



PROSIMPLUS APPLICATION EXAMPLE

BIOFUEL PRODUCTION PLANT

FROM PURE VEGETABLE OIL WITH AN ALKALINE CATALYST

EXAMPLE PURPOSE

This example illustrates the production of biofuel from pure vegetable oil with an alkaline catalyst. The process involves a transesterification reaction that requires using an alcohol (usually methanol) and allows producing biofuel and glycerol from oil. It uses mainly simple reactors (for transesterification and catalyst neutralization), scrubbers and splitters to separate heavy components from light ones, and distillation columns to separate products and purify the biofuel. Specifications are imposed on columns output streams in order to reach required purities.

ACCESS	<input checked="" type="checkbox"/> Free-Internet	<input type="checkbox"/> Restricted to ProSim clients	<input type="checkbox"/> Restricted	<input type="checkbox"/> Confidential
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CORRESPONDING PROSIMPLUS FILES [Biofuel_production_1.pmp3](#)

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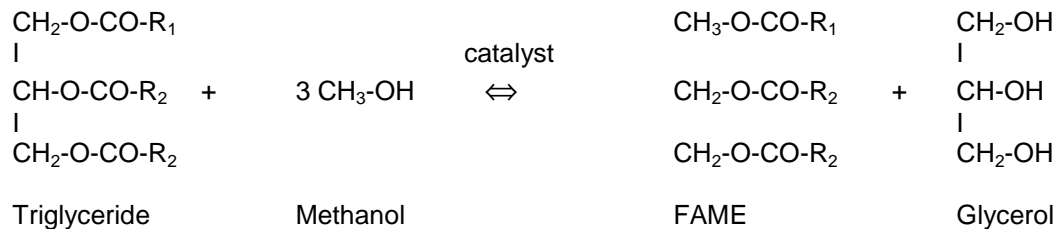
1. Process Modeling

1.1. Process description

Biofuel production is mainly done through transesterification. Transesterification is a catalytic reaction that allows producing biofuel (and glycerol as a byproduct) from oils (waste vegetable oil or pure plant oil) and alcohol. During the transesterification reaction, the ester exchanges the alkyl from the -COO-R group with an alcohol, thus producing a new ester.

Pure plant oils are mainly composed of triglycerides (resulting from the glycerol alcohols functions esterification by three fat acid molecules). When the triglycerides react with alcohol (usually methanol), the three fat acid strings come apart from the glycerol skeleton to settle down on the alcohol, thus producing an oil ester (the biofuel for instance, hereafter noted **FAME**: Fatty Acid Methyl Esters).

The chemical equation of this reaction is as follows:



This reaction can be catalyzed by an alkaline, acid or enzymatic catalyst. Only the first will be illustrated in this example.

The main characteristics of processes that imply an alkaline catalyst are:

- Alcohol-oil molar ratio of 6 to 1
- The conversion ratio of oil into methyl ester is 90% to 98% in 90 minutes.
- The process is highly sensitive to the reactants purity: the presence of water into the reaction medium can lead to saponification (fat acids react with the alkaline catalyst to produce soap and water). This saponification not only leads to a catalyst deficiency, but the soap also takes part in emulsions formation, which generate difficulties to separate and purify biofuel.
- The use of anhydride reactants is particularly important and is limiting for processes using waste vegetable oils. A pre-treatment step is required.

The process presented hereafter is using pure vegetable oils as raw material. Biofuel can be produced from different pure vegetable oils: colza, sunflower seed, soya and even waste vegetable oils. Taking into consideration its extensive industrial use, colza oil was selected in this example.

The process involves reactors, distillation columns, extraction columns and components splitters.

Methanol and Sodium hydroxide feed streams (C101 and C103) are mixed (MIX101) and their pressure is brought to 400 kPa by a centrifugal pump (P101). The pressure of oil feed (stream C105) is also brought to 400 kPa (P103) and its temperature to 60°C by a cooler/heater (E101). These three streams, with the methanol recycle stream (C201A) constitute the feed of the transesterification reactor (R101).

After the transesterification, the mixture is brought in a distillation column with total condenser (T201, from stream C102) in order to separate the methanol from other components. The distillate that contains almost pure methanol is recycled at the reactor inlet (stream C201), whereas the residue (stream C202) is cooled to 60°C (E201) and its pressure set to 200 kPa (P202). It is then washed with water in an extraction column (T301 from stream C203). The washing separates the biofuel from methanol, glycerol and catalyst.

The overhead flow (stream C301) is sent to a gravity splitter (modeled with a component splitter (X301)) that allows recovering NaOH at the bottom (stream C301B) and the FAME, oil and a fraction of water and methanol at the head (stream C301A). The FAME, oil, water and methanol recovery ratios in the organic phase of the splitter X301 are set to 1.

These components are then separated by a distillation column with partial condenser (T401). This additional separation is required to obtain a biofuel purity that meets the ASTM specifications (American Society for Testing and Materials) and that has to exceed 99.6%. The partial condenser facilitates the FAME and water-methanol separation (at the top of the column).

