PROSIMPLUS APPLICATION EXAMPLE

PRODUCTION AND VALORIZATION OF BIOGAS PRODUCED BY METHANIZATION

EXAMPLE PURPOSE
This example presents the simulation of a methanization process producing biogas. The produced biogas is upgraded and used to generate steam with a boiler.

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CORRESPONDING PROSIMPLUS FILES	*PSPS_EX_EN-Production-and-valorisation-biogaz-methanisation-water-absorption.pmp3* *PSPS_EX_EN-Production-and-valorisation-biogaz-methanisation-amines-absorption.pmp3*

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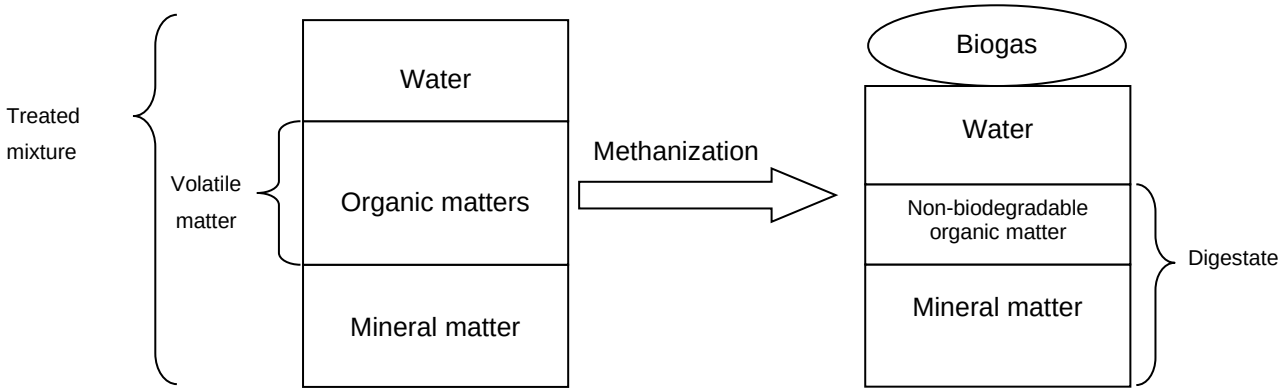
1. PROCESS MODELING

1.1. Process description

Methanization is a process which produces biogas from organic matter.



Volatile matter (VM) is the organic part of the treated mixture, *i.e.,* the components capable of producing biogas. The treated mixture is composed of all the components entering the "Methanization reactor".

This material is, once placed in anaerobic digesters (deprived of oxygen), broken down by micro-organism to form biogas, consisting mainly of methane (CH_4) and carbon dioxide (CO_2) and digestate (organic or inorganic material remaining after the anaerobic digestion).

However, the biogas contains several pollutants, including sulfur compounds, organo-halogens, VOCs.

In order to improve the biogas quality (biogas upgrading), it is usually purified to remove these undesired substances. The main reason of this biogas upgrading is to avoid corrosive phenomena and mechanical wear of the downstream equipment.

The biogas can be used in different ways: heat production (combustion in a boiler), electricity production (gas boiler with a steam turbine, fuel engine, and gas turbine), cogeneration (production of electricity and wasted heat recovery), and production of fuel or even gas grid injection.

The treatment of municipal waste by anaerobic digestion started at industrial scale in 1988 with the world's first installation in Amiens (France), treating 80 000 t/year of household waste and using a digester developed by the Valorga company. Since then, improvements in the quality of collected and/or sorted waste has allowed a significant development of this technology in Europe and around the world [APE07].

The Valorga process is based on anaerobic treatment of wet organic waste. The process is composed of an upstream input sorted by a waste-sorting line in order to eliminate as much undesirable products as possible (metals, scrap iron, glass, etc.). A boiler is powered downstream to produce steam with the biogas. The process treats 110 000 t/year of waste, 30 000 t/year of which are removed by sorting. In the end, 80 000 t/year of waste is treated in the digesters ([ROB21] and [VAL21]).

This example presents the valorization of the gas, by heat production with a boiler.

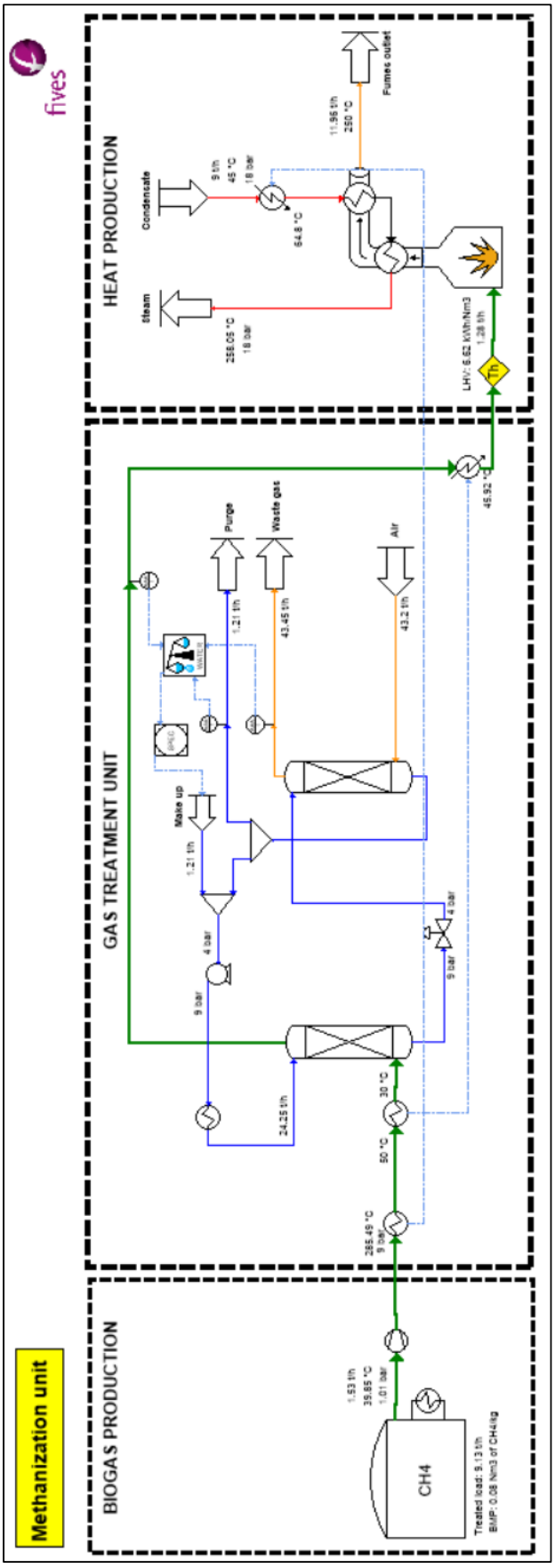
In this context, the process is separated into 3 parts:

- ✓ A part for biogas production;
- ✓ A part for biogas treatment (biogas upgrading);
- ✓ A part for heat production.

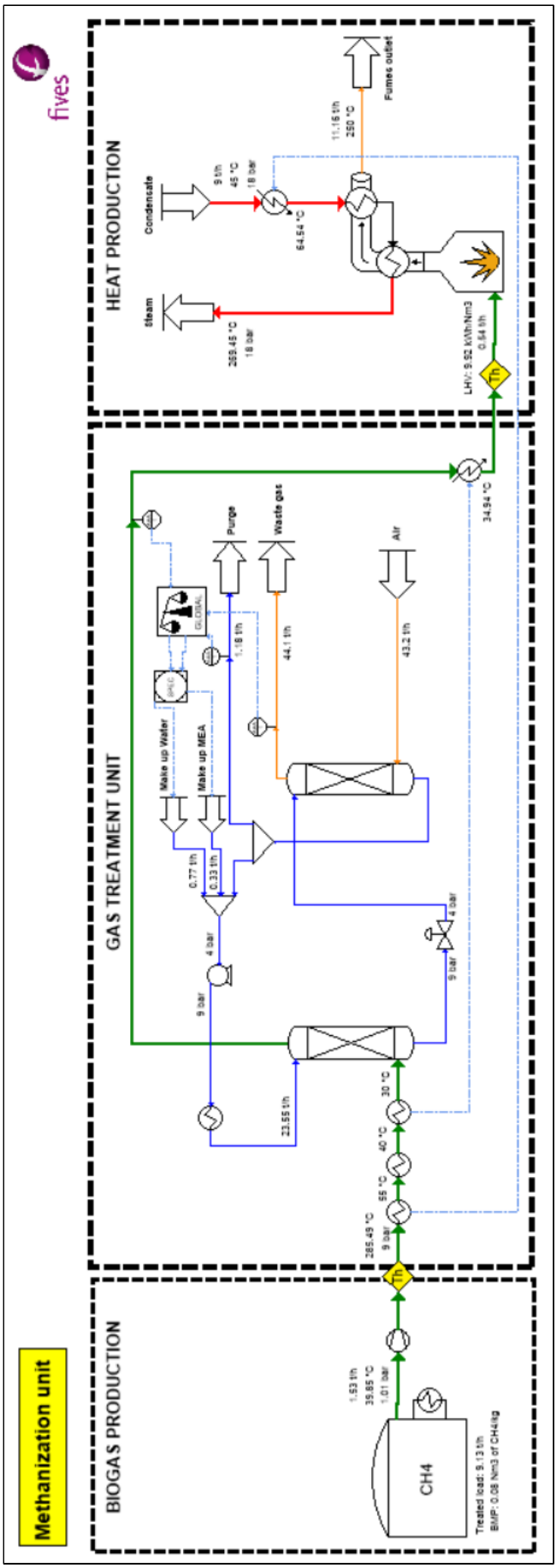
This example also presents 2 upgrading methods for the treatment of the biogas:

- ✓ Absorption-desorption treatment with water (water washing);
- ✓ Absorption-desorption treatment with a mixture of monoethanolamine (MEA) and water (amine gas treatment).

