

Supporting Information for

Optimizing Renewable Energy Integration for Sustainable Fuel Production: A Techno-Economic Assessment of Dimethyl Ether Synthesis via a Hybrid Microgrid-Hydrogen System

Mohammed M. Alotaibi^{1,2} and *Abdulaziz A. Alturki*^{3,*}

1 Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

2 King Abdullah Petroleum Studies and Research Center (KAPSARC), Riyadh 11672, Saudi Arabia

3 Department of Chemical and Materials Engineering, Faculty of Engineering–Rabigh Branch, King Abdulaziz University, Jeddah 21589, Saudi Arabia

* Correspondence: aaaaltrki@kau.edu.sa

S1 – Kinetic calculation

Table 2 shows the pre-exponential factor and activation energy of each reaction constant for methanol synthesis reaction calculation, which A_1 is the rearranged parameter.

$$A_1 = e^{(A_1)} \times \text{Density} \times \frac{1 - \text{Fix Bed Porosity}}{\text{Fix Bed Porosity}}$$

$$E_{a,i} = -\frac{B_1}{R}, R \text{ is the gas constant which equals } 8.314$$

$$k_i = A_i \exp\left(\frac{E_i}{RT}\right)$$

$$r_{DME} = \frac{1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) \left(C_{CH_3OH}^2 - \frac{C_{DME} C_{H_2O}}{0.1103 \exp\left(\frac{2708.6 \times 8.314}{RT}\right)} \right)}{\left(1 + 46.4 \times 10^{-3} \exp\left(\frac{35280.5}{RT}\right) C_{CH_3OH}^{0.5} + 84.7 \times 10^{-3} \exp\left(\frac{42152}{RT}\right) C_{H_2O} \right)^4}$$

$$r_{DME} = \frac{1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) C_{CH_3OH}^2 - 1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) \times \frac{C_{DME} C_{H_2O}}{0.1103 \exp\left(\frac{2708.6 \times 8.314}{RT}\right)}}{\left(1 + 46.4 \times 10^{-3} \exp\left(\frac{35280.5}{RT}\right) C_{CH_3OH}^{0.5} + 84.7 \times 10^{-3} \exp\left(\frac{42152}{RT}\right) C_{H_2O} \right)^4}$$

$$r_{DME} = \frac{1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) C_{CH_3OH}^2 - 1.242 \times 10^{11} \exp\left(\frac{-2544}{RT}\right) \times C_{DME} C_{H_2O} \frac{1}{\exp\left(\frac{2708.6 \times 8.314}{RT}\right)}}{\left(1 + 46.4 \times 10^{-3} \exp\left(\frac{35280.5}{RT}\right) C_{CH_3OH}^{0.5} + 84.7 \times 10^{-3} \exp\left(\frac{42152}{RT}\right) C_{H_2O} \right)^4}$$

$$r_{DME} = \frac{1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) C_{CH_3OH}^2 - 1.242 \times 10^{11} \exp\left(\frac{-2544}{RT}\right) \times C_{DME} C_{H_2O} \times \exp\left(\frac{-2708.6 \times 8.314}{RT}\right)}{\left(1 + 46.4 \times 10^{-3} \exp\left(\frac{35280.5}{RT}\right) C_{CH_3OH}^{0.5} + 84.7 \times 10^{-3} \exp\left(\frac{42152}{RT}\right) C_{H_2O} \right)^4}$$

$$r_{DME} = \frac{1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right) C_{CH_3OH}^2 - 1.242 \times 10^{11} C_{DME} C_{H_2O} \exp\left(\frac{-25063.3}{RT}\right)}{\left(1 + 46.4 \times 10^{-3} \exp\left(\frac{35280.5}{RT}\right) C_{CH_3OH}^{0.5} + 84.7 \times 10^{-3} \exp\left(\frac{42152}{RT}\right) C_{H_2O} \right)^4}$$

