Supplementary Material

Process Modeling and Evaluation of Plasma-assisted Ethylene Production from Methane

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Table of content

1. Shale gas dehydration unit

Water (coming from the extraction process) is contained in raw shale gas. Although most of the liquid water is removed in simple separators, water vapour is still present. Therefore, absorbers are used to remove the water vapour. In this case, a water vapour content of 3% is considered. The mass flow, composition, temperature and pressure conditions of all streams involved in the raw shale gas dehydration unit are presented in Table S1.

Table S1. Streams mass flow, composition, temperature and pressure conditions of the dehydration unit.

Material		**Raw shale gas**	**Lean TEG**	**Dehydrated shale gas**	**Rich TEG**	**Absorber top**	**Regenerated TEG**	**Stripper feed**	**Recycled TEG**	**Make-up TEG**
Mole flow										
CH_4	kmol/hr	10.0	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	kmol/hr	1.9	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0
CO_2	kmol/hr	0.4	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.4	0.0	0.0	0.4	0.4	0.0	0.4	0.0	0.0
$C_6H_{14}O_4$ (TEG)	kmol/hr	0.0	0.1	0.0	0.1	0.0	0.1	0.1	0.1	$1.8\ 10^{-6}$
Mass flow										
CH_4	kg/hr	161.0	0.0	160.9	0.1	0.1	0.0	0.1	0.0	0.0
C_2H_6	kg/hr	57.3	0.0	57.0	0.3	0.3	0.0	0.3	0.0	0.0
CO_2	kg/hr	16.8	0.0	16.7	0.0	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	6.9	0.5	0.5	6.9	6.4	0.5	6.9	0.5	0.0
$C_6H_{14}O_4$ (TEG)	kg/hr	0.0	12.0	0.0	12.0	0.0	12.0	12.0	12.0	$2.7\ 10^{-4}$
Mole Flows	kmol/hr	12.7	0.1	12.3	0.5	0.4	0.1	0.5	0.1	0.0
Mass Flows	kg/hr	241.9	12.5	235.1	19.3	6.8	12.5	19.3	12.5	$2.7\ 10^{-4}$
Volume Flow	cum/hr	61.4	0.02	62.1	0.02	11.4	0.01	0.06	0.01	$2.3\ 10^{-7}$
Temperature	°C	25	29.6	29.8	25.8	98.5	142.6	84.6	29	25
Pressure	bar	5	5	5	5	1	1	5	1	5

It is worth mentioning that the composition of the dehydrated gas delivered (T-101 top; Table S1) is slightly different than the one used in the simulation (Table S2 and Table S7). This difference is attributed to the fact that raw shale gas of real composition (CH_4:C_2H_6:CO_2:H_2O = 80:14:3:3 ref) is used in the simulation of the dehydration unit, resulting in dehydrated gas composition of CH_4:C_2H_6:CO_2:H_2O = 84:13.5:1:0.5 (v:v), while dehydrated shale gas with composition equal to the one fed in the experiments (CH_4:C_2H_6:CO_2 = 86:13:1) was used in the process simulation. This minor difference does not affect the validity of the simulation results.

2. One-step process

2.1 Streams mass flow, composition and conditions

The mass flow, composition, temperature and pressure conditions of all the streams involved in the one-step plasma-assisted ethylene production process are presented in Table S2.

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process.

