ProSim

PROSIMPLUS APPLICATION EXAMPLE

ENERGY ANALYSIS OF AN ESTERIFICATION PROCESS FROM VEGETABLE OIL

EXAMPLE PURPOSE
This example illustrates the simulation of a production unit of ester and glycerin (glycerol) by esterification of vegetable oil. The "Pinch analysis" module is used to perform an energy analysis of the process.

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

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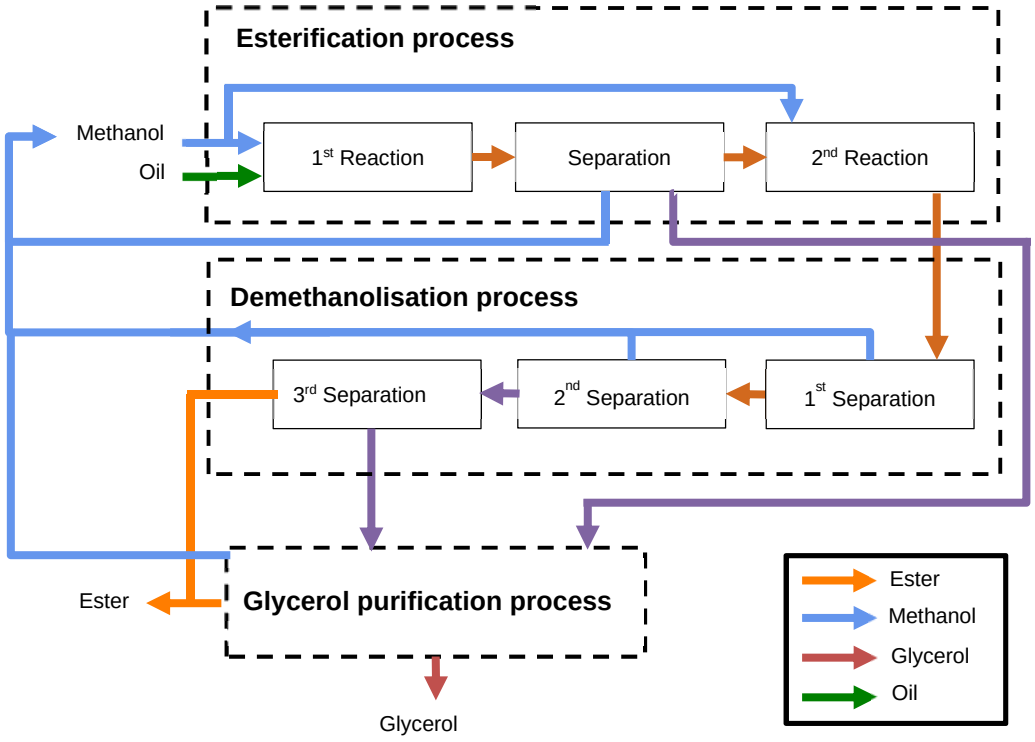
1. PROCESS MODELLING

1.1. Process description

This example illustrates the simulation of a production unit of ester and glycerin (glycerol) by esterification of vegetable oil. The example presented in this document is an esterification unit producing 10 t/h of ester and 1 t/h of glycerol from 10 t/h of vegetable oil.

The process is divided into 3 parts:

- "Esterification process" (section #1): this part deals with the oil and methanol reaction which produces ester and glycerol. The reaction is not complete using a single reactor, therefore there are 2 reactors in series. These reactions are catalytic reactions occurring at high temperature and pressure. The first reactor converts 70% of the oil. The second reactor called "finisher" then reaches the total conversion of glycerol in oil and ester.
- "Demethanolization process" (section #2): this part of the process is dedicated to recover most of the methanol fed in excess in the reaction section. For this example, the recovery (separation) of the methanol is carried out by a series of flashes.
- "Glycerol purification process" (section #3): this part of the process is used to purify the glycerol. This purification involves the use of a distillation column.



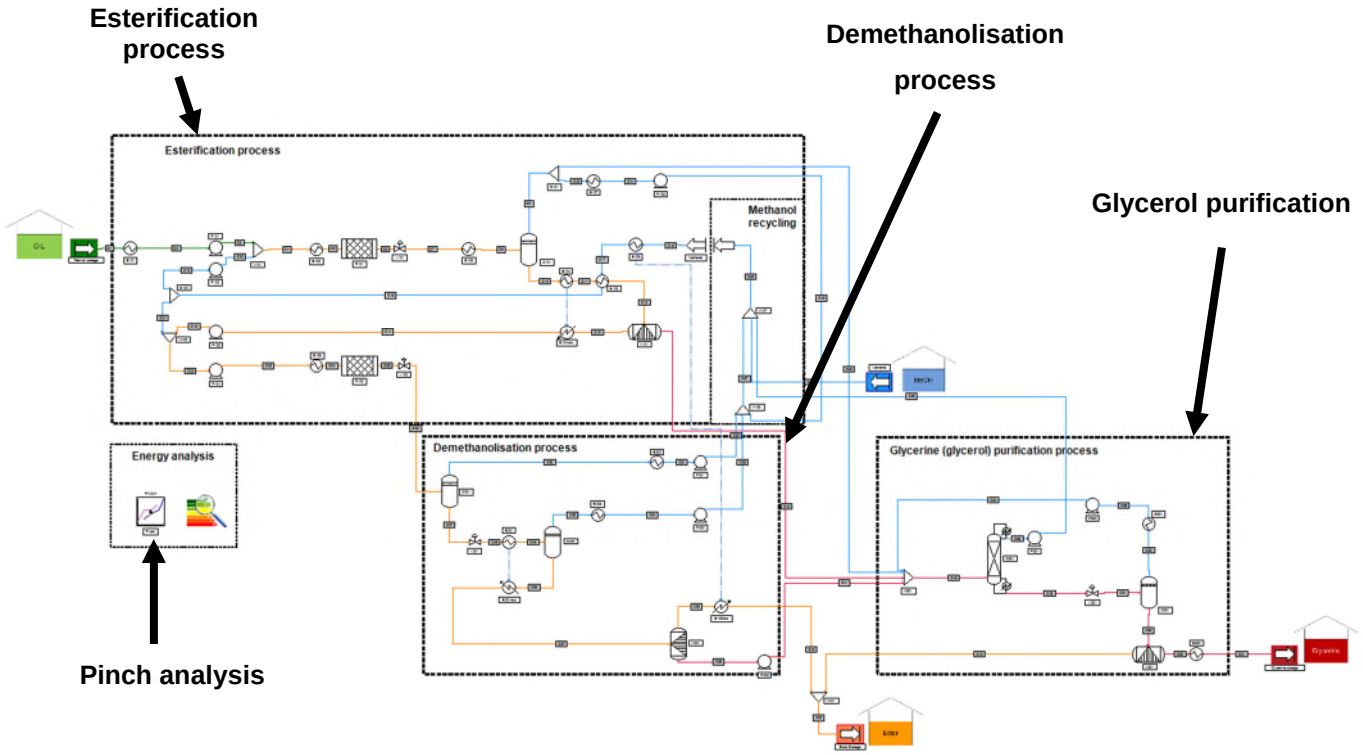
Block diagram of the esterification process from vegetable oil

The input data and the results of this example are based on several references [EJI10], [FUK01], [REF10] and [SIL10].