Then the formula is written as below to keep consistency with the data table in the first reactor:

$$r_{DME} = \frac{k_1 C_{CH_3OH}^2 + k_2 C_{DME} C_{H_2O}}{(1 + k_3 C_{CH_3OH}^{0.5} + k_4 C_{H_2O})^4} \left[\frac{kmol}{m^3 h} \right]$$

DME Reverse Reaction:

$$K = \frac{k_1}{k_2}, k_2 = \frac{k_1}{K}$$

$$k_1 = 1.37 \times 10^{10} \exp\left(\frac{-2544}{RT}\right)$$

$$\text{Since } K = 0.1103 \exp\left(\frac{2708.6 \times 8.314}{RT}\right)$$

$$k_2 = 1.242 \times 10^{11} \exp\left(-\frac{2544}{RT}\right) \times \exp\left(-\frac{2708.6 \times 8.314}{RT}\right) = 1.242 \times 10^{11} \exp\left(-\frac{25063.3}{RT}\right)$$

S2 – Mass balance

This appendix discussed the mass balance calculations of the proposed DME synthesis technology. The general mass balance equation is show by Eq. S1.

$$\text{In} - \text{Out} + \text{Production} - \text{Consumption} = \text{Accumulation} \quad \text{Eq. S1}$$

The mass balanced was calculated based on the following basis:

- A feed rate of 100 kmol/h of CO₂.
- A feed rate of 300 kmol/h of H₂.

Mass Balance on methanol synthesis phase:

Excel spread sheet was developed to carry out the mass balance of the surrounded area as shown in Figure S1.