Material		Dehydrated shale gas	Recycling	Plasma Reactor feed	Reactor product	Water for washing column
Mole flow						
CO_2	kmol/hr	0.4	0.0	0.4	0.3	0.0
CO	kmol/hr	0.0	0.0	0.0	0.1	0.0
H_2	kmol/hr	0.0	40.4	40.4	54.5	0.0
CH_4	kmol/hr	10.8	27.3	38.1	28.7	0.0
C_2H_6	kmol/hr	1.9	0.0	1.9	1.2	0.0
C_2H_4	kmol/hr	0.0	0.2	0.2	3.4	0.0
C_2H_2	kmol/hr	0.0	0.0	0.0	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0	4.4	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0	110.3
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	16.0	0.0	16.0	12.8	0.0
CO	kg/hr	0.0	0.0	0.0	2.0	0.0
H_2	kg/hr	0.0	81.4	81.3	109.8	0.0
CH_4	kg/hr	173.8	437.3	611.1	460.4	0.0
C_2H_6	kg/hr	56.8	0.2	57.0	35.4	0.0
C_2H_4	kg/hr	0.0	5.4	5.4	95.2	0.0
C_2H_2	kg/hr	0.0	0.0	0.0	1.6	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	52.5	0.0
H_2O	kg/hr	0.0	0.0	0.0	0.0	1987.9
O_2	kg/hr	0.0	0.0	0.0	1.2	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	13.1	67.8	80.9	92.6	110.3
Mass Flows	kg/hr	246.6	524.3	770.9	770.9	1987.9
Volume Flow	cum/hr	323.8	230.6	298.6	768.3	2
Temperature	°C	25	-68	-50	250	25
Pressure	bar	1	5	5	5	1

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process (continued).

Material		**Water for washing column**	**Washing tower bottom product**	**Washing tower top product**	**1-stage compression outlet stream**	**Cooling of 1-stage compression outlet stream**
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.3	0.3	0.3
CO	kmol/hr	0.0	0.0	0.1	0.1	0.1
H_2	kmol/hr	0.0	0.0	54.5	54.5	54.5
CH_4	kmol/hr	0.0	0.0	28.7	28.7	28.7
C_2H_6	kmol/hr	0.0	0.0	1.2	1.2	1.2
C_2H_4	kmol/hr	0.0	0.0	3.4	3.4	3.4
C_2H_2	kmol/hr	0.0	0.0	0.1	0.1	0.1
CARBON	kmol/hr	0.0	4.4	0.0	0.0	0.0
H_2O	kmol/hr	110.3	109.9	0.5	0.5	0.5
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	12.8	12.8	12.8
CO	kg/hr	0.0	0.0	2.0	2.0	2.0
H_2	kg/hr	0.0	0.0	109.8	109.8	109.8
CH_4	kg/hr	0.0	0.0	460.4	460.4	460.4
C_2H_6	kg/hr	0.0	0.0	35.4	35.4	35.4
C_2H_4	kg/hr	0.0	0.0	95.2	95.2	95.2
C_2H_2	kg/hr	0.0	0.0	1.6	1.6	1.6
CARBO-01	kg/hr	0.0	52.5	0.0	0.0	0.0
H_2O	kg/hr	1987.9	1979.4	8.6	8.6	8.6
O_2	kg/hr	0.0	0.0	1.2	1.2	1.2
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	110.3	114.2	88.7	88.7	88.7
Mass Flows	kg/hr	1987.9	2031.9	726.9	726.9	726.9
Volume Flow	cum/hr	2	2	439.4	240.5	192.4
Temperature	°C	25	25	25	117	40
Pressure	bar	1	5	5	12	12

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process (continued).

Material		**2-stage compression outlet stream**	**Cooling of 2-stage compression outlet stream**	**3-stage compression outlet stream**	**Cooling of 3-stage compression outlet stream**	**Caustic tower (22%wt) NaOH solution**
Mole flow						
CO_2	kmol/hr	0.3	0.3	0.3	0.3	0.0
CO	kmol/hr	0.1	0.1	0.1	0.1	0.0
H_2	kmol/hr	54.5	54.5	54.5	54.5	0.0
CH_4	kmol/hr	28.7	28.7	28.7	28.7	0.0
C_2H_6	kmol/hr	1.2	1.2	1.2	1.2	0.0
C_2H_4	kmol/hr	3.4	3.4	3.4	3.4	0.0
C_2H_2	kmol/hr	0.1	0.1	0.1	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.5	0.5	0.5	0.5	5.2
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.7
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	12.8	12.8	12.8	12.8	0.0
CO	kg/hr	2.0	2.0	2.0	2.0	0.0
H_2	kg/hr	109.8	109.8	109.8	109.8	0.0
CH_4	kg/hr	460.4	460.4	460.4	460.4	0.0
C_2H_6	kg/hr	35.4	35.4	35.4	35.4	0.0
C_2H_4	kg/hr	95.2	95.2	95.2	95.2	0.0
C_2H_2	kg/hr	1.6	1.6	1.6	1.6	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	8.6	8.6	8.6	8.6	92.7
O_2	kg/hr	1.2	1.2	1.2	1.2	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	26.1
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	88.7	88.7	88.7	88.7	5.8
Mass Flows	kg/hr	726.9	726.9	726.9	726.9	118.9
Volume Flow	cum/hr	124.8	103.7	85.3	64.3	0.09
Temperature	°C	114	50	84	0	25
Pressure	bar	23	23	31	31	31