1.2. Simulation flowsheets



Simulation process with water treatment



Simulation process with amines treatment

1.3. Components

The components taken into account in the simulation are listed in the table below, as well as their chemical formula and their CAS numbers[1]. The properties of pure substances are taken from the standard database of ProSim [WIL21].

Component	Chemical formula	CAS number (1)
Water	H_2O	7732-18-5
Oxygen	O_2	7782-44-7
Hydrogen	H_2	1333-74-0
Nitrogen	N_2	7727-37-9
Carbon dioxide	CO_2	124-38-9
Methane	CH_4	74-82-8
Ammonia	NH_3	7664-41-7
Hydrogen sulfide	H_2S	7783-06-4
Sulphur dioxide	SO_2	7446-09-5
Nitric oxide	NO	10102-43-9
Nitrogen dioxide	NO_2	10102-44-0
Carbon monoxide	CO	630-08-0
Sulphur trioxide	SO_3	7446-11-9
Monoethanolamine	C_2H_7NO	141-43-5

[1] *CAS Registry Numbers® are the intellectual property of the American Chemical Society and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.*

1.4. Thermodynamic model

Four thermodynamic “calculator” are defined to simulate this example:

- “Process”: this calculator contains all the components defined above except hydrogen and sulfur trioxide. It is used for the biogas production and its treatment sections (water absorption only). “PSRK” profile is selected.
- "Fumes": this calculator contains all the components defined previously except nitrogen dioxide. It is specifically used for the heat production part. The thermodynamic model selected is the “Ideal” profile.
- "Utility": this calculator is only used for the water streams through the boiler. Therefore, the "pure water" model is selected.
- “Amine treatment”: this calculator contains all the components defined previously except hydrogen and sulfur trioxide. It is used for the gas treatment part for the amine absorption case. The “Amines and acid gases” thermodynamic profile is used.

1.5. Operating conditions

1.5.1. "Biogas production" section

✓ Methanization reactor "Methanization reactor"

Mass compositions on dry (%)	
Carbon	44.5
Hydrogen	5
Oxygen	10
Nitrogen	0.4
Sulfur	0.1
Water	45
Manganese	40
Mass flowrate (kg/h)	9129.6
Inlet pressure (atm)	1

Treated waste flow = 80 000 t/year = 9.13 t/h (operating 365 days/year, 24 hours/day).

✓ Generalized compressor "Compressor"

Type of compressor	$Isentropic$
Exhaust pressure (bar)	9
Isentropic efficiency	0.7
Mechanical efficiency	0.8
Electrical efficiency	0.9

1.5.2. "Gas treatment" section

1.5.2.1. Water absorption case

✓ Feeds

Name:	Make up	Air
Fractions:	**mass**	**molar**
Water	1	0
Oxygen	0	0.21
Nitrogen	0	0.79
Carbon dioxide	0	0
Methane	0	0
Ammonia	0	0
Hydrogen sulfide	0	0
Nitric oxide	0	0
Nitrogen dioxide	0	0
Mass flowrate (kg/h)	10	43200
Temperature (°C)	25	25
Pressure (bar)	4	1.01325

The "Make up" feed flowrate is initialized at 10 kg/h. This flowrate is an action variable of the "Constraints and recycles" module described in the following paragraphs.

✓ Coolers/Heaters

Name	Outlet temperature (°C)
HEX 1	50
HEX 2	30
HEX 3	7

✓ Stream splitter "Splitter"

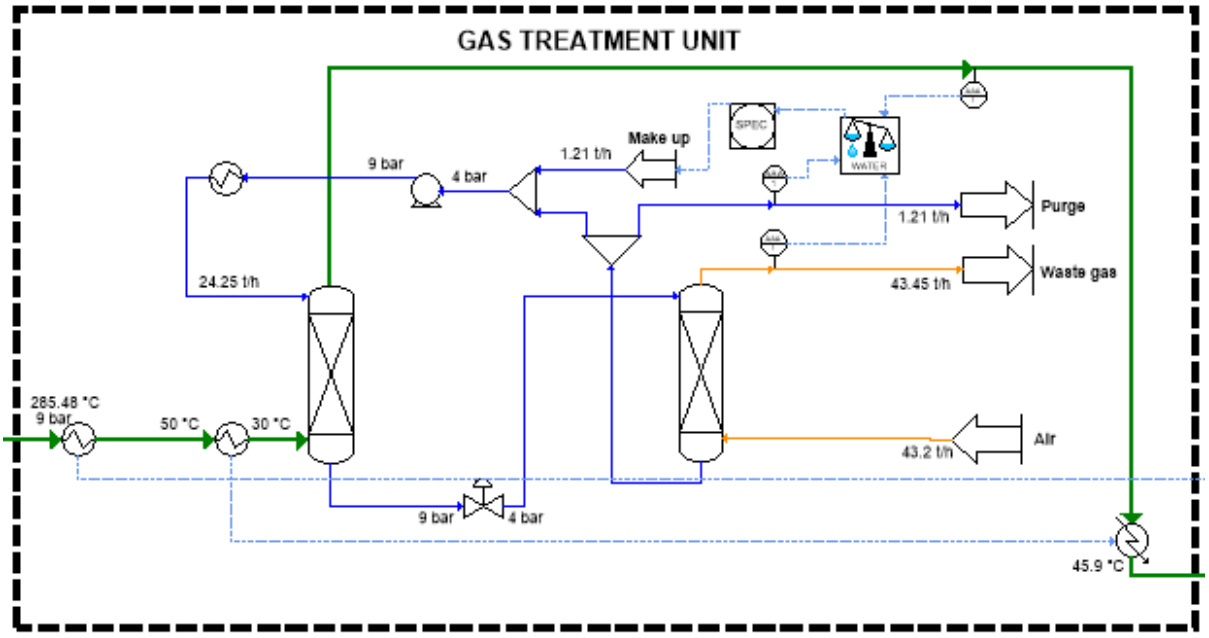
Supplied specification	*Splitting ratio*
Splitting ratio	0.95
Automatically calculated stream	*stream entering into the mixer*

✓ Centrifugal pump “pump”

Supplied specification	*Pressure*
Exhaust pressure (bar)	9
Volumetric efficiency	0.65
Mechanical efficiency	0.9
Electrical efficiency	0.98

✓ Water balance “Water balance”

Inlet		**Outlet**	
From	**To**	**From**	**To**
HEX 1	HEX 2	Water flowrate 2	Waste gas
Make up	Mixer	Water flowrate 3	Purge
Air	Stripper	Absorber	Water flowrate



✓ Columns

Name	*Absorber*	*Stripper*
Number of stages	10	10
Pressure (bar)	9	4
Stages efficiency	1	1

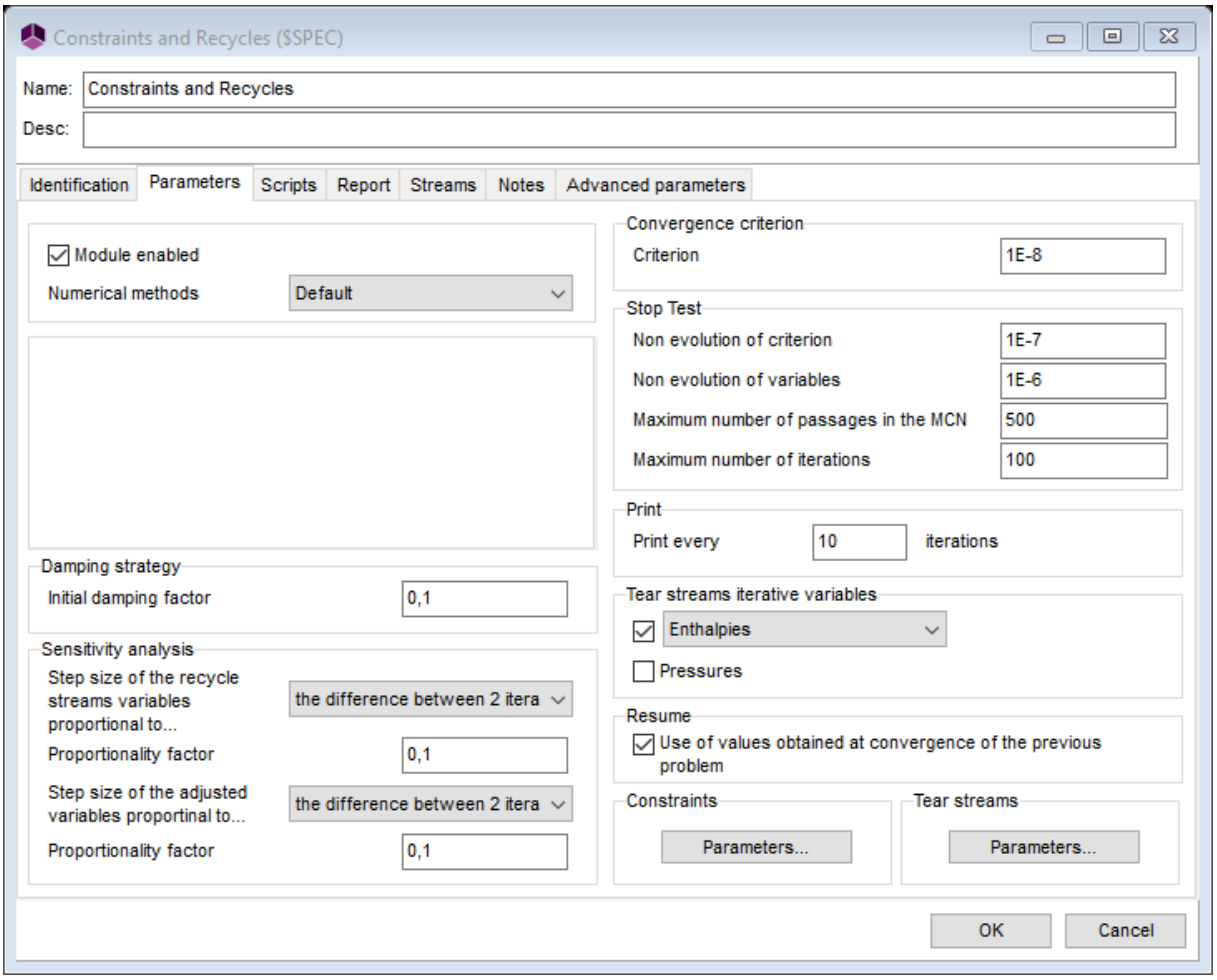
✓ Expansion valve “Valve”