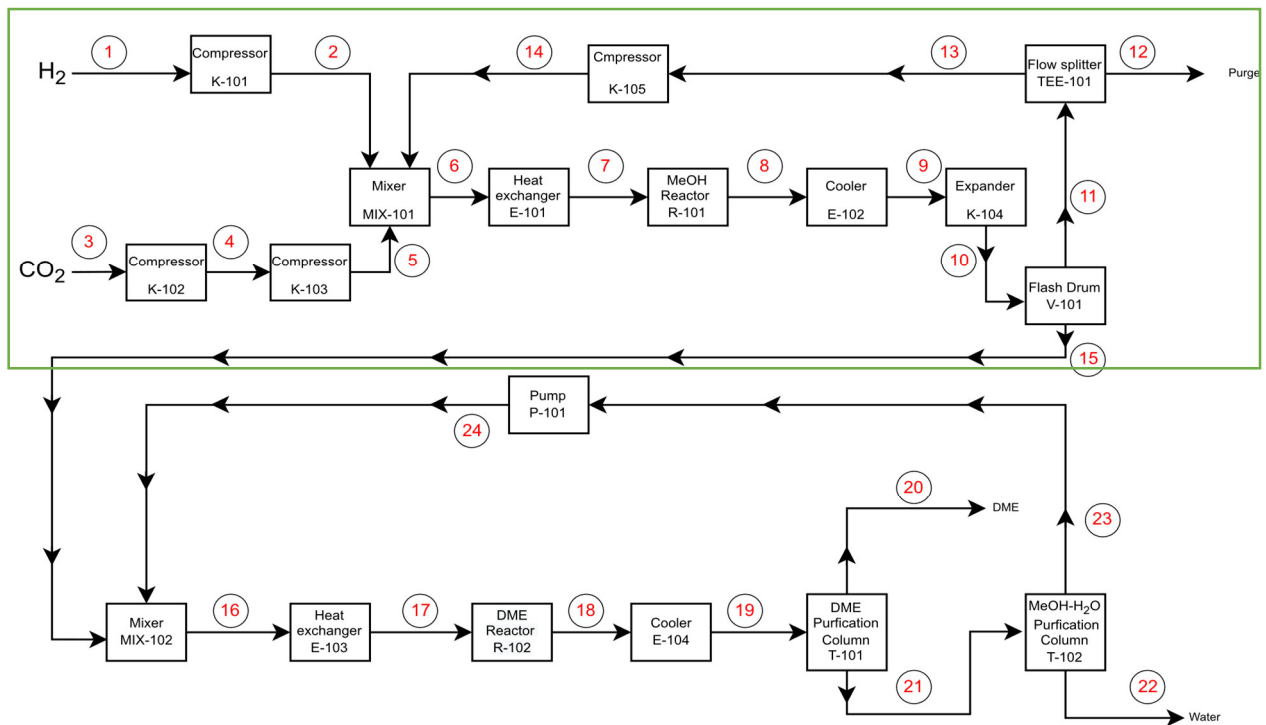


Figure S1: Methanol synthesis phase mass balance.

Just to recall, methanol conversion rate of 33% and purge ratio of 10% were used. The degree of freedom was carried out to determine the number of required equations as shown in Table S1.

Table S1: Degree of freedom analysis over methanol synthesis phase of the project.

Unit	Unknowns	Number of unknowns	Number of required equations
MIX-101	$\text{FH}_2, \text{FH}_2\text{O}, \text{FCO}_2, \text{FN}_2$	4	4
R-101	$\text{FH}_2, \text{FH}_2\text{O}, \text{FCO}_2, \text{FN}_2\text{FCH}_3\text{OH}$	5	5
V-101	$\text{FH}_2, \text{FH}_2\text{O}, \text{FCO}_2, \text{FN}_2, \text{FCH}_3\text{OH}$	5	5
TEE-101	Purge: $\text{FH}_2, \text{FCO}_2, \text{FN}_2$	6	6
	Recycled: $\text{FH}_2, \text{FCO}_2, \text{FN}_2$		
Total		20	20
DoF		0	

F represents the molar flow rate of component i in (Kmol/hr) leaving the unit.

Mass balance at MIX-101:

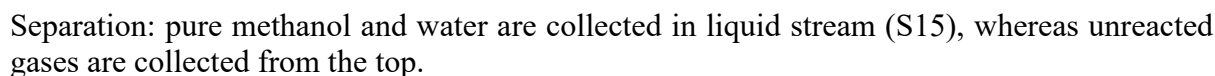
- H_2 Mass balance: $\text{FH}_{2,2} + \text{FH}_{2,14} = \text{FH}_{2,6}$
- CO_2 Mass balance: $\text{FCO}_{2,5} + \text{FCO}_{2,14} = \text{FCO}_{2,6}$
- N_2 Mass balance: $\text{FN}_{2,5} + \text{FN}_{2,14} = \text{FN}_{2,6}$
- H_2O Mass balance: $\text{FH}_{2\text{O},2} + \text{FH}_{2\text{O},14} = \text{FH}_{2\text{O},6}$

Mass balance at R-101:

Operating conditions: $T=483\text{K}$ and $P=78\text{ bar}$

Conversion rate: 33%

- H_2 Mass balance: $\text{FH}_{2,8} = \text{FH}_{2,7} - (3 \cdot \text{FCO}_{2,7} \cdot X)$
- CO_2 Mass balance: $\text{FCO}_{2,8} = \text{FCO}_{2,7} - (\text{FCO}_{2,7} \cdot X)$
- N_2 Mass balance: $\text{FN}_{2,8} = \text{FN}_{2,7}$
- H_2O Mass balance: $\text{FH}_{2\text{O},8} = \text{FH}_{2\text{O},7} + (\text{FCO}_{2,7} \cdot X)$
- CH_3OH Mass balance: $\text{CH}_3\text{OH}_{,8} = \text{FCO}_{2,7} \cdot X$



Mass Balance on DME synthesis phase:

Excel spread sheet was developed to carry out the mass balance of the surrounded area as shown in Figure S3.

