ProSim

PROSIMPLUS APPLICATION EXAMPLE

CLAUS PROCESS

INTEREST OF THIS EXAMPLE
This example corresponds to the simulation of the well-known Claus process. This process allows the recovery of elemental sulfur from acid gas containing H_2S and water, and possibly hydrocarbons and carbon dioxide. The particularity of this example lies in the use of equilibrium reactors calculated by minimization of Gibbs free energy to simulate the different steps of the process.

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CORRESPONDING PROSIMPLUS FILES	*PSPS_EX_EN-Claus-Process.pmp3*

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1. PROCESS MODELING

1.1. Process Description

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the scientist Carl Friedrich Claus, the Claus process has become the industry standard.

The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia.

Gases with an H2S content of over 25% are suitable for the recovery of sulfur in straight-through Claus plants while alternate configurations such as a split-flow set up or feed and air preheating can be used to process leaner feeds.

This example presented here corresponds to the "modified" Claus process extracted from [1] and [2].

The first step consists in a burner where the combustion of H2S and possibly of the hydrocarbons or other fuels present in the acid gas occurs:

$$H2S + 3/2\ O2 \rightarrow SO2 + H2O$$

$$CH4 + 2\ O2 \rightarrow CO2 + 2\ H2O \qquad \text{(combustion reaction of methane)}$$

The hot gas at the burner outlet is generally cooled in a heat recovery unit where steam is produced: the waste heat boiler (WHB) unit.

The main reaction that produces elemental sulfur is the following:

$$2\ H2S + SO2 \rightarrow 3/x\ Sx + 2\ H2O$$

It occurs in the combustion reactor but with a poor yield (around 70 %). In order to increase the process yield, several stages of catalytic reactor can be used in which the reaction between H2S and SO2 is carried out.

This last reaction produces gaseous sulfur under various sulfur species (S2, S3, S4, S5, S6, S7 and S8). In general, significant species in Claus process are S2, S6 and S8. In the burner, temperature is such (950-1400 °C) that the presence of S6 and S8 is negligible, while they are predominant in the catalytic converters (150-300 °C).

In this example side products such as H2, COS, CS2 and CO that could possibly be formed during the combustion are also taken into account [2].

Since the reaction scheme is complicated and not perfectly known yet, the Claus process is generally modeled assuming thermodynamic equilibrium in the reactor steps calculated by Gibbs free energy minimization. The interest of this method is that the understanding of the reaction scheme is not required, only the components have to be considered. In ProSimPlus, this method is implemented in the “Equilibrium reactor” module. This unit is particularly well adapted for the simulation of one-phase reactions (vapor or liquid phase) with possible formation of solid phase.

The steps simulated in this example are as follows:

1. Acid gas and air mixing.

2. Combustion reactor (gas phase): simulated with an “Equilibrium reactor” module.

3. Waste heat boiler (gas phase in this example): simulated with an “Equilibrium reactor” module.

4. 1st condenser (two-phase unit): it allows the recovery of liquid sulfur. It is simulated with a reactive two-phase flash. The reactions that occur in this unit are the equilibrium reaction between the sulfur species:

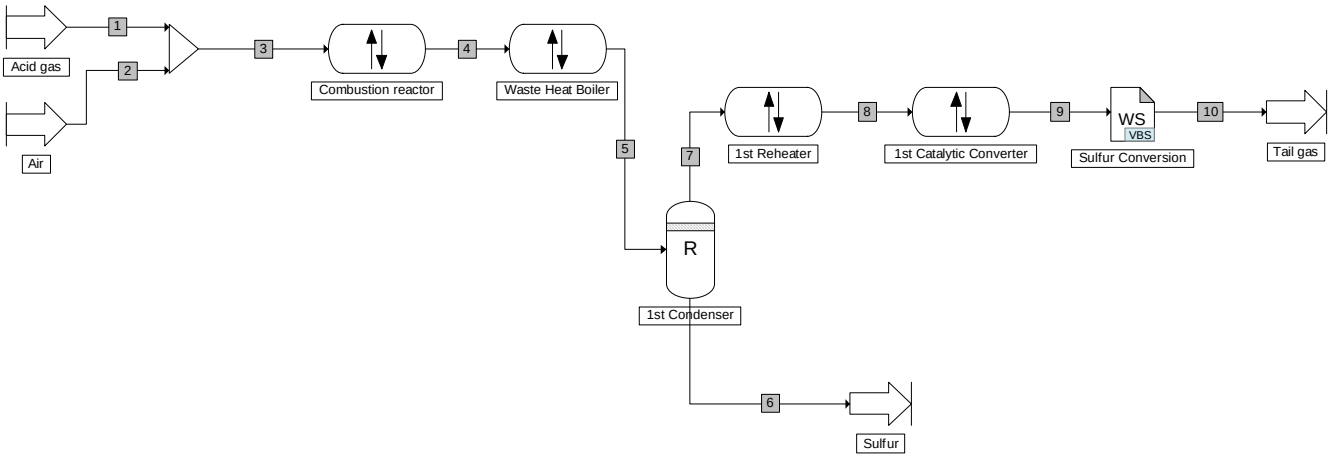
$3\ S_2 \leftrightarrow S_6$

$4\ S_2 \leftrightarrow S_8$

5. 1st reheater (gas phase): it allows the gas preheating to avoid condensation in the catalytic converter. It is simulated with an “Equilibrium reactor” module.

6. 1st catalytic converter (gas phase): simulated with an “Equilibrium reactor” module.

1.2. Process Flowsheet



Process flowsheet

1.3. Components and Thermodynamic Model

The components taken into account in the simulation are:

- Hydrogen sulfide (H_2S)
- Carbon dioxide (CO_2)
- Water (H_2O)
- Methane (CH_4)
- Sulfur dioxide (SO_2)
- Nitrogen (N_2)
- Oxygen (O_2)
- Sulfur species S_2
- Sulfur species S_6
- Sulfur species S_8
- Hydrogen (H_2)
- Carbon monoxide (CO)
- Carbonyl sulfide (COS)
- Carbon disulfide (CS_2)

Pure components properties are available in the ProSim standard database, based on the AIChE's DIPPR® database [2], except for S_2, S_6 and S_8 which were created using data from bibliographic researches, mainly [4], [5]. Properties required for simulations are:

- Chemical formula
- CAS number
- Molar weight
- Vapor pressure
- Perfect gas heat capacity
- Perfect gas enthalpy of formation
- Perfect gas free enthalpy of formation
- Perfect gas absolute entropy

The Ideal thermodynamic profile is used.

1.4. Chemical Reactions

Two-phase units (condenser and possibly waste heat boiler in other Claus process examples) are simulated with reactive two-phase flashes where the equilibrium between the sulfur species is calculated. The equilibrium laws are extracted from [6].

Reaction	*Type*	*Model*	*Law*
4 S_2 <-> S_8	Equilibrium	Fugacity	Ln(K) = -52.559 + 49539/T
3 S_2 <-> S_6	Equilibrium	Fugacity	Ln(K) = -33.876 + 33163/T

1.5. Operating conditions

./ Process feeds

	Acid gas (H_2S)	*Air*
Temperature (°C)	Dew point	82.2
Pression (kPa)	143	143
Partial flow rates (kmol/h)	H_2S: 132.06 CO_2: 70.05 H_2O : 13.50 CH_4: 2.14	N_2: 264.36 O_2: 70.31 H_2O: 9.94

./ Combustion reactor

Operating parameters	*Value*
Reactor type	Equilibrium
Method	Minimization of Gibbs free energy
Components physical state	Vapor
Specification	Adiabatic
Pressure drop (kPa)	11 (specified with « Options… » button)
Inerts	None (specified with « Atomic decomposition » button)

./ Waste Heat Boiler

Operating parameters	*Value*
Reactor type	Equilibrium
Method	Minimization of Gibbs free energy
Components physical state	Vapor
Specification	Equilibrium temperature = 371 °C
Pressure drop (kPa)	0
Inerts	All except S_2, S_6 and S_8