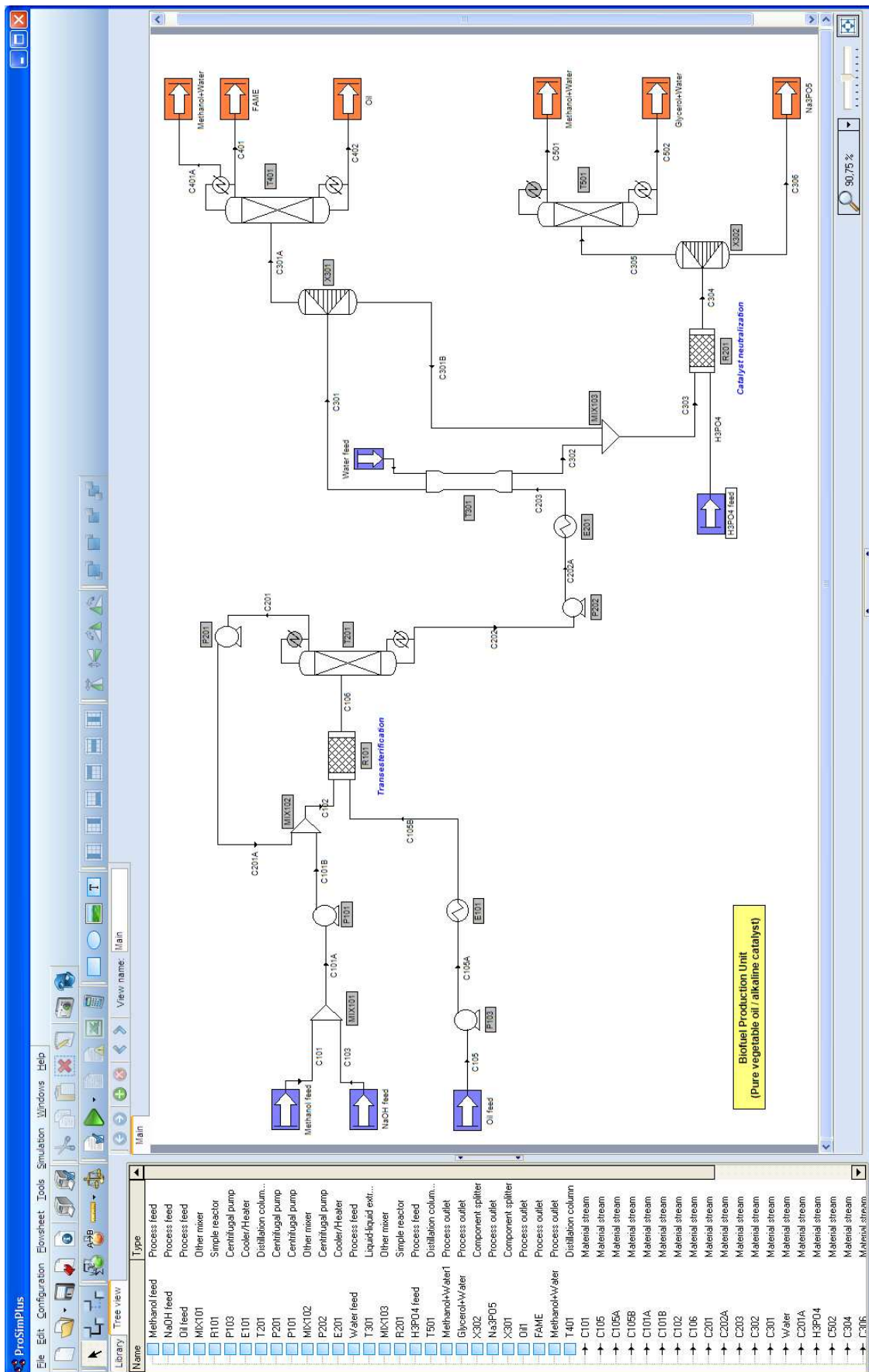
It should be noted that vacuum operating conditions are required in order to keep the temperature low enough to avoid the biofuel degradation.

The extraction column's (T301) and the components splitter's (X301) bottom streams are sent to a reactor in order to neutralize NaOH by adding pure phosphoric acid (stream H3PO4).

The produced Na_3PO_4 is separated from other components in a components splitter (X302). After recovery of Na_3PO_4 (stream C306), the stream C305 contains more than 82% mass in glycerol. However, glycerol is considered as a secondary product that must have about 92% purity. Consequently an additional separation is required and the head stream (C305) is sent to a distillation column with total condenser (T501).

This example is taken from [1].

1.2. Process flowsheet



Biofuel production plant from pure vegetable oil with an alkaline catalyst process flowsheet

1.3. Components

Components taken into account in the simulation are taken from the ProSimPlus standard database:

Name	Chemical formula	CAS Number	Use in the process
Colza oil : triolein or triacylglycerol	$C_{57}H_{104}O_6$	122-32-7	Raw material, main reactant.
Methanol	CH_3OH	67-56-1	Reactant.
Sodium hydroxide	$NaOH$	1310-73-2	Alkaline catalyst.
Sulfuric acid	H_2SO_4	7664-93-9	Acid catalyst.
Methyl oleate (biofuel, FAME)	$C_{19}H_{36}O_2$	112-62-9	Main product.
Glycerol	$C_3H_8O_3$	56-81-5	Secondary product.
Oleic acid	$C_{18}H_{34}O_2$	112-80-1	Impurities in waste vegetable oils.
Phosphoric acid	H_3PO_4	7664-38-2	Allows neutralizing NaOH.
Sodium phosphate	Na_3PO_4	7601-54-9	Product coming from NaOH neutralization.
Calcium oxide	CaO	1305-78-8	Allows neutralizing H_2SO_4 .
Calcium sulfate	$CaSO_4$	7778-18-9	Product coming from H_2SO_4 neutralization.
Water	H_2O	7732-18-5	Allows separating FAME from other products, by scrubbing.
Hexane	C_6H_{14}	110-54-3	Allows separating FAME from other products, by scrubbing.

