# Towards Greater Sustainable Development within Current Mega-Methanol (MM) Production<sup>†</sup>.

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Electronic Supplementary Information (ESI) †

#### 1. ASPEN Plus Simulation Models

#### 1.1 Front End Models

#### 1.1.1 Feed Gas Preparation

The natural gas feedstock was assumed to be completely desulphurized before reforming. A feed gas compressor (C-100) was used to maintain front-end pressure for each technology. Compressed natural gas was mixed with medium pressure (MP) steam in accordance with steam to carbon ratios (**Table 1-Main Article**), and preheated to 480° C via heat integration attached to the primary reformer convection section (SMR and CMR) or a fired heater (ATR).

#### 1.1.2. Pre-Reforming

Pre-reforming was necessary as to convert heavier hydrocarbons to methane to allow for easier shift conversion as well as to prevent onset coking. Natural gas and steam reacted as shown below, to produce carbon monoxide and hydrogen. The reactions were modelled using an adiabatic RSTOIC reactor (R100) assuming 100% conversion of higher hydrocarbons.

The water –shift reactions were modelled using an adiabatic equilibrium reactor R101 with a temperature approach of  $0^{\circ}$ F.

#### 1.1.3 Steam-Methane Reforming

Steam-methane reforming was utilized within the SMR and CMR cases only. The process gas leaving the pre-reformer was mixed with make-up MP steam (CMR) or CO<sub>2</sub> (SMR), and subsequently preheated to 520°C- 675°C before reforming. The reformer unit comprised of an isothermal radiant section with heat derived from natural gas and purge gas combustion, modelled as an equilibrium reactor with similar stoichiometry as pre-reforming. Waste heat recovery was achieved in the convection section to preheat process gas, combustion air, and produce superheated steam across the MP and high pressure (HP) units (**Table S1**). The overall thermal efficiency of the reformer furnace was within 60-67% in accordance with operating data.

For the CMR model, the methane slip was 43 mol% while the SMR model gave 1.9%, at an outlet temperature of 652 °C and 873 °C respectively. For the CMR model, the effluent reformed gas was utilized for auto-thermal reforming.

#### 1.1.4 Auto-thermal Reforming

For both the CMR and ATR models, the process gas was mixed with  $O_2$  and medium pressure steam prior to reforming in accordance with the  $O_2$ : carbon ratio shown in **Table 1-Main Article**. The inlet temperature

and pressure to the reactor was maintained at 598 °C at 35.5 bars using an adiabatic RSTOIC reactor (R103) with 100% conversion of  $O_2$ , facilitating the partial and complete combustion of  $CH_4$ :

Water-shift reactions were modelled using an adiabatic equilibrium reactor (R104) with a temperature approach of  $0^{\circ}F$  and are shown previously. The heat required for maximum shift conversion was derived from the combustion energy within the auto-thermal reforming unit.

The effluent temperatures were 973 °C, and 1017 °C for the CMR and ATR models with a methane slip of 1.5% and 2.2% respectively. Additional heat required for preheating process streams and producing steam was achieved using a fired heater utilizing natural gas and purge gas combustion.

|--|

	CMR	SMR	ATR
Convection section duty (MW)	119	209	-
Radiant section duty (MW)	69	410	-
Fired Heater duty (MW)	-	-	133

# 1.1.5 Waste Heat Recovery

The waste heat recovery system comprises a waste heat boiler H-106 (170MW), HP and MP Boiler Feed water (BFW) heaters H-107 (31.6MW) and H-109 (24.7MW), topping and distillation column reformed gas boilers H-108 (34.5MW) and H-110 (69.5MW), and a demineralized water heater, H-111 (35MW). Final cooling of the synthesis gas was achieved using cooling water via H-112 (46.8MW) and subsequently flashed at 40 °C via V-102, with effluent process condensate recovered within the steam system. The pressure drop from feed gas compression to synthesis gas dehydration was approximately 15 bars.

Process gas flow ----- ; Steam, Cooling water, Boiler feed water, HP Steam generation, MP Steam generation ----- Oxygen gas flow ----- Air flow ----- ; Purge gas flow ----- ; Natural gas feed/ fuel ----- Flue gas flow ----- Carbon Dioxide flow ----- Hydrogen recycle flow -----



Figure S1: CMR Front End Synthesis gas production section for configurations: Base Design, Series I and Series II



Figure S2: SMR Front End Synthesis gas production section for configurations: Base Design, Series I and Series II



Figure S3: ATR Front End Synthesis gas production section for configurations: Base Design, Series I and Series II



Figure S4: CMR Front End Synthesis gas production section for Series III configuration



Figure S5: SMR Front End Synthesis gas production section for Series III configuration



Figure S6: ATR Front End Synthesis gas production section for Series III configuration

#### 1.2 Back End Models

#### 1.2.1 Reactor Kinetics

In an effort to characterize and validate the methanol synthesis process, the LHHW kinetics were transposed to fit the Aspen Plus framework given by Luyben<sup>1</sup> as shown in **Table S2**. The general form of the LHHW kinetics are described in **Eq. 1-5**:

$$rate = \frac{(kinetic \ factor)(driving \ force \ expression)}{adsorption \ term}$$

(1)

Where:

kinetic factor = 
$$ke^{\left(\frac{-E}{RT}\right)}$$
 (2)

Driving Force Expression =  $k_1 \prod_{i=1}^{N} C_i^{\alpha i} - k_2 \prod_{j=1}^{N} C_j^{\beta i}$  (3)

Adsorption Term = 
$$\left[\sum_{i=1}^{M} K_{i} \left(\prod_{j=1}^{N} C_{j}^{vi}\right)\right]^{m}$$
(4)

Driving force and Adsorption tern rate constants follow:

$$\ln K = A + \frac{B}{T} + C\ln T + DT$$

(5)

Nomenclature	

rate	Rate of reaction	-
k	Pre-exponential rate constant	kmol/[kg catalyst.sec]
m	Adsorption term exponent	
Ε	Activation Energy	kJ/kmol
R	Gas law constant	-
$k_1, k_2$	Driving force rate constant for individual terms	Aspen derived
Κ	Adsorption term rate constant	Aspen derived
С	Component concentration	Partial pressure
N,M	Number of respective components	-
α	Driving force exponent, term 1	-
β	Driving force exponent, term 2	-
V	Individual exponent for adsorption terms	-
A,B,C,D	Rate law constants	Aspen derived

# Table S2: Kinetic LHHW Parameters used for Methanol Synthesis<sup>2</sup>

$R_1(CO_2 + 2H_2 \rightarrow CH)$	$H_3OH + H_2O)$
Kinetic factor	$k = 1.07 \times 10^{-3}$
	$E = -36696 \frac{kJ}{k}$
	kmol
Driving force ex	pressions
1 <sup>st</sup> term	
Concentration exponents for reactants:	$CO_2 = 1; H_2 = 1$
Concentration exponents for products:	$CH_3OH = 0; H_2O = 0$
Coefficients:	A = -23.03; B = C = D = 0
2 <sup>nd</sup> term	CO = 0.11 = 2
Concentration exponents for reactants:	$CU_2 = 0; H_2 = -2$
Concentration exponents for products:	$CH_3OH = 1, H_2O = 1$
Coefficients:	A = 24.39; B = -7059.73; C = D = 0
Adsorption ex	pression
Adsorption term exponent:	3
Concentration exponents:	
1 <sup>st</sup> term:	$H_2 = 0; H_2 O = 0$
2 <sup>nd</sup> term:	$H_2 = -1; H_2 O = 1$
Adsorption constants:	
1 <sup>st</sup> term:	A = 0; B = 0; C = 0; D = 0
2 <sup>nd</sup> term:	A = 8.15; B = 0; C = 0; D = 0

$R_2(CO_2 + H)$	$_2 \rightarrow CO + H_2O)$
Kinetic factor	$k = 1.22 \times 10^9$
	$E = 94.765 \frac{kJ}{k}$
	kmol
Driving for	e expressions
1 <sup>st</sup> term	
Concentration exponents for reactants:	$CO_2 = 1; H_2 = 0$
Concentration exponents for products:	$CO = 0; H_2O = 0$
Coefficients:	A = -11.51; B = C = D = 0
2 <sup>nd</sup> term	
Concentration exponents for reactants:	$CO_2 = 0; H_2 = -1$
Concentration exponents for products:	$C0 = 1; H_2 O = 1$
Coefficients:	A = -16.18; B = 4773.26; C = D = 0

	Adsorption expression
Adsorption term exponent:	1
Concentration exponents:	
1 <sup>st</sup> term:	$H_2 = 0; H_2 O = 0$
2 <sup>nd</sup> term:	$H_2 = -1; H_2 O = 1$
Adsorption constants:	
1 <sup>st</sup> term:	A = 0; B = 0; C = 0; D = 0
2 <sup>nd</sup> term:	A = 8.15; B = 0; C = 0; D = 0

Within the back-end model, kinetic equations were considered for the methanol synthesis as  $CO_2$  and CO react with  $H_2$  to produce  $CH_3OH$  as shown in **Eq. 6-7** 

$$CO + 2H_2 \leftrightarrow CH_3 OH \qquad \qquad \Delta H^\circ = -90.7 \frac{kJ}{mol} \tag{6}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \qquad \Delta H^\circ = -41.2 \frac{kJ}{mol} \tag{7}$$

The reactions were modelled on Aspen Plus using Eq. 8-9 as the water gas shift reaction takes precedence.

$$CO_{2} + 3H_{2} \leftrightarrow CH_{3}OH + H_{2}O \qquad \Delta H^{\circ} = -41.2 \frac{kJ}{mol}$$

$$CO_{2} + H_{2} \leftrightarrow CO + H_{2}O \qquad \Delta H^{\circ} = 41 \frac{kJ}{mol}$$
(8)
(9)

LHHW-type equations (Langmuir-Hinchelwood-Hougen-Watson) were used to describe the kinetics of methanol synthesis using **Eq. 10-12** as follows:

$$R = (kinetic term) \frac{(driving force term)}{(adsorption term)}$$
(10)

Reaction rate for the production of methanol from CO<sub>2</sub>:

$$R_{1} = (k_{4}p_{CO_{2}}p_{H_{2}}) \frac{\left[1 - \frac{1}{K_{E1}} \left(\frac{p_{CH_{3}OH}p_{H_{2}O}}{p_{CO_{2}}p_{H_{2}}^{3}}\right)\right]}{\left[1 + k_{3} \left(\frac{p_{H_{2}O}}{p_{H_{2}}}\right) + k_{1} \sqrt{p_{H_{2}}} + k_{2}p_{H_{2}O}\right]^{3}}$$
(11)

Reaction rate for water-shift reaction:

$$R_{2} = (k_{5}p_{CO_{2}}) \frac{\left[1 - \frac{1}{K_{E2}} \left(\frac{p_{CO}p_{H_{2}O}}{p_{CO_{2}}p_{H_{2}}}\right)\right]}{\left[1 + k_{3} \left(\frac{p_{H_{2}O}}{p_{H_{2}}}\right) + k_{1} \sqrt{p_{H_{2}}} + k_{2}p_{H_{2}O}\right]}$$
(12)

Two isothermal plug flow reactors (RPLUG) were used to model the methanol synthesis reactions- R-200 and R-201. The packed tubular reactor has 5955 tubes with a length of 8m and diameter, 0.0445m. The

# kg

density of the catalyst in 2000  $\overline{m^3}$  with a reactor void volume of 0.5.