./ 1st Condenser

Operating parameters	*Value*
Unit type	Reactive two-phase flash
Reaction set	Global set
Behavior	Output temperature specified = 177 °C
Pressure drop (kPa)	3.44
Output stream physical state	Diphasic
Method of the residual functions calculation	Logarithmic (specified with « Numerical parameters… » button)

./ 1st Reheater

Operating parameters	*Value*
Reactor type	Equilibrium
Method	Minimization of Gibbs free energy
Components physical state	Vapor
Specification	Equilibrium temperature = 246 °C
Pressure drop (kPa)	3.44
Inerts	All except S_2, S_6 and S_8

./ 1st Catalytic Converter

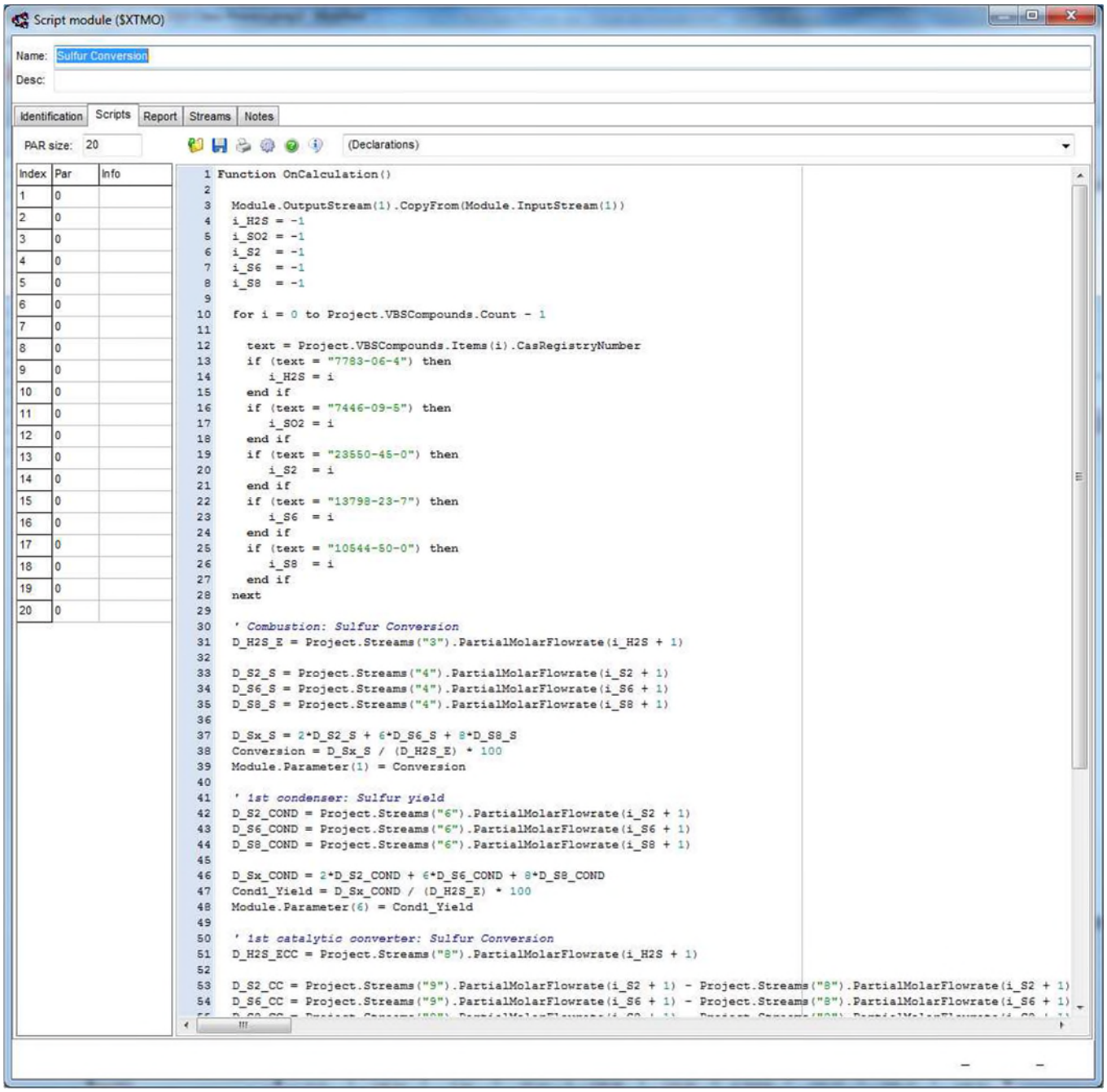
Operating parameters	*Value*
Reactor type	Equilibrium
Method	Minimization of Gibbs free energy
Components physical state	Vapor
Specification	Adiabatic
Pressure drop (kPa)	3.45
Inerts	CO_2, CH_4, N_2, O_2

