ProSim

PROSIMPLUS APPLICATION EXAMPLE

BIOETHANOL PRODUCTION PLANT

EXAMPLE PURPOSE
In this example, a bioethanol production unit is presented. Ethanol is produced from biomass by hydrolysis and sugar fermentation. First, the biomass is pre-treated with acid and enzyme to produce sugar. The sugar is then fermented into ethanol. The ethanol produced still contains a significant amount of water, which is removed by using fractional distillation. This example illustrates how to add new components to the database and how to use multiple complex reaction sets in ProSimPlus.

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CORRESPONDING PROSIMPLUS FILE	*PSPS_EX_EN-Bioethanol-Plant.pmp3*

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1. INTRODUCTION

There are two types of ethanol industrially produced: synthetic ethanol and fermentation ethanol. Fermentation ethanol (or bioethanol) can be produced from biomass materials containing sugars, starches or cellulose (starch and cellulose are more complex forms of sugar). All these production processes require a fermentation step to convert the sugar into ethanol, as well as a more or less advanced distillation step to separate the alcohol from the water.

Ethanol is a widely used biofuel. In addition to being renewable, ethanol has a major advantage in that it can be easily blended with gasoline. In some cases ethanol is first converted to its ether form (ETBE), obtained in reaction with refinery isobutene. When small amounts of ethanol are added to gasoline, there are many advantages, in particular the reduction of carbon monoxide and other toxic pollution from exhaust gases of vehicles. Because ethanol is made from crops that absorb carbon dioxide and give off oxygen, it helps reduce greenhouse gas emissions. Ethanol is also added to gasoline as an octane enhancer.

For all these reasons many ethanol producers or engineering firms are today focusing on designing and building-up new plants as rapidly as possible in order to satisfy a growing demand. In parallel, rigorous process simulation (as it can be performed with ProSimPlus) is today increasingly used to design and optimize the bioethanol production processes.

2. PROCESS MODELING

2.1. Process description

The feedstock used in this process is corn stover. The main compounds are cellulose, hemicellulose and lignin. The modeling starts just after the washing of the feedstock which step induces an increase of the feedstock moisture. Three reaction steps follow:

1. Hydrolysis (reactor R101): the feedstock is heating (190°C) at high pressure (12.1 atm) with an acid catalyst (H_2SO_4). Most of the hemicellulose is converted to xylose.
2. Saccharification (reactor R102): this is an enzymatic reaction that converts the cellulose into glucose.
3. Fermentation (reactor R103): most of the glucose and xylose are converted to ethanol and carbon dioxide.

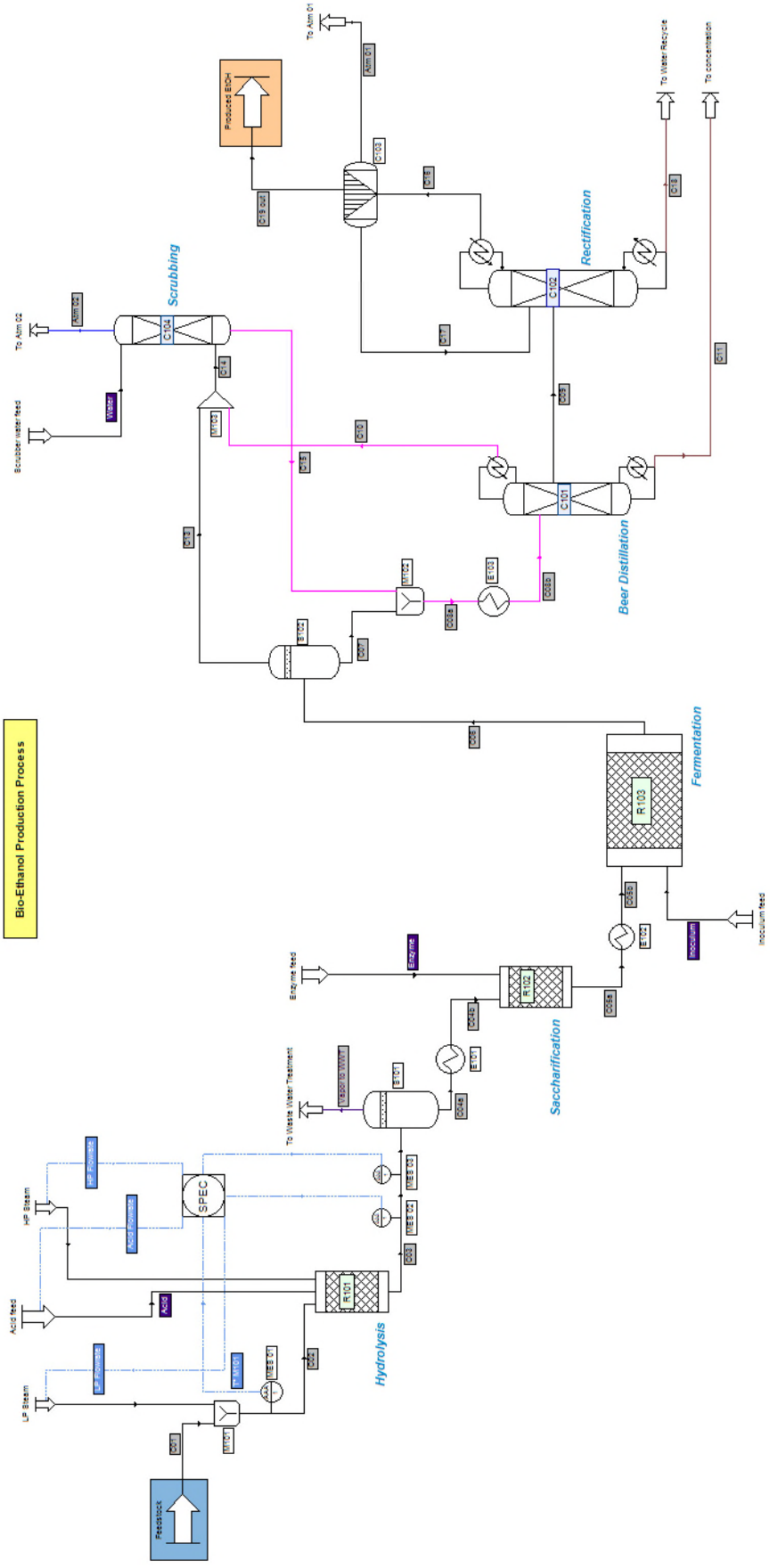
A flash separation (S101) at atmospheric pressure is present between the hydrolysis reactor and the saccharification reactor to evacuate part of the water and some by-products. Another flash (S102) is used after the fermentation reactor (R103) to separate the incondensable (CO_2).

The first distillation column (C101) separates the rest of the incondensable (CO_2), which is recovered at the vapor distillate (stream C10). The water, sugars and the un-reacted part of the feedstock are produced at the bottom (stream C11) and the ethanol (≈ 40% mass) is withdrawn at a side-stream (stream C09). This side-stream goes to a second distillation column (C102). The ethanol (≈ 92% mass), is recovered at the vapor distillate (stream C16). At the bottom, water is recovered and recycled in the process (stream C18). The ethanol is dried in a molecular sieve adsorption unit (C103). This part of the process is modeled by a component splitter.