Triolein properties were estimated with PROPRED, pure components properties estimation software, developed by the CAPEC consortium [2].

The predictive methods implemented in this software (Marrero and Gani, Constantinou and Gani, Joback and Reid, Wilson...) are based on the decomposition of the molecule into functional groups.

The developed chemical formula of triolein is the one that is supplied on the NIST [3] website.

The properties thus obtained were regressed with the regression service of Simulis[®] Thermodynamics software.

It is to be noted that as electrolytic species involved in the process only intervene in reaction steps as catalysts or catalysts neutralizers, they are considered as non-volatile ($P_i^0 = \exp(-30)$, $\Delta H^{vap} = 0$) and the missing thermodynamic properties (liquid density, liquid specific heat...) are assimilated to those of water.

The following table summarizes the properties that were supplied for electrolytes:

Component	Properties
NaOH, H_2SO_4	UNIFAC decomposition = 1[H ₂ O]
H_3PO_4	UNIFAC decomposition = 1[H ₂ O] Vapor pressure: $P_i^0 = \exp(-30)$ Perfect gas specific heat equal to water's one.

Na ₃ PO ₄	UNIFAC decomposition = 1[H ₂ O] Vapor pressure: $P_i^0 = \exp(-30)$ Vaporization enthalpy equal to water's one. Liquid and perfect gas specific heats are assimilated to water's ones
CaO, CaSO ₄	UNIFAC decomposition = 1[H ₂ O] Vapor pressure: $P_i^0 = \exp(-30)$ Vaporization enthalpy equal to water's one. Vapor and liquid thermal conductivity (only vapor for CaO), vapor and liquid viscosity, liquid molecular weight and surface tension equal to water's ones.

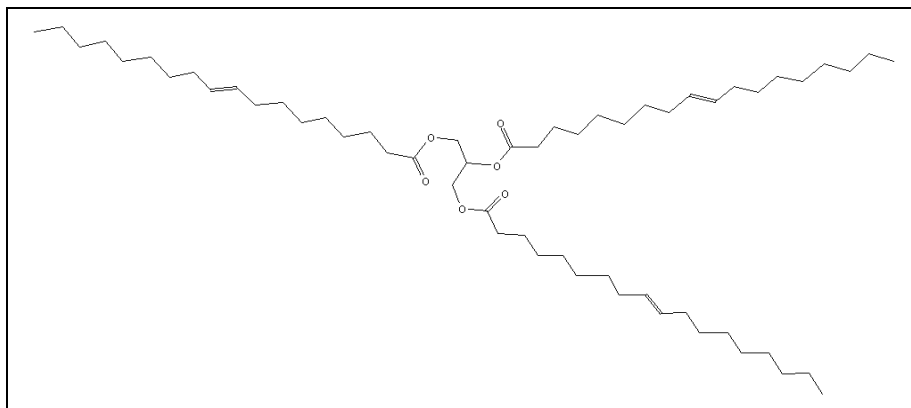
1.4. Thermodynamic model

The system contains polar components (such as methanol and glycerol), which implies strong interactions in liquid phase. The operating pressure being low (from 0.1 to 4 bars), the vapor phase behavior can be assimilated to an ideal gas.

From those two considerations, an heterogeneous approach ($\gamma - \Phi$) is retained. The equilibrium data for the binary systems not being available, a predictive model, based on group contribution, the Dortmund modified version of UNIFAC [4] model was selected.

Since the UNIFAC decompositions are not available for all the components, such as the triolein and all the inorganic components, the following assumptions were made:

- The UNIFAC decomposition of non organic components is assimilated to water's one (it mainly leads to neglect the pH influence on equilibrium, this approximation is reasonable if we consider the low content in inorganic components that only act as catalysts).
- The triolein UNIFAC decomposition is obtained from its chemical structure :



Triolein chemical structure

The triolein UNIFAC decomposition is as follows:

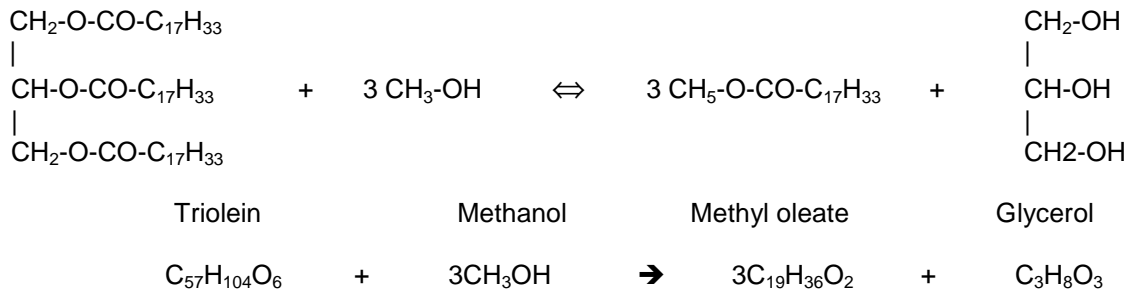
Sub-group	Frequency
CH=CH	3
CH ₂	44 4
CH	1
CH ₃	3

CH ₂ COO	3
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1.5. Chemical reactions

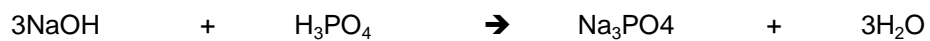
Two main reactions are taking place: a transesterification reaction and a neutralization reaction.