1.6. Windows Script Module

A Windows Script module “Sulfur Conversion” is added to the flowsheet to calculate:

- H_2S conversion in sulfur species in the combustion reactor and the catalytic converter
- The sulfur yield in the 1st condenser that corresponds to the ratio between the molar flow rate of elemental sulfur in the liquid stream and the molar flow rate of H_2S in the acid gas feed of the plant (stream 1).

The code written to perform these calculations can be viewed (and modified if needed) in the appropriate window:



2. RESULTS

The table below presents the mass and energy balances obtained.

Streams		1	2	3	4	5	6	7	8	9	10
Partial flows		kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h	kmol/h
	H2S	132.0600	0.0000	132.0600	21.8834	21.8834	0.0022	21.8811	21.8811	4.4148	4.4148
	CO2	70.0500	0.0000	70.0500	62.3477	62.3477	0.0016	62.3461	62.3461	62.3461	62.3461
	H2O	13.5000	9.9400	23.4400	128.8537	128.8537	0.3840	128.4697	128.4697	145.9360	145.9360
	CH4	2.1400	0.0000	2.1400	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	SO2	0.0000	0.0000	0.0000	20.3852	20.3852	0.0055	20.3798	20.3798	11.6466	11.6466
	N2	0.0000	264.3600	264.3600	264.3600	264.3600	0.0000	264.3600	264.3600	264.3600	264.3600
	O2	0.0000	70.3100	70.3100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	S2	0.0000	0.0000	0.0000	44.4140	0.9628	0.0000	0.0000	0.0046	0.0624	0.0624
	S6	0.0000	0.0000	0.0000	0.0000	5.1254	0.3828	0.0136	0.1442	1.3273	1.3273
	S8	0.0000	0.0000	0.0000	0.0000	7.0188	10.4351	0.3711	0.2720	2.6451	2.6451
	H2	0.0000	0.0000	0.0000	9.0429	9.0429	0.0000	9.0429	9.0429	9.0429	9.0429
	CO	0.0000	0.0000	0.0000	8.8807	8.8807	0.0000	8.8807	8.8807	8.8807	8.8807
	COS	0.0000	0.0000	0.0000	0.9597	0.9597	0.0001	0.9596	0.9596	0.9596	0.9596
	CS2	0.0000	0.0000	0.0000	0.0018	0.0018	0.0000	0.0018	0.0018	0.0018	0.0018
Total flow	kmol/h	217.7500	344.6100	562.3600	561.1292	529.8222	11.2114	516.7065	516.7426	511.6235	511.6235
Physical state		Vapor	Vapor	Vapor	Vapor	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor
Temperature	℃	44.10	82.20	65.62	1094.05	371.00	177 .00	177.00	246.00	294.95	294.95
Pressure	kPa	143.00	143.00	143.00	132.00	132.00	128.56	128.56	125.12	121.67	121.67
Enthalpic flow	kJ/h	147177	578598	725776	22210133	6643366	-644931	2568417	3772943	4677686	4677686

The results in terms of conversion and yield calculated in the Windows Script module are as follows:

- Sulfur conversion in the combustion reactor: 67.26 %
- Sulfur conversion in the 1st catalytic converter: 79.82 %
- Sulfur yield in the 1st condenser: 64.95 %

3. REFERENCES

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