This example also illustrates the use of the "Pinch" module in order to perform the energy diagnosis of the process (pinch analysis).

1.2. Simulation flowsheet

The simulation flowsheet is divided into several sections corresponding to the block diagram presented above.



1.3. Equipment nomenclature

All equipment (unit operations) of the process follow the same nomenclature.

*Example: P203 pump: **P** for pump, **2** for the section in which the pump is installed and **03** corresponding to the third pump present in this section.*

The ids of the equipment are:

B : Boiler

C : Distillation column

D : Liquid-Vapor separator (drum)

E : Heat exchanger

H : Heat pump

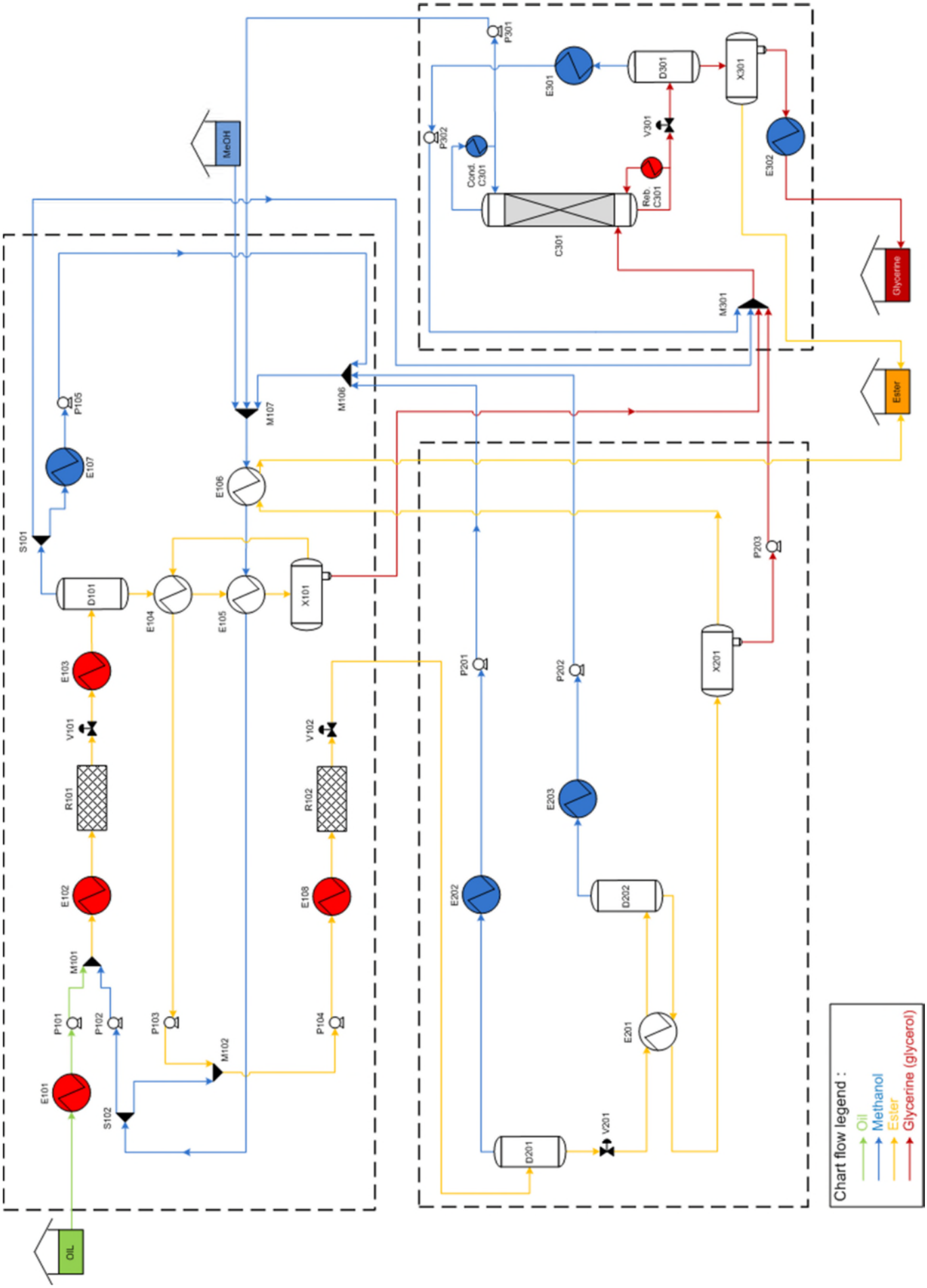
M : Mixer

P : Pump

R : Reactor

S : Stream splitter

X : Component splitter



1.4. Compounds

The compounds used in this example are listed in the following table:

Name	Chemical formula	CAS
METHANOL	CH_4O	67-56-1
GLYCEROL	$C_3H_8O_3$	56-81-5
ESTER (METHYL OLEATE)	$C_{19}H_{36}O_2$	112-62-9
OIL (TRIOLEIN)	$C_{57}H_{104}O_6$	122-32-7

Remarks:

Triolein compound has been modified compared to the "Standard" compounds basis in order to adapt the calculator to the case study. The modified properties are:

- *Liquid and ideal gas specific heat (Cp)*
- *Vaporization enthalpy (ΔHvap)*

These values are used especially for flash calculations in the process. They are particularly necessary for the calculation of thermodynamic properties (enthalpy, entropy ...).