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process (continued).

Material		**Caustic tower bottom product**	**Caustic tower top product**	**Cooling of caustic tower top product**	**Demethanizer top product**	**Demethanizer bottom product**
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2	kmol/hr	0.0	54.5	54.5	54.5	0.0
CH_4	kmol/hr	0.0	28.7	28.7	28.7	0.0
C_2H_6	kmol/hr	0.0	1.2	1.2	0.0	1.2
C_2H_4	kmol/hr	0.0	3.4	3.4	0.2	3.2
C_2H_2	kmol/hr	0.0	0.1	0.1	0.0	0.1
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	5.9	0.0	0.0	0.0	0.0
O_2	kmol/hr	0.04	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.3	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.1	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2	kg/hr	0.0	109.8	109.8	109.8	0.0
CH_4	kg/hr	0.0	460.4	460.4	460.3	0.0
C_2H_6	kg/hr	0.0	35.4	35.4	0.2	35.1
C_2H_4	kg/hr	0.0	95.2	95.2	5.7	89.5
C_2H_2	kg/hr	0.0	1.6	1.6	0.0	1.6
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	106.4	0.1	0.1	0.0	0.1
O_2	kg/hr	1.2	0.0	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	30.8	0.0	0.0	0.0	0.0
HCOONa	kg/hr	4.9	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	6.3	87.8	87.8	83.4	4.4
Mass Flows	kg/hr	143.3	702.5	702.5	576.1	126.4
Volume Flow	cum/hr	20.0	64.0	33.9	30.3	0.3
Temperature	°C	25	0	-115	-126	-7
Pressure	bar	31	31	31	31	31

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process (continued).

Material		PSA outlet stream-H2 removal	PSA outlet stream to be recycled	Heated PSA outlet stream prior to recycling	Recycling stream after the expansion	Purge stream
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2	kmol/hr	12.0	42.5	42.5	42.5	2.1
CH_4	kmol/hr	0.0	28.7	28.7	28.7	1.4
C_2H_6	kmol/hr	0.0	0.0	0.0	0.0	0.0
C_2H_4	kmol/hr	0.0	0.2	0.2	0.2	0.0
C_2H_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2	kg/hr	24.1	85.7	85.7	85.7	4.3
CH_4	kg/hr	0.0	460.3	460.3	460.3	23.0
C_2H_6	kg/hr	0.0	0.2	0.2	0.2	0.0
C_2H_4	kg/hr	0.0	5.7	5.7	5.7	0.3
C_2H_2	kg/hr	0.0	0.0	0.0	0.0	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	0.0	0.0	0.0	0.0	0.0
O_2	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	12.0	71.4	71.4	71.4	3.6
Mass Flows	kg/hr	24.1	551.9	551.9	551.9	27.6
Volume Flow	cum/hr	4.8	24.5	55.1	242.7	12.1
Temperature	°C	-126	-126	15	-68	-68
Pressure	bar	31	31	31	5	5

Table S2. Streams mass flow, composition, temperature and pressure conditions; one-step process (continued).