A scrubber (C104) separates ethanol and water contained in the gas stream coming from the flash separator (S102) after the fermentation reactor and the vapor distillate of the first distillation column (C101).

This example is taken from a publication [1].

2.2. Process flowsheet



Bioethanol plant process flowsheet

2.3. Specifications

The main specifications imposed on the process are:

- ✓ A temperature of 100°C after mixer *M101* by acting on the *LP Steam* flowrate
- ✓ A temperature of 190°C at the outlet of hydrolysis reactor *R101* by acting on the *HP Steam* flowrate
- ✓ A H_2SO_4 mass fraction of 1.1% at the outlet of hydrolysis reactor *R101* by acting of the total flowrate of the *Acid* stream.

2.4. Components

The components used in this example are listed in the following table.

Name	Chemical formula	CAS Number	Use in the process
Acetate	$C_2H_4O_2$	-	Acetate groups present in the hemicellulose polymer
Acetic acid	$C_2H_4O_2$	64-19-7	Coming from acetate hydrolysis and fermentation by-product
Carbon dioxide	CO_2	124-38-9	Fermentation product
Cellobiose	$C_{12}H_{22}O_{11}$	-	Coming from cellulose hydrolysis and saccharification
Cellulose	$C_5H_{10}O_5$	-	Feedstock
Corn steep liquor (CSL)	Unknown (modeled as water)	-	Bacteria feed nitrogen source
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	7783-28-0	Bacteria feed nitrogen source
Enzyme	$CH_{1.57}N_{0.29}O_{0.31}S_{0.007}$	-	Saccharification enzyme
Ethanol	C_2H_6O	64-17-5	Desired product
Furfural	$C_5H_4O_2$	98-01-1	Hemicellulose hydrolysis by-product
Glucose	$C_6H_{12}O_6$	50-99-7	Coming from cellulose hydrolysis and saccharification
Glycerol	$C_3H_8O_3$	56-81-5	Fermentation by-product
Hemicellulose	$C_5H_8O_4$	-	Feedstock
Lactic acid	$C_3H_6O_3$	598-82-3	Fermentation by-product
Lignin	$C_{10}H_{13.9}O_{1.3}$	-	Feedstock
Oxygen	O_2	7782-44-7	Fermentation product
Succinic acid	$C_4H_6O_4$	110-15-6	Fermentation by-product
Sulfuric acid	H_2SO_4	7664-93-9	Acid catalyst
Water	H_2O	7732-18-5	Product moisture, washing and reaction product
Xylitol	$C_5H_{12}O_5$	-	Fermentation by-product
Xylose	$C_5H_{10}O_5$	-	Coming from hydrolysis and saccharification
Z. mobilis	$CH_{1.8}O_{0.5}N_{0.2}$	-	Fermentation bacteria

Some of these compounds are not included in the ProSim standard database provided with ProSimPlus. Consequently, some components have been represented with similar components and some properties have been estimated as detailed in the following table.

Component	Properties
Acetate	Modeled as Acetic acid.
Cellobiose	Modeled as Glucose. Modification: molecular weight(E)
Cellulose	Modeled as Glucose. Modification: molecular weight(E), ideal gas heat of formation(E), liquid molar volume(E), liquid heat capacity(E)
CSL	Modeled as Water. Modification: glucose vapor pressure
Enzyme	Modeled as Glucose.
Hemicellulose	Modeled as Glucose. Modification: molecular weight(E), ideal gas heat of formation(E), liquid molar volume(E), liquid heat capacity(E)
Lignin	Modeled as Glucose. Modification: molecular weight(E), liquid molar volume(E), liquid heat capacity(E)
Xylitol	Modeled as Hemicellulose. Modification: molecular weight(E)
Xylose	Modeled as Glucose. Modification: molecular weight(E), critical temperature(E), critical pressure(E), critical volume(E), acentric factor(E), ideal gas heat of formation(E), liquid molar volume(E), liquid heat capacity(E)
Z. mobilis	Modeled as Glucose. Modification: ideal gas heat of formation(E), liquid molar volume(E), liquid heat capacity(E)

*Note: (E) e*stimated property.

2.5. Thermodynamic model

This system contents polar compounds (like water and ethanol), which induce strong interactions in the liquid phase. The working pressure being weak (from 1 to 5 atm), the vapor phase behavior can be assimilated to that of an ideal gas. Consequently the NRTL model has been selected. The required binary interaction parameters that were not available in ProSimPlus database were estimated with a predictive model, using the dedicated functionality offered by Simulis Thermodynamics.

The following table shows the binary interaction parameters taken into account.

Component		c_{12}^0	c_{21}^0	a_{12}^0	$c_{12}(T)$	$c_{21}(T)$	$a_{12}(T)$	Note
1	2							
Water	CO_2	922.65	2256.3	0.3	7.1259	-5.548	0	A
Water	Ethanol	1616.81	-635.56	0.1448	2.0177	0.9907	0	B
Water	Furfural	2602.6374	436.9686	0.3958	0	0	0	C
CO_2	Ethanol	2.0708	-3.5177	0.3	927.13	-18.62	0	A

Note A: The binary interaction parameters are estimated from activity coefficients at infinite dilution calculated with UNIFAC-PSRK model.

Note B: These binary interaction parameters are available in ProSim's software binary interaction parameters database.

Note C: From [2].

2.6. Chemical reactions

Three chemical reaction sets are defined.

For all the chemical reactions, heats of reaction are calculated from standard enthalpies of formation at 298.15 K.

- ✓ Pretreatment hydrolyser reactions:

Reactions	*Reactant*	*Fraction converted to product*
Cellulose + H_2O ➔ Glucose	Cellulose	0.077
Cellulose + 0.5 H_2O ➔ 0.5 Cellobiose	Cellulose	0.007
Hemicellulose + H_2O ➔ Xylose	Hemicellulose	0.925
Hemicellulose ➔ Furfural + 2 H_2O	Hemicellulose	0.05
Acetate ➔ Acetic acid	Acetate	1

- ✓ Saccharification reactions:

Reactions	*Reactant*	*Fraction converted to product*
Cellulose + H_2O ➔ Glucose	Cellulose	0.94
Cellulose + 0.5 H_2O ➔ 0.5 Cellobiose	Cellulose	0.012
Cellobiose + H_2O ➔ 2 Glucose	Cellobiose	1

✓ Fermentation reactions:

Reactions	*Reactant*	*Fraction converted to product*
Glucose ➔ 2 Ethanol + 2 CO_2	Glucose	0.95
Glucose + CSL + 0.018 DAP ➔ 6 Z.mobilis + 2.4 H_2O + 0.3 O_2	Glucose	0.02
Glucose + 2 H_2O ➔ 2 Glycerol + O_2	Glucose	0.004
Glucose + 2 CO_2 ➔ 2 Succinic acid + O_2	Glucose	0.006
Glucose ➔ 3 Acetic acid	Glucose	0.015
Glucose ➔ 2 Lactic acid	Glucose	0.002
3 Xylose ➔ 5 Ethanol + 5 CO_2	Xylose	0.85
Xylose + 0.833 CSL + 0.015 DAP ➔ 5 Z.mobilis + 2 H_2O + 0.25 O_2	Xylose	0.019
3 Xylose + 5 H_2O ➔ 5 Glycerol + 2.5 O_2	Xylose	0.003
Xylose + H_2O ➔ Xylitol + 0.5 O_2	Xylose	0.046
3 Xylose + 5 CO_2 ➔ 5 Succinic acid + 2.5 O_2	Xylose	0.009
2 Xylose ➔ 5 Acetic acid	Xylose	0.014
3 Xylose ➔ 5 Lactic acid	Xylose	0.002

2.7. Operating conditions

✓ Process feed

	Feed
Eau (kg/h)	45 007
Cellulose (kg/h)	31 178
Hemicellulose (kg/h)	22 924
Lignin (kg/h)	15 002
Acetate (kg/h)	2 435
Temperature (°C)	45
Pressure (atm)	1

✓ Steam inlet

	LP Steam	*HP Steam*
Water (kg/h)	6 700 (initialization)	10 000 (initialization)
Temperature (°C)	164	268
Pressure (atm)	4.42	13

✓ Catalyst feed

	Catalyst Acid feed
Water (kg/h)	98 256
Sulfuric acid (kg/h)	2 104 (initialization)
Temperature (°C)	745
Pressure (atm)	4

✓ Scrubber feed

	Scrubber Water feed
Water (kg/h)	36 000 (initialization)
Temperature (°C)	26
Pressure (atm)	1

✓ Reactors inlet

Characteristics	*Saccharification enzyme inlet Enzyme*	*Fermentation bacteria inlet Inoculum*
Water (kg/h)	6 255	33 881
Enzyme (kg/h)	568	
Z. mobilis (kg/h)		193
Diammonium Phosphate (kg/h)		136
Corn Steep Liquor (kg/h)		1 087
Temperature (°C)	20	41
Pressure (atm)	1	1

✓ Reactors

Operating parameters	*Hydrolysis reactor R101*	*Saccharification reactor R102*	*Fermentation reactor R103*
Type of reactor	Simple	Simple	Simple
Reaction set	Hydrolysis	Saccharification	Fermentation
Temperature outlet (°C)	Adiabatic	65	41
Pressure outlet (atm)	12,1	1	1

✓ Separators

Operating parameters	*S101 Water evaporation*	*S102 Reactor R102 vent*
Separator type	Liquid-Vapor separator	Liquid-Vapor separator
Temperature (°C)	Adiabatic	Inlet temperature
Pressure (atm)	1	Inlet pressure

✓ Heat exchangers

Name	*Type*	*Output temperature (°C)*
E101	Cooler / Heater	65
E102	Cooler / Heater	41
E103	Cooler / Heater	100

✓ Columns

Operating parameters	*C101*	*C102*	*C104*
Column type	Two-phase distillation column	Two-phase distillation column	Absorber
Number of stages	34	62	4
Feed stage	5	Scrubber bottom: 20 C101 side stream: 45	-
Side streams			
Stage	9	-	-
Flowrate (kmol/h)	2472,5		
Sate	Vapor		
Vapor distillate flowrate (kg/h)	491	30 740	-
Molar reflux ratio	3	3.2	
Pressure			
Overhead (atm)	1.86	1.7	1
Side stream (atm)	1.91	-	-
Bottom (atm)	2.1		
Tray efficiency	0.48	0.57	1

Additional column C104 specification:

Specification		*Product type*	*Compounds*	*Value*	*Phase*	*Type*	*Action*
1:	Recovery ratio	Vapor distillate	CO_2	0.998	Vapor	Mass	Water inlet flowrate

✓ Molecular sieve adsorption unit *C103 (modeled as a component splitter)*

Operating parameters	*Overhead product*	*Bottom product*	*Other product*
Temperature (°C)	Inlet temperature	70	Bubble point temperature
Pressure (atm)	Inlet pressure	1.53	Inlet pressure
Recovery ratio	Carbon dioxide: 1 Oxygen: 1		Water: 0.05 Ethanol: 0.80

✓ Mixer *M102*

	Operating parameter
Outlet pressure (atm)	4.76

3. RESULTS

3.1. Comments on results

The calculation sequence (order of calculation of the unit operations) is automatically generated. No initialization is required to converge the flowsheet (no tear stream initialized). Although there are two recycle streams and three specifications, convergence of the flowsheet is easily reached.

Three input flowrates are adjusted in order to reach the right operating conditions for the hydrolysis reactions. 6,7 t/h of LP Steam and 38,2 t/h of HP Steam are needed to reach the working temperature level in the hydrolysis reactor. 2,9 t/h of pure H_2SO_4 is needed to reach the working acid mass fraction in the hydrolysis reactor.

To have a recovery ratio de 99.8% of CO_2 in the scrubber, a water flowrate of 41,7 t/h is required.

The production is about 22,8 t/h of ethanol on dry basis (99.5% mass) for a feedstock of 71,6 t/h on dry basis (39% mass moisture).

3.2. 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).

Main inlet streams

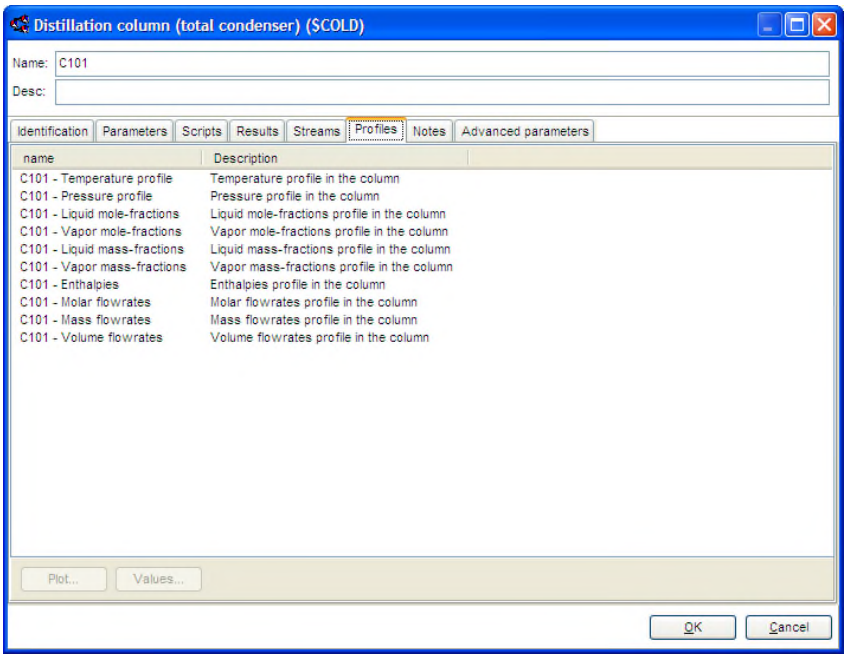
Streams		C01	Acid	Inoculum	Enzyme
From		Feedstock	Acid feed	Inoculum feed	Enzyme feed
To		M101	R101	R103	R102
Partial flows		t/h	t/h	t/h	t/h
WATER		45,00	98,25	33,88	6,25
CARBON DIOXIDE		0	0	0	0
ETHANOL		0	0	0	0
SULFURIC ACID		0	2,88	0	0
GLUCOSE		0	0	0	0
XYLOSE		0	0	0	0
CELLULOSE		31,18	0	0	0
HEMICELLULOSE		22,92	0	0	0
LIGNIN		15,00	0	0	0
FURFURAL		0	0	0	0
CELLOBIOSE		0	0	0	0
ENZYME		0	0	0	0,56
Z. MOBILIS		0	0	0,19	0
DIAMMONIUM PHOSPHATE		0	0	0,13	0
OXYGEN		0	0	0	0
CSL		0	0	1,08	0
GLYCEROL		0	0	0	0
SUCCINIC ACID		0	0	0	0
ACETIC ACID		0	0	0	0
LACTIC ACID		0	0	0	0
XYLITOL		0	0	0	0
ACETATE		2,43	0	0	0
Total flow	kg/h	116,55	101,14	35,29	6,82
Physical state		Liquide	Liquide	Liquide	Liquide
Temperature	°C	45	74	41	20
Pressure	atm	1,00	4,00	1,00	1,00
Enthalpy	kcal/h	-36684723,5	-52927597,9	-19943770	-3846201,37
Vapor fraction		0	0	0	0

