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Supplementary information

Upgrading the value of anaerobic digestion via chemical production from grid injected biomethane

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Table S1. Main technical design data

Biogas yield (Nm^{-3} biogas kg^{-1} fresh matter)	
Energy crops	210
Agricultural residues	100
Organic fraction municipal solid waste	100
Sewage sludge	80
Food waste	210
Manure	28
Biogas production rate (Nm^3 h^{-1})	1 000
Energy density methane (kWh Nm^{-3})	10.85
Energy density biogas (kWh Nm^{-3})	6.50
Mass density biogas (kg Nm^{-3})	1.22
Energy density biogas (MWh ton$^{-1}_{biogas}$)	5.33
Raw biogas composition	
CH_4 content (vol.%)	60
O_2 content (vol.%)	0.1
N_2 content (vol.%)	0.4
H_2S content (ppmv)	50
CO_2 content (vol.%)	39.5

Table S2. Feed and product flow rates for super-dry reforming (SDR), dry reforming of methane (DRM) and sorption-enhanced steam reforming of methane (SESR).

	Feed (ton day^{-1})			**Product (ton day^{-1})**				**Energy input**	
Case	CH_4 [a]	CO_2	H_2O	CO	H_2	CO_2	H_2O	(GJ ton^{-1} CH_4)	(GJ ton^{-1} CO_2)
SDR	176	1455	-	1234	-	-	396	21.0	2.55
DRM	176	485	-	617	44	-	-	16.3	5.94
SESR	176	-323	397	-	88	808	-	15.8	-

[a] The feed flow rate of CH_4 corresponds with 6000 Nm^3 h^{-1} (which in turn corresponds with 10000 Nm^3 h^{-1} biogas or about 10 large scale AD plants).

Table S3. Biogas production cost compared to average and extreme reference systems

Biogas production cost	Average	Min	Max
Feedstock cost (€ ton^{-1})[a]	**4.91**	2.00	50.00
Capital investment (€)[b]	**4 000 000**	3 500 000	4 500 000
CAPEX (€ $year^{-1}$)[c]	**305 000**	266 875	343 125
OPEX (€ $year^{-1}$)[d]	**300 000**	175 000	450 000
Biogas production (MWh $year^{-1}$)[e]	**57 052**	57 052	57 052
Production cost (€ MWh^{-1})	**21.4**	9.8	41.1
Production cost (€ ton^{-1}_{biogas})[f]	**114.4**	52.2	219.0

[a] Assumed that every substrate represents 20 % of the total biogas production. Assumed transport cost is 2.8 € ton^{-1}. Only maize silage was assumed to have a feedstock cost (30 € ton^{-1}). [1]

[b] Assumed investment: 3000 (Min), 4000 (Avg) and 5000 (Max) € Nm^{-3} h^{-1} installed biogas capacity. Investment without investment subsidy or support.

[c] Calculated according to the annuity method with an interest of 5% and 20 years depreciation.

[d] Assuming 5 % (Min), 7.5% (Avg) and 10 % (Max) of the total investment.

[e] Assumed methane content is 60 vol.% (Calculated under the assumption that no plant shutdown occurs).

[f] Assuming 4.91 MWh ton^{-1} $_{biogas.}$

Table S4. Power and heat production cost contributions

Power and heat production cost	Average	Min	Max
Installed power (kW_e)	**2500**	2500	2500
Efficiency (%)			
Electricity	**35**	35	35
Heat	**45**	45	45
Capital investment (€)[a]	**1 250 000**	1 000 000	1 500 000
CAPEX (€ $year^{-1}$)[b]	**231 250**	185 000	277 500
OPEX (€ $year^{-1}$)[c]	**100 000**	50 000	200 000
Production cost (€ MWh_e^{-1})	**17**	12	24
Production cost (€ ton^{-1})	**31.0**	22.0	44.6

[a] Assumed investment in the CHP plant is 500 € kW_e^{-1}.[2]

[b] Depreciation period of 5 years for the engine and 10 years for other installations. Engines represent approximately 35% of the investment.

[c] Assuming 20 € kW_e^{-1} (Min), 40 € kW_e^{-1} (Avg) and 100 € kW_e^{-1} (Max).