Due to the exothermic reaction occurring in R-200 and R-201, the effluent temperature was maintained at 263 °C. This was in accordance with the specifications for the methanol synthesis catalyst. This also facilitates the production of medium pressure steam (374 °C, 48bar) to drive compressors.

#### 1.2.2 Methanol Synthesis

Synthesis gas was compressed from 32 bars to 74.8 bar via C-200 in both ATR & CMR cases; however, for the SMR case, the feed gas was compressed from 16 bars to 74.8 bar system pressure via two-stage compression with intermittent cooling.

For the base design consideration, reactors R-200 and R-201 were arranged in a parallel configuration, with incoming feed gas heated to 240°C utilizing effluent heat recovery. Effluent was cooled to 40°C using cooling water and separated. For the Series I case, a series configuration was utilized without intermittent removal of methanol between reactors. The inlet temperature to the R-200 was maintained at 240°C while the effluent at an outlet temperature of 263°C was subsequently cooled to 240°C using cooling water before further synthesis within the reactor R-201, followed by cooling and methanol separation. For the Series II progression, a similar configuration was utilized with intermittent methanol removal between reactors facilitated by cooling and separation.

Heat recovery within the synthesis section was utilized in two instances. The first employed MP steam generation utilizing boiling water reactors across each configuration, while the second case was preheating of incoming feed gas by effluent cooling.

To facilitate the removal of inerts such as methane and argon, a set purge gas to recycle gas split ratio of 0.023 was constant for all cases considered. Purge gas leaving the synthesis unit was further processed for hydrogen recovery using a membrane unit within the CMR and ATR technologies, in an effort to increase the stoichiometric ratio required for methanol synthesis. Within both technologies, the effluent purge gas from hydrogen recovery was used as fuel within the reforming section in the front-end. For the SMR case, no hydrogen recovery was required and the full purge gas effluent was utilized as fuel.

Initial separation of crude methanol from light ends was achieved using high- and low-pressure flash units V-200, V-201 and V-202. Crude methanol let-down from these units were routed to methanol purification to achieve the desired purity. The estimated pressure drop for each model case from synthesis gas compression to high pressure crude methanol separation was 4.5 bars for base design, Series II and Series III and 8 bars for Series I.

#### 1.2.3 Methanol Purification

Crude methanol at 2 bars was further purified to the desired design specification of 99.99% (mol). This was achieved using two distillation columns. Crude methanol enters the topping distillation column, V-203 of 40 trays, at stage 5 (top-down) while the reflux stream enters at stage 1 at a reflux ratio of 1.3. The topping condenser using cooling water, had duties ranging from 12MW -15MW while the topping reboiler duties were from 15MW to 35MW. The bottoms of V-203 was then sent to the refining column V-204 to achieve the design specification. The methanol molar compositions of the feed stream range from 75%-82% (mol) methanol composition. There are 85 trays in V-204 with the feed at stage 77 with a reflux ratio of 1.3. The distillate contains methanol at 99.99% molar while the bottoms stream (almost 100% water) is cooled and emitted to the environment or recovered as cooling water. The refining column condenser, utilizing an aircooler design, had duties ranging from 140MW- 200MW with respective reboiler duties of 142MW - 205MW.

#### 1.2.4 Purge Gas Recovery

With respect to the ATR and CMR models, purge gas recovery was facilitated by a gas separation membrane utilizing **Eq. 13**. A polysulfone membrane was used assuming perfectly mixed conditions<sup>3</sup>. The permeance for components  $H_2$ ,  $CH_4$ , CO and  $CO_2$  were 14, 2.5, 2.5, 5.6 barrer respectively<sup>4</sup>- methanol was assumed to be fully rejected by the membrane. The purge gas feed conditions were 70 bars and 40°C while the permeate side operated at 2 bars and 40°C. The hydrogen permeate concentration was specified at 99.9 mol%. Hydrogen was recovered in accordance with stoichiometric value of feed gas required for methanol synthesis.

For a multicomponent gas mixture, the mass transfer equation follows:

$$L_{p}y_{i} = \frac{P_{i}}{\delta} (p_{u}x_{i} - p_{p}y_{i})A_{i} \qquad i = 1, 2... n$$
(13)

where  $L_p = total molar flowrate of the permeate (molhr<sup>-1</sup>);$ 

 $y_i$  = mole fraction of gas component in the permeate;

 $P_i = permeability \ coefficient \ (molms^{-1}atm^{-1}m^{-2});$ 

 $\delta$  = membrane thickness (m);

 $x_i$  = mole fraction of gas component in retentate;

 $p_{\mu} = permeance of retentate;$ 

 $p_p = permeance of permeate;$ 

 $A_t = overall membrane surface area (m^2)$ 

#### 2.1.3.1 Carbon Capture Applications

Within each configuration across technology,  $O_2$  was substituted to promote easy  $CO_2$  capture and storage. For SMR, enriched air (24 mol %  $O_2$ ) was utilized in an effort to lower the total flue gas exiting the convection section. An activated methyl di-ethanolamine (aMDEA)  $CO_2$  capture system was utilized for the SMR case and energy demand considerations taken from a rate-based Aspen Plus simulation, with an absorption efficiency of 90%, heating duty of 5.3 GJ/tonne  $CO_2$  and cooling duty of 1.97 GJ/tonne  $CO_2$ . For the CMR and ATR cases oxy-fuel was utilized<sup>5, 6</sup>. In an effort to stabilize the temperatures of the convection section within 1200-1500 °C, a fraction of the exiting flue gas was recycled. It is well known that oxy-fuel combustion allows for higher thermal efficiencies and high  $CO_2$  purity without the need for capture<sup>6, 7</sup>. Thus, the thermal efficiency of the reforming furnace was increased to 80% across SMR using enriched air and CMR/ATR oxy-fuel at 100% - efficiency enhancement values were approximated from Aspen Simulations based on heat released assuming no losses. Effluent  $CO_2$  from each technology was compressed giving a concentration of 95-100 mol%, and subsequently transported for utilization.



Figure S7: CMR/ATR Base Design configuration



Figure S8: CMR/ATR Series I configuration



Figure S9: CMR/ATR Series II/III configuration



Figure S10: SMR Base Design configuration



Figure S11: SMR Series I configuration



Figure S12: SMR Series II/III configuration

#### 2. Novelty and Literature Review

**Table S3** gives the indicators investigated for various grass roots process design cases evaluating methanol production pathways and technologies. In all studies represented, environmental profiles and assessments are absent, illustrating the gap in the research area and providing the needs basis for a more holistic overview on technological performance.

Study	Technology Investigated	Economic Indicator	Environmental Indicator	Environmental Assessment/ Profile evaluated?
Gao et al. <sup>8</sup>	Direct methanol conversion using waste synthesis gas	Total Capital Cost, Production Cost	Minimize CO <sub>2</sub> generation	None
Hernandez-Perez et al. <sup>9</sup>	SMR, DMR, CMR, POX, ATR	Net Profit, Total Annualized Cost	Minimize CO <sub>2</sub> generation	None
Zhang et al. <sup>10</sup>	SMR, CDR	Annualized Cost, IRR	None	None
Chen et al. <sup>11</sup>	CMR,SMR,ATR	Total Capital Cost, IRR	Minimize CO <sub>2</sub> generation	None
Blumberg et al. <sup>12</sup>	SMR, ATR, DMR	Net Revenue, Annualized Cost	None	None
Noureldin et al. <sup>13</sup> .	SMR, DMR, POX	Economic Potential	Minimize CO <sub>2</sub> generation	None
Chen et al. <sup>14</sup>	Coal gasification	Production Cost, IRR	GHG emission quantification	None
Blumberg et al. <sup>15</sup>	SMR, ATR, DMR, CMR,	Net Revenue, Levelized Costing	None	None
Julián-Durán et al. <sup>16</sup>	POX, SMR, CMR, ATR	ROI	CO <sub>2</sub> emissions quantification	None
Blumberg et al. <sup>17</sup>	SMR, CDR	None	CO <sub>2</sub> emissions quantification	None

<u></u>	Table	<b>S3:</b>	Literature	Review	on Methanol	<b>Technologies</b>
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CDR- CO<sub>2</sub> direct Reforming, CMR- Combined Reforming, SMR- Steam Methane Reforming, DMR- Dry Methane Reforming, POX- Partial Oxidation, ATR- Autothermal Reforming, IRR- Internal Rate of Return, ROI- Return on Investment

# 3. Equipment Design and Costing

**Table S4** gives equipment costing based on design calculations taken from Aspen Plus. Reactors were costed based on volume with a space time equivalent (reforming reactions), while distillation columns were calculated based on diameter and column height as well as tray height, and flooding parameters taken from Aspen Sizing. All other equipment were sized based on known equipment properties.