Other streams

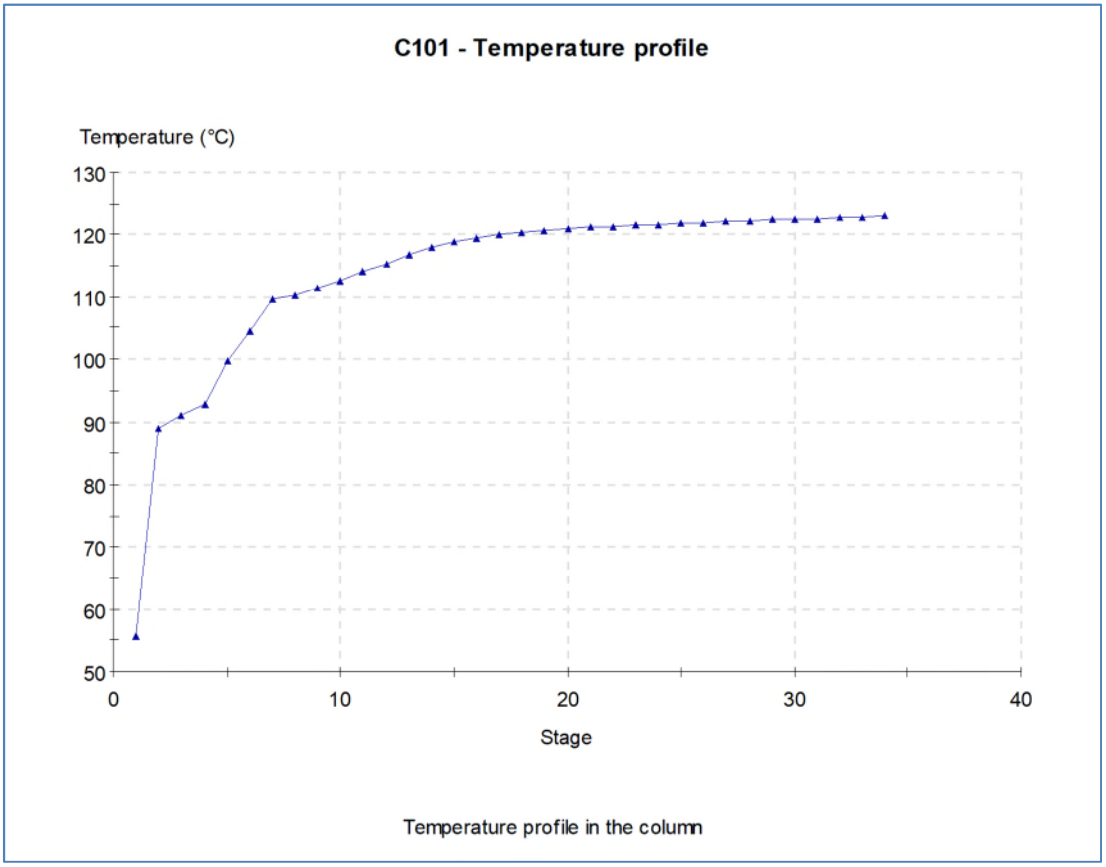
Streams		C02	C05a	C06	C09	C19 out
From		MES 01	R102	R103	C101	C103
To		R101	E102	S102	C102	Produced EtOH
Partial flows		t/h	t/h	t/h	t/h	t/h
WATER		51,73	152,81	186,79	34,09	0,12
CARBON DIOXIDE		0	0	25,00	002	0
ETHANOL		0	0	26,39	26,38	22,75
SULFURIC ACID		0	2,88	2,89	6,10E-05	0
GLUCOSE		0	32,74	0,10	0	0
XYLOSE		0	24,09	1,37	0	0
CELLULOSE		31,18	1,37	1,37	0	0
HEMICELLULOSE		22,92	0,57	0,57	0	0
LIGNIN		15,00	15,00	15,00	1,14E-07	0
FURFURAL		0	0,46	0,47	0,32	0
CELLOBIOSE		0	0,36	0,36	0	0
ENZYME		0	0,56	0,57	0	0
Z. MOBILIS		0	0	1,11	8,40E-09	0
DIAMMONIUM PHOSPHATE		0	0	0,12	0	0
OXYGEN		0	0	0,29	7,45E-08	0
CSL		0	0	0,98	7,41E-09	0
GLYCEROL		0	0	0,21	1,09E-05	0
SUCCINIC ACID		0	0	0,54	3,76E-06	0
ACETIC ACID		0	2,15	2,98	0,225972	0
LACTIC ACID		0	0	0,11	9,61E-05	0
XYLITOL		0	0	1,12	0	0
ACETATE		2,43	0	0	0	0
Total flow	kg/h	123,28	233,04	268,34	61,03	22,87
Physical state		Liquide	Liquide	Liq./Vap.	Vapeur	Liquide
Temperature	°C	100	65	41,00	111,40	92,08
Pressure	atm	1,00	1,00	1,00	1,91	1,70
Enthalpy	kcal/h	-36310578	-96472244,9	-115966771,74	2188935,52	-3952048,52
Vapor fraction		0	0	0,05	1	0