- Transesterification (Reaction 1, set of reactions R1) :



- Alkaline catalyst neutralization (Reaction 2 set of reaction R2):

The following reaction takes place (sodium hydroxide neutralization by phosphoric acid)



1.6. Operating conditions

- ✓ Process feed

	C101	C103	C105
Total flow (kg/h)	117.2	10.0	1050.0
Pure component	Methanol	NaOH	Oil
Temperature (°C)	25	25	25
Pressure (kPa)	100	100	100

- ✓ Heat exchanger E101

Operating parameters	Value
Type of exchanger	Cooler/heater
Output temperature (°C)	60

- ✓ Pumps P101, P103 and P201

Operating parameters	Value
Type of pump	Centrifugal pump
Volumetric efficiency	0,65
Output pressure (kPa)	400

✓ Reactor R101 (transesterification, Reaction 1)

<i>Operating parameters</i>	<i>Value</i>
Type of reactor	Simple
Reaction set	(R1)
Operating temperature (°C)	60
Pressure (kPa)	400
Conversion rate of oil into biofuel (%)	95
Methanol – oil molar ratio on input	6 : 1

✓ Distillation column T201 (methanol recovery)

<i>Operating parameters</i>	<i>Value</i>
Type of column	Distillation column (total condenser)
Number of theoretical stages	5
Feed stage	2
Overhead pressure (kPa)	20
Bottom pressure (kPa)	30
Liquid distillate flowrate (kg/h)	111
Reflux ratio	2

Column T201 additional specification:

	<i>Specification</i>	<i>Product type</i>	<i>Component</i>	<i>Value</i>	<i>Phase</i>	<i>Type</i>	<i>Action</i>
1 :	Recovery ratio	Liquid distillate	Methanol	0.9258	Liq.	Mol.	Liquid distillate flowrate

✓ Heat exchanger E201

<i>Operating parameters</i>	<i>Value</i>
Type of heat exchanger	Heater/Cooler
Output temperature (°C)	60

✓ Pump P202

<i>Operating parameters</i>	<i>Value</i>
Type of pump	Centrifugal pump
Volumetric efficiency	0,65
Outlet pressure (kPa)	200

- ✓ Liquid-liquid extraction column T301 (water wash)

This separation is done by adding 11 kg/h of water, at 25°C.

<i>Operating parameters</i>	<i>Value</i>
Column type	Extraction column
Number of theoretical stages	4
Operating pressure (°C)	60
Pressure (kPa)	120

- ✓ Distillation column T401 (FAME purification)

<i>Operating parameters</i>	<i>Value</i>
Column type	Distillation column (partial condenser)
Number of theoretical stages	5
Feed stage	2
Overhead pressure(kPa)	10
Bottom pressure(kPa)	20
Vapor distillate flowrate (kg/h)	7.82
Liquid distillate flowrate(kg/h)	999.88
Reflux ratio	2

- ✓ Reactor R-201 (catalyst neutralization, Reaction 2)

Specifications of the H₃PO₄ feed are: 8.2 kg/h, at 60°C and 110 kPa

<i>Operating parameters</i>	<i>Value</i>
Reactor type	Simple
Reaction set	(R2)
Operating pressure (°C)	60
Pressure (kPa)	110
NaOH conversion rate (%)	100

- ✓ Distillation column T501 (glycerol purification)

<i>Operating parameters</i>	<i>Value</i>
Column type	Distillation column with partial condenser
Number of theoretical stages	4
Feed stage	2
Overhead pressure (kPa)	40
Bottom pressure (kPa)	50

Liquid distillate flowrate (kg/h)	9.02
Reflux ratio	2

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 every stream. Results are also available at the unit operation level (result tab in the configuration window).

Feed streams (C101, C103, C105, H3PO4 feed, Water feed)