Constraint type	*Pressure specification*
Pressure specification (bar)	4

✓ Simple heat exchanger “HEX2-bis”

Heat duty (kcal/h)	Transferred (information stream) from HEX2

✓ Management of constraints and recycle (SPEC). The “Constraints and Recycles” module is necessary in order to adjust the make-up flowrate. The configuration of this module is as described below.



The value of the initial damping factor has been changed from 1 to 0.1 to ensure convergence of the simulation file.

This “Constraints and Recycles” (SPEC) gets the deviation between the water inlets and outlets calculated with the "Water balance" module and adjusts the "Make up" feed water flowrate in order to determine the water make up.

1.5.2.2. Amine treatment case

It should be noted that a more detailed example about CO_2 treatment with aqueous solution of alkanolamines is available in the ProSimPlus examples library. This detailed example is named: "PSPS_E19_EN_CO2-capture-with-amine-process.pmp3".

✓ Calculator Switch

Thermodynamic model	"*Amine treatment*"

✓ Feeds

Name:	**Make up Water**	**Make up MEA**	**Air**
Fractions:	**mass**	**mass**	**mole**
Water	1	0	0
Oxygen	0	0	0.21
Nitrogen	0	0	0.79
Carbon dioxide	0	0	0
Methane	0	0	0
Ammonia	0	0	0
Hydrogen sulfide	0	0	0
Nitric oxide	0	0	0
Nitrogen dioxide	0	0	0
Monoethanolamine	0	1	0
Mass flowrate (kg/h)	725	320	43200
Temperature (°C)	25	25	25
Pressure (bar)	4	4	1.01325

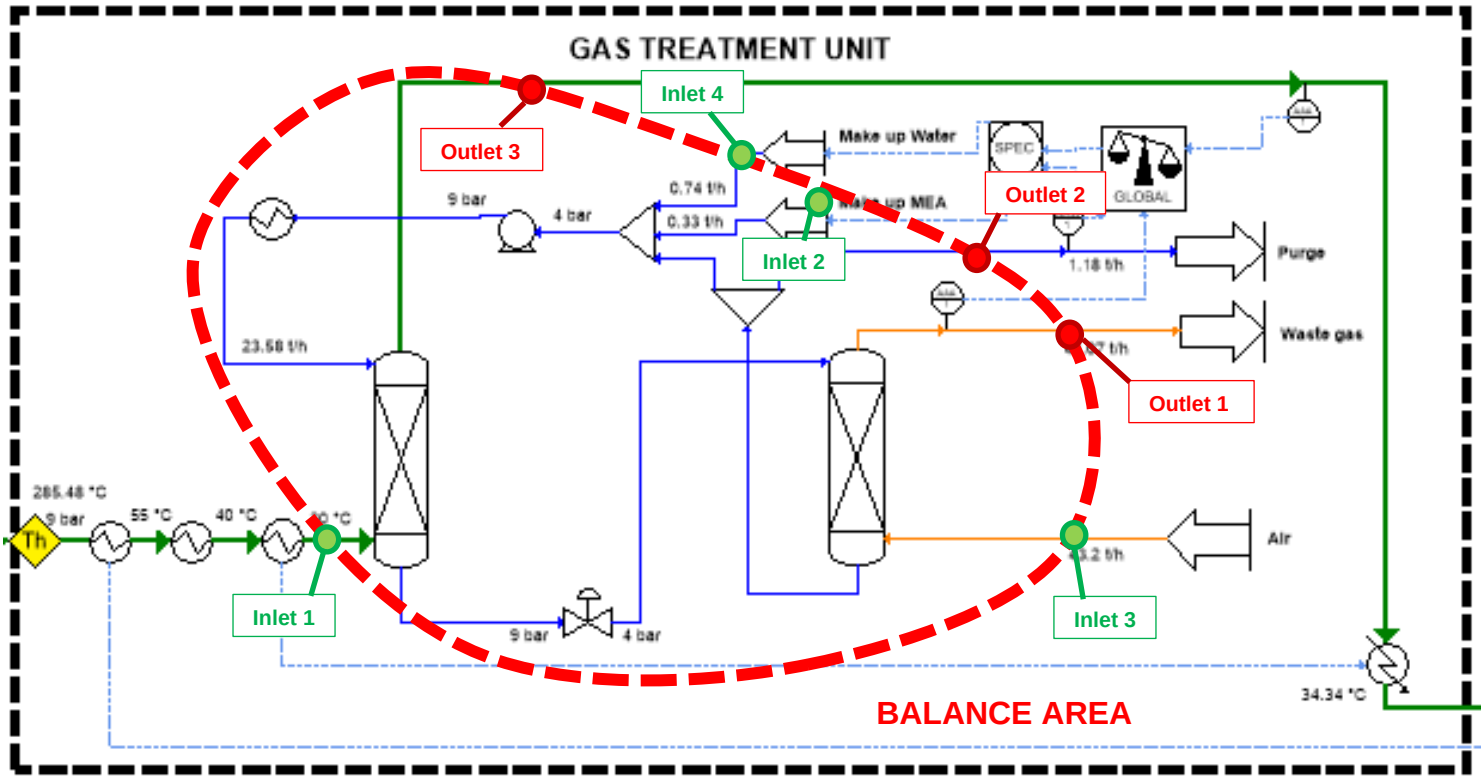
The "Make up Water" and "Make up MEA" feed flowrates are respectively initialized at 725 kg/h and 320 kg/h. These flowrates are action variables of the “Constraints and recycles” module, as described in the following paragraphs.

✓ Coolers/Heaters

Name	Outlet temperature (°C)
HEX 1	55
HEX 2	30
HEX 3	7
HEX 4	40

✓ Generalized balance “Generalized balance”

Inlet		Outlet	
From	**To**	**From**	**To**
HEX 2	Absorber	Water flowrate 2	Waste gas
Make up MEA	Mixer	Water flowrate 3	Purge
Air	Stripper	Absorber	Water flowrate
Make up water	Mixer		



- ✓ Simple heat exchanger “HEX2-bis”

Heat duty (kcal/h)	Transferred (information stream) from HEX2

The “Splitter”, “Pump”, “Absorbers”, “Valve” and “Constraints and Recycles” modules are configured with the same parameters as in the water treatment case. The module “Contraints and recycles” gets the deviation between water and monoethanolamine (MEA) inlets and outlets calculated with the “Generalized balance” and adjusts the “Make up water” and “Make up MEA” feeds flowrates in order to determine the water and monoethanolamine make-ups.