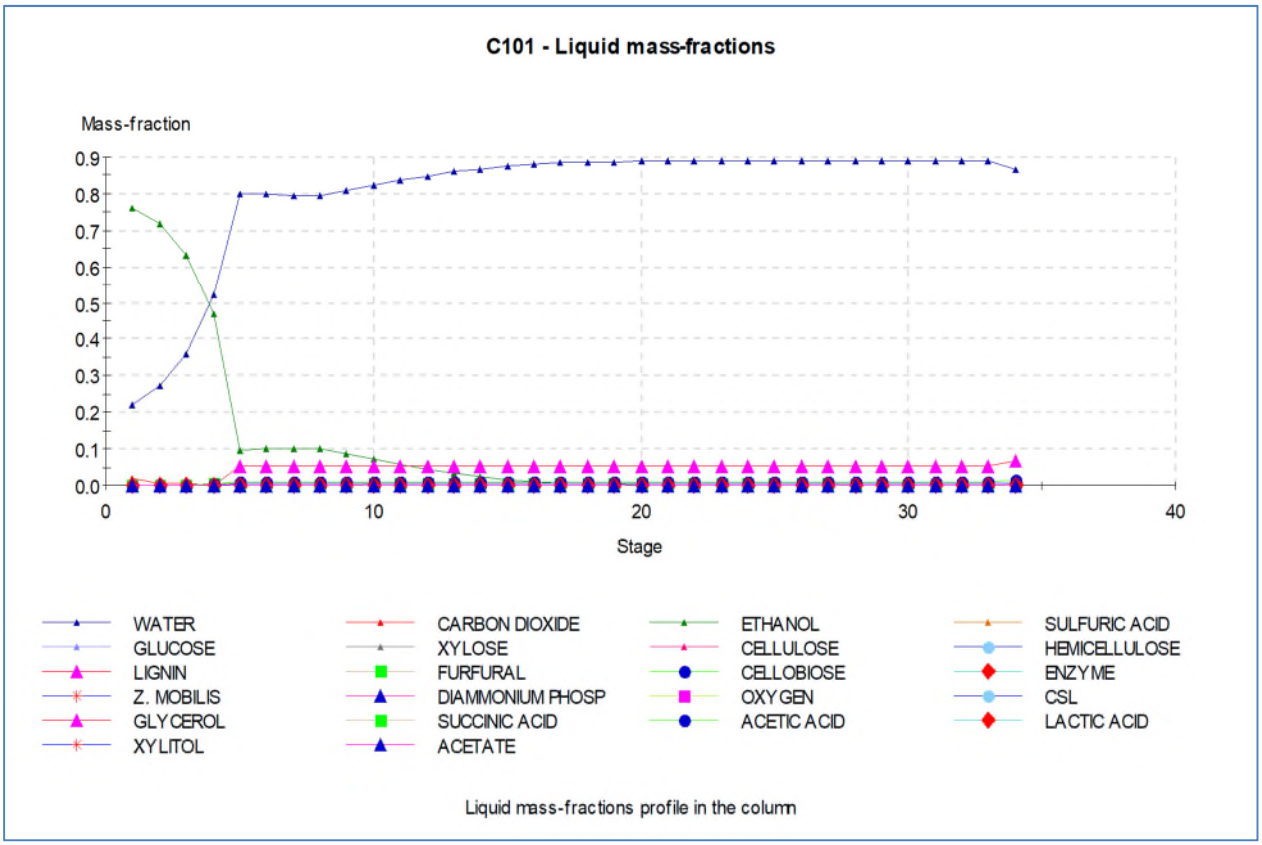
3.3. Column profiles

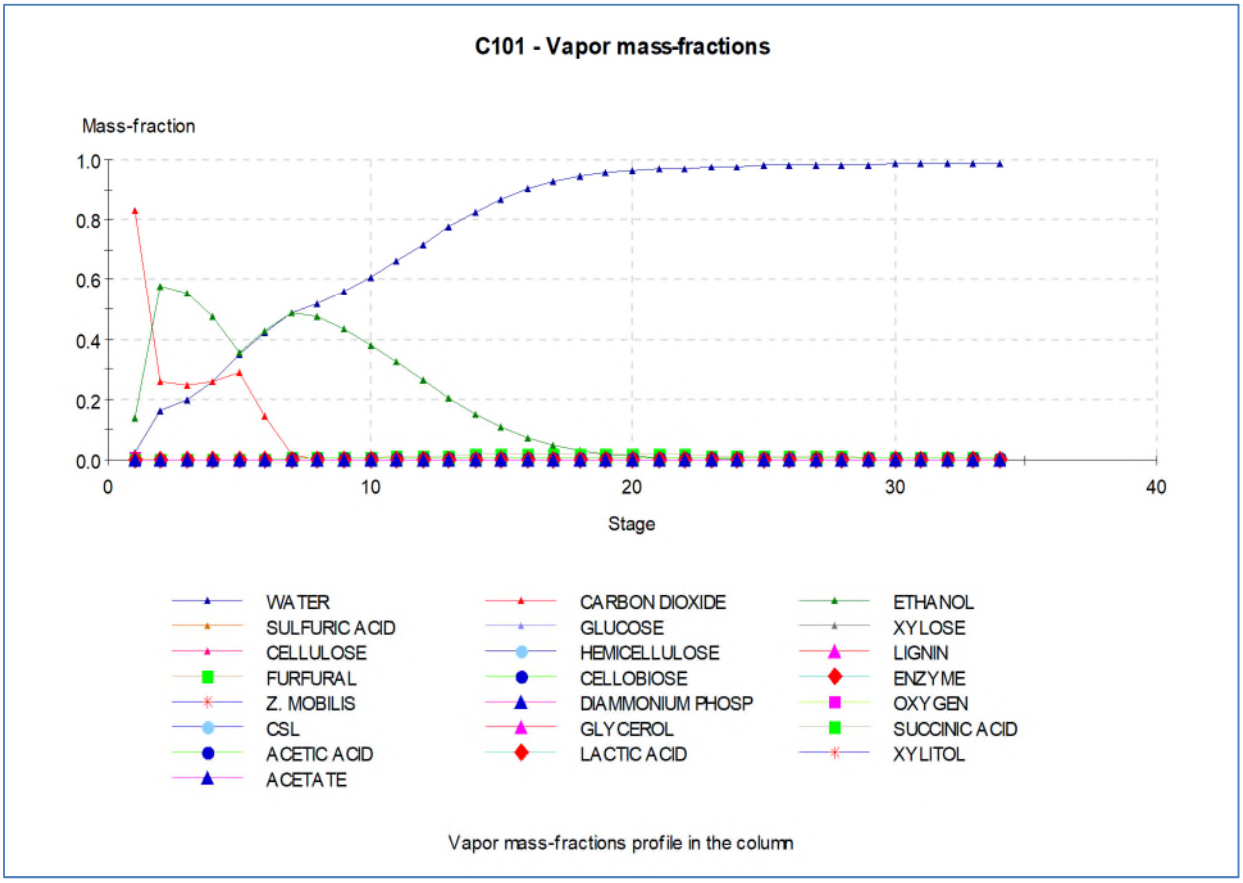
Composition profiles can be accessed after the simulation in each column configuration window, in the "Profiles" tab. Double clicking on the profile will generate the corresponding graph. It is important to note that, in ProSimPlus, first stage correspond to condenser and last stage to reboiler (numbering from top to bottom)