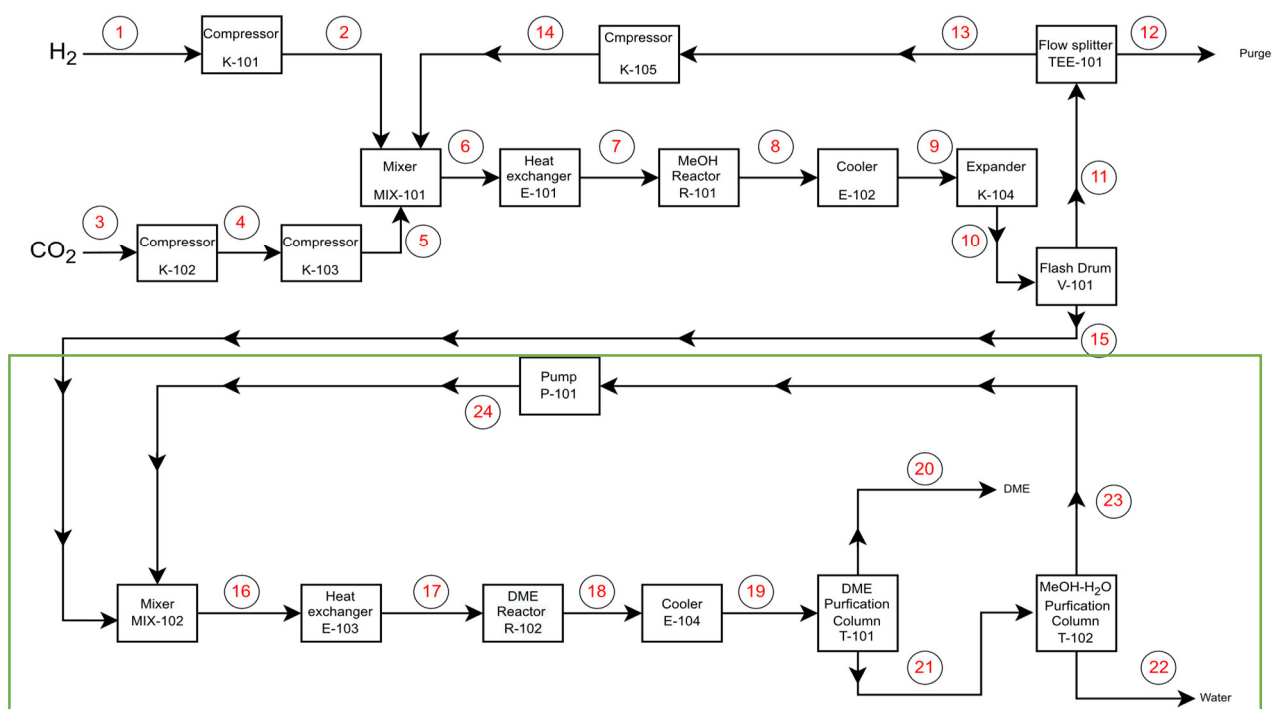


Figure S3: DME synthesis phase mass balance.

Just to recall, DME conversion rate of 78% was used. The degree of freedom was carried out to determine the number of required equations as shown in Table S2.

Table S2: Degree of freedom analysis over DME synthesis phase of the project.

Unit	Unknowns	Number of unknowns	Number of required equations
MIX-102	FCH ₃ OH	1	2
R-102	FCH ₃ OH, FH ₂ O, FCH ₃ OCH ₃	3	3
T-101	FCH ₃ OH, FH ₂ O, FCH ₃ OCH ₃	3	3
T-102	FCH ₃ OH, FH ₂ O	2	2

Total	10	10
DoF	0	

F represents the molar flow rate of component i in (Kmol/hr) leaving the unit.