1.5.3. "Heat production" section

✓ Feed

Name:	**Condensate**
Molar fractions:	
Water	1
Oxygen	0
Nitrogen	0
Carbon dioxide	0
Methane	0
Ammonia	0
Hydrogen sulfide	0
Nitric oxide	0
Nitrogen dioxide	0
Mass flowrate (kg/h)	9000
Temperature (°C)	45
Pressure (bar)	18

✓ Calculator Switch

Thermodynamic model	"*Fumes*"

✓ Boiler "Boiler"

Exchanger type	*Pure counter current*
Fumes temperature at the outlet of the unit provided (°C)	250
Combustive type	*Air*
% mass content of O_2 in fumes at the combustion outlet	3
Inlet pressure (atm)	1

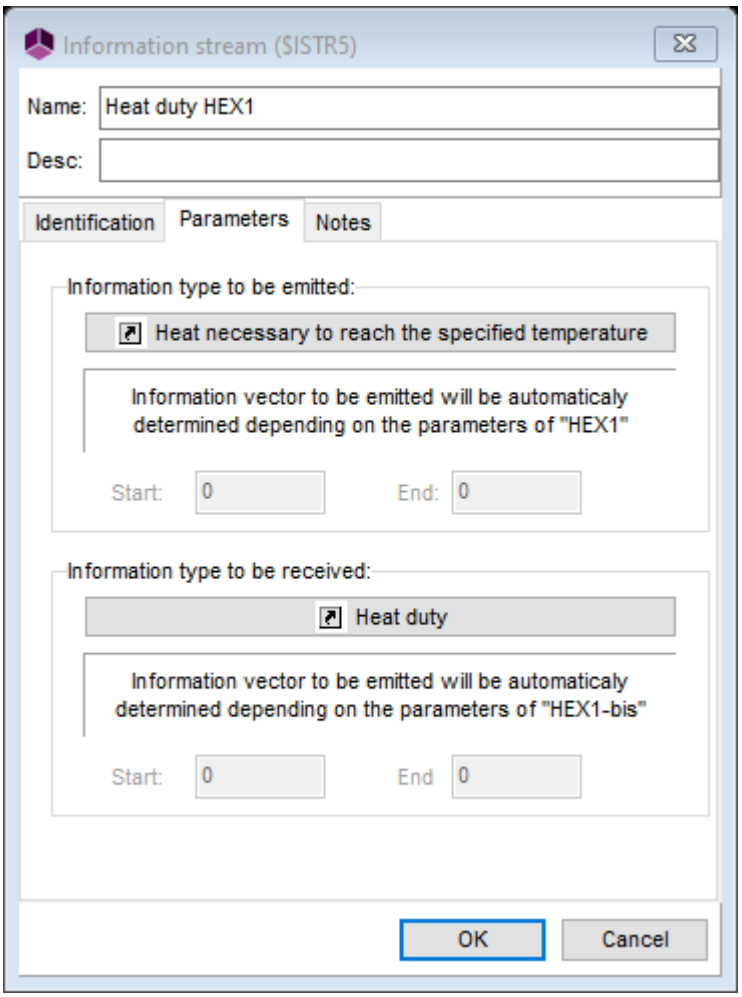
✓ Simple heat exchanger "HEX1-bis"

Heat duty (kcal/h)	Transferred (information stream) from HEX1

Note: All mixers are configured with default values (outlet pressure is the lowest of all feeds).

1.5.4. Heat recovery

The 2 coolers/heaters of the "Gas treatment unit" part are connected to 2 simple heat exchangers by information streams. These information streams are used to transfer the heat duties calculated by the coolers to heat the biogas and the condensates of the boiler. The streams are configured as below:



1.6. Initialization

1.6.1. Water treatment case

The calculation sequence is automatically determined by ProSimPlus. A tear stream is detected: the material stream "16" (pump outlet upstream of the absorber). The following initialization is used:

Material stream	16
Mass flowrate (kg/h)	
Water	25 500

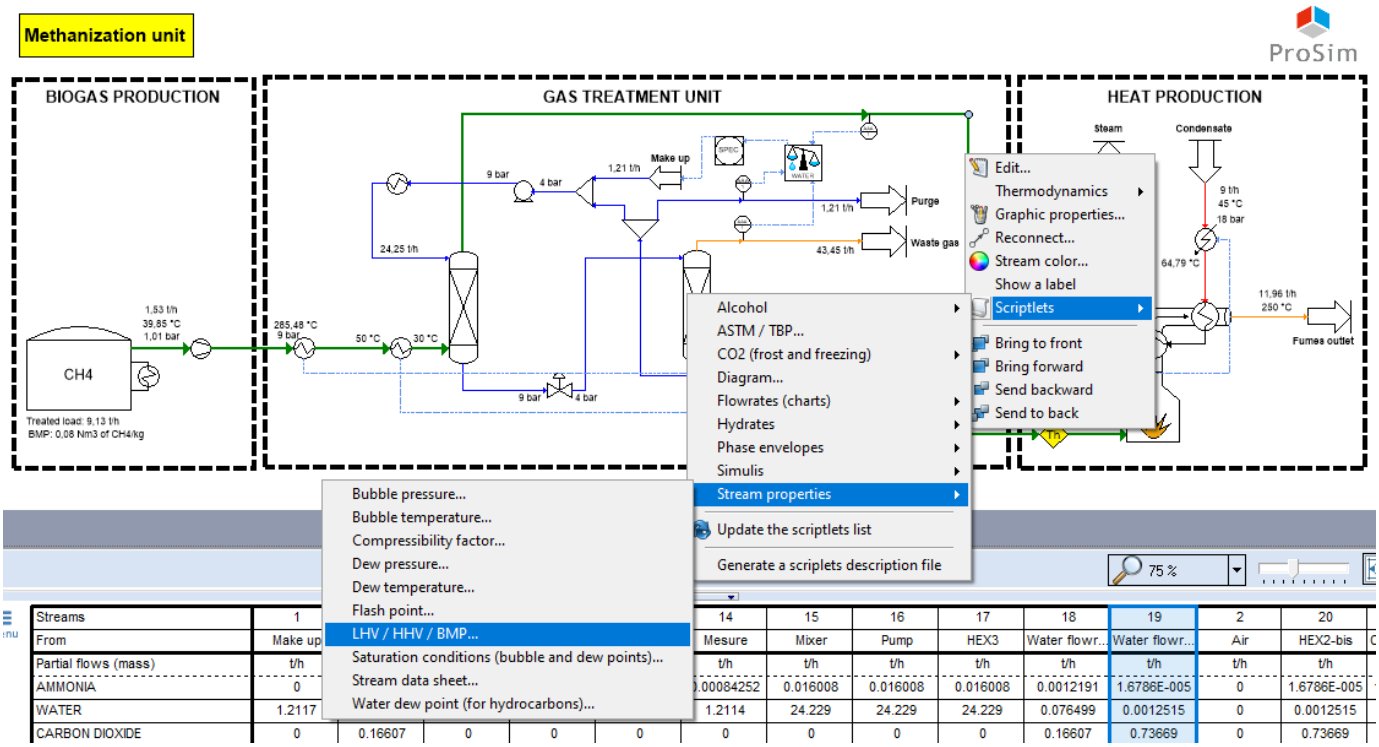
1.6.2. Amine treatment case

The calculation sequence is automatically determined by ProSimPlus. A tear stream is detected: the material stream "19" (pump output upstream of the absorber). The following initialization is used:

Material stream	19
Mass flowrate (kg/h)	
Water	819.09
Oxygen	$1.76 * 10^{-2}$
Nitrogen	$3.05 * 10^{-2}$
Carbon dioxide	50.24
Methane	0
Ammonia	1,93
Hydrogen sulfide	$4.75 * 10^{-5}$
Nitric oxide	0
Nitrogen dioxide	0
Monoethanolamine	108.21

1.7. “Tips and tricks”

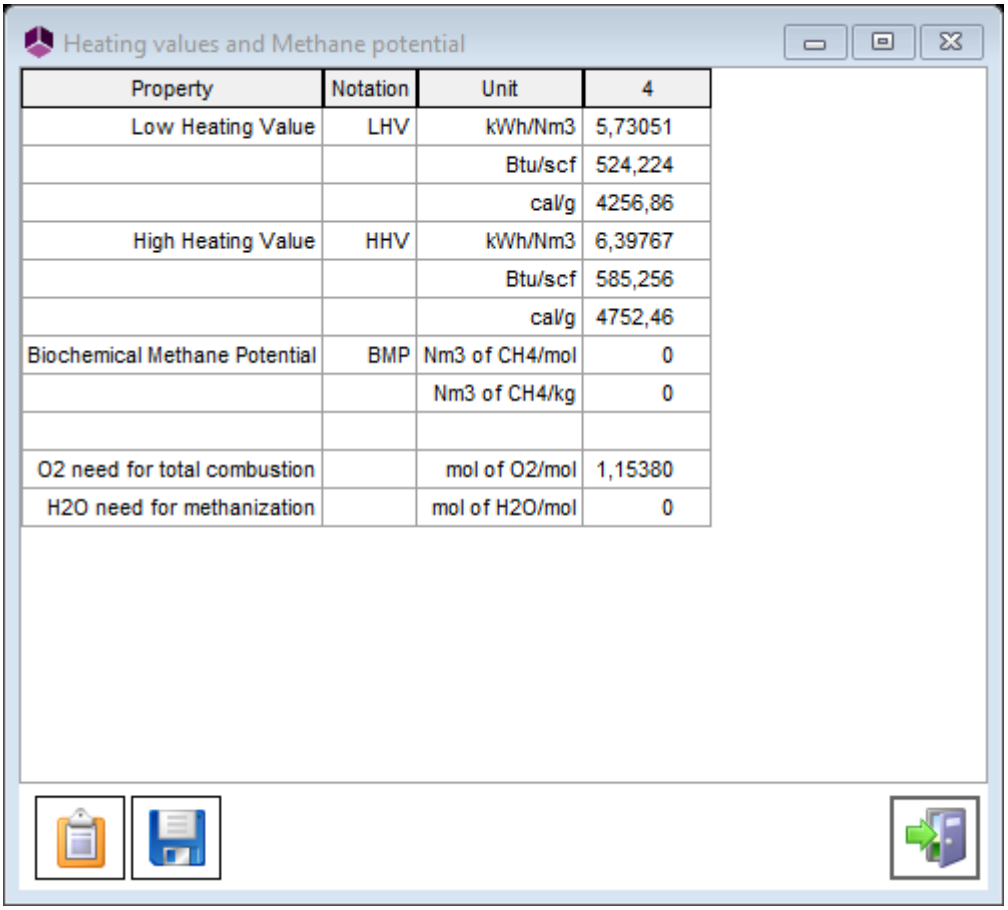
1.7.1. LHV calculation



Streams	1					14	15	16	17	18	19	2	20
From	Make up					Mesure	Mixer	Pump	HEX3	Water flowr...	Water flowr...	Air	HEX2-bis
Partial flows (mass)	t/h					t/h	t/h	t/h	t/h	t/h	t/h	t/h	t/h
AMMONIA	0					0.00084252	0.016008	0.016008	0.016008	0.0012191	1.6786E-005	0	1.6786E-005
WATER	1.2117					1.2114	24.229	24.229	24.229	0.076499	0.0012515	0	0.0012515
CARBON DIOXIDE	0	0.16607	0	0	0	0	0	0	0	0.16607	0.73669	0	0.73669