Equipment	Design Parameter		Unit
Pre-Reformer	Space Time	1.16	S
SMR	Space Time	2.03	S
ATR	Space Time	2.03	S
Methanol Synthesis Reactors	Volume	74	m <sup>3</sup>
Topping Column	Number of trays	40	
	Tray spacing	1.37	
Refining Column	Number of trays	85	
-	Tray spacing	1.37	
Storage Tank	Residence time	7	days
Flash Drum	Superficial Velocity	0.1-1.1	m/s
Pumps	Power	18-8500	kW
Compressors/ Generators	Power	1.75-50	MW
Coolers	Surface Area	52-6200	m <sup>2</sup>
Boilers	Duty	30-125	MW
Heat Exchangers	Surface Area	44-4300	m <sup>2</sup>
Membrane	Surface Area	135000-220000	m <sup>2</sup>
Furnace	Duty	267-410	MW
Fans	Volumetric Flowrate	36-380	m <sup>3</sup> s <sup>-1</sup>

#### **Table S4: Design Parameters of Equipment**

#### 4. Fixed Capital Investment Estimates

Allocation of costing factors for estimation of Fixed Capital Investment (FCI) were taken from R.K Sinnott<sup>18</sup> and are given in **Table S5**. Installed costs were generally estimated based on bare module costing (**Eq. 14**) using design specific parameters given in **Table S4**. Overall heat transfer coefficients for heat exchangers were assumed based on stream properties<sup>19</sup>, while refining column air-cooled exchangers were modelled using Aspen EDR. Reactor volumes were estimated on average space time for reforming reactions while furnace costs were calculated using duty requirements. Methanol synthesis reactor was costed using both volume and heat transfer surface area. Costing for pumps, compressors, boilers and generators were sized in terms of specific duty requirements while distillation columns were sized based on the height and diameter of the column and flash vessels and storage tanks were estimated based on volume and residence time. For purge gas recovery, gas separation membrane was costed based on surface area at a price of US\$ 100/m<sup>2 20</sup>.

$$C_{BM} = C_p^0 F_{BM} = C_p^0 \left( B_1 + B_2 F_M F_P \right)$$
(14)

Where  $C_{BM} = bare module cost$ ;  $C_p^0 = purchased cost equipment on base conditions$ ;  $F_M = material factors$ ;  $F_p = pressure factor$ ;  $B_1, B_2 = constants for bare module factor$ 

Installed costs associated with the aMDEA system was calculated using Eq.15<sup>21</sup>.

$$MDEA \ Capital \ Cost = C_0 \left(\frac{S}{S_0}\right)^{sf}$$

$$C_0 = base \ cost \ (MM\$);$$

$$S = cost \ flow;$$

$$S_0 = base \ case \ flow;$$

$$sf = scaling \ factor;$$

$$(15) \qquad \text{Where}$$

All installed costs were scaled using Chemical Engineering Plant Cost Index (CEPCI) for 2018.

Fixed capital cost of the project given as a function of the total installed equipment cost by **Eq. 16** while Total Capital Investment (TCI) was estimated from **Eq. 17-19**.

$$C_f = f_L C_e$$
 (16)  
 $C_f$   
 $= fixed capital cost; C_e = installed equipment cost; f_L = Lang factor$ 

Fixed Capital Investment = Direct costs + Indirect Costs		(17)
Working Capital = $15\%$ of Fixed Capital Investment	(18)	

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# Total Capital Investment = Fixed capital investment + Working Capital(19)

The internal rate of return (IRR) was used to measure project profitability by giving an indication of the maximum interest payable by a project, while still breaking even at the end of project lifetime. IRR was calculated using **Eq. 20**.

$$0 = NPV = \sum_{t=1}^{T} \frac{C_t}{(1 + IRR)^t} - C_0$$
(20)

where:

 $C_t$  = Net cash inflow for the period, t

 $C_0 = Total Capital Investment$ 

IRR- Internal rate of return

t= Project lifetime in years.

An IRR >7% was chosen as a benchmark for estimating project profitability. Furthermore, set process parameters such as methanol, natural gas,  $O_2$  and  $CO_2$  prices and fixed capital investment (FCI), were manipulated (± 10%) in an effort to assess sensitivities in economic profitability.

Item	Costing Factor	
Direct Costs		
$f_1$ Equipment Erection	0.4	
$f_{2}$ Piping	0.7	
$f_{3}$ Instrumentation	0.2	
$f_{4}$ Electrical	0.1	
f <sub>5</sub> Ancillary Building	0.15	
Total physical plant cost (PPC)		
$PPC = (1 + f_1 + + f_5)$	2.55	
Fixed Capital = PPC $\times$	2.55	
Indirect Costs		
$f_6$ Design and Engineering	0.2	
$f_7$ Contingency	0.05	
$PPC = (1 + f_6 + f_7)$		
Fixed Capital = PPC $\times$	1.25	

#### Table S5: Parameters for TCI Estimation<sup>18</sup>

#### 5. Operating Costs Estimates

Estimates for Total Operating Costs (OPEX) was taken from production cost allocations<sup>18</sup> are given in **Table S6**. Operating costs associated with utilities - cooling water, and process water, were obtained from Turton et al<sup>22</sup> while costing for raw materials such as natural gas and  $O_2$  as well as methanol product were derived from global market trends for last quarter 2018. Electricity rates were obtained from a local supplier<sup>23</sup>. Electricity power consumption reflected the duties of pumping utilities taken from the Aspen Plus simulations. Offsite electrical demand was estimated at 47% of the total electrical demand for the base plant design, and kept constant throughout all subsequent cases. For Series III models where carbon capture was considered, operating costs were averaged at \$US 22 per tonne  $CO_2^{24}$ , associated with dehydration and transport. For the SMR model (Series III), operating costs associated with the aMDEA system was priced at \$US 55/tonne  $CO_2$  captured<sup>25</sup>.

Raw material costs were calculated directly from mass and energy balances using Aspen Plus, while operating labour was derived from key unit operations within each model according to **Eq. 21-22** from Turton et al<sup>22</sup>.

No of operators = $[6.29 + (No of equipment \times 0.23)]^{0.5}$	(21)
Labour costs = (Approximate No of operators $\times$ 4.5) $\times$ 66910 $\times$ 1.19	(22)

Item	Values				
Variable Costs					
Raw materials	-				
Miscellaneous	10% of Maintenance costs				
Fixed Costs					
Maintenance	5% of FCI				
Operating Labour	-				
Laboratory Costs	21.5% of Operating Labour				
Supervision	20% of Operating Labour				
Plant Overheads	50% of Operating Labour				
Capital Charges	10% of Operating Labour				
Royalties	10% of FCI				

#### Table S6: Parameters for OPEX estimation<sup>18</sup>.

#### 6. Life Cycle Inventory and Planetary Boundary Data

**Table S7** contains the datasets used from the Ecoinvent v3.4 LCA database. Datasets were aligned to reflect processes within Trinidad and Tobago energy sector by specifying heating and electricity consumption affiliated with natural gas combustion only. **Table S8** gives the life cycle inventory (LCI) across reforming technologies and methanol synthesis configurations. The power consumption for cryogenic air separation was modified to reflect current large scale oxygen production- approximately 0.245kW/kg  $O_2^{26}$ 

Process Stream	Dataset	Year
Heating Utility	Heat, district or industrial natural gas	2013
Natural Gas Feedstock	Natural gas, low pressure	2015
Process Water	Water, deionized	2010
Electricity	Electricity, high voltage, produced	2012
Oxygen	Air Separation, cryogenic	2017

Table S7: LCA dataset information retrieved from Ecoinvent v3.4.

LCA Inventory	Ammonia		CMR	Cases			SMF	R Cases			ATR (	Cases	
Parameters	Base <sup>1</sup>	Base	Series	Series	Series	Base	Series	Series	Series	Base	Series	Series	Series
			I	II	III		Ι	II	III		I	II	III
Inputs from Technosphere													
Natural Gas Heating	16896.12	1153	1409	1945	1404	12070	13381	13161	14417	1387	1964	1212	0
[MJ]													
Natural Gas Feedstock	39.79	35.9	35.9	35.1	34.8	30.4	30.5	29.3	29	36.7	36.7	36.7	36.7
[m <sup>3</sup> ]													
Oxygen [kg]	0	537.5	537.5	524.7	781.8	0	0	0	261.8	579.5	579.9	579.9	781.6
Process Water [kg]	877.145	179.6	179.6	175.4	173.8	576.2	578.5	557.1	550.6	61.5	61.5	61.5	61.5
Electricity [MWh]	0.0168	0.0143	0.014	0.0143	-0.011	0.016	0.0161	0.0155	0	0.0184	0.0169	0.0192	-0.0274
				]	Process Ai	r Emissio	ns						
CO <sub>2</sub> [kg]	525.05	181.8	173.6	142.3	0	270	277	214	72.4	214.1	258.4	215.1	0
CO <sub>2</sub> Avoided Credit	985.95	0	0	0	203.3	0	0	0	651.4	0	0	0	210.98

Table S8: Normalized LCI for methanol model scenarios (Functional unit – 1000kg CH<sub>3</sub>OH) and ammonia system boundary (Functional unit- 1000kg NH<sub>3</sub>)

<sup>1</sup> Data taken from an industrial case study within the energy sector of Trinidad and Tobago

# Table S9: Data sources for determining the share of total safe operating space assigned to the TT energy sector (aS<sup>TTEnergy</sup>) and characterized impact scores (IS<sub>p</sub>).