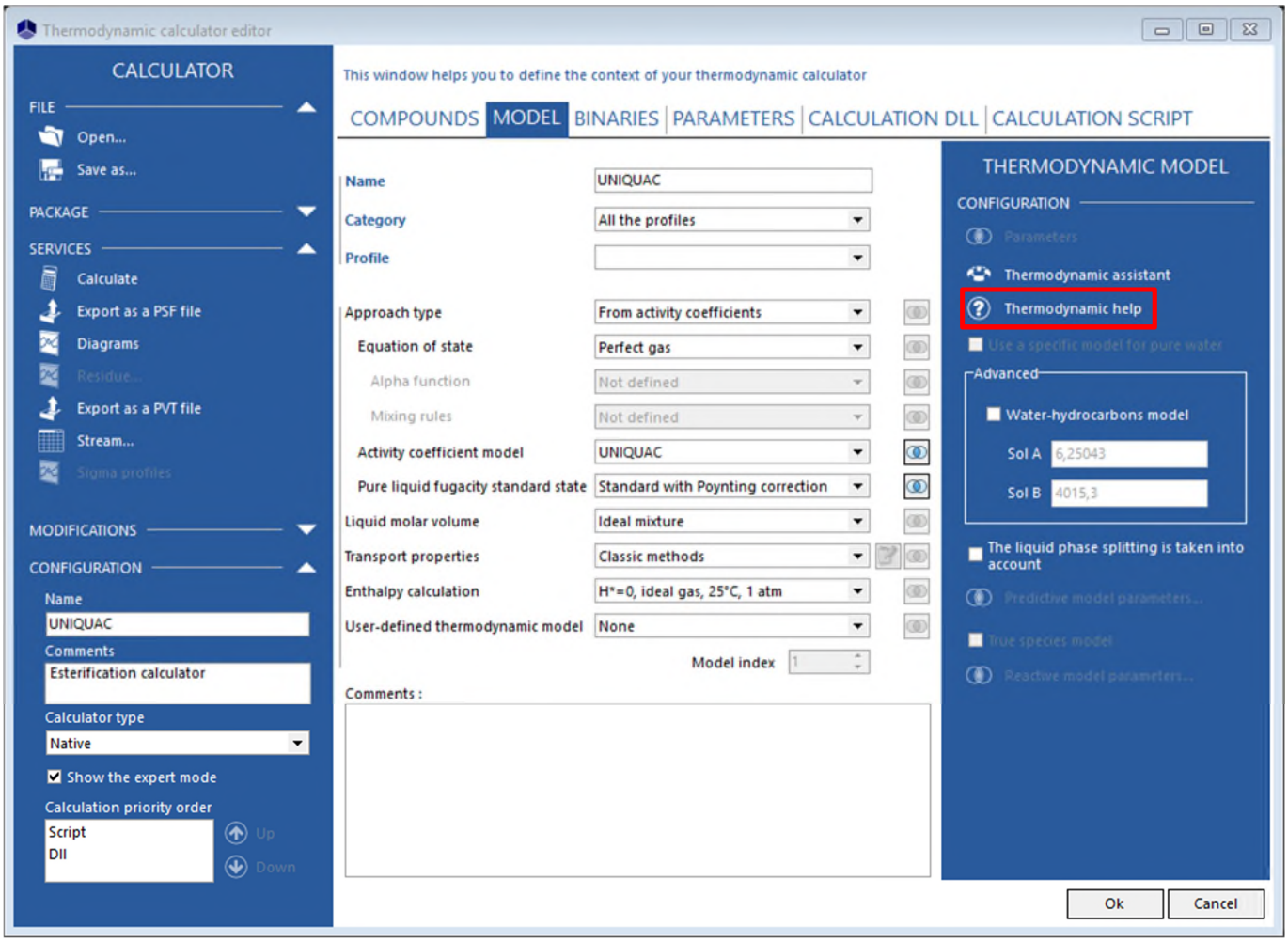
The values of the modified properties are presented in the appendix of this document.

1.5. Thermodynamic model

The thermodynamic model used for the simulation is the standard UNIQUAC thermodynamic profile.
The binary interaction parameters are:

Name	Aij0	Aji0
Methanol - Glycerol	80.446	65.4210
Methanol - ESTER	27.381	594.131
Glycerol - ESTER	-282.2	334.778

For more information on the thermodynamic models available in ProSimPlus, it is possible to access the user guide of thermodynamic models, available from the "MODEL" tab of the calculator editor window.



Window for the definition of thermodynamic profile in the "MODEL" tab

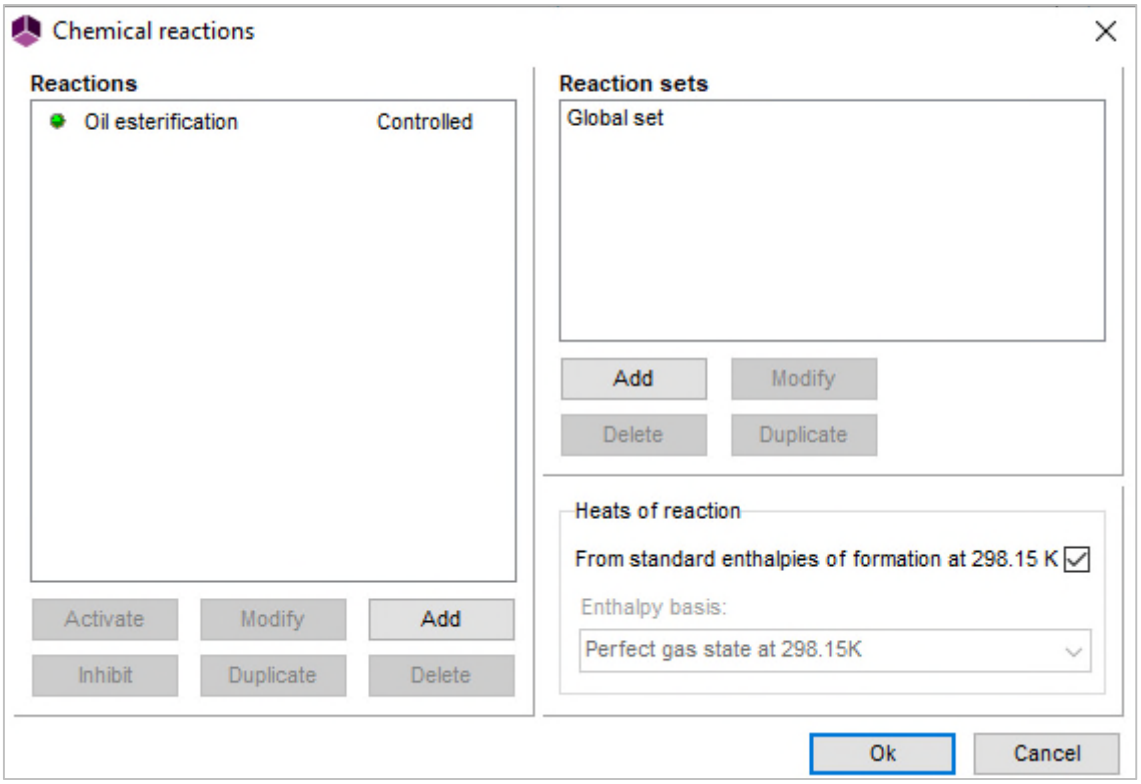
1.6. Reactions

To simplify the simulation process, the esterification and transesterification reactions are modelled by a single reaction.