Table S5. Biomethane composition and technicalities of the gas upgrading unit and additional components for the different upgrading techniques

Biomethane composition	*PWS*[a]	*PSA*[b]	*AS*[c]	*GP*[d]
Volume flow ($Nm^3\ h^{-1}$)	606.2	606.2	618.3	615.5
CH_4 content (vol.%)	97	97	97	97
O_2 content (vol.%)	0.47	0.07	0.16	0.08
N_2 content (vol.%)	1.57	0.33	0.65	0.65
H_2S content (ppmv)	0.68	0.26	0.44	0.33
CO_2 content (vol.%)	0.96	2.6	2.19	2.28
Technical parameters of biogas upgrading plant	*PWS*	*PSA*	*AS*	*GP*
Methane slip (vol.%)	2	2	0.04	0.5
Biomethane pressure (bar)	8	7	1	6
Technical parameters of grid injection	*PWS*	*PSA*	*AS*	*GP*
Length of biomethane pipeline (m)	100	100	100	100
Gas grid pressure (bar)	14	14	14	14

[a] *PWS = pressurized water scrubbing*
[b] *PSA = pressurized swing adsorption*
[c] *AS = amine scrubbing*
[d] *GP = gas permeation*

Table S6. Estimated CAPEX contribution to reforming processes.

	Foster Wheeler, 2013 [3]	Salkuyeh, 2017 [4]	Compagnoni, 2017 [5]
Reforming process	SRM[a]	SRM[a]	SRE[b]
Plant capacity (ton CH_4 day^{-1})	553[c]	1814	55[c]
Capital investment (M€)[d]	85.7	217	16.2
Depreciation time (years)[e]	15	15	30
Interest (%)[f]	5	5	5
Percentage of time on stream (%)[g]	95	95	96
CAPEX (M€ year^{-1})[h]	8.00	20.3	0.946
CAPEX (k€ day^{-1})	21.9	55.5	2.59
CAPEX (€ ton^{-1} CH_4)	41.8	32.2	49.0

[a] Steam reforming of methane (SRM)

[b] Steam reforming of ethanol (SRE)

[c] The reported plant capacity in terms of H_2 production was converted into CH_4 processing capacity by assuming a 3.1 mol_{H2} mol_{CH4}^{-1} yield (based on our Aspen Simulations for SESR).

[d] The conversion factor between US$ and € was obtained from https://www.statista.com/statistics/412794/euro-to-u-s-dollar-annual-average-exchange-rate/ taking into account the year of publication of the source data.

[e] The depreciation time was assumed 15 years in case it was not specified in the reference.

[f] The interest on capital investment was assumed to be 5%.

[g] Percentage of the time on stream is assumed 95% in case it was not specified in the reference.

[h] Calculated according to the annuity method taking into account the specific depreciation time and interest.

Table S7. Overview of fuels, raw chemicals, bulk chemicals and other chemicals and their global production volume/capacity as well as the amount of carbon involved. The amount of CO that would be necessary to meet the production volume/capacity according to the reaction scheme of paragraph 2.3.3. Error! Reference source not found. **is determined and linked to the amount of CO_2 that can be converted by SDR.**

Fuels and raw chemicals	**Mt year^{-1}**	**Mt C year^{-1}**	**Mt CO year^{-1}**	**Mt CO_2 year^{-1} [b]**	**%BMPP[c]**	**%SCE[d]**	**Year**
Coal production [6]	7860	2360-6680[e]					2015
Oil production [6]	4400	3740	8800	10370	265	49	2015
Natural gas production [6]	2870	2190					2015
	15130	**8290-12610**	**8800**	**10370**	**265**	**49**	
Bulk chemicals							
Ethylene [7a]	154	132	308	363	9.3	1.73	2013
Propylene [7a]	148	127	296	349	8.9	1.66	2013
Olefins (via MTO process) [8]	*11*	*9.4*	*22*	*26*	*0.7*	*0.13*	*2014*
Ethanol [9]	68	35.4	82.5	98	2.5	0.46	2011
Methanol [7a]	98	37	86	101	2.6	0.48	2013
Methanol [10]	55	20.6	48	56	1.4	0.27	2013
Formaldehyde [11]	30	12	28	33	0.8	0.16	2016
Acetic acid [12]	6.5	1.3	3	4	0.1	0.02	2013
	560	**365**	**852**	**1004**	**25.6**	**4.8**	
Other chemicals							
Phosgene [13]	3	0.37	0.86	1.05	0.03	0.005	2014
Acetaldehyde [14]	1	0.30	0.60	0.71	0.02	0.003	2006
Polycarbonate [10]	4	0.14	0.34	0.40	0.01	0.002	2014
Dimethylcarbonate [15]	0.4	0.053	0.13	0.15	0.004	0.001	2014
	8.4	**0.86**	**1.9**	**2.31**	**0.06**	**0.011**	