Mass balance at MIX-102:

- H₂O Mass balance: $F_{H_2O,15} = F_{H_2O,16}$
- CH₃OH Mass balance: $F_{CH_3OH,15} + F_{CH_3OH,24} = F_{CH_3OH,16}$

Mass balance at R-102:

Operating conditions: T = 573K and P = 17.5 bar

Conversion rate: 78%

- H₂O Mass balance: $F_{H_2O,18} = F_{H_2O,17} + (2 * F_{CH_3OH,17} * X)$
- CH₃OCH₃ Mass balance: $F_{CH_3OCH_3,18} = (2 * F_{CH_3OH,17} * X)$
- CH₃OH Mass balance: $F_{CH_3OH,18} = F_{CH_3OH,17} - (2 * F_{CH_3OH,17} * X)$

Mass balance at T-101:

Operating conditions: T = 393 K and P = 10 bar

Separations: pure DME (99.99 mol%) was collected from the top.

- H₂O Mass balance: $F_{H_2O,21} = F_{H_2O,19}$
- CH₃OCH₃ Mass balance: $F_{CH_3OCH_3,21} = F_{CH_3OCH_3,19}$
- CH₃OH Mass balance: $F_{CH_3OH,20} = F_{CH_3OH,19}$

Mass balance at T-102:

Operating conditions: T = 393 K and P = 1 bar

Separation: pure methanol (99.99 mol%) was collected from the top.

- H₂O Mass balance: $F_{H_2O,21} = F_{H_2O,22}$
- CH₃OH Mass balance: $F_{CH_3OH,21} = F_{CH_3OH,23}$

A screenshot of the excel spreadsheet is shown in Figure S4.

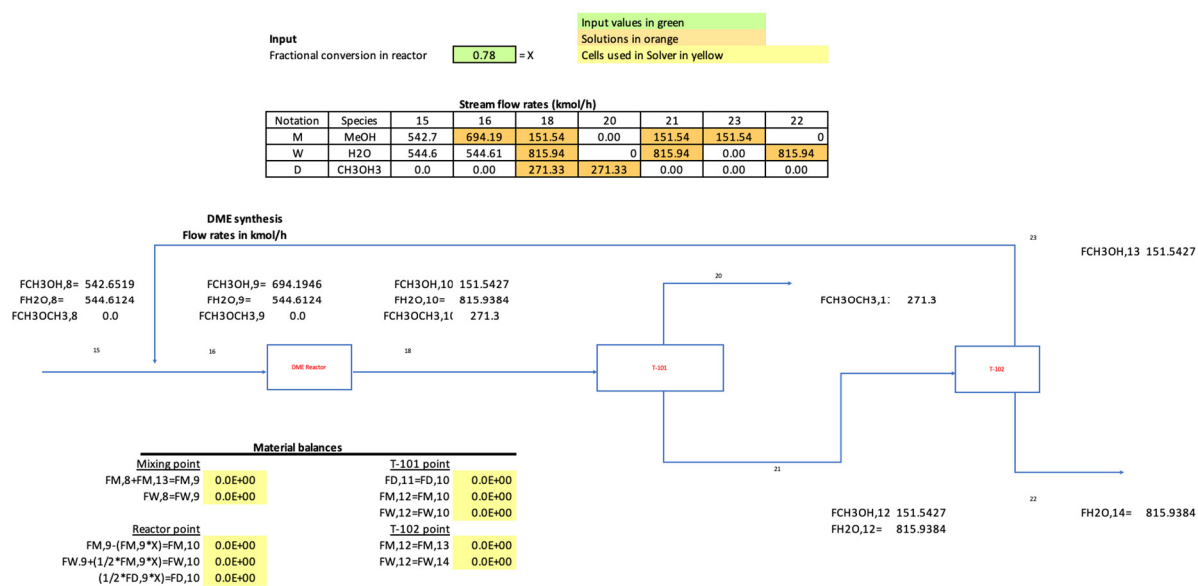


Figure S4: DME synthesis excel spreadsheet.