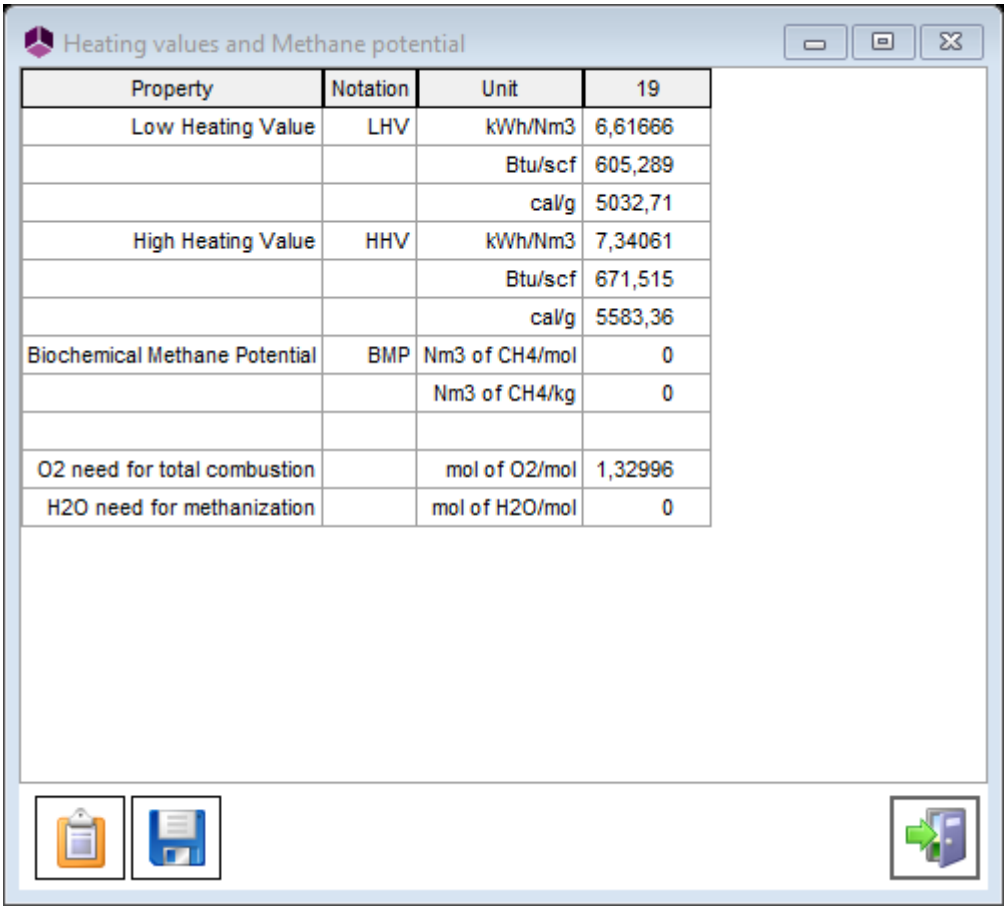
The scriptlet “LHV / HHV / BMP” is used to compute the Lower Heating Value (LHV, amount of heat released by the complete combustion of a fuel under normal atmospheric pressure) of the biogas from the digester and the biogas after treatment.

Biogas heating value before treatment:



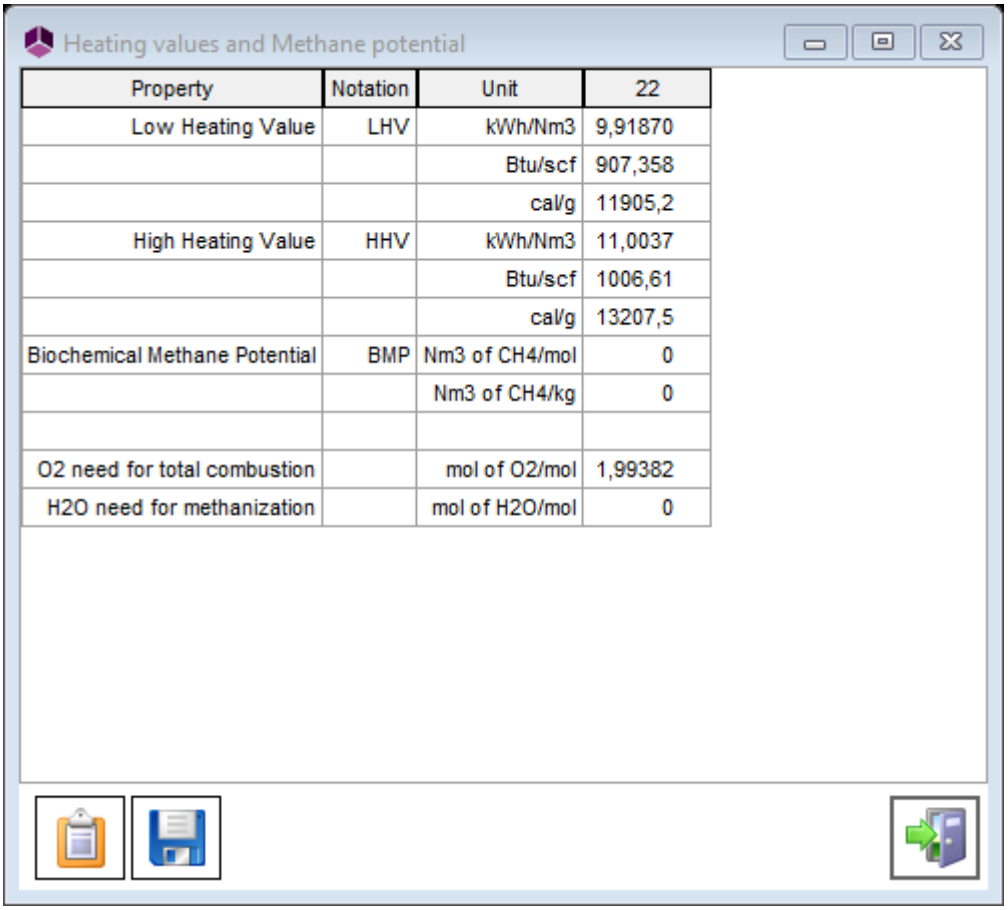
Property	Notation	Unit	4
Low Heating Value	LHV	kWh/Nm3	5,73051
		Btu/scf	524,224
		cal/g	4256,86
High Heating Value	HHV	kWh/Nm3	6,39767
		Btu/scf	585,256
		cal/g	4752,46
Biochemical Methane Potential	BMP	Nm3 of CH4/mol	0
		Nm3 of CH4/kg	0
O2 need for total combustion		mol of O2/mol	1,15380
H2O need for methanization		mol of H2O/mol	0

Biogas heating value after treatment with water:



Property	Notation	Unit	19
Low Heating Value	LHV	kWh/Nm3	6,61666
		Btu/scf	605,289
		cal/g	5032,71
High Heating Value	HHV	kWh/Nm3	7,34061
		Btu/scf	671,515
		cal/g	5583,36
Biochemical Methane Potential	BMP	Nm3 of CH4/mol	0
		Nm3 of CH4/kg	0
O2 need for total combustion		mol of O2/mol	1,32996
H2O need for methanization		mol of H2O/mol	0

