Supplementary Materials

Supplementary Material A

A1: The detailed simulation of the once-through reactor methanol production

HYSYS Documentation

The decision variables in this case are

Pressure of the equilibrium reactor (ERV-100): 70 bar

Temperature of the equilibrium reactor (ERV-100): 190˚C

Temperature of cooler (E-101): 60˚C

Fluid package: Peng Robinson

Component: CO_2, Hydrogen, Methanol, CO, H_2O

Reactions:

Set-1

Rxn-1 Type: Equilibrium	Stoich Coeff
CO_2	-1
H_2O	1
Methanol	1
Hydrogen	-3
Rxn-2 Type: Equilibrium	**Stoich Coeff**
CO	-1
Methanol	1
Hydrogen	-2
Rxn-3 Type: Equilibrium	**Stoich Coeff**
CO_2	-1
CO	1
Methanol	1
Hydrogen	-1

Streams:

Hydrogen

Composition Mole fraction

Hydrogen 1.0000

Temperature = 25° C

Pressure = 20 bar

Carbon dioxide

Composition Mole fraction

CO_2 1.0000

Temperature = 40°C

Pressure = 20 bar

Compressed feed (decision variable)

Pressure = 70 bar

Heated feed (decision variable)

Temperature = 190°C

Water_in

Composition Mole fraction

H_2O 1.0000

Temperature = 20°C

Pressure = 1 bar

Water_out

Composition Mole fraction

H_2O 1.0000

Temperature = 35°C

Pressure = 1 bar

Cooled product (decision variable)

Temperature = 60°C

Vessel:

ERV-100

Reaction Set: Set-1

Towers:

T-100

Number of stages: 10

Inlet Stream

Stream: Cooled product (decision variable)

Inlet Stage: 5_Main Tower

Condenser: Full Reflux

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Condenser Temperature = 25˚C

Reflux Ratio = 0.6

T-101

Number of stages: 10

Inlet Stream

Stream: Methanol-water

Inlet Stage: 5_Main Tower

Condenser: Total

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Comp Fraction

Stage: Condenser

Flow Basis: Mole Fraction

Phase: Liquid

Spec Value: 0.9950

Component: Methanol

Reflux Ratio = 30

Heat Exchanger:

For all heat exchangers:

Heat Exchanger Model: Simple Weighted

Tube Side Dalta P = 0 bar

Shell Side Delta P = 0 bar

Mixer:

MIX-100

Feed

Composition	Mole fraction
Hydrogen	0.7500
CO_2	0.2500

A2: The detailed simulation of the methanol production with a recycle

HYSYS Documentation

The decision variables in this case are

Pressure of the equilibrium reactor (ERV-100): 70 bar

Temperature of the equilibrium reactor (ERV-100): 190˚C

Temperature of a separator (E-101): 60˚C

Recycle ratio (RCY-1): 1

Fluid package: Peng Robinson

Component: CO_2, Hydrogen, Methanol, CO, H_2O

Reactions:

Set-1

Rxn-1 Type: Equilibrium	Stoich Coeff
CO_2	-1
H_2O	1
Methanol	1
Hydrogen	-3

Rxn-2 Type: Equilibrium	Stoich Coeff
CO	-1
Methanol	1
Hydrogen	-2

Rxn-3 Type: Equilibrium	Stoich Coeff
CO_2	-1
CO	1
Methanol	1
Hydrogen	-1

Streams:

Hydrogen

Composition	Mole fraction
Hydrogen	1.0000

Temperature = 25˚C

Pressure = 20 bar

Carbon dioxide

Composition	Mole fraction
CO_2	1.0000

Temperature = 40˚C

Pressure = 20 bar

Compressed feed (decision variable)

Pressure = 70 bar

Heated feed (decision variable)

Temperature = 190˚C

Water_in

Composition	Mole fraction
H_2O	1.0000

Temperature = 20˚C

Pressure = 1 bar

Water_out

Composition Mole fraction

H_2O 1.0000

Temperature = 35˚C

Pressure = 1 bar

Cooled product (decision variable)

Temperature = 60˚C

Vessel:

ERV-100

Reaction Set: Set-1

Towers:

T-100

Number of stages: 10

Inlet Stream

Stream: Cooled product (decision variable)

Inlet Stage: 5_Main Tower

Condenser: Full Reflux

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Condenser Temperature = 25˚C

Reflux Ratio = 0.6

T-101

Number of stages: 10

Inlet Stream

Stream: Methanol-water

Inlet Stage: 5_Main Tower

Condenser: Total

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Comp Fraction

Stage: Condenser

Flow Basis: Mole Fraction

Phase: Liquid

Spec Value: 0.9950

Component: Methanol

Reflux Ratio = 30

Heater:

Inlet Stream: Mixed feed

Outlet: Heated feed

Delta P: 0 bar

Heat Exchanger:

For all heat exchangers:

Heat Exchanger Model: Simple Weighted

Tube Side Dalta P = 0 bar

Shell Side Delta P = 0 bar

Mixer:

MIX-100

Feed

Composition	Mole fraction
Hydrogen	0.7500
CO_2	0.2500

MIX-101

Mixed feed

Composition	Mole fraction
Hydrogen	0.8053
CO_2	0.1886
CO	0.0013
Methanol	0.0039
H_2O	0.0009

MIX-102

Combined product

Composition	Mole fraction
Hydrogen	0.0025
CO_2	0.0154
CO	0.0000
Methanol	0.4911
H_2O	0.4910

TEE:

TEE-100

Split Fraction

To recycle = 1.00

To mixer = 0.00

Recycle:

RCY-1

Inlet Stream: To recycle

Outlet Stream: Recycle

Valves:

VLV-101

Inlet stream: To mixer

Outlet stream:

Pressure = 4 bar

VLV-102

Inlet stream: Liquid_product

Outlet stream

Pressure = 4 bar

A3: The detailed simulation of the methanol production with two reactors in series

HYSYS Documentation

The decision variables in this case are

Pressure of the first equilibrium reactor (ERV-100): 70 bar

Temperature of the first equilibrium reactor (ERV-100): 190˚C

Temperature of a separator after the first equilibrium reactor (E-101): 60˚C

Pressure of the second equilibrium reactor (ERV-101): 140 bar

Outlet temperature of the liquid stream cooler after the second equilibrium reactor: 60˚C

Fluid package: Peng Robinson

Component: CO_2, Hydrogen, Methanol, CO, H_2O

Reactions:

Set-1

Rxn-1 Type: Equilibrium	Stoich Coeff
CO_2	-1
H_2O	1
Methanol	1
Hydrogen	-3
Rxn-2 Type: Equilibrium	**Stoich Coeff**
CO	-1
Methanol	1
Hydrogen	-2
Rxn-3 Type: Equilibrium	**Stoich Coeff**
CO_2	-1
CO	1
Methanol	1

Hydrogen -1

Streams:

Hydrogen

Composition Mole fraction

Hydrogen 1.0000

Temperature = 25˚C

Pressure = 20 bar

Carbon dioxide

Composition Mole fraction

CO_2 1.0000

Temperature = 40˚C

Pressure = 20 bar

Compressed feed (decision variable)

Pressure = 70 bar

Heated feed (decision variable)

Temperature = 190˚C

Water_in_E-101

Composition Mole fraction

H_2O 1.0000

Temperature = 20˚C

Pressure = 1 bar

Water_out_E-101

Composition Mole fraction

H_2O 1.0000

Temperature = 35˚C

Pressure = 1 bar

Water_in_E-102

Composition Mole fraction

H_2O 1.0000

Temperature = 20˚C

Pressure = 1 bar

Water_out_E-102

Composition	Mole fraction
H_2O	1.0000

Temperature = 80˚ C

Pressure = 1 bar

Water_in_E-103

Composition	Mole fraction
H_2O	1.0000

Temperature = 20˚C

Pressure = 1 bar

Water_out_E-103

Composition	Mole fraction
H_2O	1.0000

Temperature = 40˚ C

Pressure = 1 bar

Cooled product (decision variable)

Temperature = 60˚C

Cooled_vapor_product

Temperature = 190˚C

Cooled_vapor_product

Temperature = 190˚C

Vessel:

ERV-100

Reaction Set: Set-1

ERV-101

Reaction Set: Set-1

Towers:

T-100

Number of stages: 10

Inlet Stream

Stream: Cooled product (decision variable)

Inlet Stage: 5_Main Tower

Condenser: Full Reflux

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Condenser Temperature = 25˚C

Reflux Ratio = 0.6

T-101

Number of stages: 10

Inlet Stream

Stream: Methanol-water

Inlet Stage: 5_Main Tower

Condenser: Total

Condenser Pressure = 4 bar

Condenser Delta P = 0 bar

Reboiler Pressure = 4 bar

Reboiler Delta P = 0 bar

Specifications:

Comp Fraction

Stage: Condenser

Flow Basis: Mole Fraction

Phase: Liquid

Spec Value: 0.9950

Component: Methanol

Reflux Ratio = 30

Heater:

Inlet Stream: Mixed feed

Outlet: Heated feed

Delta P: 0 bar

Heat Exchanger:

For all heat exchangers:

Heat Exchanger Model: Simple Weighted

Tube Side Dalta P = 0 bar

Shell Side Delta P = 0 bar

Mixer:

MIX-100

Feed

Composition	Mole fraction
Hydrogen	0.7500
CO_2	0.2500

MIX-101

Mixed_product

Composition	Mole fraction
Hydrogen	0.0041
CO_2	0.0145
CO	0.0000
Methanol	0.5116
H_2O	0.4698

MIX-102

Purge

Composition	Mole fraction

Hydrogen	0.9966
CO_2	0.0001
CO	0.0000
Methanol	0.0030
H_2O	0.0003

Valves:

VLV-100

Inlet stream: Liquid_product

Outlet stream

Pressure = 4 bar

VLV-101

Inlet stream: Liquid_product3

Outlet stream

Pressure = 4 bar

VLV-102

Inlet stream: Liquid_product4

Outlet stream

Pressure = 4 bar

Supplementary Material B

B1: An artificial neural network with eight nodes for the once-through methanol production

Mean square errors:

Data set	MSE
Training	6.88E-05
Validation	2.71E-03
Testing	1.01E-03

Weight 1, $W1_{rn}$

Neurons	Input nodes		
	1	2	3
1	0.01838	-1.70034	-1.20367
2	-1.68858	1.95475	0.00519
3	-0.08469	2.77145	-2.02880
4	-0.27928	3.05352	0.98175
5	1.21379	-2.16699	0.51323
6	-0.87896	-1.12092	2.95081
7	-0.94691	-0.92281	2.73080
8	1.99345	0.69224	1.74543

Weight 2, $W2_{r}$

Neurons	Output node
1	-0.22146
2	-1.71827
3	0.08519
4	-0.06928
5	-0.14825
6	0.73373
7	-0.64427
8	0.03067

Bias 1, $B1_{r}$

Neurons	Output node
1	-3.47132
2	2.46352
3	0.92364
4	-0.04140
5	1.52651
6	-1.48586
7	-1.48669
8	2.84496

Bias 2, $B2$	0.62038

B2: An artificial neural network with eight nodes for the methanol production with a recycle

Mean square errors:

Data set	MSE
Training	8.72E-21
Validation	1.16E-02
Testing	1.42E-03

Weight 1, $W1_{rn}$

Neurons	Input nodes			
	1	2	3	4
1	-1.00968	1.73126	-0.10196	0.75399
2	1.11953	-0.31624	1.09309	1.26681
3	-1.42018	-1.63466	-1.01587	-0.06575
4	0.11041	-0.09164	0.17686	-0.41533
5	-1.86229	3.54757	-0.26787	-1.78728
6	-1.88872	0.45065	-2.79983	-1.75360
7	-0.82886	0.56948	-0.12020	-1.32130
8	-1.94827	-1.58476	1.28377	-1.77149

Weight 2, $W2_{r}$

Neurons	Output node
1	-2.80948
2	-1.15408
3	0.61432
4	0.20542
5	-1.10762
6	-1.68792
7	-1.05462
8	2.49677

Bias 1, $B1_{r}$

Neurons	Output node
1	-2.80948
2	-1.15408
3	0.61432
4	0.20542
5	-1.10762
6	-1.68792
7	-1.05462
8	2.49677

Bias 2, *B2*	-0.33351

B3: An artificial neural network with eight nodes for the methanol production with two reactors in series

Mean square errors:

Data set	MSE
Training	4.71E-03
Validation	1.62E-02
Testing	7.21E-03

Weight 1, $W1_{rn}$

Neurons	Input nodes				
	1	2	3	4	5
1	1.6740	0.8355	0.9769	0.3482	1.0151
2	0.9246	0.1406	-0.9624	-1.6217	-0.9027
3	1.0726	-0.0086	-0.3173	1.4694	0.9207
4	-0.4479	0.2063	-1.2073	1.4524	1.1261
5	0.8234	-1.2615	-0.4674	0.2023	-1.9366
6	0.1548	-0.3474	-0.0050	-0.6043	-0.1140
7	-1.2164	0.1393	-1.5386	-0.1769	-1.3954
8	0.9263	-0.9053	1.4689	0.3428	-0.4674

Weight 2, $W2_{r}$

Neurons	Output node
1	-0.23179
2	0.09440
3	-0.04781
4	0.11484
5	0.15391
6	-1.20436
7	0.15647
8	0.13893

Bias 1, $B1_{r}$

Neurons	Output node
1	-2.70132
2	-1.22765
3	-1.84862
4	0.22289
5	0.09772
6	0.36272
7	-1.60834
8	2.25577

Bias 2, $B2$	-0.08487