Data s	ources based on Local and Regiona	al Statistics						
GVA Trinidad (USD) <sup>27</sup>	GVA Trinidad (USD) <sup>27</sup>							
Production methanol 2018 (tonne	5,010,000.00							
GVA Methanol in Trinidad and T	Cobago's Energy Sector (USD) <sup>28, 29</sup>	2,370,923,700						
Trinidad population 2018 <sup>30</sup>		1,359,193						
World population 2018 <sup>31</sup>		7,631,091,000						
• •								
aSTT methanol		1.804 x 10 <sup>-5</sup>						
Characterization	factors (CF) used for evaluation of	f Impact Scores <sup>32</sup> (IS	n)					
<b>Environmental flow</b>	Earth System Process	CF	Unit					
CO <sub>2</sub>	Climate Change-Energy	3.53 x 10 <sup>-13</sup>	W yr m <sup>2</sup> kg <sup>-1</sup>					
CH <sub>4</sub>	Imbalance	1.59 x 10 <sup>-12</sup>	, ,					
N <sub>2</sub> O		4.64 x 10 <sup>-11</sup>						
CO <sub>2</sub>	Climate Change-CO <sub>2</sub>	2.69 x 10 <sup>-11</sup>	ppm yr kg <sup>-1</sup>					
CH <sub>4</sub>	Concentration	7.40 x 10 <sup>-11</sup>						
CO <sub>2</sub>	Ocean Acidification	8.22 x 10 <sup>-14</sup>	mol yr kg <sup>-1</sup>					
CH <sub>4</sub>		2.26 x 10 <sup>-13</sup>						
Halon 1211	Stratospheric Ozone Depletion	5.16 x 10 <sup>-8</sup>	DU yr kg <sup>-1</sup>					
Halon 1301		1.15 x 10 <sup>-7</sup>						
	Biogeochemical Flows-							
Global P flows	Phosphorus	8.61 x 10 <sup>-10</sup>	Tg P yr <sup>-1</sup> kg <sup>-1</sup> yr					
			Tg N yr <sup>-1</sup> kg					
Total N Flow		2.44 x 10 <sup>-8</sup>	<sup>1</sup> yr					
			Tg N yr <sup>-1</sup> kg <sup>-</sup>					
NO <sub>x</sub>	<b>Biogeochemical Flows- Nitrogen</b>	3.04 x 10 <sup>-10</sup>	<sup>1</sup> yr					
Consumption of Blue Water	Freshwater Use	1 x 10 <sup>-9</sup>	km <sup>3</sup> m <sup>-3</sup>					
Global Forest Transformation	Land-System Change	1.56 x 10 <sup>-12</sup>	% m <sup>-2</sup>					

# 7. Mass and Energy Balances

		C	MR		SMR				ATR			
	Base	Series I	Series	Series	Base	Series I	Series	Series	Base	Series I	Series	Series
			п	Ш			п	ш			п	ш
Process Inputs												
Natural Gas Feedstock	0.57	0.572	0.557	0.552	0.474	0.476	0.459	0.453	0.582	0.583	0.583	0.583
[kg/kg]												
Natural Gas Feedstock	27.96	28.037	27.292	27.054	23.243	23.333	22.473	22.211	28.539	28.560	28.559	28.551
[MJ/kg] <sup>a</sup>												
Natural Gas Fuel [kg/kg]	0.02	0.029	0.040	0.028	0.246	0.273	0.268	0.222	0.028	0.040	0.025	0.000
Natural Gas Fuel [MJ/kg] <sup>a</sup>	1.15	1.409	1.950	1.396	12.071	13.383	13.155	10.909	1.387	1.964	1.212	0.000
Carbon Capture Unit	0.00	0.000	0.000	0.000	0.000	0.000	0.000	3.501	0.000	0.000	0.000	0.000
[MJ/kg]												
O <sub>2</sub> [kg/kg]	0.54	0.539	0.525	0.782	0.000	0.000	0.000	0.262	0.579	0.580	0.580	0.782
CO <sub>2</sub> [kg/kg]	0.00	0.000	0.000	0.000	0.350	0.351	0.338	0.334	0.000	0.000	0.000	0.000
Electricity Demand	0.05	0.051	0.052	0.000	0.058	0.058	0.056	0.000	0.049	0.049	0.049	0.000
[MJ/kg]												
	1			-	Process Outp	outs	1		1		1	1
Product Methanol [kg/kg]	1.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Product Methanol	19.92	19.920	19.920	19.920	19.920	19.920	19.920	19.920	19.920	19.920	19.920	19.920
[MJ/kg] <sup>a</sup>												
Fuel Gas [kg/kg]	0.13	0.132	0.090	0.077	0.196	0.202	0.141	0.153	0.114	0.115	0.113	0.113
Fuel Gas [MJ/kg] <sup>a</sup>	3.75	3.470	2.184	1.945	5.040	5.176	4.088	3.781	2.569	2.589	2.589	2.588
Electricity Generation	0.00	0.000	0.000	0.039	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.066
[MJ/kg] <sup>b</sup>												
Plant Efficiency (%)	81.17%	79.30%	75.46%	76.99%	70.56%	68.24%	67.28%	64.72%	75.02%	73.62%	75.48%	79.06%
Recycle Ratio	3.27	3.39	2.21	2.19	3.25	3.38	2.13	2.5	3.34	3.55	1.67	1.55

# <u>Table S10: Summary of mass and energy balances considered across all synthesis loop configurations and</u> reforming technologies (per kg Methanol basis).

<sup>a</sup>Energy load calculated using the net heating value estimated from Aspen Plus, <sup>b</sup>Total electricity generated.

KPIs were quantified through mass and energy balances carried out across different synthesis loop configurations and reforming technologies as shown in **Table S10**. For comparison purposes, the R- value was kept constant at 2.04.

Across the various technologies, natural gas was the major source of energy while methanol gave the largest energy output. Upon examining material flows of different reforming technologies, the SMR cases required a lower natural gas feedstock owing to the utilization of  $CO_2$  within the reforming section, while the ATR cases utilized higher  $O_2$  demand when compared to CMR as increased heat generated during auto-thermal reforming allows for efficient steam reforming at low steam-to-carbon ratios. From **Table 3 (main article)**, the methanol production and carbon conversion were the highest for SMR cases due to higher synthesis gas flow rates, resulting in higher electrical demand associated with pumping utilities. For the CMR and ATR cases, a higher  $CO/CO_2$  ratio increased the methanol yield considerably over the SMR models while decreasing the net heating value of the purge gas output<sup>33</sup>. However, the need for hydrogen recovery across the CMR and ATR cases decreased the recycle ratio (shown in **Table S10**) required for optimum methanol production hence, decreasing the carbon conversion.

For Series III cases, an economic pressure (82 bar) and purge gas split fraction (0.0205) was consideredusing process intensification with Series II as a benchmark for methanol synthesis, while oxy-fuel (CMR and ATR cases) and enriched air coupled with carbon capture (SMR cases) was utilized within the reforming unit for increased environmental benefits. From the results in **Table S10** for Series III, a general decrease in fuel across technologies was observed, credited to higher thermal efficiencies. For the CMR Series III case, an increase in fuel flow associated with significant decrease in purge gas heating value was observed as methanol productivity increased across the synthesis loop, whereas, for the ATR Series III case heating requirements were met directly by an efficient purge gas oxy-fuel process.

#### 7.1 Energy Efficiency and Requirements

# Table S11: Summary of energy requirements and consumption considered across all synthesis loop

		CMR			SMR				ATR			
Mass and Energy	Base	Series	Series	Series	Base	Series	Series	Series	Base	Series	Series	Series
Balances		Ι	Π	Ш		Ι	II	Ш		Ι	П	III
Energy Consumption [MJ/kg] <sup>a</sup>												
Steam Reforming	4.91	4.11	4.13	3.35	15.70	18.03	16.11	11.91	0.00	0.00	0.00	0.00
Utilities	0.00	0.77	0.00	0.00	1.41	0.53	1.13	2.78	3.96	4.55	3.80	2.59
Carbon Capture Unit	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.50	0.00	0.00	0.00	0.00
Purge Gas Recovery	-3.75	-3.47	-2.18	-1.94	-5.04	-5.18	-4.09	-3.78	-2.57	-2.59	-2.59	-2.59
TOTAL	1.16	1.41	1.94	1.40	12.07	13.38	13.15	14.41	1.39	1.96	1.21	0.00
Energy Recovery [MJ/kg]												
Waste Heat Recovery <sup>b</sup>	5.29	5.24	5.15	5.11	6.83	6.78	6.58	6.40	4.21	3.88	4.46	4.79
Steam Generation <sup>c</sup>	5.40	6.09	5.14	5.10	5.15	5.87	4.87	4.85	5.26	5.19	4.71	4.84
TOTAL	10.69	11.32	10.29	10.20	11.97	12.64	11.45	11.25	9.47	9.08	9.17	9.63
			]	Power Cor	isumptio	on [MJ/kg	ç]	I				
Utilities	0.004	0.038	0.004	0.047	0.006	0.006	0.006	0.162	0.003	0.003	0.003	0.003
Distillation	0.036	0.035	0.036	0.106	0.037	0.037	0.035	0.032	0.036	0.036	0.036	0.038
Offsite Consumption	0.012	0.012	0.011	0.011	0.015	0.015	0.014	0.014	0.010	0.010	0.010	0.010
Electricity Generation	0.000	0.000	0.000	-0.238	0.000	0.000	0.000	-0.248	0.000	0.000	0.000	-0.154
Carbon Capture	0.000	0.000	0.000	0.034	0.000	0.000	0.000	0.040	0.000	0.000	0.000	0.036
Utilization												
TOTAL <sup>d</sup>	0.051	0.084	0.051	-0.039	0.058	0.058	0.056	0.000	0.049	0.049	0.049	-0.066

#### configurations and reforming technologies.

a. Overall Energy consumption. Purge gas recovery is denoted as a negative contribution as this gas provides sufficient energy to plant operations, b. Waste heat recovery = Total heat recovered from convection section/fired heating + Reformed gas cooling, c. Steam generation = Total steam generated across waste heat boiler + methanol synthesis reactors, d. Negative values denote net electricity generation.