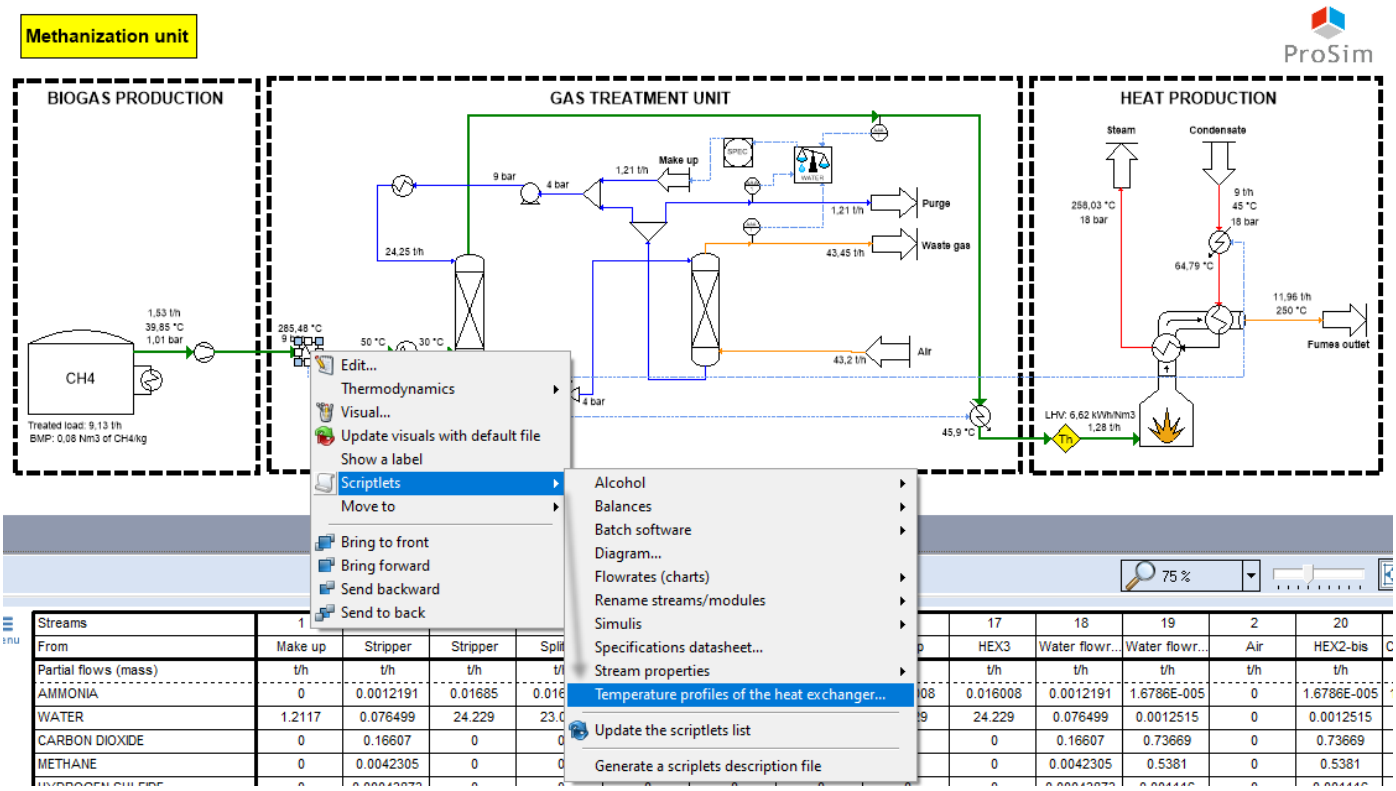
Biogas heating value after treatment with amines:



Property	Notation	Unit	22
Low Heating Value	LHV	kWh/Nm3	9,91870
		Btu/scf	907,358
		cal/g	11905,2
High Heating Value	HHV	kWh/Nm3	11,0037
		Btu/scf	1006,61
		cal/g	13207,5
Biochemical Methane Potential	BMP	Nm3 of CH4/mol	0
		Nm3 of CH4/kg	0
O2 need for total combustion		mol of O2/mol	1,99382
H2O need for methanization		mol of H2O/mol	0

The biogas heating value is better after treatment because the methane composition is higher (the treatment removed unwanted components and also part of the carbon dioxide). The LHV is even higher for the amine absorption case; this treatment is more efficient (because the amine absorption is more selective to the carbon dioxide).

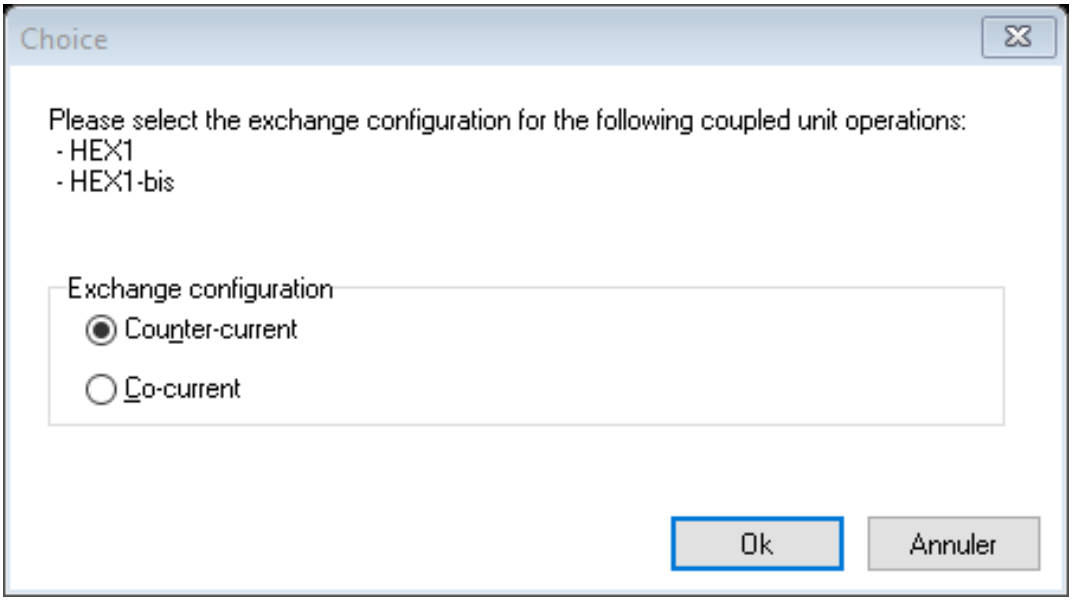
1.7.2. Temperature profiles



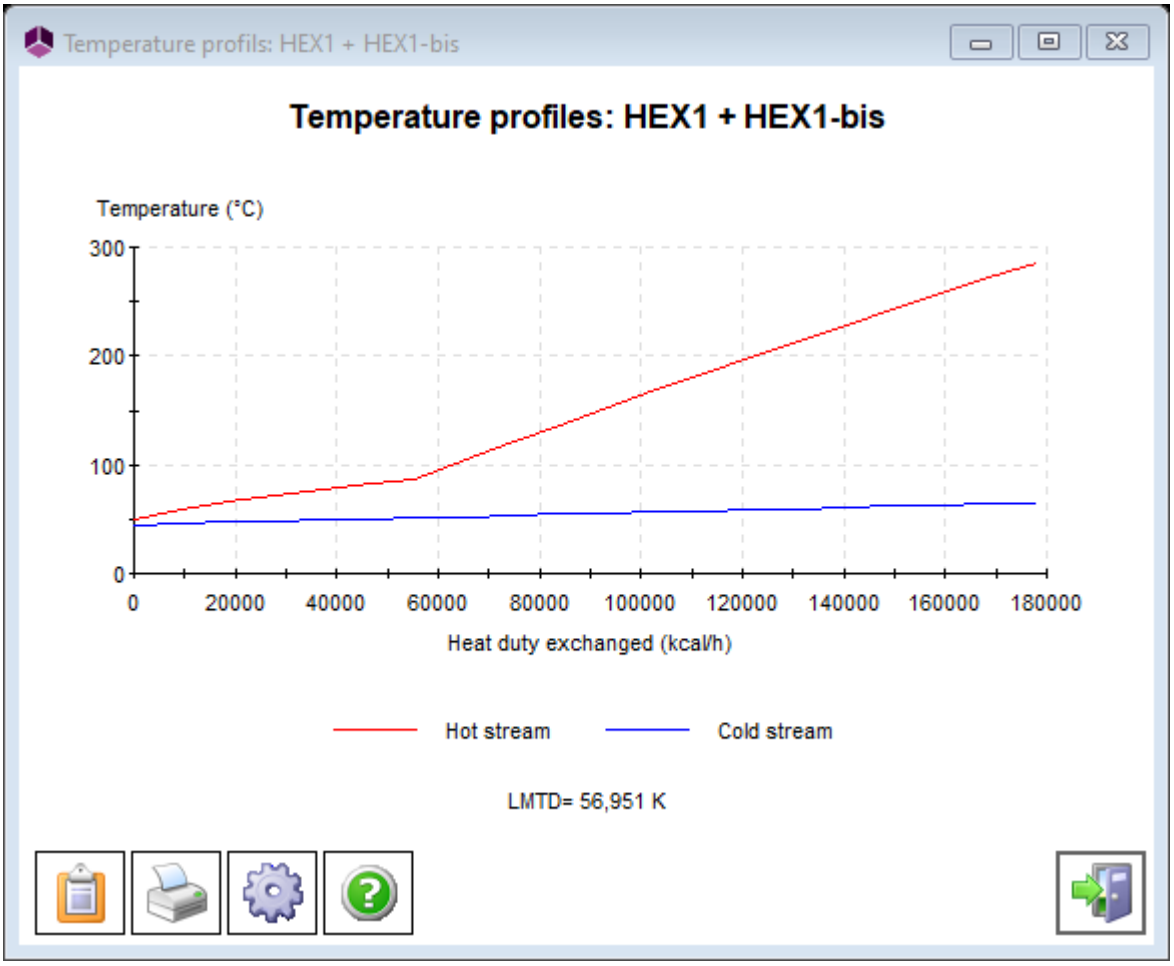
Streams	1					17	18	19	2	20
From	Make up	Stripper	Stripper	Split		HEX3	Water flowr...	Water flowr...	Air	HEX2-bis
Partial flows (mass)	t/h	t/h	t/h	t/		t/h	t/h	t/h	t/h	t/h
AMMONIA	0	0.0012191	0.01685	0.016		0.016008	0.0012191	1.6786E-005	0	1.6786E-005
WATER	1.2117	0.076499	24.229	23.0		24.229	0.076499	0.0012515	0	0.0012515
CARBON DIOXIDE	0	0.16607	0	0		0	0.16607	0.73669	0	0.73669
METHANE	0	0.0042305	0	0		0	0.0042305	0.5381	0	0.5381

This second scriptlet allows to obtain the heat exchangers temperature profiles. The simulation of a "cooler/heater – Simple heat exchanger" association (modules linked by an information stream transferring the exchanged heat duty) is the same as the simulation of a generalized heat exchanger. It is therefore possible to compare the temperature profiles of the hot source and the cold source.