Reaction "Oil esterification"

$$Oil\ (Triolein) + 3\ Methanol \rightarrow Glycerol + 3\ Ester\ (Methyl\ oleate)$$

$$C_{57}H_{104}O_6 + 3\ CH_4O \rightarrow C_3H_8O_3 + 3\ C_{19}H_{36}O_2$$



Definition of reactions

1.7. Unit operations of "Esterification process" part

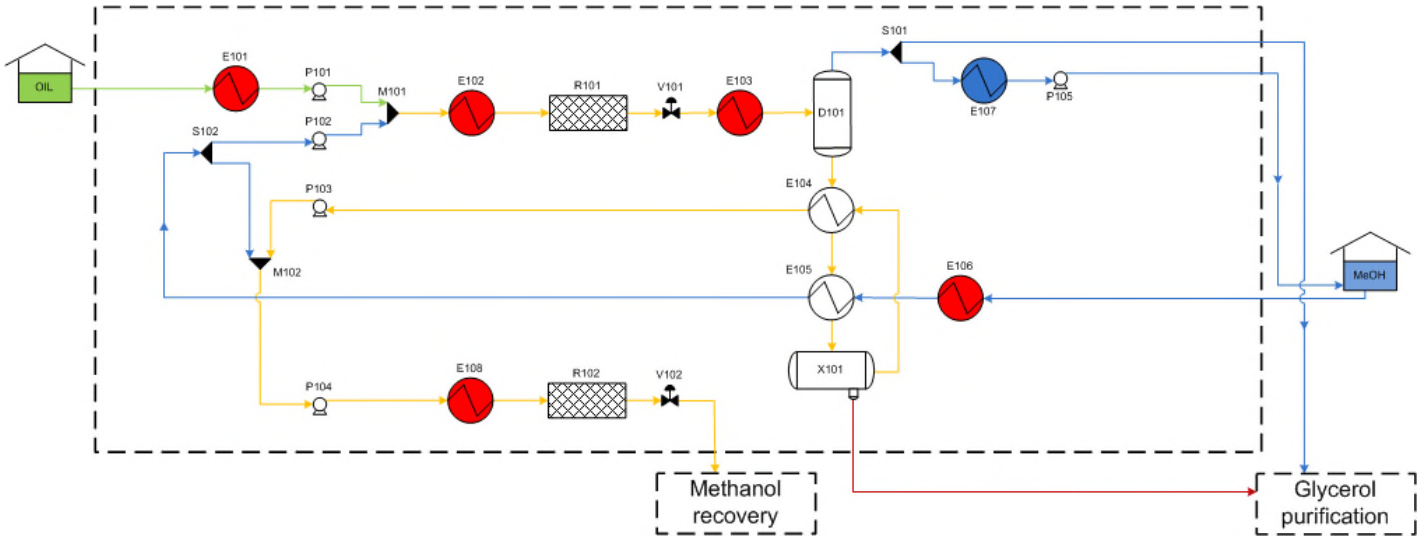
The operating conditions of the feeds are presented below:

- ✓ Vegetable oil feed

		From oil storage
Mass percent	**Oil (triolein)**	100
Total mass flowrate (t/h)		10
Temperature (°C)		25
Pressure (bar)		1

- ✓ Methanol feed

		Methanol
Mass percent	**methanol**	100
Total mass flowrate (t/h)		1.1
Temperature (°C)		20
Pressure (bar)		3



"Esterification process" section

✓ Coolers/Heaters

Name	***Outlet temperature (°C)***	***Pressure drop (bar)***
E101	135	0
E102	200	0
E103	100	0
E104	80	0
E106	54	0
E107	Subcooling of 1°C below the bubble point	0
E108	200	0

✓ *Pumps*

Operating conditions	***P101***
Outlet pressure (bar)	50
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

Operating conditions	***P102***
Outlet pressure (bar)	50
Volumetric efficiency	0.75
Mechanical efficiency	0.95

Electrical efficiency	1

Operating conditions	***P103***
Outlet pressure (bar)	3
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

Operating conditions	***P104***
Outlet pressure (bar)	55
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

Operating conditions	***P105***
Outlet pressure (barr)	2
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

- ✓ Generalized heat exchanger

Operating conditions	***E105***
Constraint: "Hot Stream"	Outlet temperature of the hot stream
Outlet temperature (°C)	65

- ✓ Two-phases separator

Operating conditions	**D101**
Separator type	Liquid-vapor separator
Pressure (bar)	Inlet pressure
Pressure Drop (bar)	0
Heat duty exchanged (W)	Adiabatic

✓ *Component splitter*

Operating conditions	***X101***
Recovery ratios to overhead product	Overhead product to the reactor R102
Methanol	0.7
Glycerol	0.1
Ester	1
Oil	1

✓ *Simple reactors*

Operating conditions	***R101***
Reaction set	Global set
Type of specification	Reactor at a constant temperature
Key component	Oil
Reaction conversion rate	0.7
Pressure drop (bar)	5

Operating conditions	***R102***
Reaction set	Global set
Type of specification	Reactor at a constant temperature
Key component	Oil
Reaction conversion rate	1
Pressure drop (bar)	5

✓ *Stream splitter*

Operating conditions	***S101***
Specification type	Splitting ratio to the purification of glycerol (E107)
Splitting ratio	65.5%

Operating conditions	***S102***
Specification type	Splitting ratio to the reactor R101
Splitting ratio	56.09%