**Table S10** gives the plant efficiencies for each technology and synthesis configuration. The plant efficiency was estimated from  $Eq.23^{34}$ , by considering the total plant inputs (natural gas feedstock, fuel and electricity) as well as the total outputs (methanol, purge gas fuel, electricity generation).

$$\eta_{plant} = \frac{m_{methanol} \cdot NHV_{methanol} + m_{fuelgas} \cdot NHV_{fuelgas} + Electricity Generation}{m_{nat.gas(feed)} \cdot NHV_{nat.gas(feed)} + m_{natgas(fuel)} \cdot NHV_{natgas(fuel)} + Electricity Demand}$$
(23)  

$$m_{i} = mass flow \left(\frac{kg}{hr}\right); NHV = net heating value \left(\frac{MJ}{kg}\right)$$

From Eq.23, increased methanol production and decreased natural gas feedstock and fuel has a net positive effect on plant efficiency. Past research has shown that CMR technologies give the best utilization of energy while SMR has lower energy efficiencies<sup>35, 36</sup> and thus, this was reflected in the model simulations as shown in **Table S10**. Analysis of synthesis loop configurations showed a decrease in plant efficiency, with Base

cases giving a more efficient utilization of energy. Within the SMR cases, even with the highest production capacity, Series III gives the lowest plant efficiency across all cases. This was directly attributed to an energy intensive CO<sub>2</sub>-aMDEA capture and stripping process.<sup>37, 38</sup> In the CMR cases, a similar trend was observed with Series III giving the lowest efficiency compared to the other cases- mainly attributed to a large decrease in purge gas flow and heating value as methanol productivity increased. For the ATR cases however, Series III gave the highest efficiency, even with a net lower methanol production rate when compared to the Base case. Thus, our results suggest that higher productivity does not significantly benefit overall plant performance as much as a reduction in energy demand.

An overview of the energy consumption with respect to heating, heat recovery as well as electricity consumption is given in **Table S11**, for reforming technologies and synthesis loop configurations. For reforming technologies, SMR had the highest energy consumption (12-14.4 MJ/kg) mainly due to the endothermic nature of the steam reforming process. This coupled with the utilization of CO<sub>2</sub>, a reversible by- product of the water-gas shift reaction, increased the added energy required for favourable methane reforming. For CMR and ATR cases the overall energy consumption was significantly lower (1.16-1.96 MJ/kg) as partial oxidation creates an energy surplus driving methane reforming; thus, energy consumption followed SMR>CMR>ATR. Overall energy recovery followed an opposing trend, with SMR giving higher energy recoveries (11.25-12.64 MJ/kg) over CMR and ATR (9.63-11.32 MJ/kg) cases as synthesis gas generation followed similarly. This increased the available duty required for energy recovery. Utility electrical consumption followed a decreasing trend attributed directly to steam-to-carbon ratios and utility pumping requirements, while electrical usage increased with higher methanol productivities; thus, SMR gave higher electrical consumption over CMR and ATR cases.

For synthesis loop considerations, CMR and ATR cases showed a general decrease in energy consumption as methanol productivity increases; with Series III cases being significantly lower than all other cases cases. This was attributed to reduced synthesis gas compression power requirements due to lower recycle ratios. For the SMR cases, lower front-end pressures as well as higher recycle ratios resulted in larger gas compression power requirements as well as low pressure steam requirements for distillation, and hence, utility steam generation increased energy demand. For Series III cases, oxy-fuel processes gave net lower energy consumption, with ATR being fully self-sufficient in energy and electrical consumption while carbon capture applications within SMR gave higher energy demand. Within the utility design for Series III cases, excess steam was routed for electrical generation largely decreasing the electrical demand for all technologies.

# 8. Economic Profitability Estimates

#### 8.1 Installed Costs

**Figure S13** represents the allocation of installed costs as well as total installed costs for different sections of the methanol process and configuration comparing each reforming technology. The capital costs range from \$260 USD million (ATR Base, Series II and III) to \$434 USD million (SMR Series III).

Results broadly showed the largest contributors to the installed costs were reforming (28-57%), distillation (19-26%) and methanol synthesis (13-17%) sections of the process.

The reforming section contributed the most to the capital costs (53-57%) with respect to the CMR technology and the least (29-39%) for the SMR technology. Analysis of Series III configurations showed lower cost contributions associated with the SMR cases due to the reduction in reforming duty owing to the addition of enriched air.

The distillation section contributed the most to the SMR technology installed costs (22- 26%), as opposed to (19-23%) for CMR and (20-24%) for ATR models, due to higher condenser and reboiler duties associated with higher methanol production.

The synthesis section contributed (13-17%) to installed costs across all technologies. The SMR technology gave marginally higher costs than the other technologies, due to higher synthesis compression.

With respect to purge gas recovery, ATR technologies gave higher installed costs (8%) over CMR (5%) due to higher hydrogen recovery while carbon capture within Series III models was the greatest for SMR (9.4%), attributed to the aMDEA system as an oxy-fuel process was not economically feasible.



Figure S13: Total installed costs across synthesis loop configurations for A) CMR, B) SMR, and C) ATR reforming technologies.

#### 8.2 Operating Costs

Insights into operating cost allocation for raw material expenditure ( $O_2$ , catalysts,  $CO_2$ ), utilities (natural gas, electricity and cooling water,), operating labour and carbon capture costs are shown in **Figure S14**. The total operating and maintenance costs range from \$209 USD million (SMR Base case) to \$329 USD million (SMR Series III).

Generally, the ATR technology gave the highest operating and maintenance costs – (M\$267-270) due to higher  $O_2$  consumption rates while the SMR had the lowest operating costs (M\$209-216). The highest contributor to the total annual operating costs was natural gas consumption throughout all technologies, for which SMR gave the highest contribution (M\$186-194) due to its higher energy demand. Furthermore, SMR was the only technology that utilized  $CO_2$  as a raw material (Base, Series I and Series II)- its consumption makes up ~6% of the total operating costs.

Considering process efficiency with respect to Base, Series I and Series II models, an increase in production rate incurred higher operating costs. For the Series III models, oxy-fuel combustion technologies increased oxygen consumption (M \$40-57), with a subsequent decrease in fuel consumption (M \$3-10). This increased operating costs by as much as 24% for CMR and ATR. Overall, the utilization of  $O_2$  as well as carbon capture gave the highest operating costs (M \$329) for the SMR technology, leading to reductions in IRR (13.44%).

The operating labour was constant for each configuration throughout, and the catalyst cost did not change. These factors, along with water consumption, electricity and cooling water, did not contribute significantly to the operating, with an overall contribution of ~ 1%.



# Figure S14: Annual operating and maintenance costs across synthesis loop configurations for A) CMR, B) SMR, and C) ATR models.

#### 8.3 Sensitivity Analysis

A sensitivity analysis was carried out on each of the technologies by varying different factors within  $\pm$  10% of their base values and observing individual effects on economic viability. For the SMR base, Series I and Series II cases, FCI, methanol, CO<sub>2</sub> and natural gas costs were varied as illustrated in **Figure S15**. For the SMR Series III case, as well as all other technologies, O<sub>2</sub> price was varied as shown in **Figures S15-S17**.

Variation in methanol costs produced the greatest effect on profitability across all models with sensitivities of up to 6% change in IRR. Similarly, for changes to FCI, all technologies gave similar sensitivities with 4-5% change in IRR. Production costs associated with natural gas and  $CO_2/O_2$  prices were the least sensitive for all cases, with a maximum 1% variation in IRR.

As previously stated, the methanol price had the greatest impact on the economic profitability, hence a study on the global methanol price trend was undertaken. The global methanol price has changed rapidly<sup>39</sup>, mainly depending on several conditions such as the price of oil and gas as well as surplus production over demand. Thus, the methanol price has seen substantial declines, such as from January 2008 at US\$ 720/MT to January 2014 at US\$ 540 M/T<sup>40</sup> – a decrease of US\$180/MT, with a further decline in 2019 to US\$ 350/MT. However, the price has been forecast to increase into  $2020^{41}$ , increasing profitability projections for new MM projects.



Figure S15: Sensitivity analysis for Base case (A), Series I (B), Series II (C) and Series III (D) across CMR technology.



Figure S16: Sensitivity analysis for Base case (A), Series I (B), Series II (C) and Series III (D) across SMR technology.



Figure S17: Sensitivity analysis for Base case (A), Series I (B), Series II (C) and Series III (D) across ATR technology.

# 9. Life Cycle Impact Assessment (LCIA)

LCIA results are given in Tables S12-S29 based on model specific inventory data specified in Table S8.

# Table S12: Individualized LCIA profiles (CML-IA Baseline) for SMR Base Design Case

Impact Category	Unit	Total	Process Emissions	Heating	Process Water	Natural Gas Feedstock	Electricity
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	4.81	0.00	3.59	0.37	0.68	0.18
Abiotic depletion	MJ						
(fossil fuels)		15592.50	0.00	14107.76	11.16	1300.99	172.59
Global Warming	kg CO <sub>2</sub> eq						
(GWP100a)		1302.44	337.48	935.83	1.08	18.24	9.81
Ozone layer	kg CFC-11 eq						
depletion (ODP)	x10 <sup>-5</sup>	8.72	0.00	7.87	0.03	0.77	0.05
Human toxicity	kg 1,4-DB eq	90.93	0.00	83.84	0.52	6.30	0.28
Fresh water aquatic	kg 1,4-DB eq						
ecotoxicity		26.20	0.00	23.42	0.44	2.19	0.15
Marine aquatic	kg 1,4-DB eq						
ecotoxicity		95876.54	0.00	85921.98	1572.75	7882.66	499.15
Terrestrial							
ecotoxicity	kg 1,4-DB eq	0.14	0.00	0.13	0.00	0.01	0.00
Photochemical							
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.90	0.00	0.82	0.01	0.06	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.10	0.00	0.09	0.00	0.01	0.00

Impact Category	Unit	Total	Process	Heating	<b>Process Water</b>	Natural Gas	Electricity
			Emissions	-		Feedstock	
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	5.09	0.00	3.86	0.37	0.68	0.18
Abiotic depletion (fossil	MJ						
fuels)		16662.85	0.00	15171.17	11.22	1307.85	172.61
Global Warming (GWP100a)	kg CO <sub>2</sub> eq	1379.00	343.40	1006.37	1.09	18.34	9.81
Ozone layer depletion (ODP)	kg CFC-11 eq						
	x10 <sup>-5</sup>	9.32	0.00	8.46	0.03	0.78	0.05
Human toxicity	kg 1,4-DB eq	97.28	0.00	90.16	0.52	6.33	0.28
Fresh water aquatic	kg 1,4-DB eq						
ecotoxicity		27.98	0.00	25.19	0.45	2.20	0.15
Marine aquatic ecotoxicity	kg 1,4-DB eq	102403.03	0.00	92398.58	1581.03	7924.20	499.22
Terrestrial ecotoxicity	kg 1,4-DB eq	0.15	0.00	0.14	0.00	0.01	0.00
Photochemical oxidation							
(POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.96	0.00	0.89	0.01	0.06	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.11	0.00	0.10	0.00	0.01	0.00