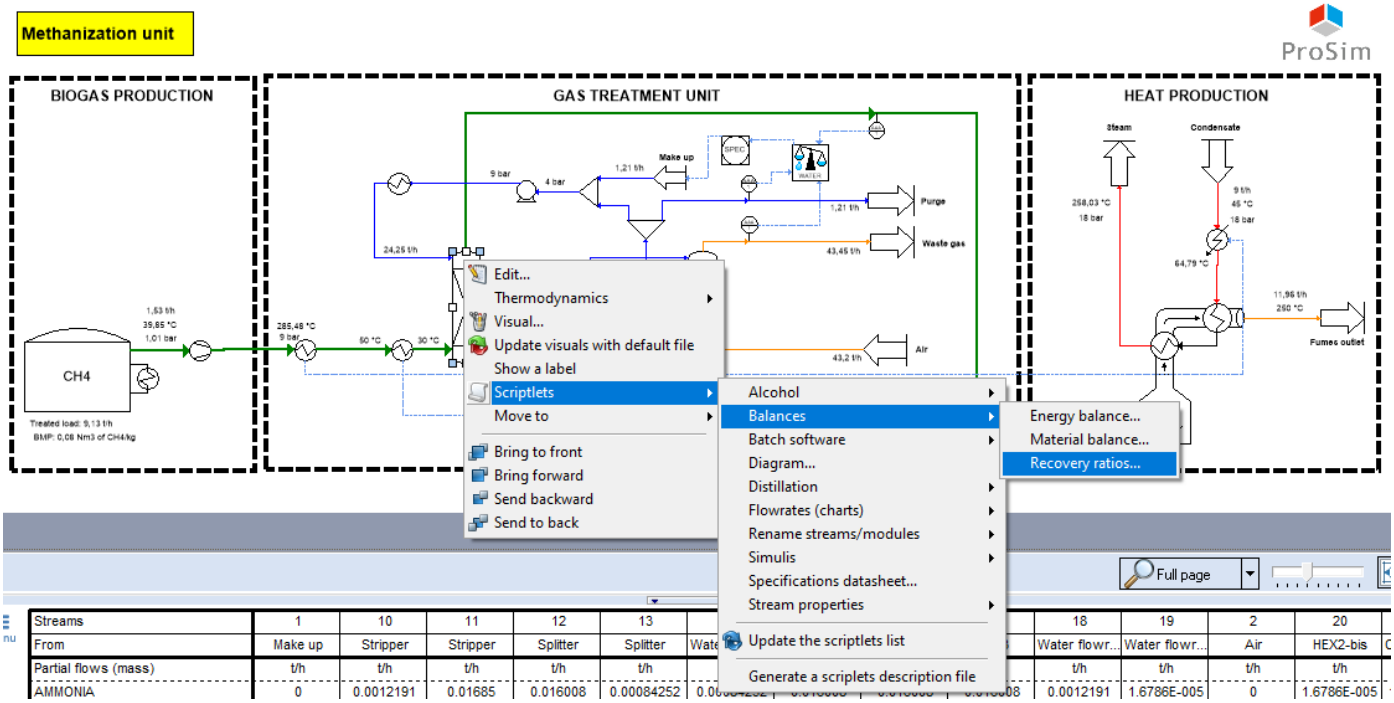
First, the exchanger type must be chosen. This one is in a counter-current configuration:



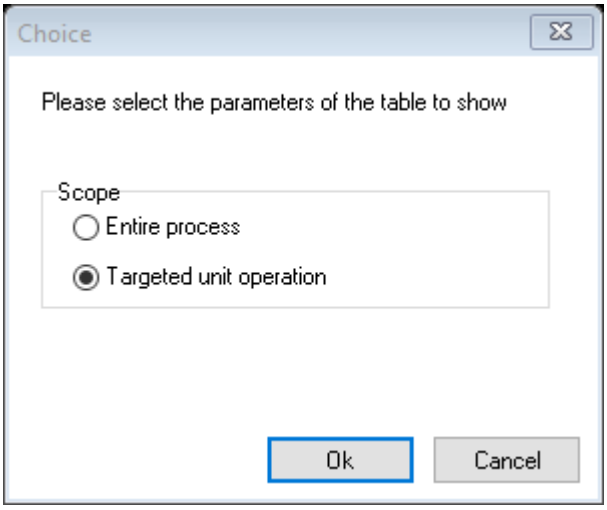
The following temperature profile is obtained:



1.7.3. Recovery ratios



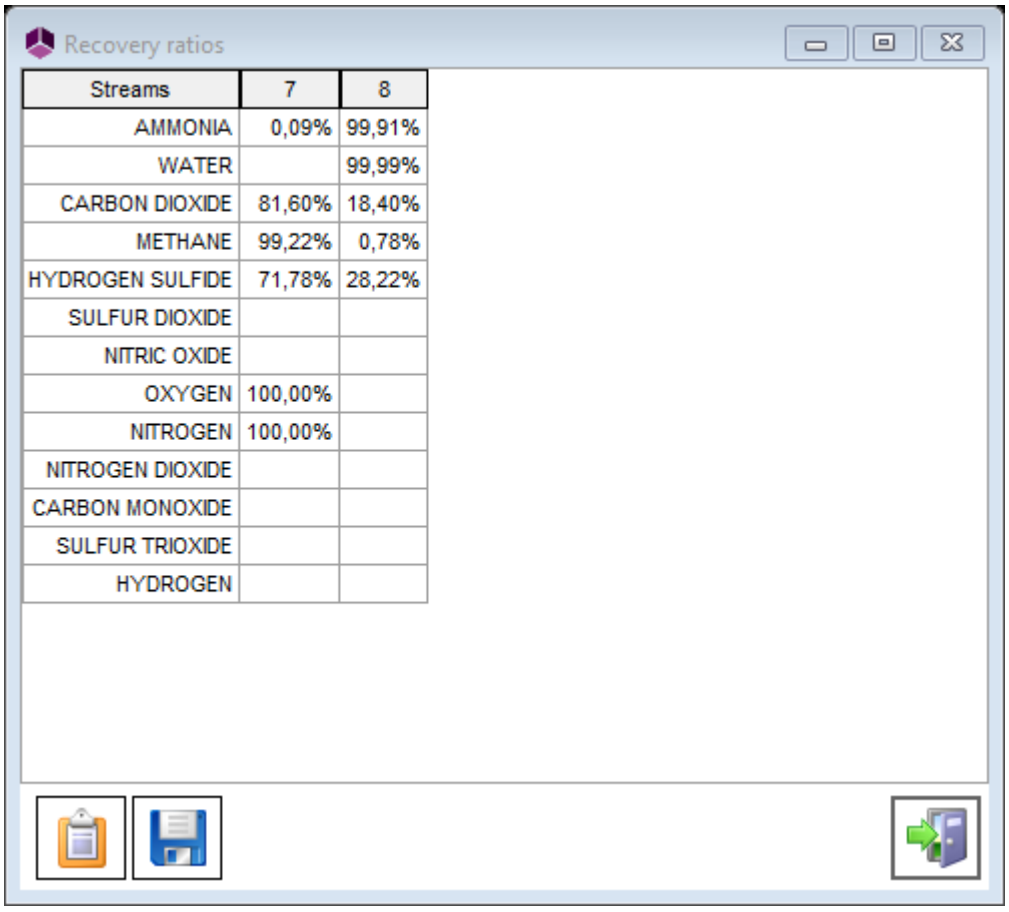
This scriptlet calculates the columns recovery ratios.