[a] Global “capacity” is reported rather than the actual production volume

[b] Amount of CO_2 that can be converted into CO to meet the demand of chemicals/fuels when considering reaction stoichiometry of SDR: $1CH_4 + 3CO_2 = 4CO + 2H_2O$

[c] Percentage of the global biomethane production potential (assumed 658 Mt biomethane year^{-1}) necessary to provide CO for chemicals/fuels production by SDR, taking into account CH_4 necessary for providing process heat. The current production reaches around 3.5% of this production potential.

[d] Percentage of stationary CO_2 emission sources (estimation for 2015) that could be valorized by production of chemicals/fuels, taking into account that 1 mol CH_4 and 3 mol CO_2 are converted into 4 mol CO according to reaction stoichiometry.

[e] The reported range of Mt C/year originates from the highly variable carbon content of coal (ranging from 30 to 86 w% carbon).

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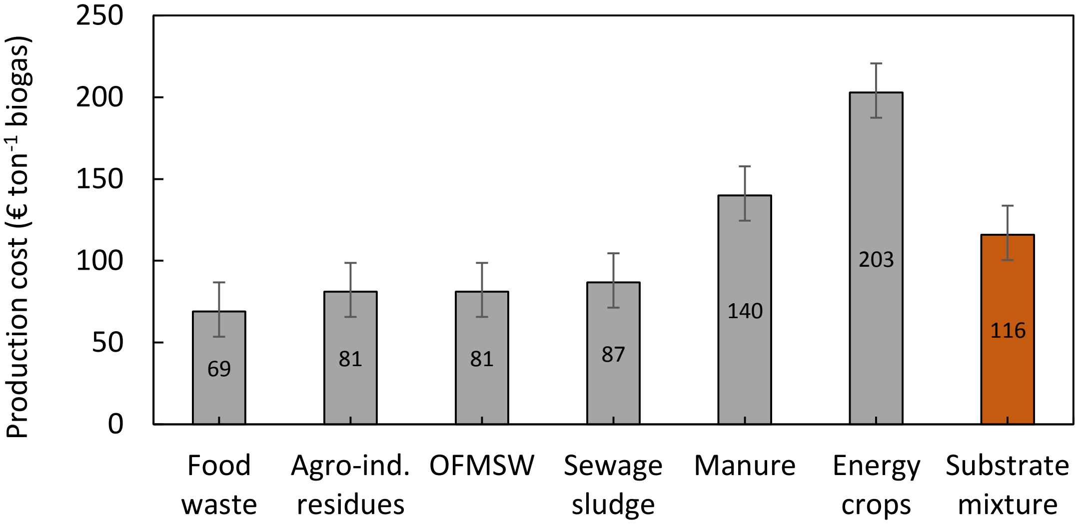

Figure S1. Specific raw biogas production cost in € ton^{-1} biogas for 6 different feedstocks, and for co-digestion of the 6 substrates (every substrate represents 1/6th of the total biogas production).