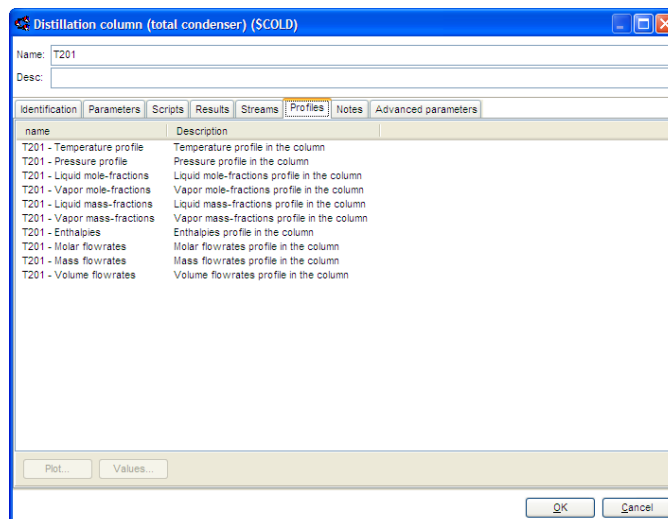
Streams		C101	C103	C105	H3PO4	Water
From		Methanol feed	NaOH feed	Oil feed	H3PO4 feed	Water feed
To		MIX101	MIX101	P103	R201	T301
Partial flowrates		kg/h	kg/h	kg/h	kg/h	kg/h
METHANOL		117,2	0	0	0	0
Triacylglycerol (oil)		0	0	1050	0	0
METHYL OLEATE (FAME)		0	0	0	0	0
GLYCEROL		0	0	0	0	0
SODIUM HYDROXIDE		0	10	0	0	0
WATER		0	0	0	0	11
PHOSPHORIC ACID		0	0	0	8,2	0
TRISODIUM PHOSPHATE		0	0	0	0	0
Total flowrate	kg/h	117,2	10	1050	8,2	11
Mass fractions						
METHANOL		1	0	0	0	0
Triacylglycerol (oil)		0	0	1	0	0
METHYL OLEATE (FAME)		0	0	0	0	0
GLYCEROL		0	0	0	0	0
SODIUM HYDROXIDE		0	1	0	0	0
WATER		0	0	0	0	1
PHOSPHORIC ACID		0	0	0	1	0
TRISODIUM PHOSPHATE		0	0	0	0	0
Physical state		Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	°C	25	25	25	60	25
Pressure	kPa	99,99	99,99	99,99	109,99	99,99
Enthalpy	kcal/h	-33230,21	-23195,65	-32686,48	-1452,96	-6402,00
Vapour fraction		0	0	0	0	0

Outlet streams (C401A, C401, C402, C501, C502, C306)

Streams		C401A	C401	C402	C501	C502	C306
From		T401	T401	T401	T501	T501	X302
To		Methanol+ Water	FAME	Oil1	Methanol+ Water1	Glycerol+ Water	Na3PO5
Partial flowrates		kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
METHANOL		1,694	0,059	0	4,85	2,30	0
Triacylglycerol (oil)		7,67E-08	0,033	52,461	0	0	0
METHYL OLEATE (FAME)		2,37	999,63	0,049	0,00029	0,0062	0
GLYCEROL		0	0	0	0,0010	103,75	0
SODIUM HYDROXIDE		0	0	0	0	0	0
WATER		3,75	0,15	0	4,16	7,43	0
PHOSPHORIC ACID		0	0	0	0	0	0,0337
TRISODIUM PHOSPHATE		0	0	0	0	0	13,66
Total flowrate	kg/h	7,82	999,88	52,51	9,02	113,49	13,69
Mass fractions							
METHANOL		0,21	5,90E-05	0	0,53	0,020	0
Triacylglycerol (oil)		9,81E-09	3,32E-05	0,99	0	0	0
METHYL OLEATE (FAME)		0,30	0,99	0,00094	3,29E-05	5,51E-05	0
GLYCEROL		0	0	0	0,00011	0,91	0
SODIUM HYDROXIDE		0	0	0	0	0	0
WATER		0,47	0,00015	0	0,46	0,065	0
PHOSPHORIC ACID		0	0	0	0	0	0,0024
TRISODIUM PHOSPHATE		0	0	0	0	0	0,99
Physical state		Vapor	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	°C	171,79	171,79	466,51	52,93	90,18	60
Pressure	kPa	9,99	9,99	19,99	39,99	49,99	109,99
Enthalpy	kcal/h	488,97	-7241,60	11285,88	-3576,57	-24756,84	-959,57
Vapour fraction		1	0	0	0	0	0