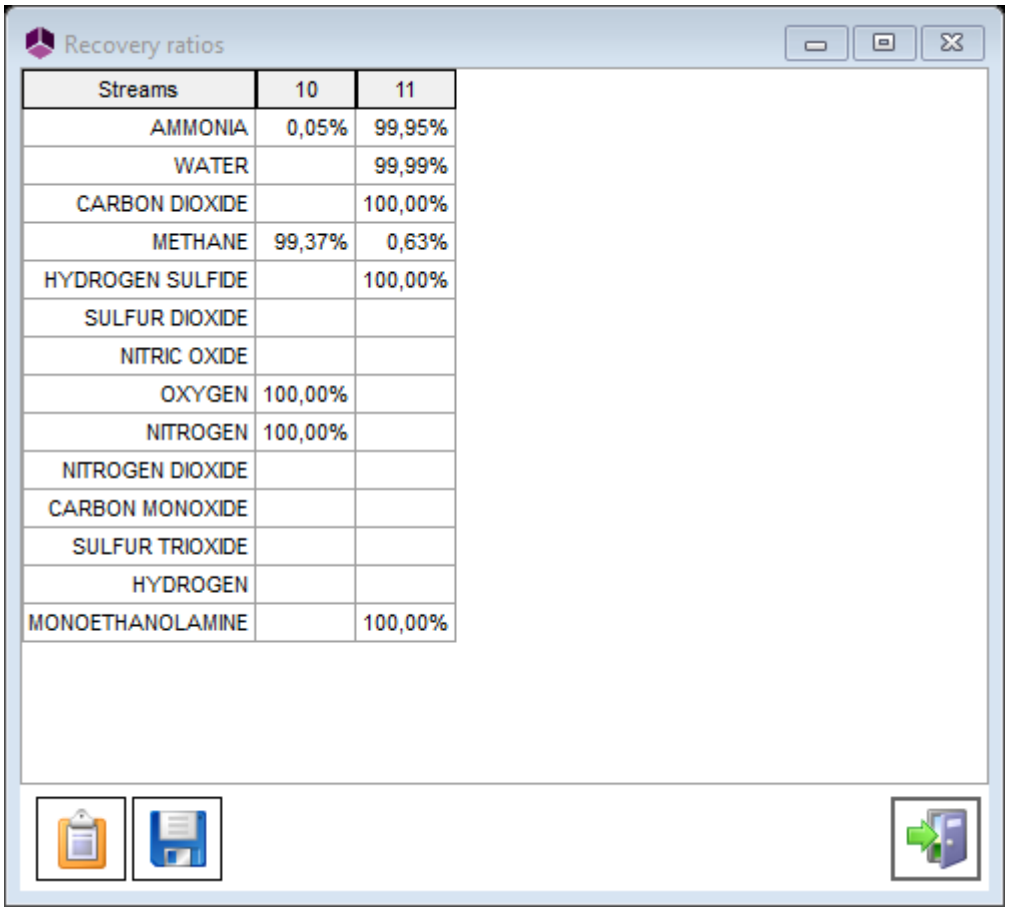
It is possible to calculate the recovery ratios on the overall process or on a targeted unit operation.

The recovery ratios are obtained for each stream and each compound, as shown in the window below.

Here the scriptlet is used to calculate the recovery ratios for the "Absorber" module for the water treatment case, and then for the amine treatment case.



Streams	7	8
AMMONIA	0,09%	99,91%
WATER		99,99%
CARBON DIOXIDE	81,60%	18,40%
METHANE	99,22%	0,78%
HYDROGEN SULFIDE	71,78%	28,22%
SULFUR DIOXIDE		
NITRIC OXIDE		
OXYGEN	100,00%	
NITROGEN	100,00%	
NITROGEN DIOXIDE		
CARBON MONOXIDE		
SULFUR TRIOXIDE		
HYDROGEN		



Streams	10	11
AMMONIA	0,05%	99,95%
WATER		99,99%
CARBON DIOXIDE		100,00%
METHANE	99,37%	0,63%
HYDROGEN SULFIDE		100,00%
SULFUR DIOXIDE		
NITRIC OXIDE		
OXYGEN	100,00%	
NITROGEN	100,00%	
NITROGEN DIOXIDE		
CARBON MONOXIDE		
SULFUR TRIOXIDE		
HYDROGEN		
MONOETHANOLAMINE		100,00%

2. RESULTS

2.1. Process Performance

Simulation results	
CH_4 yield (Nm^3 of CH_4/t of inlet VM)	251
Biogas yield (Nm^3 of biogas/t of inlet treated load)	144
Overall conversion rate	0.29
COD slaughter rate	0.29

2.2. Biogas properties

2.2.1. Water absorption case

	Before treatment	After treatment
Mass fractions:		
Ammonia	$1.36 * 10^{-3}$	$1{,}3 * 10^{-5}$
Water	0.05	$9.8 * 10^{-4}$
Carbon dioxide	0.59	0.58
Methane	0.35	0.42
Hydrogen sulfide	$1.02 * 10^{-3}$	$8.7 * 10^{-4}$
LHV of the biogas (kWh/Nm^3)	5.73	6.62

2.2.2. Amine absorption case

	Before treatment	After treatment
Mass fractions:		
Ammonia	$1.36 * 10^{-3}$	$3{,}0 * 10^{-5}$
Water	0.05	$1.45 * 10^{-3}$
Carbon dioxide	0.59	$1.22 * 10^{-4}$
Methane	0.35	0.996
Hydrogen sulfide	$1.02 * 10^{-3}$	0
LHV of the biogas (kWh/Nm^3)	5.73	9.92

2.3. Digestate properties

The simulated digestate flowrate is 7.6 t/h and 45% moisture (mass). This digestate is then pressed to obtain:

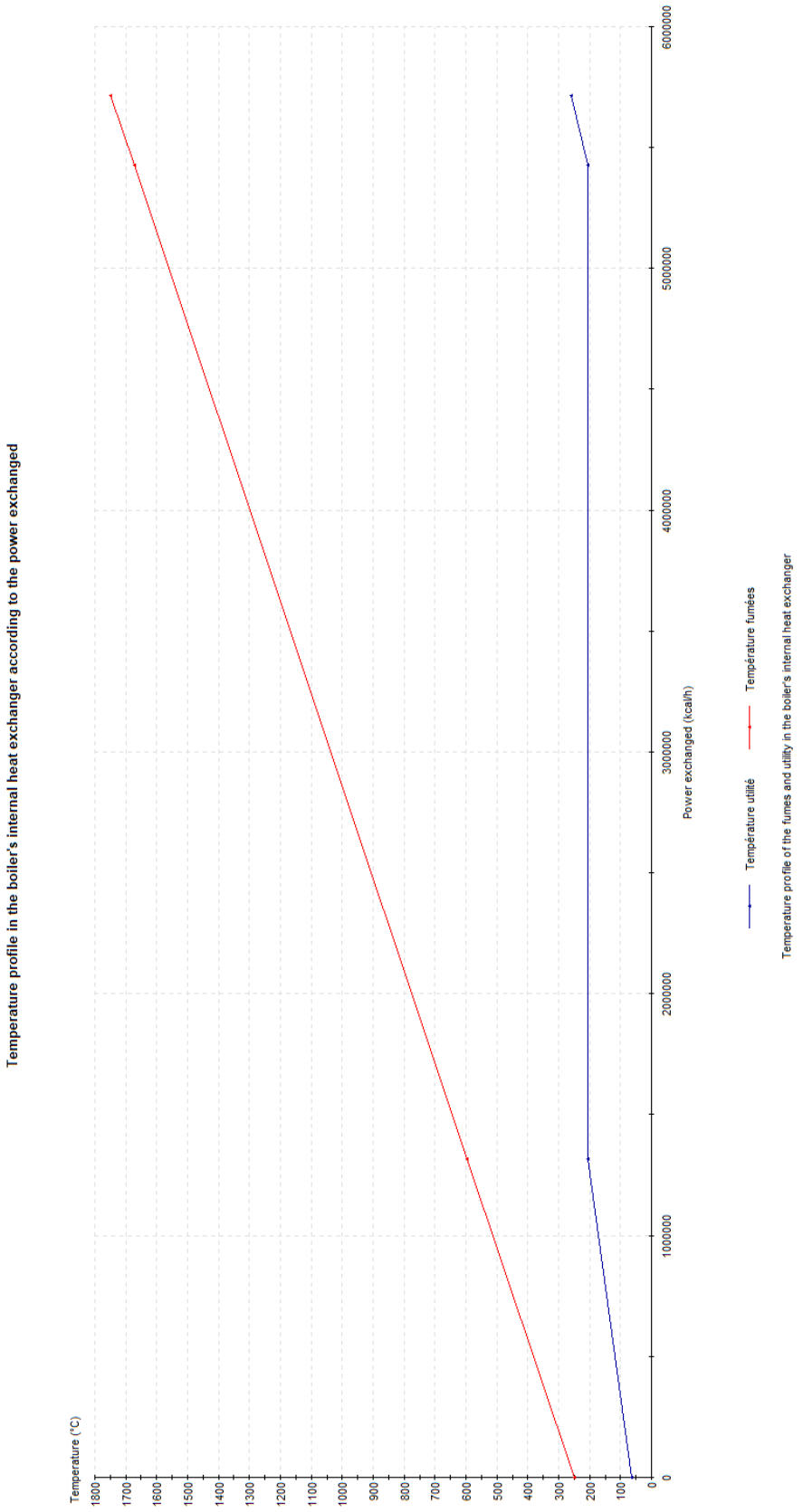
- A stream of juice (2.8 t/h or 24 500 t/year).
- An affinate stream (4.8 t/h, 0.5 t/h of water and 4.3 t/h of undegraded material, or 42 000 t/year).

For this example, the stream of digestate from the methanizer was not simulated. The information above is available in the “Methanization reactor” module report.

2.4. Boiler properties

Steam output mass flowrate (t/h)	9
Steam outlet temperature (°C)	258 (water treatment) / 269°C (amines treatment)
Outlet temperature (°C)	250
Steam outlet pressure (bar)	18
Overall useful power (MW)	6.64

The temperature profile in the boiler's internal heat exchanger according to the power exchanged:



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