ProSim

PROSIMPLUS APPLICATION EXAMPLE

METHANOL SYNTHESIS

EXAMPLE PURPOSE
This example illustrates the synthesis of methanol from a syngas. The syngas can be provided by a gasifier (e.g. "PSPS_E28_EN - IGCC Plant"). The different steps are modeled: syngas compression reaction, flash purification and then final distillation purification of the methanol produced. The synthesis reactor is modelled using Gibbs energy minimization. The particular points which are detailed in this example are the use of a Gibbs reactor, the modeling of the distillation column condenser as an outside unit operation and the use of a "Calculator Switch" to change the thermodynamic model in some part of the process.

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CORRESPONDING PROSIMPLUS FILE	*PSPS_E27_EN - Methanol synthesis.pmp3*

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1. MODELING OF THE PROCESS

1.1. Process description

Nowadays, methanol is one of the most consumed commodities around the world with a 70 million tons annual demand [DEM13]. Its main applications are as fuel, additive or reactant in the fine chemical industry, but others are emerging such as hydrogen carrier for fuel cell technology applications or denitrification agent for wastewater treatment. It can be made from any renewable biomass hydrocarbon source by partial oxidation in an oxygen-blown gasifier to produce synthesis gas, which is then converted into methanol. See ProSimPlus example "PSPS_E28_EN - IGCC Plant" to have an example of syngas production through a gasifier.

The flowsheet of the process is shown on paragraph 1.2. Synthesis gas at 51.2 bar is compressed in a two-stage compression system to 110 bar (unit K101, E101 and K102). The fresh feed is mostly hydrogen, carbon dioxide, and carbon monoxide, but it also contains small amounts of methane, water and nitrogen. The inert components must be purged out of the system. Three recycle gas streams are added "16", "21" and "28". The total gas stream is heated first by the reactor effluent and finally by the E102 heat exchanger. The reactions take place in the packed tubular reactor R101. The reactor is cooled to maintain a temperature of 267°C. Methanol from syngas synthesis involves hydrogenation of CO (1) and CO_2 (2) and reversed water-gas shift reactions (3):

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{R@298\,K} = -90.55\ kJ/mol \qquad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{R@298\,K} = -49.43\ kJ/mol \qquad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{R@298\,K} = +41.12\ kJ/mol \qquad (3)$$

Several kinetics can be found in literature for this reactive system (e.g. [LUY10], [DEM13]). In this example, the reactions are supposed to be at the chemical equilibrium, which is computed by minimizing the Gibbs energy of the system. This approach is an "ideal" case, the resulting methanol production is the theoretical one. To go further it's possible to describe Langmuir-Hinshelwood reactions in ProSimPlus:

$$r = \frac{k\left(\prod_{i=1}^{N_{reactant}} A_i^{\alpha_i} - \frac{1}{K}\prod_{j=1}^{N_{product}} A_j^{\alpha_j}\right)}{\left(K_c + \sum_{i=1}^{NC} k_i A_i^{d_i}\right)^{N_{site}}}$$

For more complex kinetics, the user-defined kinetics capability of ProSimPlus can be used.

After, the reactor effluent is cooled to 38°C (heat exchangers E102 and E104) and partially condensed. The vapor and liquid phases of the stream are separated in a tank operating at 106.5 bar and 38°C. Most of the vapor stream is compressed back up to 110 bar and recycled. A small fraction (2.2%) is vented off. This is where the inert methane and nitrogen in the synthesis gas fresh feed are removed from the system.

The liquid from the separator F102 contains significant amounts of light components because of the high pressure in the separator (106.5 bar). If this stream were fed directly into the distillation column, these inert components would build up in the condenser and blanket the condenser. Either a high pressure or a low temperature would be needed in the condenser, which may require the use of expensive refrigeration. Therefore, the flash tank F102 is used to remove most of the light components before feeding into the distillation column C101. The flash tank F102 is operated at 2 bar. The gas from the flash F102 is compressed to 110 bar and recycled to the reactor.

