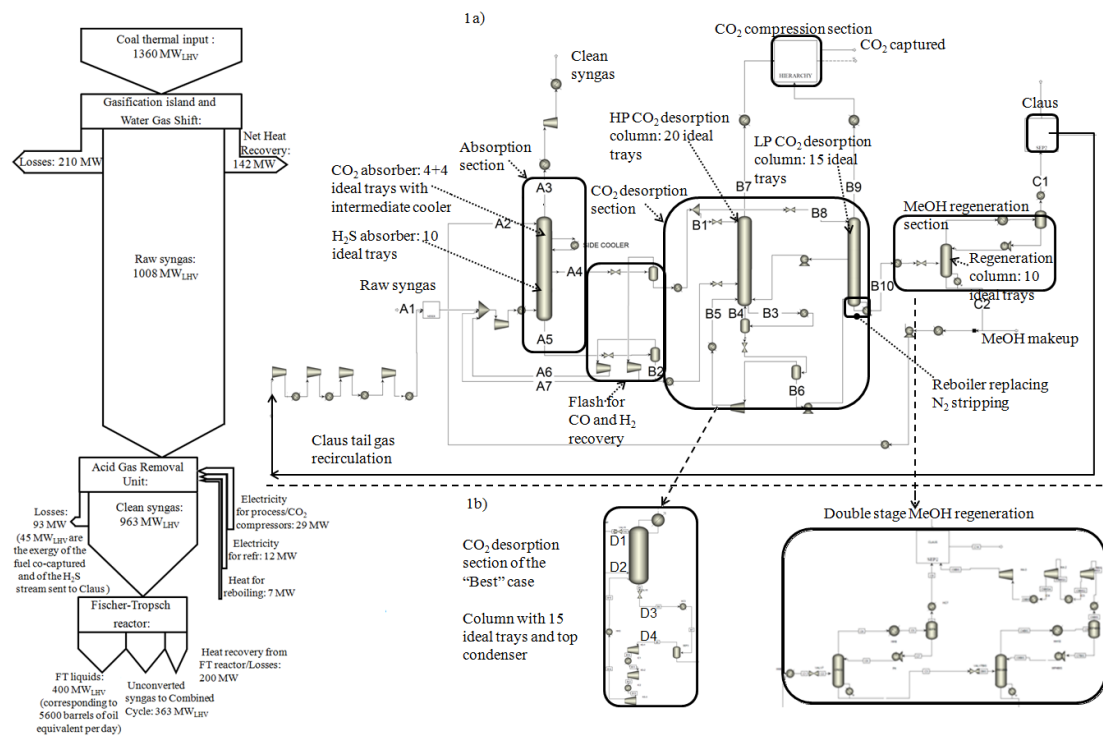


Figure 1: a) Scheme of the "Reference" case (as from Aspen Plus®); b) Flowsheet modifications introduced. The most relevant input and output energy flows are reported as well in the left portion of the picture

4. Heat integration and optimal selection of the utilities

The energy consumption of the above described methanol-based AGR process is due to the syngas and recycle compressors, methanol pumps, the compressor which brings the CO₂ stream to the capture conditions, the fraction of CO and H₂ co-captured, and the external utilities (steam and refrigeration power).

A significant amount of heat is exchanged among the different sections of the plant. For instance, the heat of absorption of CO₂ is removed from the absorption section by cooling down both the methanol and the syngas, whereas the behaviour is reversed for CO₂ desorption exploiting both the flash (pressure reduction) and thermal desorption (whose heat can be therefore recovered from the absorption section). Finally, the H₂S is removed from methanol by thermal regeneration. As a consequence, the heat integration among the process streams and the available utilities plays a crucial role in determining the thermodynamic performances. For this reason, a large reduction of the energy consumption may be obtained by tackling the process heat integration in a systematic way.

In this study, we address such task with the "heat-cascade" based technique proposed by Maréchal and Kalitventzeff (1998). The process heat integration and the design of the utility systems are tackled simultaneously within the following Mixed Integer Linear Problem: given a list of available hot and cold utilities and the minimum heat exchange temperature difference associated to each class of streams, find the utility levels and flow rates which minimize the overall exergy consumption of the utilities.

The heat integration is solved by adopting the following assumptions:

- The hot utilities available are saturated steam at 3, 1.5 and 0.5 bar
- The cooling water is available as a stream that can be heated up from 288 to 298 K
- The refrigeration cycle can be either (i) a state of the art two level cascade ethane/ammonia cycle or (ii) an improved cycle replacing the ethane level with two levels of a mixed refrigerant cycle using a mixture of ethane, propane and ammonia.
- The following $\Delta T_{min}/2$ were associated to each class of streams: $\Delta T_{min}/2$ refrigerant = 3 K; $\Delta T_{min}/2$ hot utility = 10 K; $\Delta T_{min}/2$ process streams = 5 K