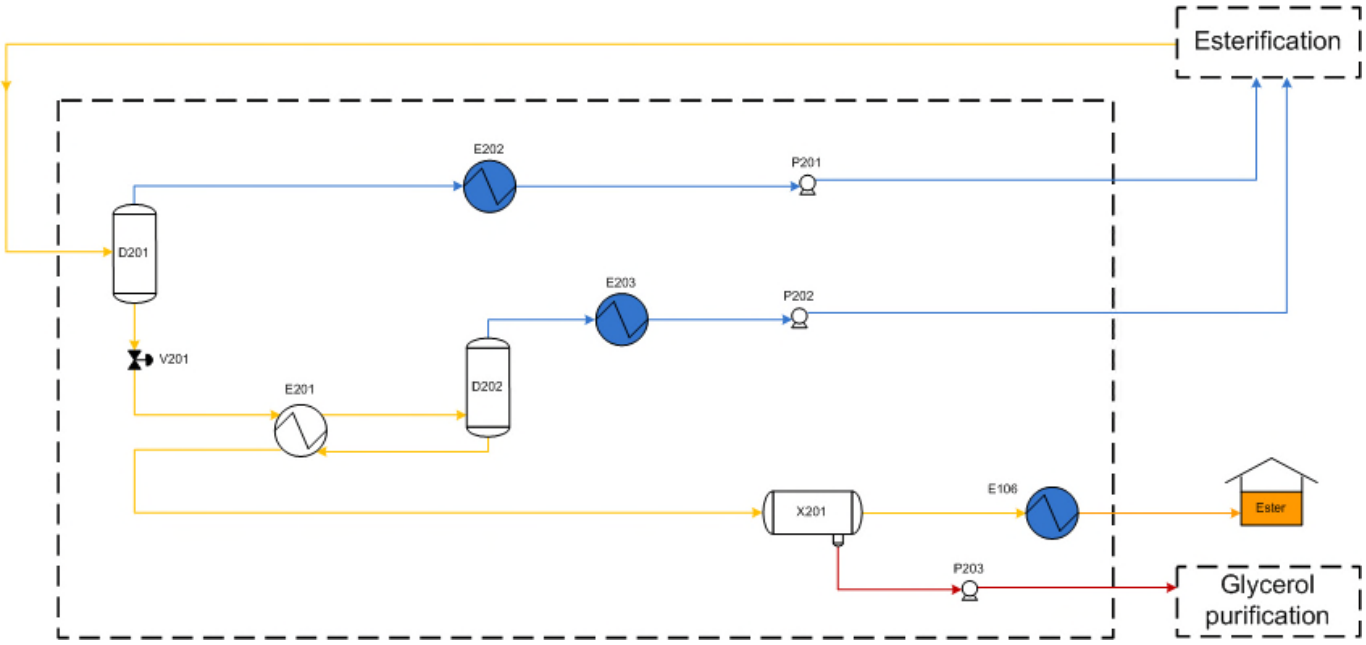
✓ Expansion valves

Operating conditions	*V101*
Constraint Type	Specified pressure
Supplied pressure (barr)	1

Operating conditions	*V102*
Constraint Type	Specified pressure
Supplied pressure (bar)	1.5

1.8. Unit operations of "Demethanolization process" part

The operating conditions of the "Demethanolization process" unit operations are presented in this section.



"Demethanolization process" section

✓ Coolers/Heaters

Name	*Outlet temperature (°C)*	*Pressure drop (bar)*
E201	70	0
E202	25	0
E203	25	0

✓ *Pumps*

Operating conditions	***P201 / P202 / P203***
Outlet pressure (barr)	2
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

✓ Expansion valve

Operating conditions	***V201***
Constraint type	Specified pressure
Supplied pressure (bar)	0.3

✓ Simple heat exchangers

Name	***Heat duty (W)***	***Pressure drop (bar)***
E201-bis	Connected by an information stream with the heat exchanger E201	0
E106-bis	Connected by an information stream with the heat exchanger E106	0

✓ Two-phases separators

Operating conditions	**D201**
Separator type	Liquid-vapor separator
Pressure (bar)	Inlet pressure
Pressure Drop (bar)	0
Heat duty exchanged (W)	Adiabatic

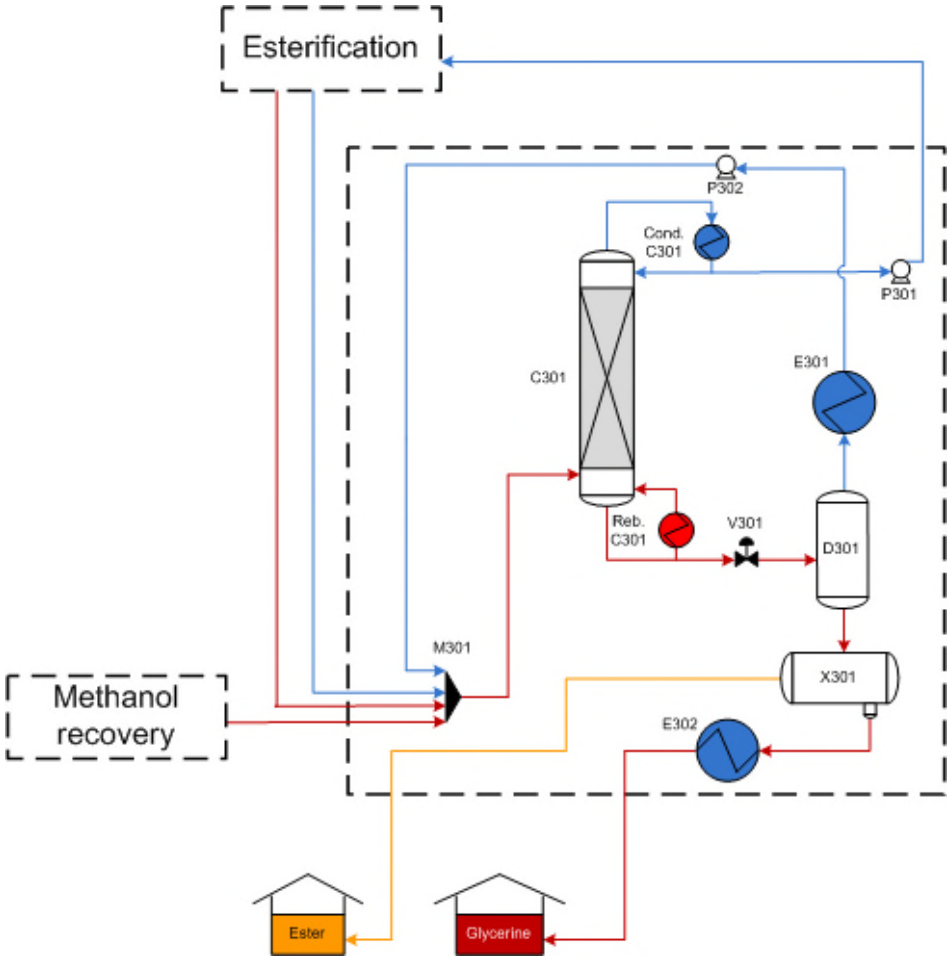
Operating conditions	**D202**
Separator type	Liquid-vapor separator
Pressure (bar)	Inlet pressure
Pressure Drop (bar)	0
Temperature (°C)	150

✓ *Component splitter*

Operating conditions	***X201***
Recovery ratios to overhead product	Overhead product to the pump P203
Methanol	0
Glycerol	1
Ester	0.005
Oil	0

1.9. Unit operations of "Glycerol purification process" part

The operating conditions for the "Glycerol purification process" part are presented in this section.