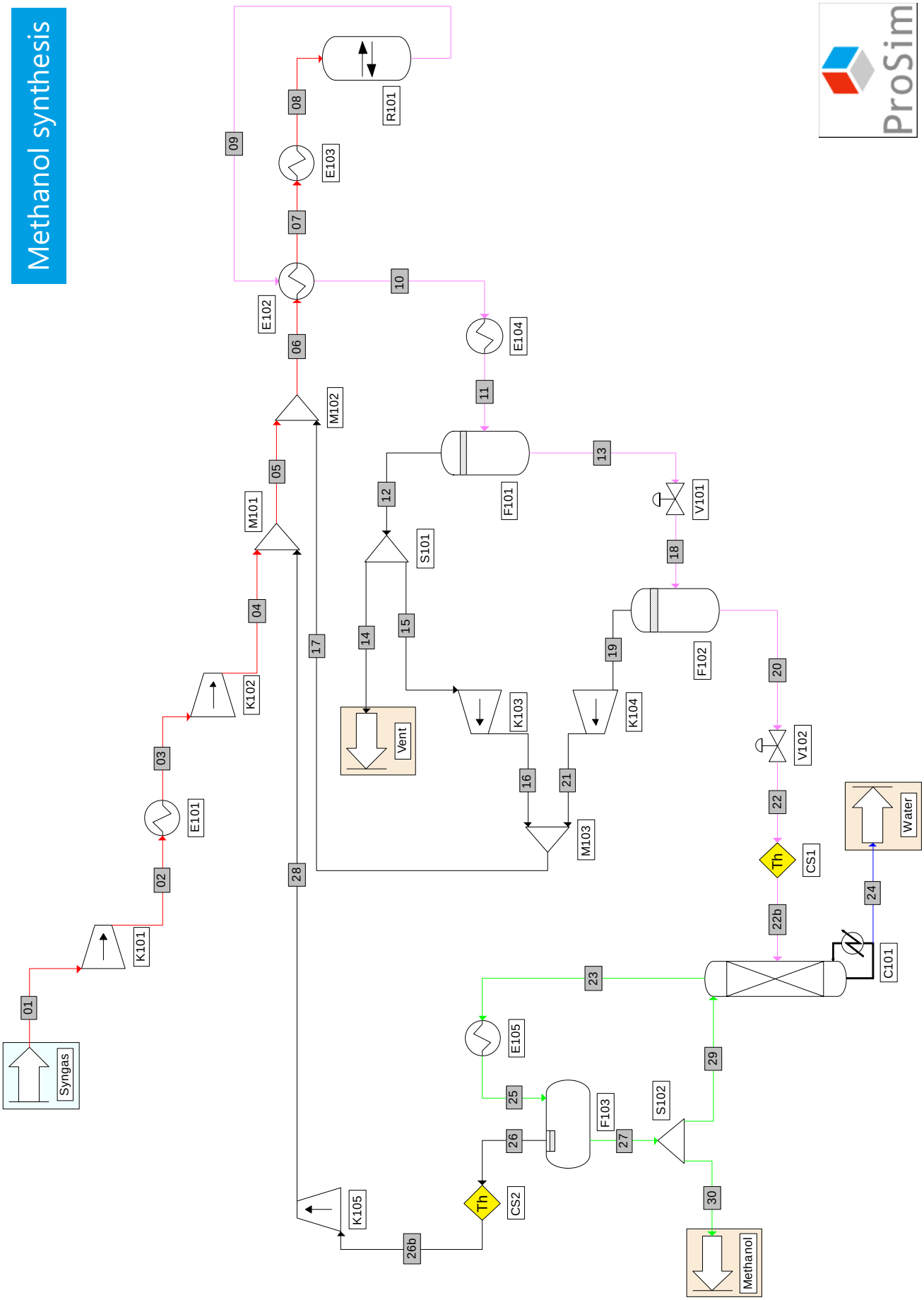
The liquid from the flash tank F102 is pumped into the distillation column C101 (42-stages, feed on stage 27). This column operates at 1 bar. Its objective is to obtain dehydrated methanol with few lights in it. There are three specifications in this column:

- ✓ 0.01 mol % of methanol at the bottoms,
- ✓ 0.1 mol % of water at the liquid distillate,
- ✓ Reflux-drum temperature at 50°C, which establishes the amount of vapor that must be removed from the top of the reflux drum for compression and recycle.

The condenser of the column is modeled as a separated unit operation: heat exchanger E105, reflux drum F103 and splitter S102. By this way it's easier to control the temperature of the condenser.

This example is adapted from [LUY10] and [DEM13].

1.2. Process flowsheet



1.3. Components

Components taken into account in the simulation, their chemical formula and CAS numbers are presented in the following table. Pure components physical properties are extracted from the ProSimPlus standard database [ROW17].