S3 – HEN Diagram Construction

The first step in HEN diagram constricting was to draw streams from the initial/supply temperature towards the desired temperature as shown at Figure S5. Then, calculate enthalpy at above and below the pinch using Eq.S2. Cold and hot pinch temperatures were used as reference temperatures.

$$Q = \dot{m} * C_p * \Delta T \quad \text{Eq. S2}$$

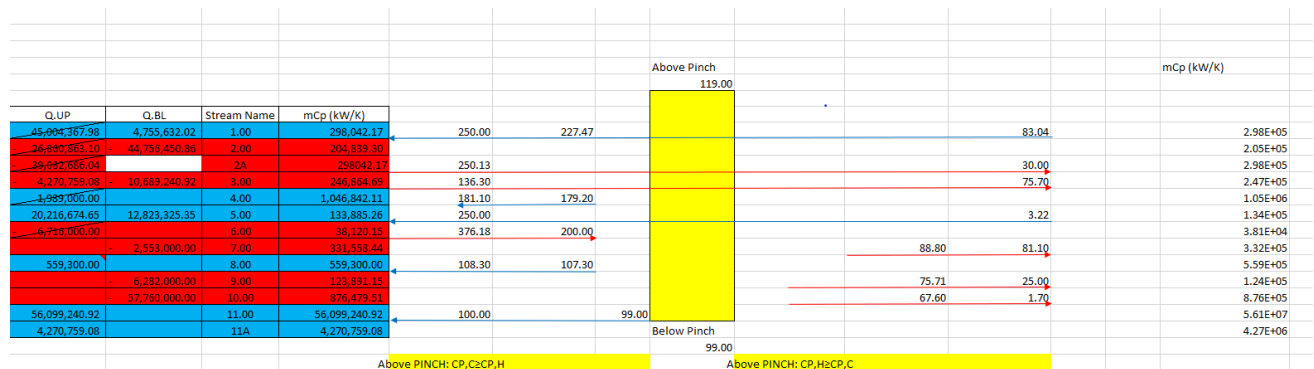


Figure S5: HEN diagram building.

Multiple conditions were taken into consideration while stream matching as listed below:

- The number of hot streams above the pinch is greater than or equal to the number of cold streams, and vice versa at below the pinch.
- Above the pinch, the heat capacity mass flow of the cold stream is greater than or equal to the hot stream's heat capacity mass flow, and vice versa at below the pinch.
- The minimum temperature differences between hot and cold streams is greater than or equal to the minimum approach temperature ($\Delta T_{\min} = 20^{\circ}\text{C}$).

Above the pinch matching

- S6-S1 match

Conditions	S6-S1	
CP	TRUE	
dT min	TRUE	
	S6	SATISFIED

S1 REM	38,288,367.98 kJ/h
S1 outlet temperature	227.47 °C

- S2A-S1 match

Conditions	S2A-S1 match	
CP	TRUE	
dT min	TRUE	
	S1	SATISFIED
	S2A REM	-794,318.05 kJ/h
	S2A outlet temperature	121.67 °C

- S2A-S4 match

Conditions	S2A-S4 match	
CP	TRUE	
dT min	TRUE	
	S2A	SATISFIED
	S4 REM	1,194,681.95 kJ/h
	S4 outlet temperature	179.96 °C

- S2-S4 match

Conditions	S2-S4 match	
CP	TRUE	
dT min	TRUE	
	S4	SATISFIED
	S2 REM	-25,666,181.15 kJ/h
	S2 outlet temperature	244.30°C

- S2-S11 match

Conditions	S2-S11 match	
CP	TRUE	
dT min	TRUE	
	S2	SATISFIED
	S11 REM	30,433,059.97 kJ/h
	S11 outlet temperature	99.46°C

- S3-S11A match

Conditions	S3-S11A match	
CP	TRUE	
dT min	TRUE	
	S3 & S11A	SATISFIED

Hence, the total amount of heating external utility must be supplied externally

$$= (30,433,059.97 \text{ kJ/h}) + (559,300.00 \text{ kJ/h}) + (20,216,674.65 \text{ kJ/h}) = 51,209,034.62 \text{ kJ/h.}$$

Matching our result showed in the cascade table.