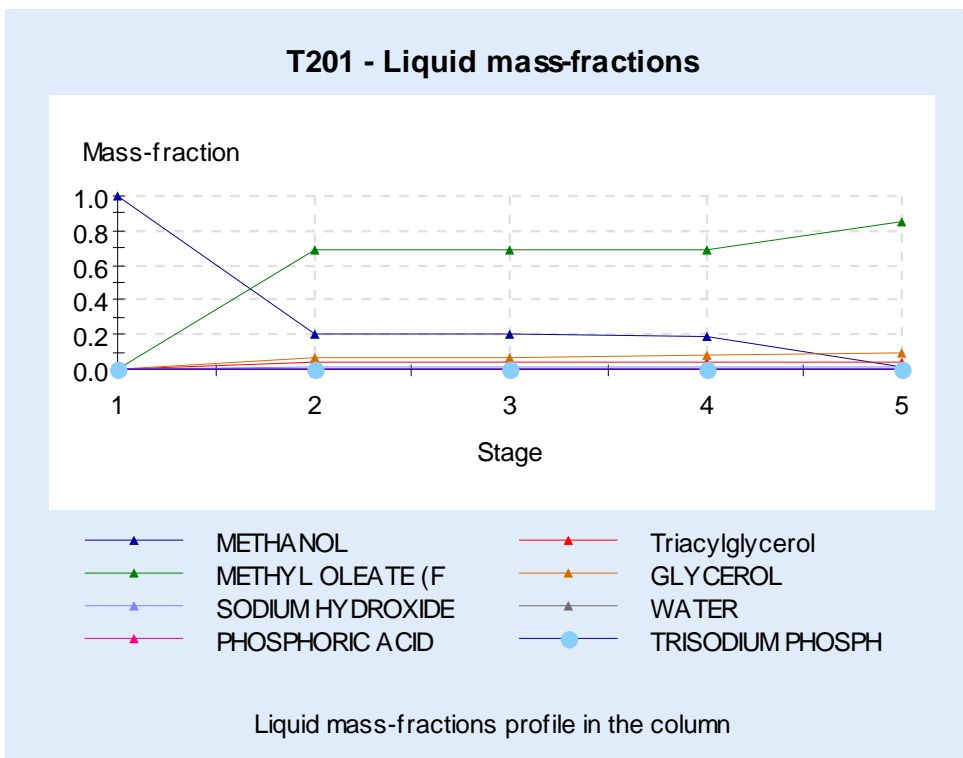
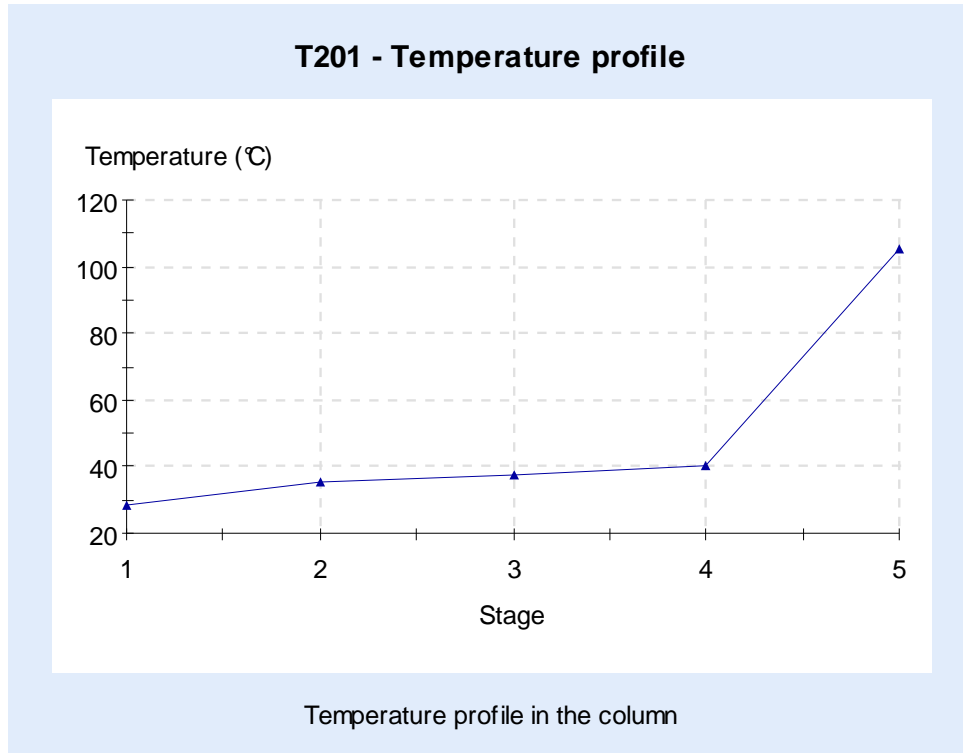
2.2. Columns profiles

Composition profiles can be accessed after the simulation in each column configuration window, in the "Profiles" tab. Double clicking on the profile will generate the corresponding graph. Here, only the liquid-mole fractions is shown for the three columns.