Impact Category	Unit	Total	Process	Heating	<b>Process Water</b>	Natural Gas	Electricity
			LIIIISSIOIIS			reeustock	
Abiotic depletion	kg Sb eq x10-5	5.02	0.00	3.82	0.36	0.67	0.17
Abiotic depletion (fossil	MJ						
fuels)		16481.46	0.00	15025.24	10.95	1276.65	168.61
Global Warming (GWP100a)	kg CO <sub>2</sub> eq	1320.90	295.66	996.69	1.06	17.90	9.59
Ozone layer depletion (ODP)	kg CFC-11 eq						
	x10 <sup>-5</sup>	9.22	0.00	8.38	0.03	0.76	0.05
Human toxicity	kg 1,4-DB eq	96.25	0.00	89.29	0.51	6.18	0.27
Fresh water aquatic	kg 1,4-DB eq						
ecotoxicity		27.67	0.00	24.95	0.43	2.14	0.15
Marine aquatic ecotoxicity	kg 1,4-DB eq	101275.96	0.00	91509.82	1543.32	7735.18	487.64
Terrestrial ecotoxicity	kg 1,4-DB eq	0.15	0.00	0.13	0.00	0.01	0.00
Photochemical oxidation							
(POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.95	0.00	0.88	0.00	0.06	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.11	0.00	0.10	0.00	0.01	0.00

# Table S14: Individualized LCIA profiles (CML-IA Baseline) for SMR Series II Case

Impact Category	Unit	Total	Process Emissions	Heating	Process Water	Natural Gas Feedstock	Process Oxygen	Carbon Capture
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	7.15	0.00	3.82	0.31	0.59	2.44	0.00
Abiotic depletion	MJ							
(fossil fuels)		16832.54	0.00	15020.35	9.24	1132.00	670.95	0.00
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		399.98	72.38	996.36	0.89	15.87	38.28	-651.43
Ozone layer	kg CFC-11 eq							
depletion (ODP)	x10 <sup>-5</sup>	9.28	0.00	8.38	0.03	0.67	0.20	0.00
Human toxicity	kg 1,4-DB eq	97.17	0.00	89.26	0.43	5.48	2.00	0.00
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		28.15	0.00	24.94	0.37	1.90	0.94	0.00
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		102885.82	0.00	91480.04	1301.79	6858.77	3245.23	0.00
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.16	0.00	0.13	0.00	0.01	0.01	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.96	0.00	0.88	0.00	0.05	0.02	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.12	0.00	0.10	0.00	0.01	0.01	0.00

# Table S15: Individualized LCIA profiles (CML-IA Baseline) for SMR Series III Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
impace category	0		Emissions		Water	Feedstock	Oxygen	j
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	6.39	0.00	0.31	0.10	0.74	5.08	0.16
Abiotic depletion	MJ							
(fossil fuels)		4191.25	0.00	1218.31	3.06	1422.14	1396.97	150.77
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		371.12	181.79	80.82	0.30	19.94	79.70	8.57
Ozone layer	kg CFC-11 eq							
depletion (ODP)	x10 <sup>-5</sup>	1.99	0.00	0.68	0.01	0.84	0.42	0.04
Human toxicity	kg 1,4-DB eq	18.68	0.00	7.24	0.14	6.88	4.17	0.24
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		6.62	0.00	2.02	0.12	2.39	1.96	0.13
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		23660.34	0.00	7420.00	430.73	8616.71	6756.86	436.04
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.04	0.00	0.01	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.02	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.19	0.00	0.07	0.00	0.07	0.05	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00

# Table S16: Individualized LCIA profiles (CML-IA Baseline) for CMR Base Design Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
			Emissions		Water	Feedstock	Oxygen	
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	6.45	0.00	0.38	0.10	0.74	5.08	0.15
Abiotic depletion	MJ							
(fossil fuels)		4458.89	0.00	1488.81	3.06	1422.14	1396.97	147.90
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		380.75	173.64	98.76	0.30	19.94	79.70	8.41
Ozone layer	kg CFC-11 eq							
depletion (ODP)	x10 <sup>-5</sup>	2.14	0.00	0.83	0.01	0.84	0.42	0.04
Human toxicity	kg 1,4-DB eq	20.28	0.00	8.85	0.14	6.88	4.17	0.24
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		7.07	0.00	2.47	0.12	2.39	1.96	0.13
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		25299.51	0.00	9067.46	430.73	8616.71	6756.86	427.75
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.01	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.21	0.00	0.09	0.00	0.07	0.05	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00

# Table S17: Individualized LCIA profiles (CML-IA Baseline) for CMR Series I Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
			Emissions	0	Water	Feedstock	Oxygen	·
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	6.46	0.00	0.52	0.10	0.72	4.96	0.16
Abiotic depletion	MJ							
(fossil fuels)		4961.44	0.00	2055.17	2.98	1388.41	1363.81	151.07
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		384.75	142.27	136.33	0.29	19.47	77.81	8.59
Ozone layer	kg CFC-11 eq							
depletion (ODP)	x10 <sup>-5</sup>	2.43	0.00	1.15	0.01	0.82	0.41	0.04
Human toxicity	kg 1,4-DB eq	23.39	0.00	12.21	0.14	6.72	4.08	0.24
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		7.91	0.00	3.41	0.12	2.33	1.91	0.13
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		28383.00	0.00	12516.82	420.50	8412.31	6596.45	436.92
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.02	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.24	0.00	0.12	0.00	0.07	0.05	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.01	0.00	0.01	0.01	0.00

# Table S18: Individualized LCIA profiles (CML-IA Baseline) for CMR Series II Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity	Carbon
LB. 2			Emissions		Water	Feedstock	Oxygen		Capture
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	8.49	0.00	0.37	0.10	0.71	7.32	-0.01	0.00
Abiotic depletion	MJ								
(fossil fuels)		4839.06	0.00	1470.18	2.93	1363.83	2013.74	-11.62	0.00
Global Warming	kg CO <sub>2</sub> eq								
(GWP100a)		27.89	0.00	97.52	0.28	19.12	114.89	-0.66	-203.26
Ozone layer	kg CFC-11 eq								
depletion (ODP)	x10 <sup>-5</sup>	2.24	0.00	0.82	0.01	0.81	0.60	0.00	0.00
Human toxicity	kg 1,4-DB eq	21.47	0.00	8.74	0.14	6.60	6.02	-0.02	0.00
Fresh water aquatic	kg 1,4-DB eq								
ecotoxicity		7.66	0.00	2.44	0.12	2.29	2.82	-0.01	0.00
Marine aquatic	kg 1,4-DB eq								
ecotoxicity		27336.87	0.00	8953.96	413.08	8263.40	9740.04	-33.61	0.00
Terrestrial									
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.01	0.00	0.01	0.02	0.00	0.00
Photochemical									
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.22	0.00	0.09	0.00	0.06	0.07	0.00	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.01	0.00	0.01	0.02	0.00	0.00

# Table S19: Individualized LCIA profiles (CML-IA Baseline) for CMR Series III Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
1 87			Emissions	8	Water	Feedstock	Oxygen	U
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	6.84	0.00	0.37	0.03	0.76	5.47	0.20
Abiotic depletion	MJ							
(fossil fuels)		4622.87	0.00	1469.79	1.05	1451.83	1506.23	193.96
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		429.02	214.10	97.50	0.10	20.36	85.93	11.03
Ozone layer	kg CFC-11							
depletion (ODP)	eq x10 <sup>-5</sup>	2.19	0.00	0.82	0.00	0.86	0.45	0.06
Human toxicity	kg 1,4-DB eq	20.62	0.00	8.73	0.05	7.03	4.50	0.31
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		7.20	0.00	2.44	0.04	2.44	2.11	0.17
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		25741.86	0.00	8951.62	147.35	8796.59	7285.34	560.97
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.01	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.21	0.00	0.09	0.00	0.07	0.05	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.01	0.00	0.01	0.02	0.00

# Table S20: Individualized LCIA profiles (CML-IA Baseline) for ATR Base Design Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
			Emissions	-	Water	Feedstock	Oxygen	
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	6.98	0.00	0.53	0.03	0.76	5.48	0.18
Abiotic depletion	MJ							
(fossil fuels)		5215.13	0.00	2075.25	1.05	1452.87	1507.32	178.65
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		512.66	258.38	137.66	0.10	20.37	85.99	10.16
Ozone layer	kg CFC-11							
depletion (ODP)	eq x10 <sup>-5</sup>	2.53	0.00	1.16	0.00	0.86	0.45	0.05
Human toxicity	kg 1,4-DB eq	24.20	0.00	12.33	0.05	7.03	4.50	0.29
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		8.20	0.00	3.45	0.04	2.44	2.11	0.16
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		29396.68	0.00	12639.10	147.45	8802.90	7290.57	516.66
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.02	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.25	0.00	0.12	0.00	0.07	0.05	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.01	0.00	0.01	0.02	0.00

# Table S21: Individualized LCIA profiles (CML-IA Baseline) for ATR Series I Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Process	Electricity
1 87			Emissions	8	Water	Feedstock	Oxygen	v
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	8.71	0.00	0.33	0.03	0.76	7.39	0.21
Abiotic depletion	MJ							
(fossil fuels)		4971.66	0.00	1282.76	1.05	1452.83	2032.18	202.84
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		448.10	215.06	85.09	0.10	20.37	115.94	11.53
Ozone layer	kg CFC-11							
depletion (ODP)	eq x10 <sup>-5</sup>	2.25	0.00	0.72	0.00	0.86	0.61	0.06
Human toxicity	kg 1,4-DB eq	21.10	0.00	7.62	0.05	7.03	6.07	0.32
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		7.64	0.00	2.13	0.04	2.44	2.85	0.18
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		27178.53	0.00	7812.56	147.45	8802.64	9829.25	586.63
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.05	0.00	0.01	0.00	0.01	0.02	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Acidification	kg SO <sub>2</sub> eq	0.22	0.00	0.07	0.00	0.07	0.07	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.01	0.00	0.01	0.02	0.00