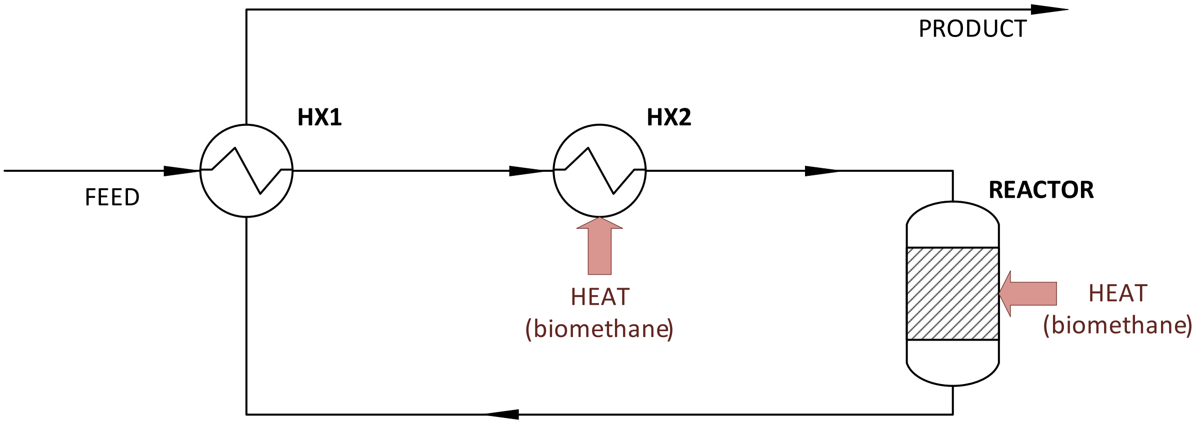

Figure S2. Flowsheet used for Aspen Plus simulation of biomethane conversion to CO, syngas or H_2. (HX1: shell-tube heat exchanger, HX2: heat exchanger, REACTOR: RYield reactor.)

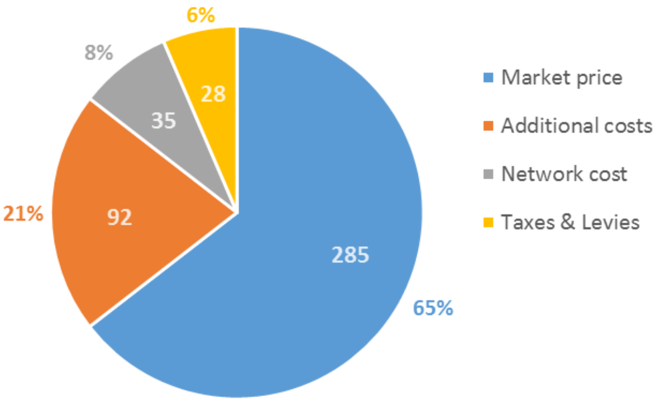

Figure S3. Pie chart representing the contributions (percentual and in € ton^{-1} CH_4) that constitute the consumer price of natural gas for industrial end-users in 2015 (average for EU-28, 2015). Values are based on a report made by the European Commission[16].

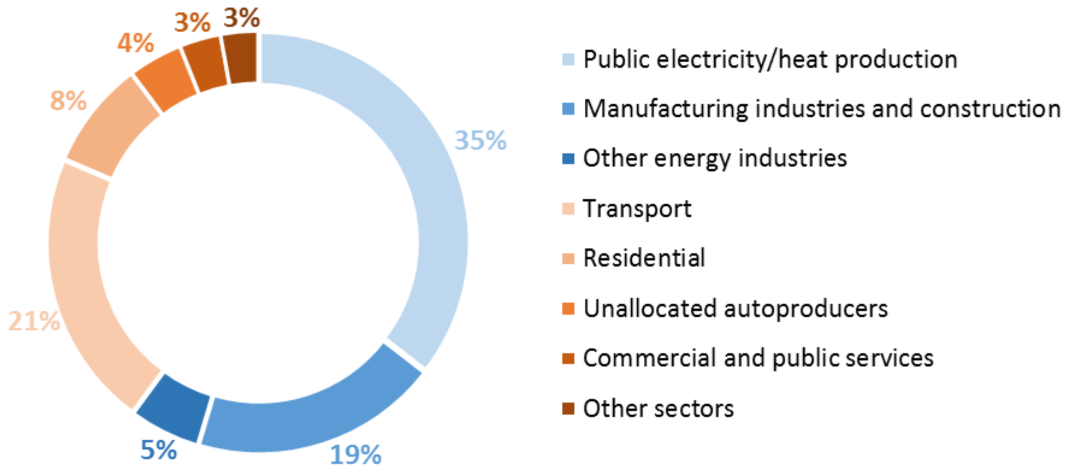

Figure S4. Contributions to global CO_2 emissions: blue contributions constitute large stationary point sources, while orange and brown contributions constitute mobile sources as well as small stationary point sources. [17]