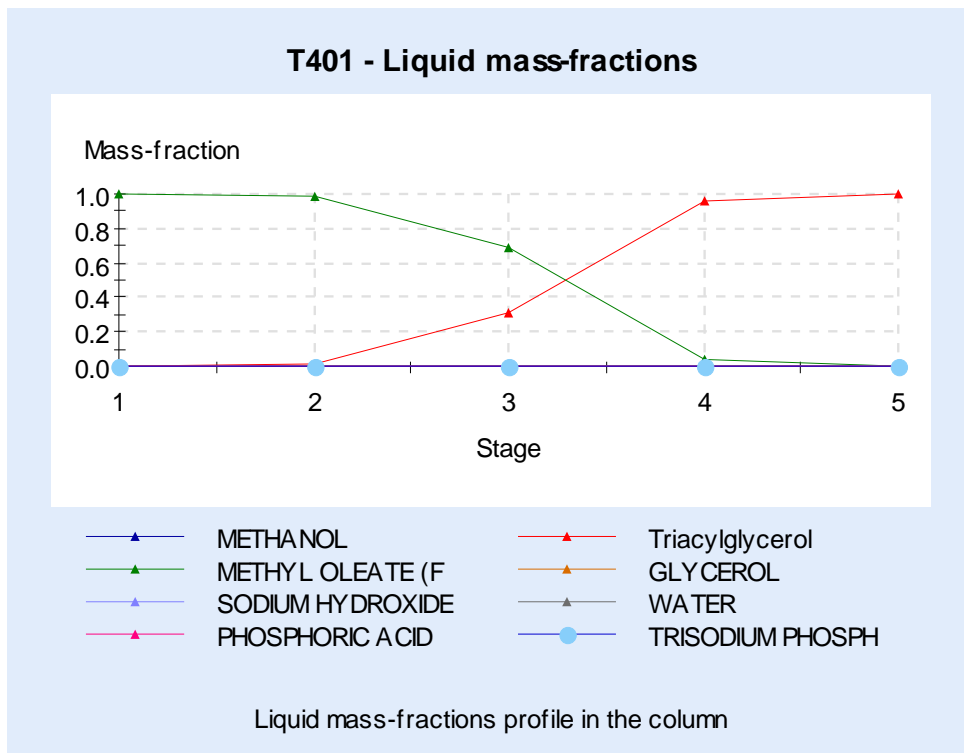
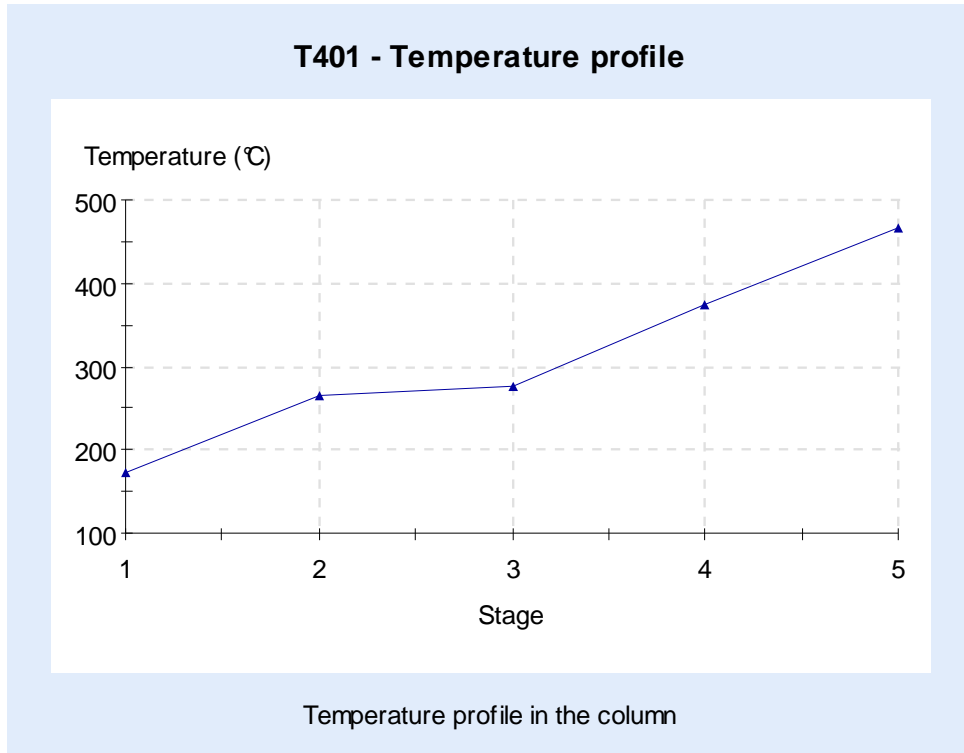


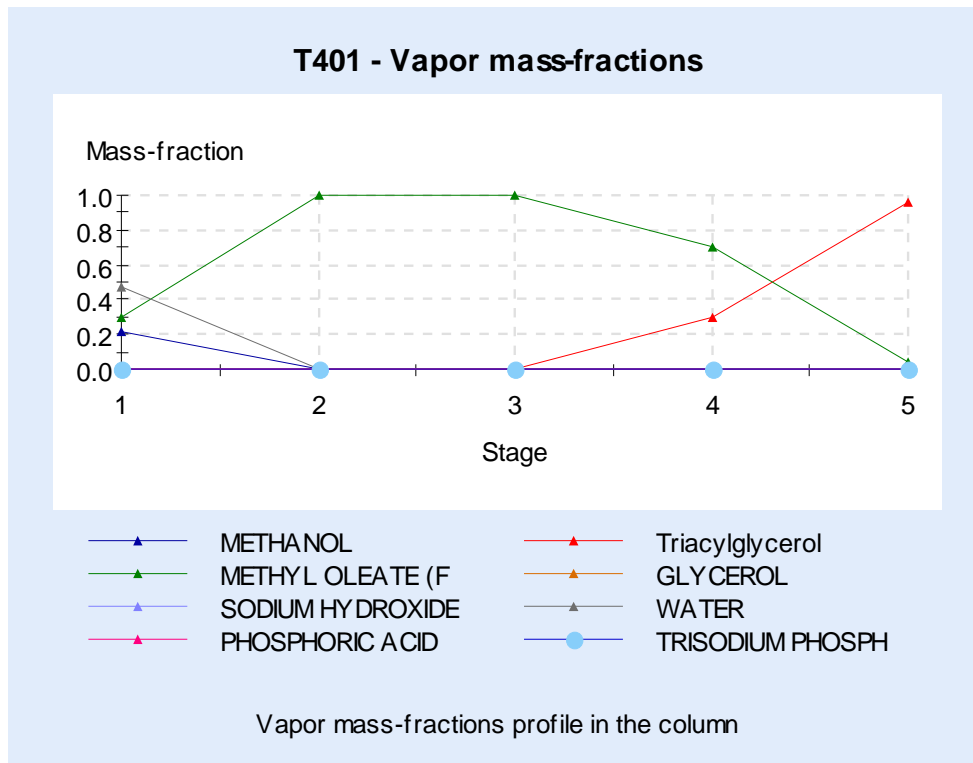
Note that in ProSimPlus the stages are numbered from top to bottom. Stage 1 is the condenser, the last stage is the boiler.