Column C101







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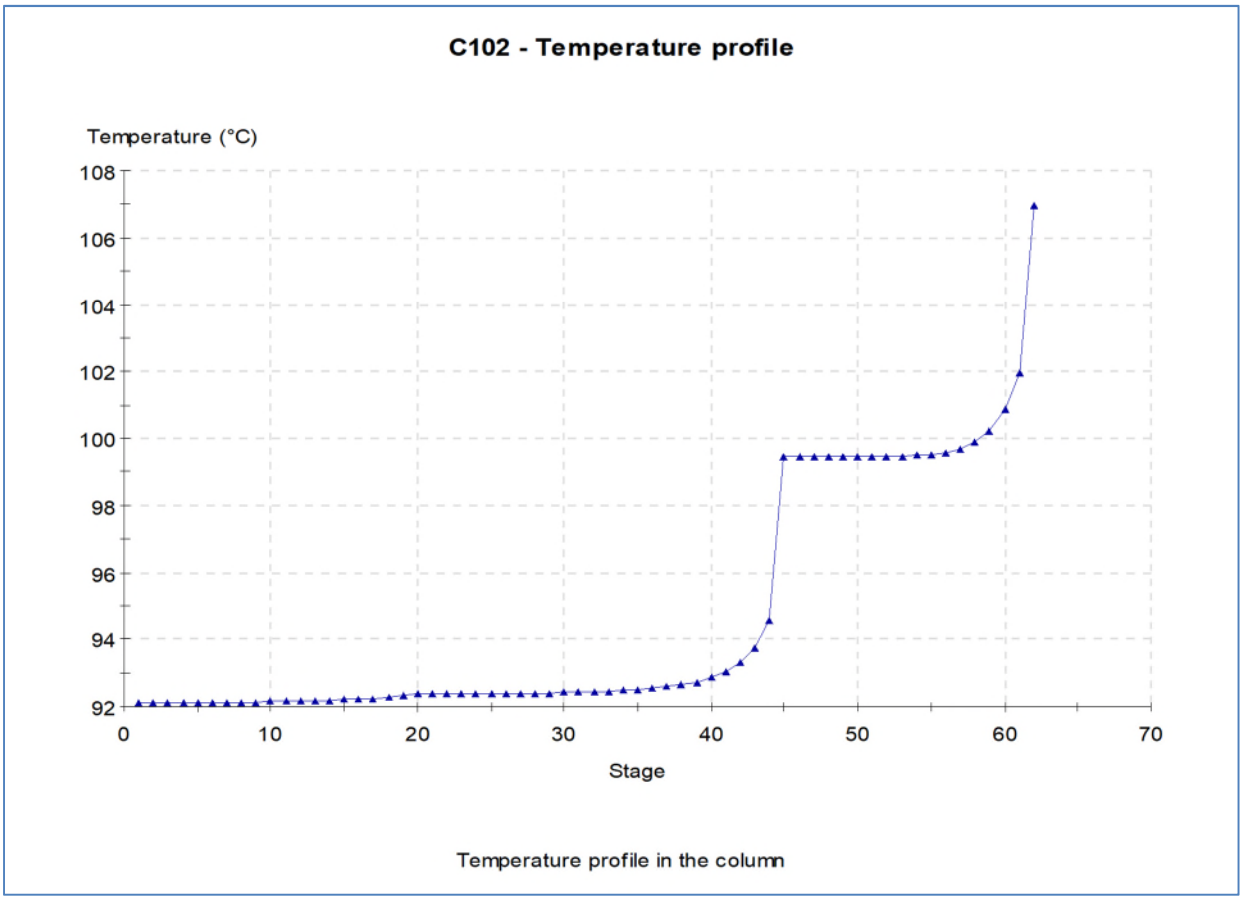
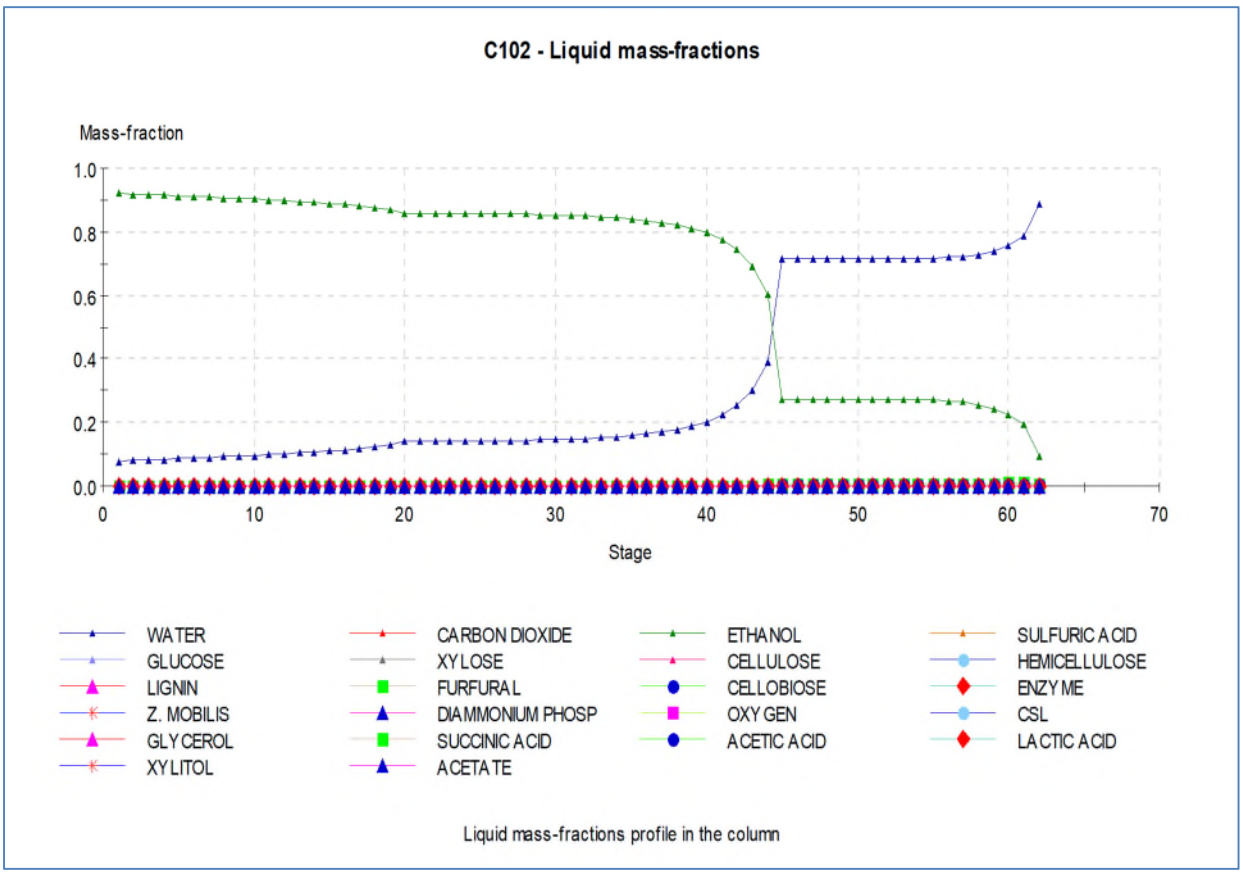
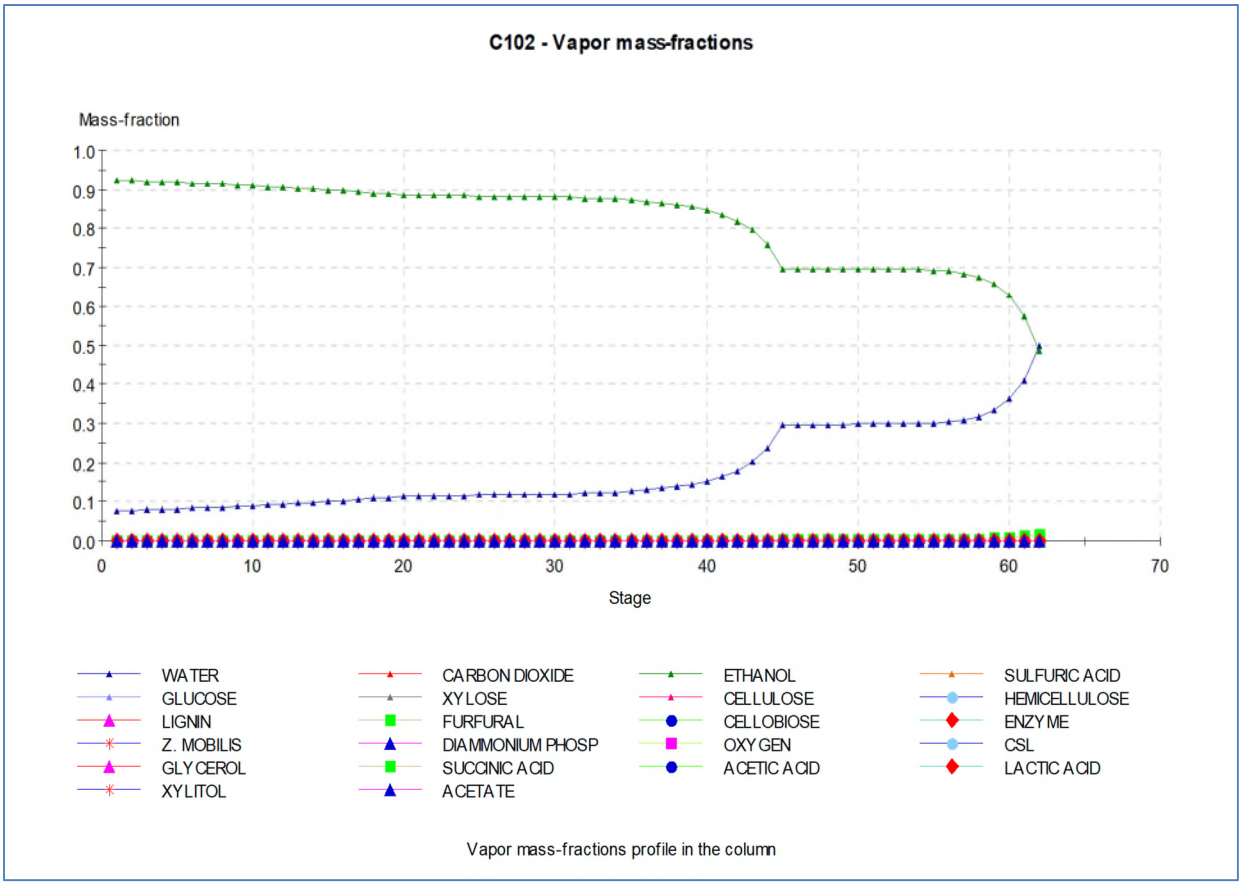