The ethane/ammonia cycle makes available two evaporation levels at 213 and 238 K. The ammonia section may serve as refrigeration utility or condenser for the ethane level. Cooling water removes the heat of the condenser of the ammonia cycle operating at 313 K. The improved cycle makes available three

evaporation levels and it is fully integrated with the process. Its temperature levels have been selected according to the indications given by Exergy Grand Composite Curves (EGCC) of the options featuring the ethane/ammonia refrigerator (see Figure 2). The EGCCs, defined by Marechal and Kalitventzeff (1998), are essentially GCCs in which surplus and deficit of heat are evaluated depending on their temperature level according to the Carnot factor ($1-T_{\text{ambient}}/T$). In such diagram the area between the EGCCs of the process and utilities corresponds to the Exergy wasted by heat transfer irreversibility. The temperature levels selected for the improved refrigeration cycle are reported in Figure 4.

5. Process simulation and thermodynamic performances

5.1 Simulation and performances of the options with a state of the art refrigerator

The merit function chosen to compare the thermodynamic performances of the proposed options is the specific equivalent exergy consumption, calculated as the sum of the exergy consumptions of both the mechanical and thermal utilities, divided by the mass flow rate of CO₂ captured. The results of the Aspen Plus® simulation and of the subsequent thermal integration are shown in Figure 2. The picture shows that two possible improvements could be introduced at the level of the process:

- The split of thermal regeneration into two subsequent columns so as to improve the thermal integration at high temperatures. This feature was implemented in “Double regeneration” case.
- The introduction of mechanical vapour recompression in correspondence to the pinch located at 250 K in order to realize an auto-refrigeration circuit directly inside the process and then reduce the refrigeration cycle consumption. This idea was included in the “Best” case.

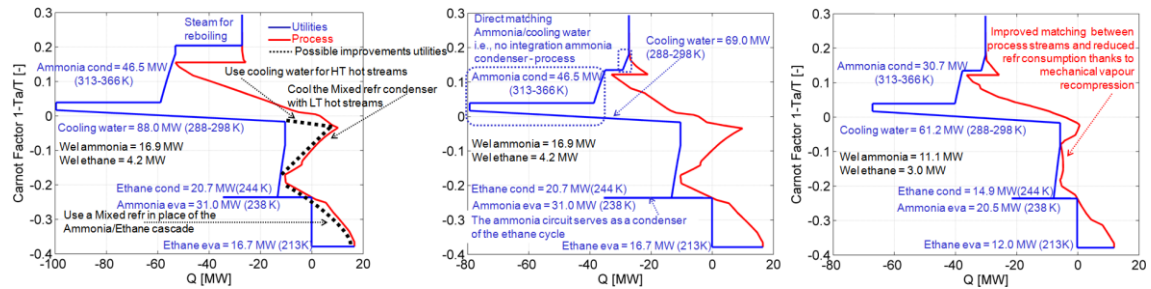


Figure 2: Exergy GCC of the cases with an ethane/ammonia refrigeration cycle. Note that the Carnot factor, i.e. $1-T_{\text{ambient}}/T$, is used and that temperatures are plotted as shifted values, i.e. $T_{\text{cor}}=T-\Delta T_{\text{min}}/2$ for hot streams and $T_{\text{cor}}=T+\Delta T_{\text{min}}/2$ for cold streams. a) Reference, b) Double Regeneration, c) Best case.

The aggregated specific consumption for the Reference case is 925 kJ/kg of CO₂ captured and it is broken-down into the single contributions in Figure 3. The “Double regeneration” case modifies the regeneration section as shown in Figure 1b). This modification causes a 8 % decrease of the specific consumption which reduces to 854 kJ/kg. As reported by Figure 1b), the “Best” case replaces the CO₂-desorption section of the “Double regeneration” case with a single column operating at 10 bar. The column is fed at the top stage with the CO₂-loaded methanol (D1), whereas the H₂S-loaded methanol (D2) is heated up to the ambient temperature and enters the column above the last stage. The liquid extracted from the bottom of the column (D3) still containing a relevant amount of CO₂ is flashed from 10 to 2 bar through a throttling valve and then partly vaporized through a heater before being separated into liquid and vapour phases in a separator. The vapour stream (D4), mainly composed of CO₂ and H₂S, is then recompressed and recycled to the desorption column in order to recover the CO₂ contained. This configuration leads to a reduction of 107 kJ/kg of CO₂ in the consumption of the refrigerator.

5.2 Simulation and performances of the options featuring a mixed refrigerant cycle

Figure 4 describes the enhancements in the process integration realized by adopting a mixed refrigerant cycle. The “Double regeneration” case obtains the most significant relative reduction thanks to the poor heat integration of the ethane/ammonia case. Its improvement in terms of specific consumption is 107 kJ/kg of CO₂. As shown by Figure 4a), this is achieved by integrating the condensers of the mixed refrigerant cycle with the process streams and by placing the ammonia evaporator at a higher temperature. Also for the “Best” case the improved exergy efficiency is a consequence of the appropriate placement of the evaporators and condensers of the mixed refrigerant cycle. This configuration represents the most efficient option, reporting an additional reduction of 33 kJ/kg of CO₂ compared to the “Best” case with a state of the art refrigerator, and an overall relative improvement of 211 kJ/kg of CO₂ with respect to the “Reference” case. Figure 4c) shows the tight matching between the CC of the “Best” case.