# Table S22: Individualized LCIA profiles (CML-IA Baseline) for ATR Series II Case

Impact Category	Unit	Total	Process	Process	Natural Gas	Process	Electricity	Carbon
LB. 2			Emissions	Water	Feedstock	Oxygen		Capture
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	7.80	0.00	0.03	0.75	7.31	-0.30	0.00
Abiotic depletion	MJ							
(fossil fuels)		3164.82	0.00	1.04	1438.42	2012.35	-286.97	0.00
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		-92.22	0.00	0.10	20.17	114.81	-16.32	-210.98
Ozone layer	kg CFC-11 eq							
depletion (ODP)	x10 <sup>-5</sup>	1.37	0.00	0.00	0.85	0.60	-0.09	0.00
Human toxicity	kg 1,4-DB eq	12.56	0.00	0.05	6.96	6.01	-0.46	0.00
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		5.03	0.00	0.04	2.42	2.82	-0.25	0.00
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		17764.63	0.00	145.99	8715.30	9733.31	-829.96	0.00
Terrestrial								
ecotoxicity	kg 1,4-DB eq	0.04	0.00	0.00	0.01	0.02	0.00	0.00
Photochemical								
oxidation (POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.02	0.00	0.00	0.01	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.13	0.00	0.00	0.07	0.07	-0.01	0.00
Eutrophication	kg PO <sub>4</sub> eq	0.04	0.00	0.00	0.01	0.02	0.00	0.00

# Table S23: Individualized LCIA profiles (CML-IA Baseline) for ATR Series III Case

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	CO <sub>2</sub>	Electricity
			Emissions	8	Water	Feedstock	Product	v
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	4.49	0.00	3.24	0.33	0.63	0.12	0.17
Abiotic depletion (fossil	MJ							
fuels)		14494.2	0.00	12753.68	9.80	1203.25	358.45	169.03
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		1192.62	270.00	846.01	0.95	16.87	49.18	9.61
Ozone layer depletion	kg CFC-11 eq x10 <sup>-5</sup>							
(ODP)		8.10	0.00	7.11	0.03	0.71	0.20	0.05
Human toxicity	kg 1,4-DB eq	84.40	0.00	75.79	0.45	5.82	2.06	0.27
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		24.33	0.00	21.18	0.39	2.02	0.60	0.15
Marine aquatic	kg 1,4-DB eq	89017.7						
ecotoxicity		0	0.00	77675.09	1381.60	7290.44	2181.70	488.86
Terrestrial ecotoxicity	kg 1,4-DB eq	0.13	0.00	0.11	0.00	0.01	0.00	0.00
Photochemical oxidation								
(POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.08	0.00	0.07	0.00	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.83	0.00	0.75	0.00	0.06	0.02	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.10	0.00	0.09	0.00	0.01	0.00	0.00

Table S24: Individualized LCIA profiles (CML-IA Baseline) for SMR Base Design system boundary definition sensitivity (Case B)

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	CO <sub>2</sub>	Electricity
			Emissions	0	Water	Feedstock	Product	· ·
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	4.84	0.00	3.59	0.33	0.63	0.12	0.18
Abiotic depletion (fossil	MJ							
fuels)		15885.93	0.00	14138.94	9.84	1207.21	359.84	170.09
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		1291.72	276.90	937.90	0.95	16.93	49.37	9.67
Ozone layer depletion	kg CFC-11 eq x10 <sup>-5</sup>							
(ODP)		8.88	0.00	7.88	0.03	0.72	0.20	0.05
Human toxicity	kg 1,4-DB eq	92.66	0.00	84.02	0.46	5.84	2.07	0.27
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		26.64	0.00	23.48	0.39	2.03	0.60	0.15
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		97495.54	0.00	86111.88	1387.12	7314.42	2190.20	491.91
Terrestrial ecotoxicity	kg 1,4-DB eq	0.15	0.00	0.13	0.00	0.01	0.00	0.00
Photochemical oxidation								
(POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.91	0.00	0.83	0.00	0.06	0.02	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.11	0.00	0.09	0.00	0.01	0.00	0.00

# Table S25: Individualized LCIA profiles (CML-IA Baseline) for SMR Series I system boundary definition sensitivity (Case B)

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	CO <sub>2</sub>	Electricity
			Emissions	8	Water	Feedstock	Product	U U
Abiotic depletion	kg Sb eq x10 <sup>-5</sup>	4.74	0.00	3.53	0.31	0.60	0.11	0.17
Abiotic depletion (fossil	MJ							
fuels)		15586.23	0.00	13906.48	9.48	1159.71	346.81	163.75
Global Warming	kg CO <sub>2</sub> eq							
(GWP100a)		1210.55	214.00	922.48	0.92	16.26	47.58	9.31
Ozone layer depletion	kg CFC-11 eq x10 <sup>-5</sup>							
(ODP)		8.71	0.00	7.75	0.03	0.69	0.19	0.05
Human toxicity	kg 1,4-DB eq	90.95	0.00	82.64	0.44	5.61	1.99	0.26
Fresh water aquatic	kg 1,4-DB eq							
ecotoxicity		26.13	0.00	23.09	0.38	1.95	0.58	0.14
Marine aquatic	kg 1,4-DB eq							
ecotoxicity		95642.76	0.00	84696.10	1335.57	7026.64	2110.86	473.58
Terrestrial ecotoxicity	kg 1,4-DB eq	0.14	0.00	0.12	0.00	0.01	0.00	0.00
Photochemical oxidation								
(POCP)	kg C <sub>2</sub> H <sub>4</sub> eq	0.09	0.00	0.08	0.00	0.01	0.00	0.00
Acidification	kg SO <sub>2</sub> eq	0.90	0.00	0.81	0.00	0.06	0.02	0.01
Eutrophication	kg PO <sub>4</sub> eq	0.10	0.00	0.09	0.00	0.01	0.00	0.00

# Table S26: Individualized LCIA profiles (CML-IA Baseline) for SMR Series II system boundary definition sensitivity (Case B)

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Electricity
			Emissions		Water	Feedstock	
Climate Change Human Health	DALY x 10 <sup>-5</sup>	122.45	31.32	88.20	0.10	1.91	0.92
Climate change Ecosystems	species.yr x10 <sup>-6</sup>	3.70	0.94	2.66	0.00	0.06	0.03
Ozone depletion	DALY x10 <sup>-6</sup>	0.08	0.00	0.07	0.00	0.01	0.00
Particulate matter formation	DALY x10 <sup>-6</sup>	151.19	0.00	138.02	1.54	10.63	1.00
Terrestrial acidification	species.yr x10 <sup>-6</sup>	0.15	0.00	0.14	0.00	0.01	0.00
Freshwater eutrophication	species.yr x10-9	6.78	0.00	5.72	0.33	0.63	0.10
Terrestrial ecotoxicity	species.yr x10-9	0.57	0.00	0.45	0.02	0.08	0.02
Freshwater ecotoxicity	species.yr x10-9	0.93	0.00	0.81	0.02	0.09	0.01
Marine ecotoxicity	species.yr x10-9	0.21	0.00	0.18	0.00	0.02	0.00
Human non-carcinogenic toxicity	DALY x10 <sup>-6</sup>	7.48	0.00	6.42	0.17	0.77	0.13
Mineral resource scarcity	\$	0.05	0.00	0.05	0.00	0.01	0.00
Fossil resource scarcity	\$	135.40	0.00	122.55	0.05	11.30	1.50

# Table S27: Individualized LCIA profiles (ReCiPe Endpoint- Hierarchist V1.13 World) for SMR Base Design

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Electricity
			Emissions		Water	Feedstock	
Climate Change Human Health	DALY x 10 <sup>-5</sup>	129.66	31.87	94.85	0.10	1.92	0.92
Climate change Ecosystems	species.yr x10 <sup>-6</sup>	3.91	0.96	2.86	0.00	0.06	0.03
Ozone depletion	DALY x10 <sup>-6</sup>	0.08	0.00	0.08	0.00	0.01	0.00
Particulate matter formation	DALY x10 <sup>-6</sup>	161.65	0.00	148.42	1.55	10.69	1.00
Terrestrial acidification	species.yr x10 <sup>-6</sup>	0.16	0.00	0.15	0.00	0.01	0.00
Freshwater eutrophication	species.yr x10-9	7.22	0.00	6.15	0.33	0.64	0.10
Terrestrial ecotoxicity	species.yr x10-9	0.60	0.00	0.48	0.02	0.08	0.02
Freshwater ecotoxicity	species.yr x10-9	1.00	0.00	0.87	0.02	0.09	0.01
Marine ecotoxicity	species.yr x10-9	0.22	0.00	0.19	0.00	0.02	0.00
Human non-carcinogenic toxicity	DALY x10 <sup>-6</sup>	7.97	0.00	6.90	0.17	0.78	0.13
Mineral resource scarcity	\$	0.06	0.00	0.05	0.00	0.01	0.00
Fossil resource scarcity	\$	144.70	0.00	131.79	0.05	11.36	1.50

Table S28: Individualized LCIA profiles (ReCiPe Endpoint- Hierarchist V1.13 World) for SMR Series I

Impact Category	Unit	Total	Process	Heating	Process	Natural Gas	Electricity
			Emissions	_	Water	Feedstock	-
Climate Change Human Health	DALY x 10 <sup>-5</sup>	124.25	27.44	93.94	0.10	1.87	0.90
Climate change Ecosystems	species.yr x10 <sup>-6</sup>	3.75	0.83	2.83	0.00	0.06	0.03
Ozone depletion	DALY x10 <sup>-6</sup>	0.08	0.00	0.07	0.00	0.01	0.00
Particulate matter formation	DALY x10 <sup>-6</sup>	159.91	0.00	147.00	1.51	10.43	0.97
Terrestrial acidification	species.yr x10 <sup>-6</sup>	0.16	0.00	0.15	0.00	0.01	0.00
Freshwater eutrophication	species.yr x10-9	7.13	0.00	6.09	0.32	0.62	0.09
Terrestrial ecotoxicity	species.yr x10-9	0.60	0.00	0.48	0.02	0.08	0.02
Freshwater ecotoxicity	species.yr x10-9	0.99	0.00	0.87	0.02	0.09	0.01
Marine ecotoxicity	species.yr x10-9	0.22	0.00	0.19	0.00	0.02	0.00
Human non-carcinogenic toxicity	DALY x10-6	7.88	0.00	6.83	0.16	0.76	0.12
Mineral resource scarcity	\$	0.06	0.00	0.05	0.00	0.01	0.00
Fossil resource scarcity	\$	143.13	0.00	130.52	0.05	11.09	1.47

# Table S29: Individualized LCIA profiles (ReCiPe Endpoint- Hierarchist V1.13 World) for SMR Series II

#### 10. Cradle-to-Gate Life Cycle Impact Assessment (LCIA)

#### 10.1 Contributional Analysis

The LCIA was examined based on a functional unit of 1 metric tonne of methanol produced per hour to identify the main contributors to environmental burden throughout the cradle-to-gate methanol life cycle. Detailed contributional analyses and LCI are presented in the **Tables S12-S29**. For the methanol and ammonia processes, natural gas was utilized both as a fuel and a feedstock as well as a raw material for electricity generation. Thus, major contributors to environmental burden were affiliated with natural gas combustion, extraction and utilization.