Component name	Chemical formula	CAS number
Hydrogen	H_2	1333-74-0
Nitrogen	N_2	7727-37-9
Carbon monoxide	CO	630-08-0
Carbon dioxide	CO_2	124-38-9
Methane	CH_4	74-82-8
Methanol	CH_4O	67-56-1
Water	H_2O	7732-18-5

1.4. Thermodynamic models

Considering the temperature and pressure conditions of this process and that polar components are also present (methanol, water), a EoS/G^E combined model, PSRK [HOL91], [GME95], [CHE02], has been chosen. This model is a predictive model based on group contributions. This model is used for all the process except the column and the unit operations used to model its condenser (E105, F103, S102).

For the column and the unit operations used to model its condenser (E105, F103, S102), given the polar nature of major components (water, methanol) and the pressure level (1 bar), the activity coefficient model NRTL [REN68] is chosen. Water-methanol binary interaction parameters come from the database provided with ProSimPlus.

1.5. Operating conditions

1.5.1. Process feed

	Syngas
Mole fraction (-)	
Hydrogen	0.6746
Nitrogen	0.0031
Carbon monoxide	0.2297
Carbon dioxide	0.0686
Methane	0.0217
Water	0.0023
Total flow rate (kmol/h)	11 450
Temperature (°C)	50
Pressure (bar)	51.2

1.5.2. R101 reactor

Operating parameters	Value
Reactor type	Gibbs
Method	Minimization of Gibbs free energy
Components physical state	Vapor
Specification	Equilibrium temperature
Equilibrium temperature (°C)	267
Equilibrium pressure (bar)	107,5
Inert compounds	Nitrogen Methane

1.5.3. Heat exchangers

✓ Cooler/Heater

	E101	E103	E104	E105
Operating parameters	**Value**			
Outlet temperature (°C)	Dew temperature	150	38	50

	Select the NRTL thermodynamic model for the E105 cooler/heater.

✓ E102 generalized heat exchanger

Operating parameters	Value
Specification	Cold stream outlet temperature
Outlet temperature (°C)	145

1.5.4. Compressors

	K101	K102	K103	K104	K105
Operating parameters	**Value**				
Exhaust pressure (bar)	75	110	110	110	110
Isentropic efficiency	0.77	0.94	0.81	0.74	0.80
Mechanical efficiency	1				
Electrical efficiency	1				

1.5.5. Flashs

	F101	F102	F103
Operating parameters	**Value**		
Type	Constant pressure and enthalpy flash		
Pressure	The lowest of the feed streams		
Heat duty	Adiabatic		

	Select the NRTL thermodynamic model for the F103 flash.

1.5.6. Expansion valves

	V101	V102
Operating parameters	**Value**	
Outlet pressure (bar)	2	1

1.5.7. Calculator switch

This module is used to change the thermodynamic model from:

- ✓ PSRK, defined as the default calculator, (the one used in most of the process) to NRTL (the one used in the column and the unit operations used to model its condenser) for the CS1 calculator switch,
- ✓ NRTL to PSRK for the CS2 calculator switch.

The calculation of the enthalpies being not the same between these two models, the use of a “Calculator switch” module is necessary in order to not distort the enthalpy balance.

	CS1	CS2
Operating parameters	**Value**	
Thermodynamic model	NRTL	PSRK
Outlet physical state	Calculated	

1.5.8. C101 distillation column

Operating parameters	Value
Type	Absorber with a reboiler
Number of stages	41
Feed stage	26
Overhead vapor flow rate (kmol/h)	5 900
Pressure drop (bar)	0.4
Objectives/Constraints Specification Adjusted variable	 0.01 %mol. of methanol in the bottom stream Vapor distillate flow rate

	Select the NRTL thermodynamic model for the C101 distillation column.

	The value of the overhead vapor flow rate is automatically adjusted to reach the defined specification.

1.5.9. Stream splitters

	Operating parameters	Value
S101	Vent stream splitting ratio (stream “14”)	0.022
S102	Reflux stream splitting ratio (stream “29”)	0.440

Select the NRTL thermodynamic model for the S102 stream splitter.

1.5.10. Mixers

Default parameters for the M101, M102 and M103 mixers.

1.6. Initializations

The calculation sequence is automatically determined by ProSimPlus. Three tear streams are detected: “07” (gas inlet of the reactor), “10” (inlet of the F101 flash) and “25” (overhead of the distillation column). The following initializations of these streams are used in the simulation.