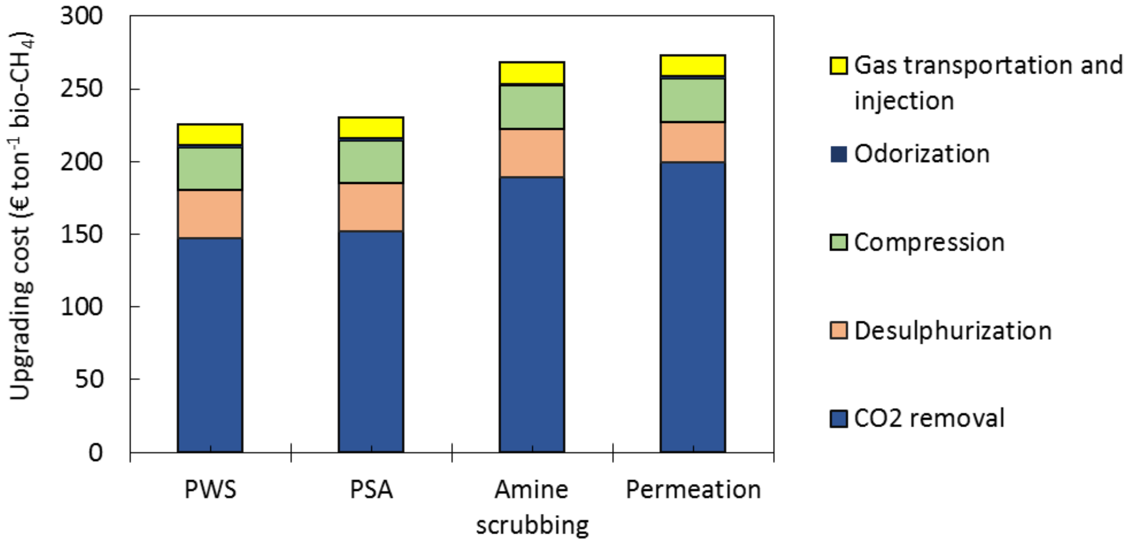

Figure S5. The impact of the upgrading technology on the overall biogas upgrading cost (PWS = pressurized water scrubbing; PSA = pressurized swing adsorption).

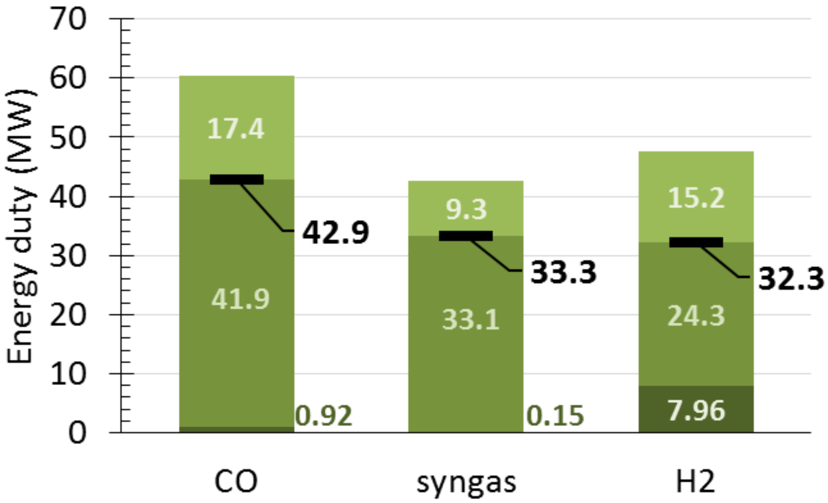

Figure S6. Energy duty for heat exchanger HX1 (top light green), HX2 (lower dark green) and reforming reactor (middle green) in the CO production (SDR), syngas production (DRM) and H_2 production (SESR) case. The solid black line represents the net heat input, the sum of the energy duty for heat exchanger HX2 and the reactor.