Material		Deethanizer feed	Deethanizer bottom product	Deethanizer top product	Purifier feed	Purifier bottom product	Purifier top product
Mole flow							
CO_2	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
H_2	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	kmol/hr	1.2	1.0	0.2	0.2	0.2	0.0
C_2H_4	kmol/hr	3.2	0.0	3.2	3.2	0.0	3.2
C_2H_2	kmol/hr	0.1	0.0	0.0	0.0	0.0	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0	0.0
Mass flow							
CO_2	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
H_2	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	kg/hr	35.1	28.7	6.5	6.5	6.5	0.0
C_2H_4	kg/hr	89.5	0.6	89.0	89.0	0.0	89.0
C_2H_2	kg/hr	1.6	0.4	1.2	1.2	1.2	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	0.1	0.1	0.0	0.0	0.0	0.0
O_2	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	4.4	1.0	3.4	3.4	0.3	3.2
Mass Flows	kg/hr	126.4	29.7	96.7	96.7	7.7	89.0
Volume Flow	cum/hr	1.5	0.1	3.5	57.7	0.0	43.3
Temperature	°C	-34	-19	-38	-67	-89	-104
Pressure	bar	15	15	15	1	1	1

2.2 *Heat integration*

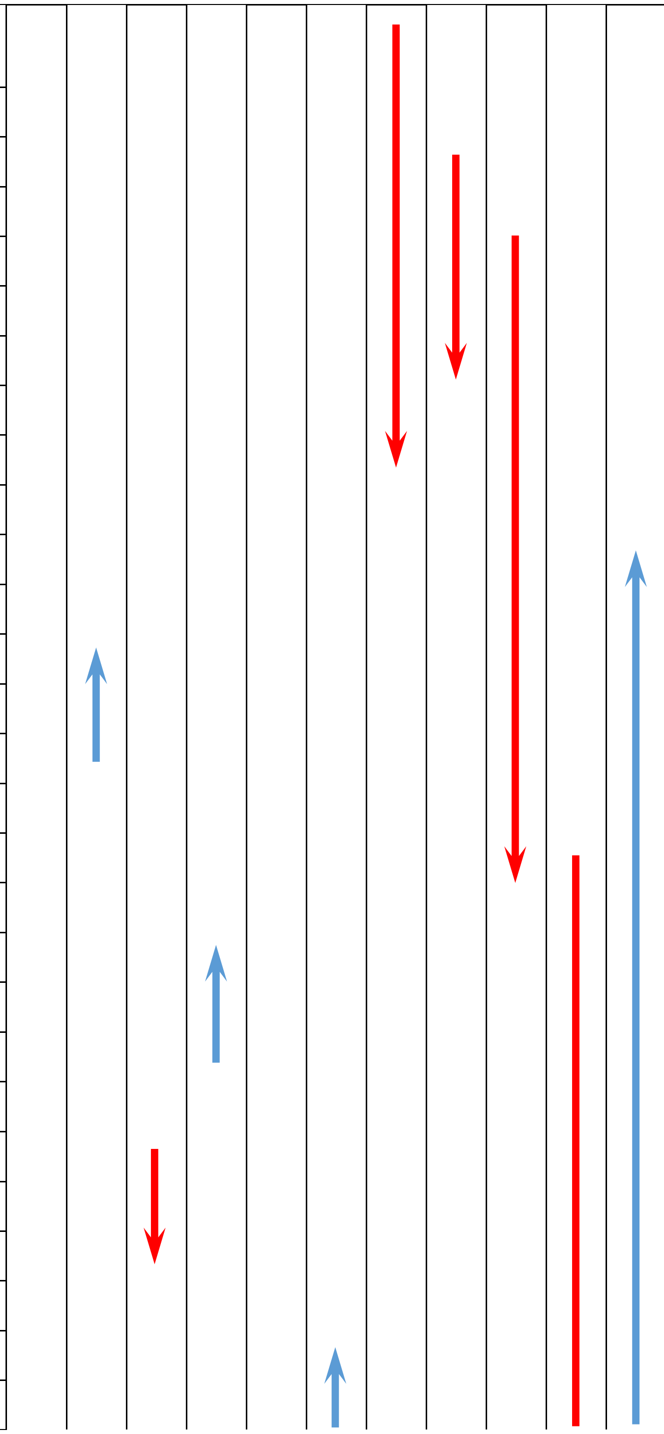
Seven hot and four cold process streams can be integrated to reduce the external hot and cold utility demand. The supplied and targeted temperatures, the temperature intervals and the energy content of these streams are presented in Table S3.