Stream	07	10	25
Mole fraction (-)			
Hydrogen	0.549186	0.457502	0.000046
Nitrogen	0.034575	0.040267	0.000005
Carbon monoxide	0.077576	0.025484	0.000005
Carbon dioxide	0.089494	0.086770	0.003760
Methane	0.242841	0.282825	0.000314
Methanol	0.005338	0.088541	0.994847
Water	0.000990	0.018611	0.001023
Molar flow rate (kmol/h)	46 819	40 200	5 940
Temperature (°C)	145	175	50
Pressure (bar)	110	107.5	1

2. RESULTS

2.1. Mass and energy balances

This document presents only the most relevant stream results. In ProSimPlus, mass and energy balances are provided for all streams. Stream results are also available at the unit operation level (“Stream” tab in the configuration window).

Streams		01	08	09	12	13	14
Total flow	t/h	129.26	574.51	574.51	446.47	128.04	9.8224
Total flow	kmol/h	11450	46819	40200	35841	4359.1	788.5
Mass fractions							
HYDROGEN		0.12046	0.090225	0.064538	0.082812	0.00081188	0.082812
NITROGEN		0.0076924	0.078926	0.078926	0.10126	0.0010334	0.10126
CARBON MONOXIDE		0.56991	0.17707	0.049941	0.064022	0.00083638	0.064022
CARBON DIOXIDE		0.26743	0.32092	0.26716	0.3306	0.045932	0.3306
METHANE		0.030836	0.31746	0.31746	0.40532	0.011106	0.40532
METHANOL		0	0.013937	0.19851	0.01525	0.83757	0.01525
WATER		0.0036703	0.001453	0.02346	0.0007351	0.10271	0.0007351
Mole fractions							
HYDROGEN		0.6746	0.54921	0.45753	0.51174	0.011829	0.51174
NITROGEN		0.0031	0.034572	0.040265	0.04503	0.0010835	0.04503
CARBON MONOXIDE		0.2297	0.077574	0.025481	0.028473	0.00087703	0.028473
CARBON DIOXIDE		0.0686	0.08948	0.086755	0.093578	0.030655	0.093578
METHANE		0.0217	0.24284	0.28282	0.31474	0.020334	0.31474
METHANOL		0	0.0053375	0.088541	0.0059287	0.76777	0.0059287
WATER		0.0023	0.00098966	0.018611	0.00050831	0.16745	0.00050831
Physical state		Vapor	Vapor	Vapor	Vapor	Liquid	Vapor
Temperature	°C	50	150	267	38	38	38
Pressure	bar	51.2	110	107.5	106.5	106.5	106.5
Enthalpic flow	MW	2.4505	53.425	94.959	1.0783	-43.688	0.023723
Vapor molar fraction		1	1	1	1	0	1

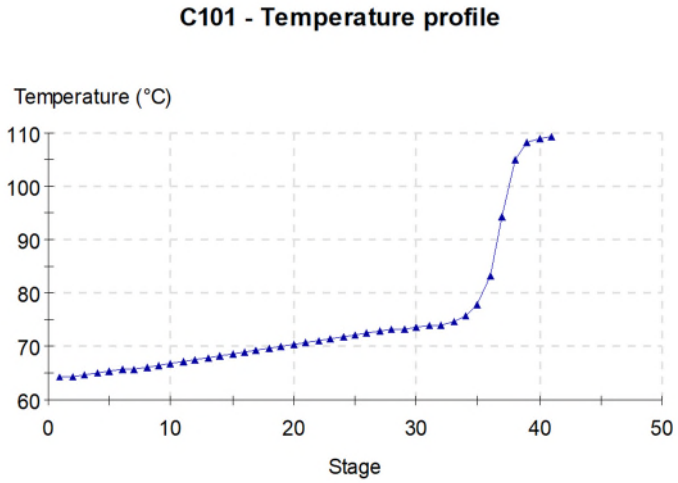
Streams		19	20	23	24	26	30
Total flow	t/h	8.1089	119.93	190.46	13.052	0.48694	106.39
Total flow	kmol/h	302.14	4057	5939.8	724.42	14.362	3318.2
Mass fractions							
HYDROGEN		0.012751	4.6083E-006	2.9016E-006	0	0.0011349	0
NITROGEN		0.016221	6.5298E-006	4.1597E-006	0	0.0015842	1.0991E-007
CARBON MONOXIDE		0.013113	6.2748E-006	3.9696E-006	0	0.0015361	4.2555E-008
CARBON DIOXIDE		0.64605	0.0053549	0.0051597	0	0.42875	0.0040739
METHANE		0.17212	0.00021865	0.00015689	0	0.044286	4.3778E-005
METHANOL		0.13491	0.88509	0.9941	0.00017785	0.5226	0.99531
WATER		0.0048423	0.10932	0.00057488	0.99982	0.00010982	0.00057603
Mole fractions							
HYDROGEN		0.16976	6.7574E-005	4.6155E-005	0	0.019089	0
NITROGEN		0.01554	6.8904E-006	4.7615E-006	0	0.0019174	1.258E-007
CARBON MONOXIDE		0.012564	6.6221E-006	4.5444E-006	0	0.0018594	4.8711E-008
CARBON DIOXIDE		0.39397	0.0035968	0.0037594	0	0.33032	0.0029679
METHANE		0.28795	0.00040291	0.0003136	0	0.093602	8.7495E-005
METHANOL		0.113	0.81654	0.99485	0.0001	0.55301	0.99592
WATER		0.0072137	0.17938	0.0010232	0.9999	0.0002067	0.0010252
Physical state		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Temperature	°C	34.038	34.038	64.137	109.33	50	50
Pressure	bar	2	2	1	1.4	1	1
Enthalpic flow	MW	0.02296	-43.711	2.9513	-7.5358	0.0041433	-31.94
Vapor molar fraction		1	0	1	0	1	0