Temperature profile in the column



Liquid mass-fractions profile in the column



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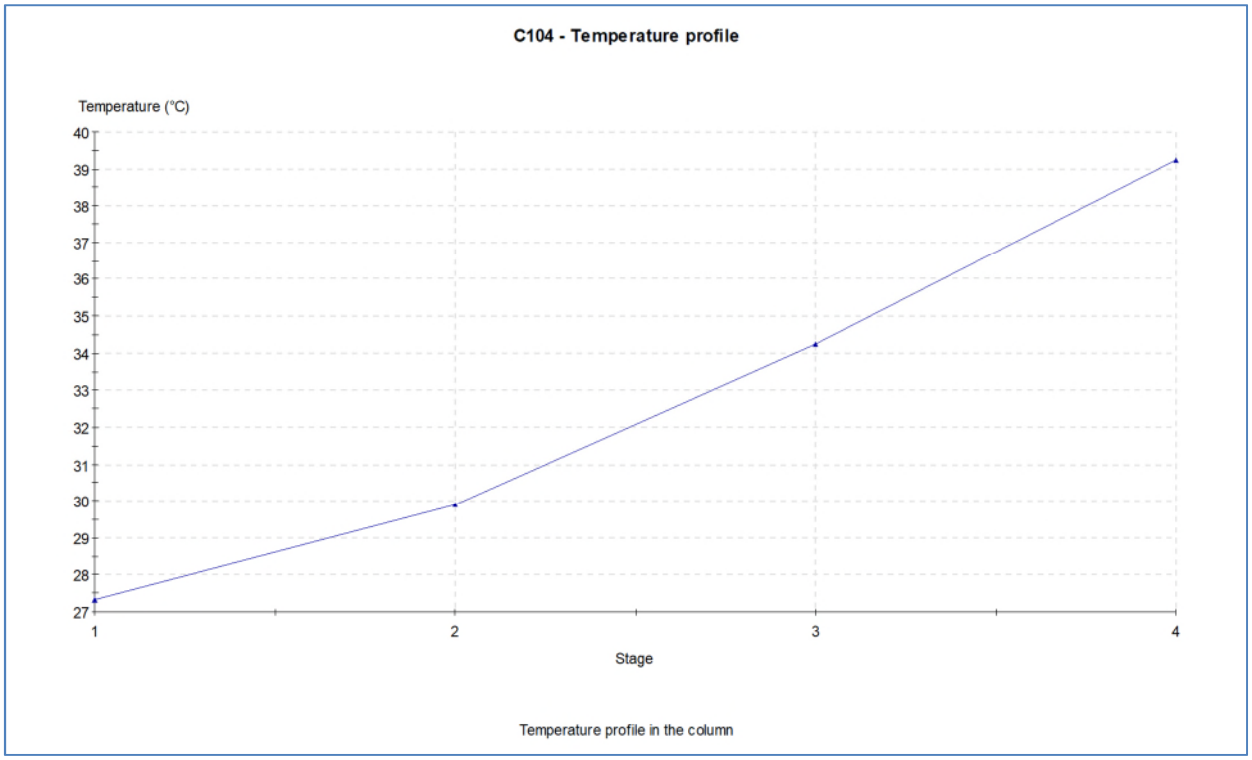