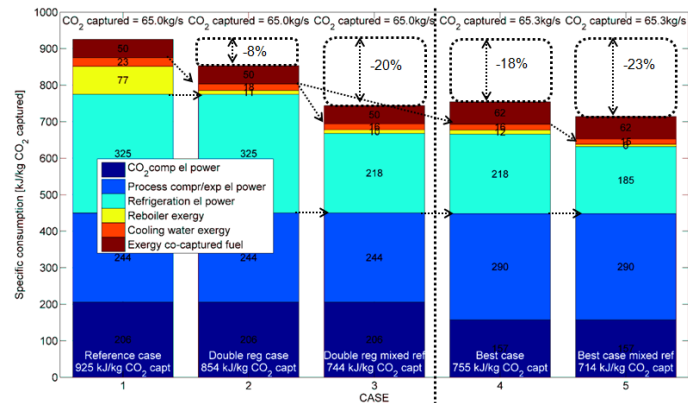


Figure 3: Performance summary and breakdown analysis of the specific consumption for each case. Note that the contribution related to syngas compression from 35 bar to 60 bar, which is 185 kJ/kgCO₂ for all the options, could be removed by adopting an operating pressure of the gasifier of 60 bar

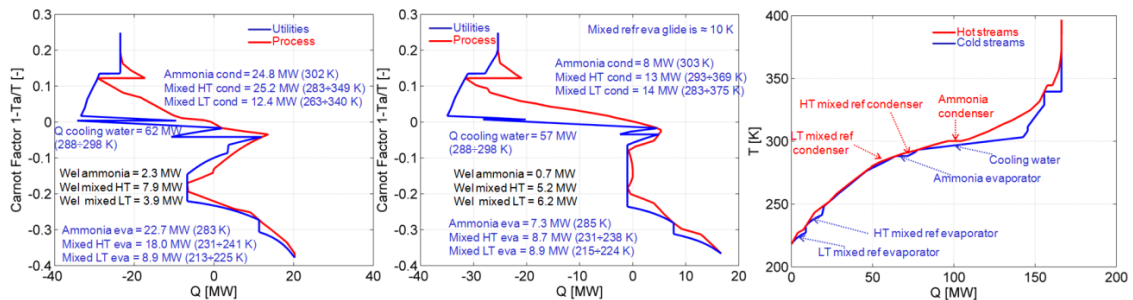


Figure 4: Exergy GCC of the cases with mixed refrigerant: 4a) refers to the “Double regeneration” case while 4b) refers to the “Best” case. 4c) is the Composite Curve (CC) of the “Best” case

6. Conclusions

The paper compares the thermodynamic performances of five different configurations of a methanol absorption based AGR process applied to a partly shifted syngas derived from coal gasification. The specific consumption is estimated as a result of the process simulation performed with Aspen Plus, and the thermal integration optimised with the improved heat cascade methodology. The graphical analysis of the EGCC suggests two main process improvements to reduce the energy consumption: splitting the methanol regeneration in two subsequent stages and including mechanical vapour recompression. Indeed, the “Best” scheme, including the above mentioned process changes and a specifically designed refrigeration cycle, shows an overall equivalent exergy specific consumption of 714 kJ/kg of CO₂ captured, representing a 23 % saving compared to the “Reference” Case.

References

- Bell D.A., Towler B.F., Fan M., 2011, Coal Gasification and its Applications. Elsevier, Amsterdam.
- Gross J., Sadowski G., 2001, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules, Ind. Eng. Chem. Res., 40(4), 1244-1260.
- Kasper M., 2009, Syngas Conditioning by Lurgi Rectisol. Technical presentation from IEA Task 33 Gasification Meeting, Karlsruhe, Germany. <www.ieatask33.org>.
- Marechal F., Kalitventzeff B., 1998. Process Integration - Selection of the Optimal Utility System, Comput. Chem. Eng., 22, 149-156.
- NETL, 2010. Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity. Report. DOE/NETL-2010/1397. <www.netl.doe.gov/energy-analyses/baseline_studies.html>, accessed 10.12.2012.
- Prelipceanu A., Kabbalo H.-P., Kerestecioglu U., 2007, Linde Rectisol Wash Process. 2nd Int Freiberg Conference on IGCC & Xtl Technologies, Freiberg, Germany, <www.iec.tu-freiberg.de/conference>.
- Ranke G., Weiss H., 1982, Separation of gaseous components from a gaseous mixture by physical scrubbing. US Patent number 4324567.
- Sun L., Smith R., 2013, Rectisol wash process simulation and analysis, Journal of Cleaner Production, 39, 321–328.