**Figures S18-S20** gives the LCA contributional analysis for the SMR, CMR and ATR reforming technologies and configurations, where all data across different impact categories are normalized to 100%.

For the SMR technology (**Figure S18**), heating gave the largest environmental burden contribution of 53%-93% throughout all impact categories. This directly aligned with the energy-intensive nature of the reforming unit within the SMR process. Significant contributions were observed for fossil fuel depletion (89%-91%), marine and freshwater toxicities (88%-91%), human toxicity and acidification (90%-93%) mainly attributed to the release of toxic compounds such as barium, beryllium, cobalt, vanadium, zinc and copper ions as well the presence of SO<sub>2</sub> and mercury during fossil fuel extraction and utilization.

For both CMR and ATR technologies (**Figures S19 and S20**),  $O_2$  consumption, carried the largest environmental burden across all impact categories, followed by heating and natural gas feedstock utilization. The largest contributions were observed for abiotic depletion (76%-91%), fossil fuel depletion (27%-58%), terrestrial ecotoxicity (39%-64%), POCP (28%-50%) and eutrophication (41%-75.2%). These burdens were attributed mainly to fossil fuel combustion associated with the heating, natural gas extraction and un-decarbonized electricity consumption.

Process based emissions, attributed to purge gas combustion, caused relatively high environmental impacts on GWP<sub>100a</sub> compared with other impact category. Contributions varied with SMR process burdens 22%-25% while for the CMR and ATR cases were 36%-48% and 48-51% respectively. These burdens were mainly attributed to GHG emissions- predominantly CO<sub>2</sub>. Heating within the SMR process contributed 72%-88% to the GWP<sub>100a</sub> environmental burden while O<sub>2</sub> consumption within the CMR and ATR cases contributed between 19%-42%; attributed to both CO<sub>2</sub> and CH<sub>4</sub> emissions.

Apart from negative environmental impacts, environmental benefits (negative burdens) were also observed mainly associated carbon capture and electrical generation (Series III). Lower energy demand associated with CMR and ATR processes lead to significant environmental benefits associated with global warming.

Lastly, process water and electricity contributions were mostly low with burdens affiliated with the SMR process around 0.05%-7.5%, and CMR and ATR giving 0.06%-5%.



Figure S18: Characterized LCIA Profiles (Method CML-IA Baseline World 2000; functional unit 1 tonne CH<sub>3</sub>OH) for SMR technology.



Figure S19: Characterized LCIA Profiles (Method CML-IA Baseline World 2000; functional unit 1 tonne CH<sub>3</sub>OH) for CMR technology.



Figure S20: Characterized LCIA Profiles (Method CML-IA Baseline World 2000; functional unit 1 tonne CH<sub>3</sub>OH) for ATR technology.

#### 11. LCSA Results

**Tables S30-S33** gives normalized parameters for models across each reforming technology. For the environmental domain, major impact categories were chosen while for the economic domain, IRR was normalized using a reverse score indicating a minimum value for the highest economic profitability. For the social domain, job creation was assessed in terms of the total number of operators needed based on specific model unit operations. All other jobs related to engineering, maintenance and administration are plant specific and did not change across models.

Category	Base Design				
	CMR	SMR	ATR		
Fossil Fuel Depletion	0.269	1.000	0.296		
GWP 100a	0.285	1.000	0.329		
ODP	0.229	1.000	0.251		
РОСР	0.268	1.000	0.294		
Eutrophication	0.307	1.000	0.336		
Human Toxicity	0.205	1.000	0.227		
IRR (Reverse Score)	1.000	0.810	0.684		
Job Creation (Reverse Score)	1.000	0.941	0.941		

Table S30: Normalized Sustainability Parameters for Base Design models

#### Table S31: Normalized Sustainability Parameters for Series I models

Category	Series I				
	CMR	SMR	ATR		
Fossil Fuel Depletion	0.268	1.000	0.313		
GWP 100a	0.276	1.000	0.372		
ODP	0.230	1.000	0.271		
РОСР	0.267	1.000	0.310		
Eutrophication	0.303	1.000	0.350		
Human Toxicity	0.208	1.000	0.249		
IRR (Reverse Score)	1.000	0.777	0.655		
Job Creation (Reverse Score)	1.000	0.944	1.000		

Category	Series II			
	CMR	SMR	ATR	
Fossil Fuel Depletion	0.301	1.000	0.302	
GWP 100a	0.291	1.000	0.339	
ODP	0.264	1.000	0.244	
РОСР	0.300	1.000	0.294	
Eutrophication	0.336	1.000	0.359	
Human Toxicity	0.243	1.000	0.219	
IRR (Reverse Score)	1.000	0.803	0.685	
Job Creation (Reverse Score)	1.000	0.944	1.000	

Table S32: Normalized Sustainability Parameters for Series II models

# Table S33: Normalized Sustainability Parameters for Series III models

Category	Series III				
	CMR	SMR	ATR		
Fossil Fuel Depletion	0.287	1.000	0.188		
GWP 100a	0.213	1.000	0.000		
ODP	0.241	1.000	0.148		
РОСР	0.284	1.000	0.188		
Eutrophication	0.354	1.000	0.228		
Human Toxicity	0.221	1.000	0.129		
IRR (Reverse Score)	0.89	1.000	0.553		
Job Creation (Reverse Score)	1.000	1.000	1.000		

#### 12. PB and LCA Limitations and Sensitivities

#### 12.1 LCA Sensitivities

In an effort to assign burden contributions to CO<sub>2</sub> feedstock utilized within the SMR process, a system boundary expansion approach was considered as shown in **Figure S21**. For the original case study (**Case A-Figure S21**), the system boundary incorporated the co-production of ammonia and methanol whereby burdens were shared between products based on economic value. Within the second case (**Case B-Figure S21**), ammonia manufacture was excluded from the system boundary, and burdens were shared between methanol and the by-product captured CO<sub>2</sub>. **Figure S22** gives the impact contributions while **Tables S23-S25** gives overall burden contributions for each system boundary considered. Comparing the results across both cases, impact contributions were relatively similar, and thus the allocation approach was deemed not a sensitive factor for environmental profiles within the methanol process.

For the endpoint approach, the ReCiPe Endpoint Hierarchist version 1.13 / World was used. Impact contributions are given in **Tables S26-S28**. This method comprises of 12 impact categories, climate change human health, ozone depletion (**ODP**), human toxicity, particulate matter formation (**PM**), climate change ecosystems (**Eco**), terrestrial acidification, freshwater eutrophication, terrestrial ecotoxicity (**ecotox**), freshwater ecotoxicity (**ecotox**), marine ecotoxicity (**ecotox**), metal depletion (**dep**) and fossil depletion (**dep**). The sensitivity analysis was conducted across the SMR technology. Comparing **Figures S22 A and S23**, the results of both methods gave broadly similar results. Thus, the characterization model was not a sensitive factor for environmental profiles within the methanol process.

#### 11.2 Limitations within the PB Framework

- The allocation of the share of the safe operating space assumes static shares of PBs related to each Earth System. MM processes however, has the ability to reduce its own burdens while maintaining given outputs and thus, can promote cross-sector share allocations with other industrial partners that show stricter adherence to PBs in which the MM process has poor performance. This dynamic share allocation can be considered in future work as the main aim of this study was to examine design considerations that can promote sustainable development within the current MM process technologies.
- Uncertainties in estimating the population and gross value added for Trinidad and Tobago are largely dependent on local reporting which are not updated. Hence, the latest data was used (2018) for which the current share of the operating space was estimated.
- Total impacts on for land-system change was excluded as LCI information was unavailable for MM process plants within Trinidad and Tobago.
- The software used to quantify burdens for the PB-LCIA analysis (Ecoinvent database v3.4 on SimaPro v9.0.0.30) has not been updated to reflect the current global industrial policies with respect

to halon, HCFC and CFC use<sup>42</sup>. The absence of further data relating to stratospheric ozone depletion limited us in quantifying shares associated with the stratospheric ozone depletion PB for each scenario. Consequently, the transgression for each scenario was assumed to be zero given that legislation has restricted the utilization of these specific chemicals with respect to fire extinguishers etc.

• Uncertainties guided by incorrect estimation of ecological limits as well as characterization factors for determining impact as these values change annually and are assumed relatively constant within this study. Also, focus was made on PBs for which characterization factors are available, thus, biosphere integrity was omitted due to lack of methods for generating impact. Furthermore, uncertainties in calculating elementary flows were not considered.



Figure S21: System boundary expansion across SMR technology.

![](_page_62_Figure_0.jpeg)

Figure S22: Sensitivity analysis on system boundary definition using Method CML-IA Baseline World 2000; functional unit 1 tonne CH<sub>3</sub>OH. A) SMR LCIA profiles for system boundary (A), B) SMR LCIA profiles for system boundary (B)

![](_page_63_Figure_0.jpeg)

Figure S23: Characterized profiles for SMR using ReCiPe (H) endpoint method

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