"Glycerol purification process" section

✓ Coolers/Heaters

Name	***Outlet temperature (°C)***	***Pressure Drop (bar)***
E301	Subcooling of 5°C below the bubble point	0
E302	70	0

✓ *Pumps*

Operating conditions	***P301 / P302***
Outlet pressure (barr)	2
Volumetric efficiency	0.75
Mechanical efficiency	0.95
Electrical efficiency	1

✓ Two-phases separators

Operating conditions	**D301**
Separator type	Liquid-vapor separator
Pressure (bar)	Inlet pressure
Pressure Drop (bar)	0
Temperature (°C)	140

✓ *Component splitter*

Operating conditions	***X301***
Recovery ratios to overhead product	Overhead product to the ester storage
Methanol	0
Glycerol	0
Ester	1
Oil	0

✓ Expansion valve

Operating conditions	***V301***
Constraint Type	Specified pressure
Supplied pressure (bar)	0.1

✓ Distillation column

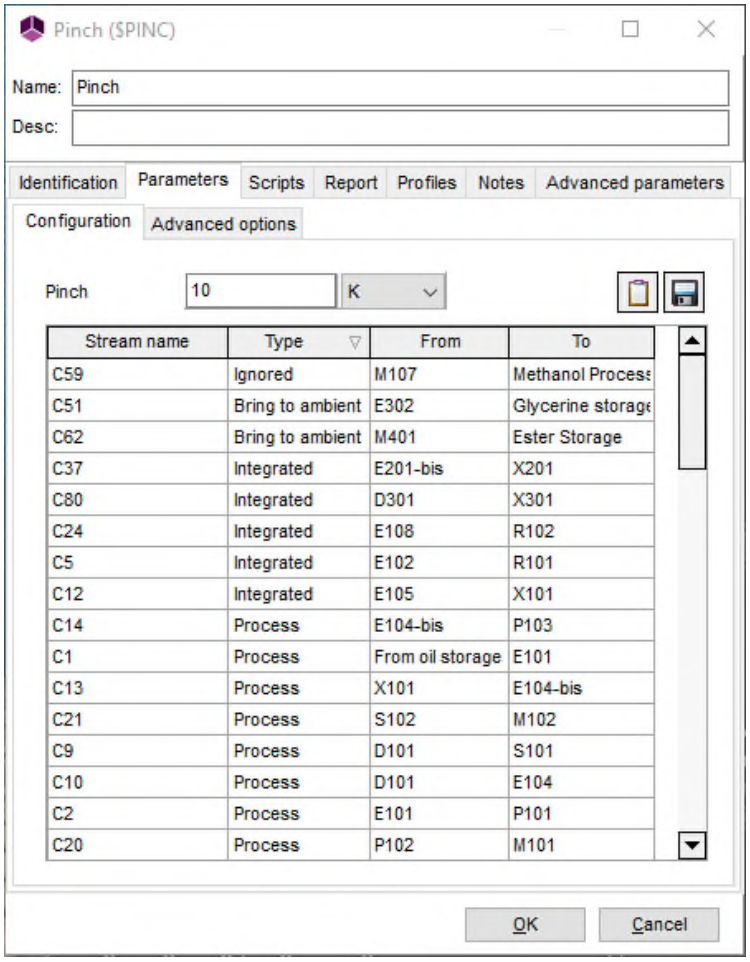
Operating conditions	*C301*
Number of theoretical stages	10
Feed stage	9
Specifications for the operating conditions	Reflux flowrate and reboiler heat duty
Reboiler heat duty (Mcal/h)	650
Reflux flowrate (t/h)	2

2. ENERGY ANALYSIS OF THE PROCESS

An energy analysis of the process is then performed to provide a balance on energy consumption and to suggest improvements of the process.

2.1. Setting of the parameters of the "Pinch Analysis" module

The "Pinch analysis" module enables to apply the "Pinch" method (also called "Pinch analysis") directly on the simulated process.



Main interface of the "Pinch" module

The main interface of the module presents the entire list of the streams of the process. The user can specify the type of each stream among the following choices:

- Process (by default);
- Hot utility;
- Cold utility;
- Integrated;
- Bring to ambient (available only for process outlets);
- Ignored (available only for process outlets).

Only **Process** or **Bring to ambient** streams are integrated into the energy analysis.

For the energy analysis of the process, some streams have to be defined:

- The process outlets (streams to the ester storage tank and to the glycerol storage tank) are brought to ambient temperature;
- The process outlet of methanol for the recycle is configured as "ignored" (not taken into account for the analysis);
- Inlet streams of the two reactors (R101 and R102) and of component splitters (X101, X102 and X103) are defined as "Integrated" (not taken into account for the analysis).