Below the pinch matching

- S10-S1 match

Conditions	S10-S1	
CP	TRUE	
dT min	TRUE	
	S1	SATISFIED
	S1 REM	-53,004,367.98 kJ/h
	S10 outlet temperature	62.17 °C

- S10-S6 match

Conditions	S10-S5	
CP	TRUE	
dT min	TRUE	
	S5	SATISFIED
	S10 REM	-40,181,042.64 kJ/h
	S10 outlet temperature	47.54 °C

Hence, the total amount of cooling external utility must be supplied externally

$$= (40,181,042.64 \text{ kJ/h}) + (44,756,450.86 \text{ kJ/h}) + (10,689,240.92 \text{ kJ/h}) + (2,553,000.00 \text{ kJ/h}) + (6,282,000.00 \text{ kJ/h})$$

$$= 104,461,734.42 \text{ kJ/h.}$$

Matching our result showed in the cascade table.

S4 – Cost optimization

The GAMS model builder is show in Figures S6-S10.

```
1 Set
2 i /1*20/;
3
4 Parameters
5 Hot(i)
6 /
7 1 4047589.27396668
8 2 757394.235948845
9 3 26526064.7431314
10 4 595101.785946696
11 5 402305.176287095
12 6 31631244.4855723
13 7 6597766.18008208
14 8 149949.231365504
15 9 6072943.87030281
16 10 149949.231365504
17 11 11963128.5830598
18 12 10679205.353131
19 13 8326045.40757181
20 14 4044280.0333851
21 15 5067.89547502422
22 16 5076858.22698504
23 17 56522280.2771738
24 18 5001853.32336179
25 19 1558790.81782001
26 20 18863181.8680677
27 /
28
```

Figure S6: Hot streams deficit energy.

```
29 Cold(i)
30 /
31 1 0
32 2 8581795.23589314
33 3 21178005.0133544
34 4 1626646.49393419
35 5 1183015.63195216
36 6 27168235.6411854
37 7 3800961.4251579
38 8 645685.486935408
39 9 3498612.22088396
40 10 60456385.4869355
41 11 6891937.21439948
42 12 1907029.7327407
43 13 1030916.52203072
44 14 722203.761062966
45 15 776.656984549676
46 16 1084470.62707128
47 17 5034085.87381234
48 18 669426.31300696
49 19 238110.662658875
50 20 0
51 /
52 ;
```

Figure S7: Cold streams deficit energy.

```

54 Free Variable
55 *Total Cost
56 COST;
57
58 POSITIVE VARIABLES
59 *Fired Heat (1000)
60 QFH,
61 *HOT OIL
62 QHO,
63 *HIGH PRESSURE STEAM
64 QHP,
65 *MEDIUM PRESSURE STEAM
66 QMP
67 *LOW PRESSURE STEAM
68 QLP
69 *COOLING WATER
70 QCW,
71 *Refrigerant 1 Generation
72 QRF
73 *R ENERGY BALANCE
74 R(i);
75
76 EQUATIONS
77 *INTERVAL ENERGY BALANCES,
78 EB1 , EB2 , EB3 , EB4 , EB5 , EB6 ,
79 EB7 , EB8 , EB9 , EB10 , EB11 , EB12 ,
80 EB13 , EB14 , EB15 , EB16 , EB17 , EB18 , EB19 , EB20,
81 *TOTAL COST
82 TC;