Column T201

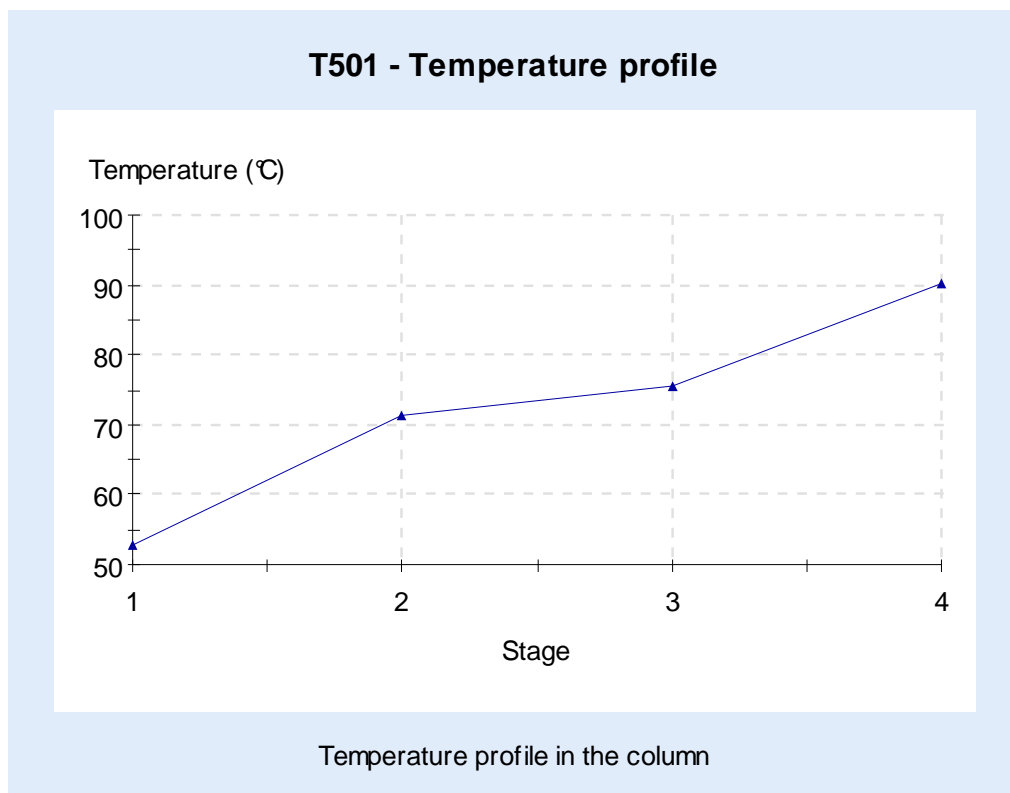


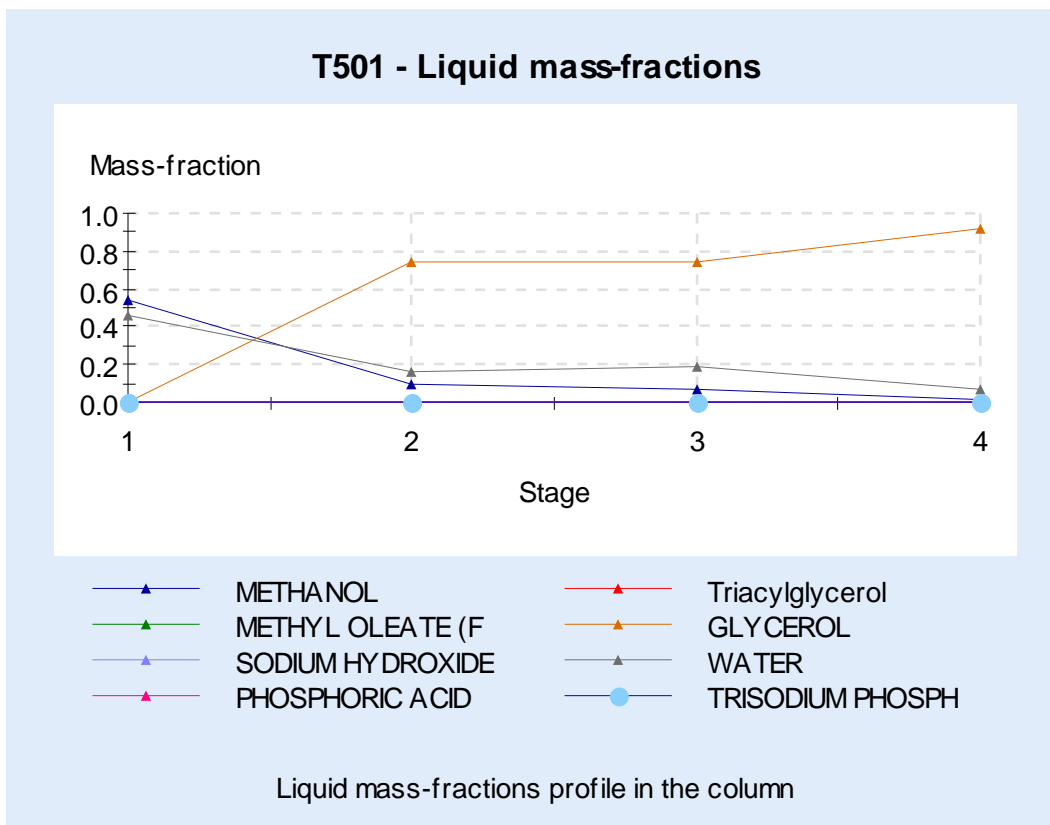
Column T401





Column T501





3. REFERENCES

- [1] Zhang, Y., Dubé, M.A., McLean, D.D., Kates, M.
 "Biofuel production from waste cooking oil: 1.Process design and technological assessment"
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