2.2. Process performance

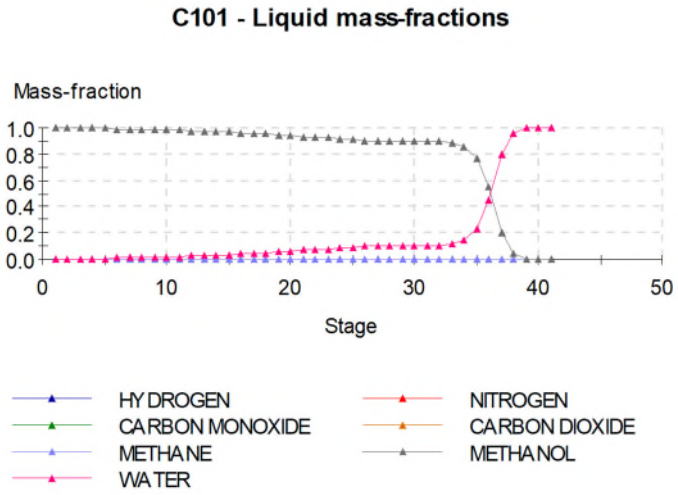
This process produces 2 555 t/d of methanol at a purity of 99.5% mass. 313 t/d of water at a purity of 99.98% mass are recovered.

2.3. C101 column profiles

The column stages are numbered from top to bottom (plate 1: top plate; plate 40: bottom plate; 41 reboiler).

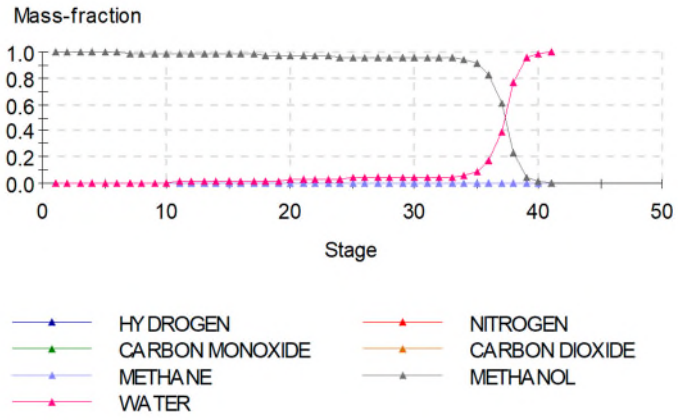


Temperature profile in the column



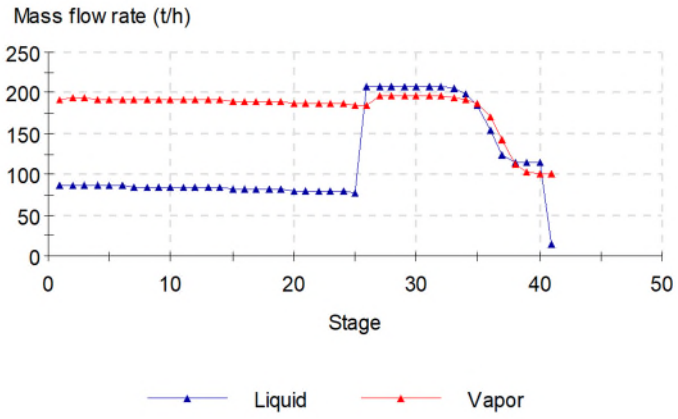
Liquid mass-fractions profile in the column

C101 - Vapor mass-fractions



Vapor mass-fractions profile in the column

C101 - Mass flowrates



Mass flow rates profile in the column

3. REFERENCES

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