```

Figure S8: variables definition.

```

76 EQUATIONS
77 *INTERVAL ENERGY BALANCES,
78 EB1 , EB2 , EB3 , EB4 , EB5 , EB6 ,
79 EB7 , EB8 , EB9 , EB10 , EB11 , EB12 ,
80 EB13 , EB14 , EB15 , EB16 , EB17 , EB18 , EB19 , EB20,
81 *TOTAL COST
82 TC;
83 *ENERGY BALANCES (=20)
84 EB1.. R('1') =E= QFH + HOT('1');
85 EB2.. R('2') + COLD('2') =E= R('1') + HOT('2') + QHO;
86 EB3.. R('3') + COLD('3') =E= R('2') + HOT('3') + QHP;
87 EB4.. R('4') + COLD('4') =E= R('3') + HOT('4') ;
88 EB5.. R('5') + COLD('5') =E= R('4') + HOT('5') ;
89 EB6.. R('6') + COLD('6') =E= R('5') + HOT('6') + QMP;
90 EB7.. R('7') + COLD('7') =E= R('6') + HOT('7') ;
91 EB8.. R('8') + COLD('8') =E= R('7') + HOT('8') ;
92 EB9.. R('9') + COLD('9') =E= R('8') + HOT('9') ;
93 EB10.. R('10') + COLD('10') =E= R('9') + HOT('10') +QLP ;
94 EB11.. R('11') + COLD('11') =E= R('10') + HOT('11') ;
95 EB12.. R('12') + COLD('12') =E= R('11') + HOT('12') ;
96 EB13.. R('13') + COLD('13') =E= R('12') + HOT('13') ;
97 EB14.. R('14') + COLD('14') =E= R('13') + HOT('14') ;
98 EB15.. R('15') + COLD('15') =E= R('14') + HOT('15') ;
99 EB16.. R('16') + COLD('16') =E= R('15') + HOT('16') ;
100 EB17.. R('17') + COLD('17') + QCW =E= R('16') + HOT('17') ;
101 EB18.. R('18') + COLD('18') =E= R('17') + HOT('18') ;
102 EB19.. R('19') + COLD('19') =E= R('18') + HOT('19') ;
103 EB20.. QRF + COLD('20') =E= R('19') + HOT('20') ;
104

```

Figure S9: Energy balance equations.

```

104
105 *TOTAL COST CALCULATION ($/yr)
106 TC.. COST =E= ((QFH*4*10**(-6)) + (QHO*3.5*10**(-6)) + (QHP*2.5*10**(-6)) + (QCW*2.125*10**(-7))+
107 (QMP*2.26*10**(-6))+(QLP*1.9*10**(-6)) + (QRF*2.739*10**(-6)))*8000 ;|
108
109 MODEL UTIL /ALL/;
110 SOLVE UTIL USING LP MINIMIZING COST;
111 Display COST.L, QFH.L, QHO.L, QHP.L, QCW.L , R.L ;

```

Figure S10: Selected solver.

The obtained Results is shown in Figure S11 and S12.

	LOWER	LEVEL	UPPER	MARGINAL
---- VAR COST	-INF	1499828.6958	+INF	.
---- VAR QFH	.	.	+INF	0.0040
---- VAR QHO	.	3776811.7260	+INF	.
---- VAR QHP	.	.	+INF	0.0048
---- VAR QMP	.	.	+INF	0.0029
---- VAR QLP	.	4.7432223E+7	+INF	.
---- VAR QCW	.	7.9945445E+7	+INF	.
---- VAR QRF	.	2.4516289E+7	+INF	.

Figure S11: Cost results and recommended utilities amount.

	LOWER	LEVEL	UPPER	MARGINAL
1	.	4047589.2740	+INF	.
2	.	.	+INF	0.0128
3	.	5348059.7298	+INF	.
4	.	4316515.0218	+INF	.
5	.	3535804.5661	+INF	.
6	.	7998813.4105	+INF	.
7	.	1.0795618E+7	+INF	.
8	.	1.0299882E+7	+INF	.
9	.	1.2874214E+7	+INF	.
10	.	.	+INF	0.0169
11	.	5071191.3687	+INF	.
12	.	1.3843367E+7	+INF	.
13	.	2.1138496E+7	+INF	.
14	.	2.4460572E+7	+INF	.
15	.	2.4464863E+7	+INF	.
16	.	2.8457251E+7	+INF	.
17	.	.	+INF	0.0202
18	.	4332427.0104	+INF	.
19	.	5653107.1655	+INF	.

Figure S12: Interval balance.