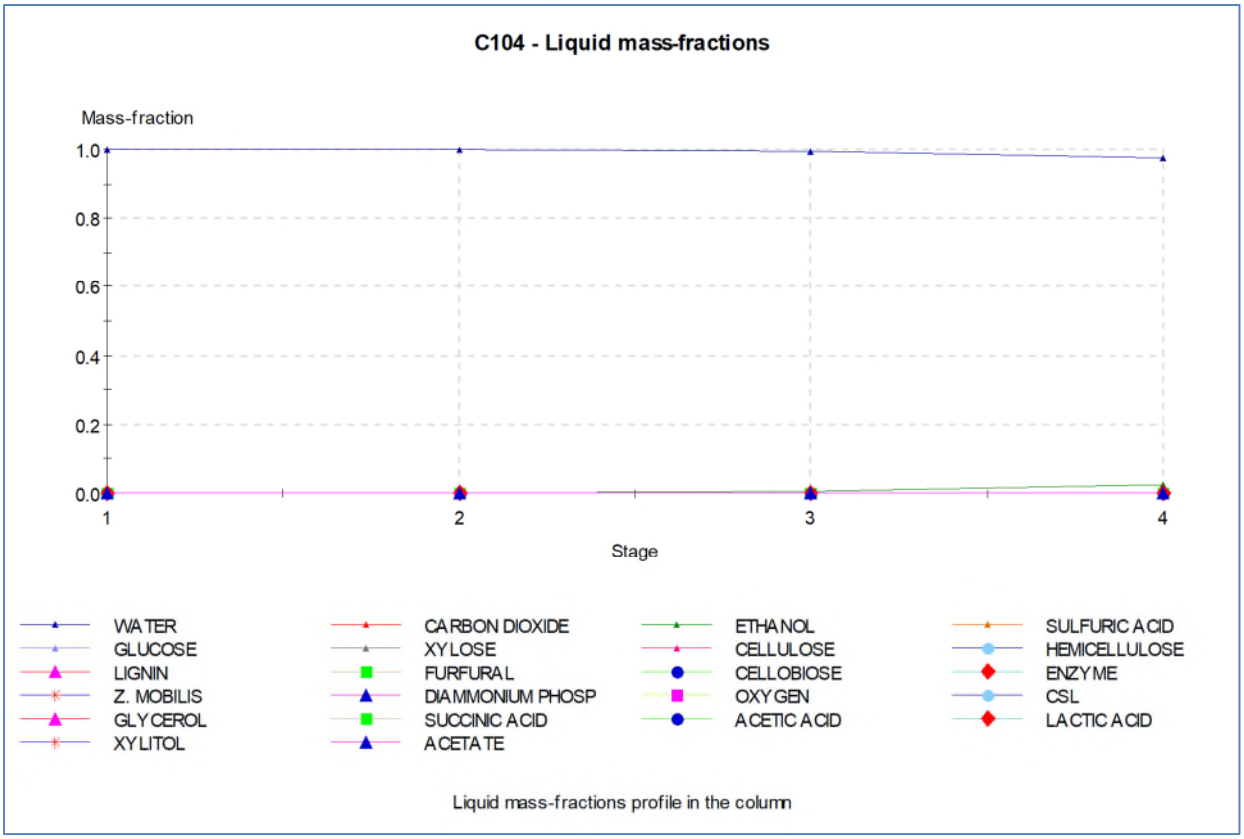

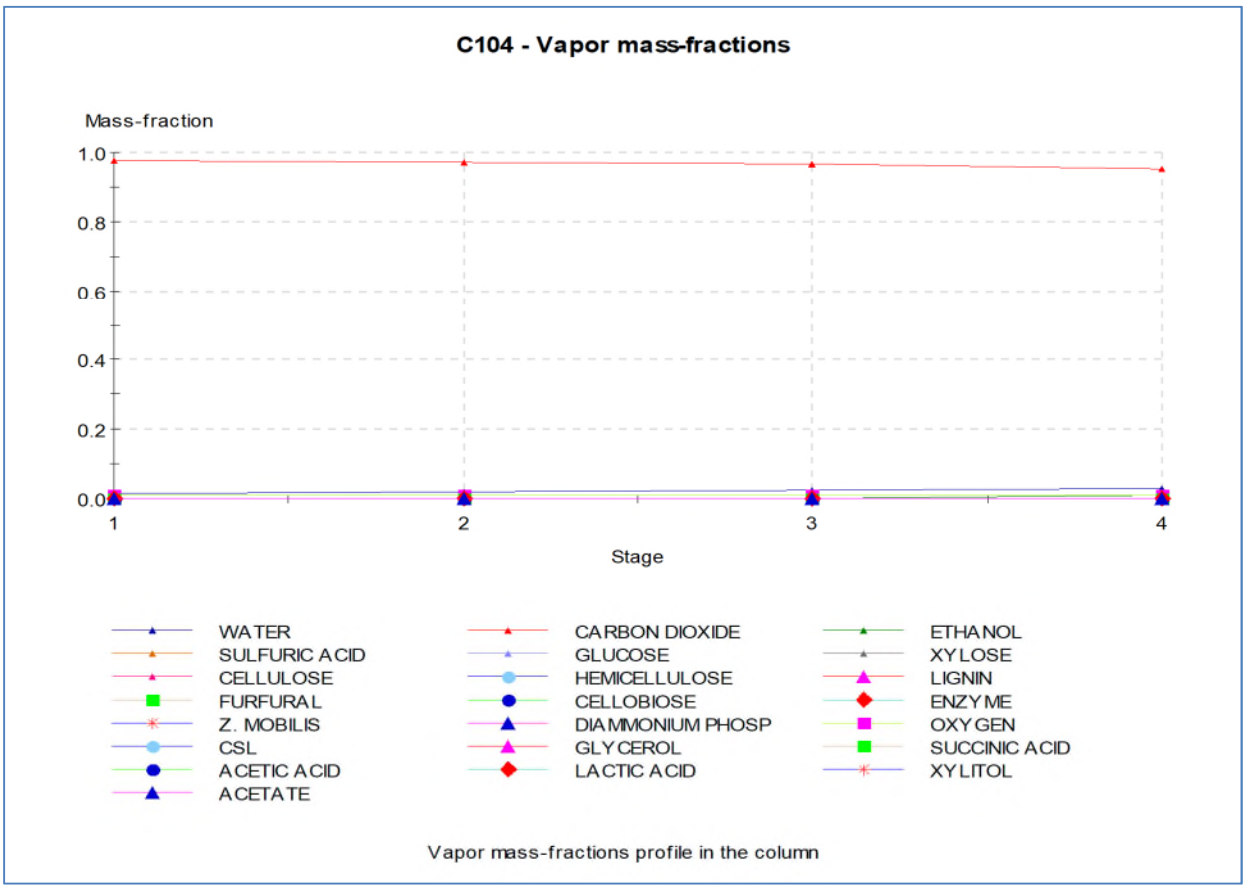

4. REFERENCES

[1] A. Aden, M. Ruth, K. Ibsen, J; Jechura, K. Neeves, J. Sheehan, B. Wallace
Lignocellulosic Biomass to Ethanol Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover.
NREL, NREL/TP-510-32438, 2002.

[2] DECHEMA
Deutsche Gellelschaft Für Chemische Technik und Biotechnology e.V.