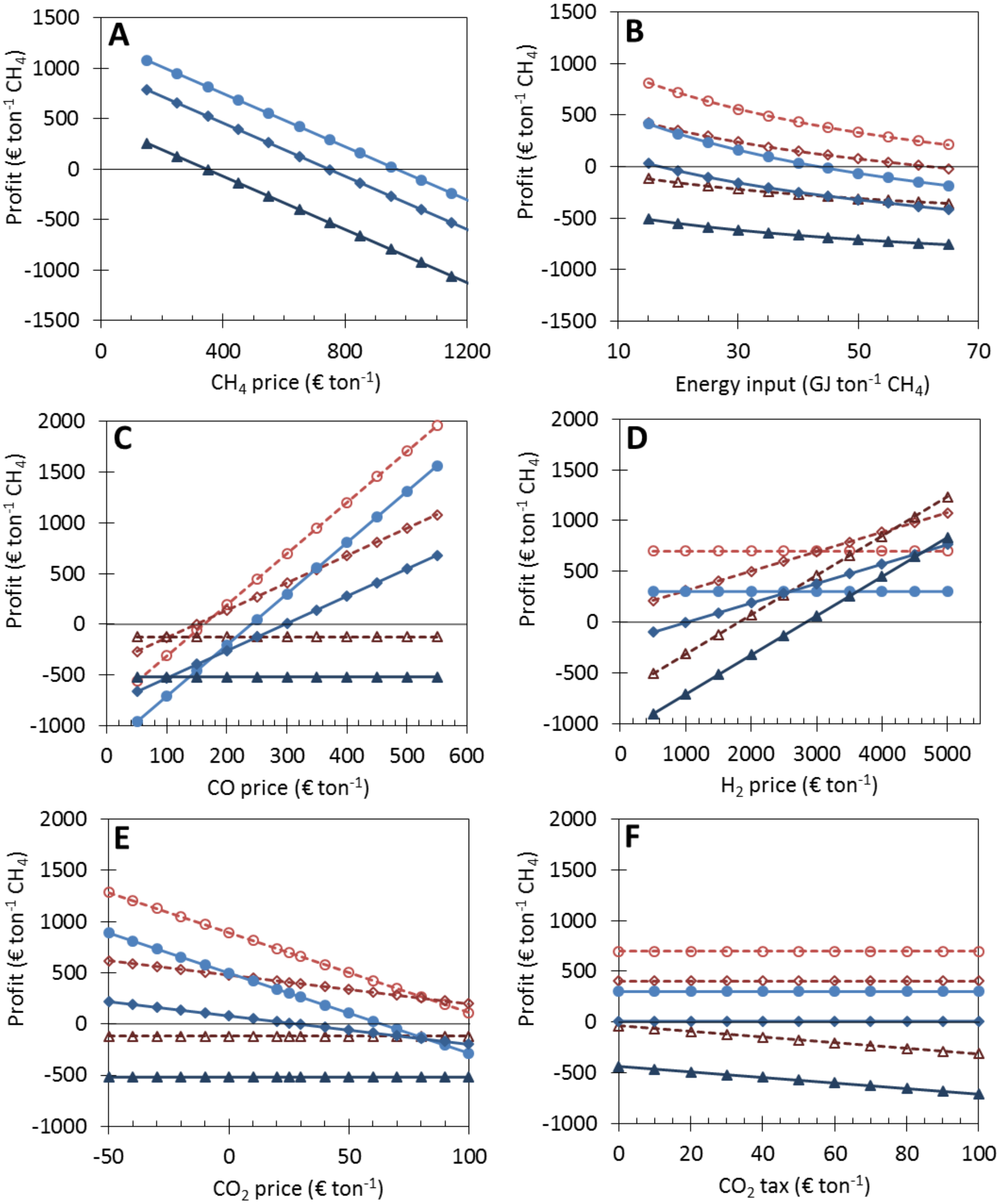

Figure S7. Economic analysis for the production of chemicals from biomethane or natural gas. Effect of CH_4 price (A), required energy input (B), CO price (C), H_2 price (D), CO_2 price (E) and CO_2 tax (F) on calculated profit. Circles – super-dry reforming process (SDR); Diamonds – dry reforming of methane (DRM); Triangles – sorption-enhanced steam reforming of methane (SESR). Full symbols and full lines (blue) represent margin of the case studies with biomethane as source of CH_4, while hollow symbols and dashed lines (red) represent the margin of the case studies with natural gas (NG) as source of CH_4 in an EU context.

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