In the simulation file associated with this document, these streams are:

Stream name	Type	From	To
C59	Ignored	M107	Methanol Process
C51	Bring to ambient	E302	Glycerine storage
C62	Bring to ambient	M401	Ester Storage
C37	Integrated	E201-bis	X201
C80	Integrated	D301	X301
C24	Integrated	E108	R102
C5	Integrated	E102	R101
C12	Integrated	E105	X101

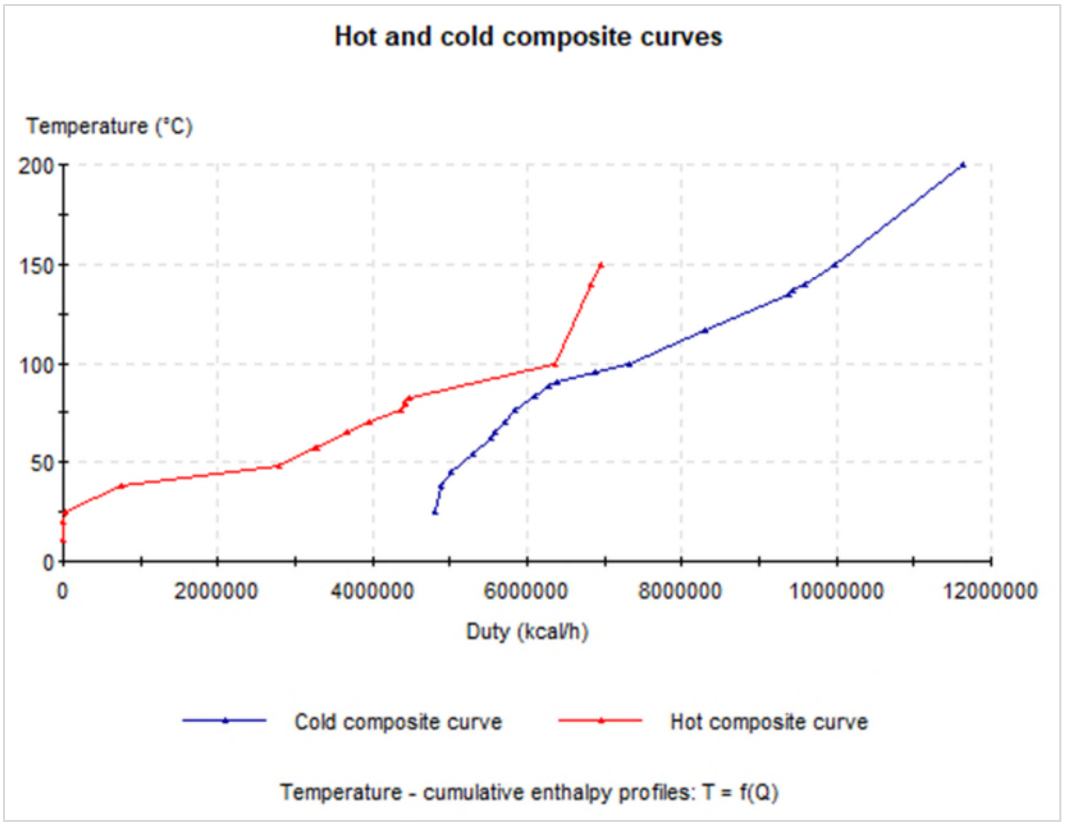
Configuration table of streams defined in the "Pinch analysis" module

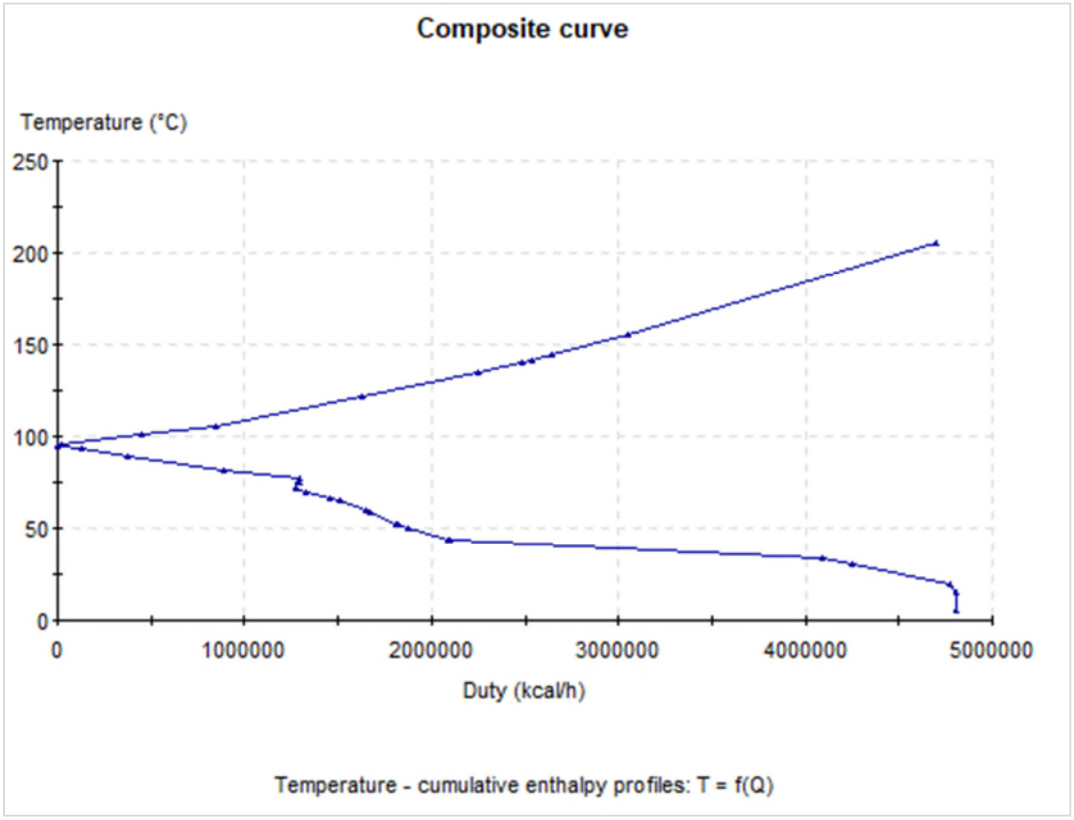
Other streams of the flowsheet are defined by default as "Process" stream.

2.2. Results analysis of the "Pinch" method

The main results are summarized in the following table:

Stream	Physical state	F*Cp (kcal/hr/k)	T in (°C)	T out (°C)	Q (kcal/hr)
C1	L	5598.5	25.0	135.0	615829.7
C16	L	12863.6	45.0	54.0	115772.8
C4	L	17535.5	96.0	200.0	1824282.7
C7	LV	53389.9	90.8	100.0	491272.7
C17	L	13172.4	54.0	61.8	102886.1
C13	L	6140.5	65.0	88.0	141286.3
C23	L	15527.9	76.6	200.0	1915438.4
C28	LV	12990.1	38.6	70.0	408208.4
C29	LV	6902.6	70.0	150.0	552205.7
Rebo.C301	L	12420.4	83.9	136.2	650000.0
C61	LV	865.0	116.9	140.0	19961.2
C10	L	7064.3	100.0	80.0	141286.3
C11	L	6859.1	80.0	65.0	102886.1
C43	V	86842.1	100.0	82.1	1556510.7
C26	LV	225.0	76.7	76.7	2.3
C30	V	42039.9	76.7	25.0	2173071.9
C33	V	5143.6	150.0	25.0	642947.8
C36	L	5811.4	150.0	79.8	408208.4
C39	L	5149.4	79.8	57.3	115772.8
Cond.C301	V	152710.2	48.4	38.5	1515115.0
C52	V	189.7	140.0	11.0	24471.3
C62	L	4952.8	57.7	20.0	186791.5
C51	L	623.5	70.0	20.0	31175.7
C50	L	701.4	140.0	70.0	49098.9





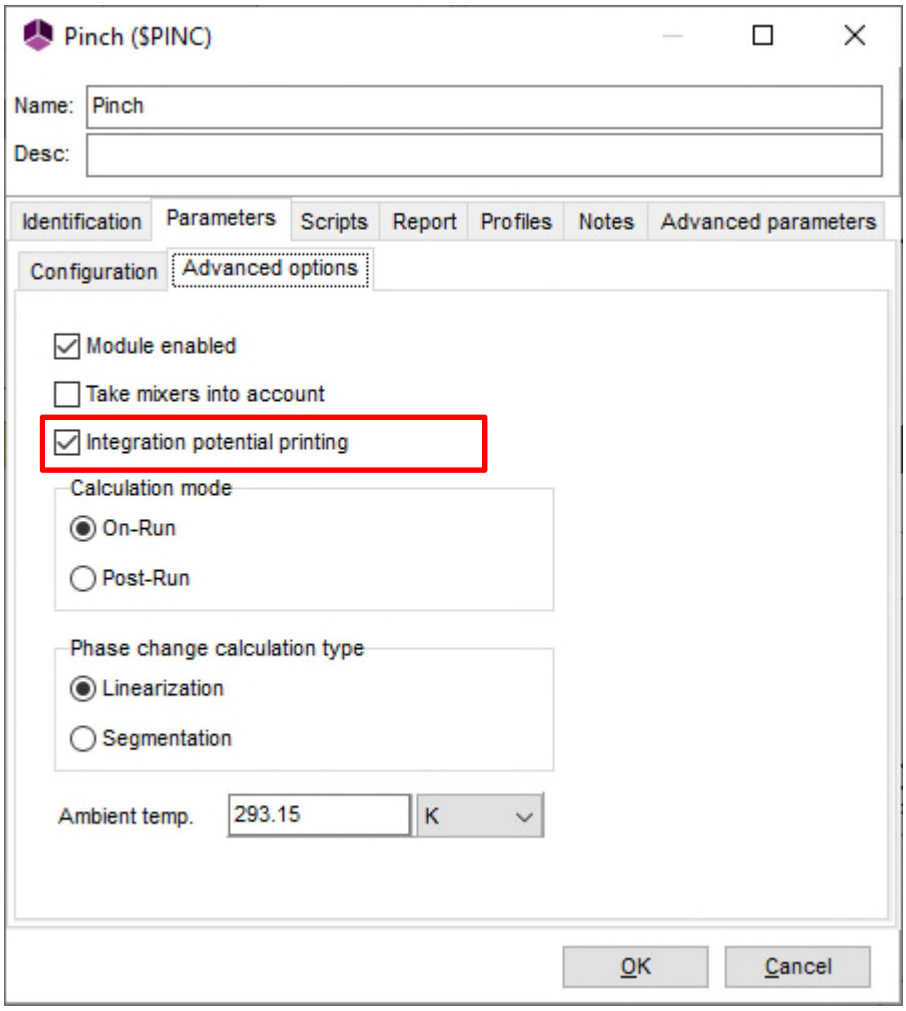
Profiles of hot and cold composite curves and the grand composite curve of "Profiles" tab in the " Pinch analysis" module

The results of the module are:

Cold utility (kcal/h)	*4810723*
Maximum energy recovery (kcal / h)	***2136616***
Hot utility (kcal / h)	*4700528*

It is possible to recover 2.1 Gcal/h of energy using integration exchangers in order to exchange the hot and cold “process” streams together. This theoretical value is called the Maximum Energy Recovery (MER).

The process presented in this case study proposes 4 integration heat exchangers: E104, E105, E106 and E201.
It is possible to display the energy recovery percentages of these exchangers compared to MER. To display these results, the user has to check the "Integration potential printing":



Window interface of the advanced options of the "Pinch" module

After a re-run of the simulation, the results of integration potential are:

	HEAT DUTY (KCAL/HR)			SATISFACTION RATIO (%)
	MINIMUM	REAL	MAXIMUM	
COLD FLUID	4.810723E+06	6.179185E+06	6.947339E+06	11.057
HOT FLUID	4.700528E+06	6.068990E+06	6.837144E+06	11.235

Maximum energy recovery	=	2.136616E+06	(KCAL/HR)
Pinch temperature	=	95.0000	(C)
Real integration ratio	=	35.952	(%)

The total heat duty recovered by the integration heat exchangers is 0.76 Gcal/h. Thus, 4 integration heat exchangers can recover ≈ 36% of MER.

It is still possible to recover energy in the process by adding integration heat exchangers.
ProSim has developed a dedicated tool in the design of heat exchanger network, named Simulis Pinch, with the main objective of providing an efficient heat exchangers network.
Simulis Pinch can quickly find an efficient network for the best compromise between capital and operating costs to achieve a main objective of reducing energy consumptions. All the constraints of the plant (distances, incompatible exchanges...) can be taken into account in this software.

3. REFERENCES

[EJI10] P.M. Ejikeme, “Catalysis in Biodiesel Production by Transesterification Processes-An Insight”, E-Journal of Chemistry, 2010, 7(4), 1120-1132.

[FUK01] H. Fukuda, “Biodiesel Fuel Production by Transesterification of Oils”, Journal of Bioscience and Bioengineering, Vol. 92, No. 5, 405-416, 2001.

[REF10] A. A. Refaat, “Different techniques for the production of biodiesel from waste vegetable oil”, Int. J. Environ. Sci. Tech., 7(1), 183-213, Winter 2010.

[SIL10] C. C. Silva, “Biodiesel production from soybean oil and methanol using hydrotalcites as catalyst”, Fuel Processing Technology, 91, 205–210, 2010.

4. APPENDIX: MODIFIED PROPERTIES FOR TRIOLEIN COMPOUND