Table S3. Process streams available for heat integration in the one-step plasma-assisted ethylene production process.

Streams	No/Type	Actual temperature		Interval temperature		CP_M	ΔH	Total demand
		°C		°C		kW/°C	kW	kW
		T_{sup}	T_{targ}	T_{sup}	T_{targ}			
T-203/Condenser	1/Hot	-83	-126	-88	-131	3.7	-159	400 (Hot utility)
T-203/Reboiler	2/Cold	-8	-7	-3	-2	129.8	146	
T-204/Condenser	3/Hot	-38	-39	-43	-44	38.6	-58	
T-204/Reboiler	4/Cold	-19	-18	-14	-13	105.2	64	
T-205/Condenser	5/Hot	-104	-105	-109	-110	111.8	-95	
T-205/Reboiler	6/Cold	-92	-91	-87	-86	93	93	
HEX-201	7/Hot	117	40	112	35	0.8	-64	-596 (Cold Utility)
HEX-202	8/Hot	114	50	109	45	0.8	-54	
HEX-203	9/Hot	84	0	79	-5	0.9	-74	
HEX-204	10/Hot	0	-115	-5	-120	0.8	-92	
HEX-211	11/Cold	-126	15	-121	20	0.7	97	

The process streams heat balances and the problem table algorithm involved in the pinch analysis for the one-step process are presented in Table S4. Hot utility of 105.9 kW should be added to balance the heat cascade. The pinch temperature is at -87°C.

Table S4. Heat balances for the temperature intervals and problem table algorithm of the on-step process.



Temperature °C	Streams overlapping	ΔT °C	ΣCPm kW/°C	ΔH kW	S/D[1]	Unb C.[2] kW	B C.[3] kW
112							Add: 1105.9
		3	-0.8	-2.5	Surplus		
109						2.5	108.4
		30	-1.7	-49.7	Surplus		
79						52.2	158.1
		34	-2.5	-86.5	Surplus		
45						138.8	244.7
		10	-1.7	-17.1	Surplus		
35						155.9	261.8
		15	-0.9	-13.3	Surplus		
20						169.2	275.1
		22	-0.2	-4.4	Surplus		
-2						173.5	279.4
		1	129.6	129.6	Deficit		
-3						43.9	149.8
		2	-0.2	-0.4	Surplus		
-5						44.3	150.2
		8	-0.1	-0.9	Surplus		
-13						45.2	151.1
		1	105.1	105.1	Deficit		
-14						-59.8	46.1
		29	-0.1	-3.3	Surplus		
-43						-56.5	49.4
		1	-38.7	-38.7	Surplus		
-44						-17.8	88.1
		42	-0.1	-4.8	Surplus		
-86						-13.0	92.9
		1	92.9	92.9	Deficit		

-87																**-105.9**	**0.0**
												1	-0.1	-0.1	Surplus		
-88																-105.8	0.1
												21	-3.8	-80.6	Surplus		
-109																-25.2	80.7
												1	-115.6	-115.6	Surplus		
-110																-90.4	196.3
												10	-3.8	-38.4	Surplus		
-120																-128.8	234.7
												1	-3.0	-3.0	Surplus		
-121																-131.8	237.7
												10	-3.7	-37.2	Surplus		
-131																-169.1	275.0
	1	2	3	4	5	6	7	8	9	10	11						

[1]S/D = Surplus/Deficit

[2]Unb C. = Unbalanced cascade

[3]B C. = Balanced cascade

2.3 *Electric power and energy requirements*

Table S5. Electric power demand distribution over the different process steps involved in the on-step process.

Electricity demand	**kW**	**Source**
CH_4 compress/Cooling	400	Simulation
CH_4 expansion/Cooling	-109	Simulation
CH_4 feed	152	Simulation
Water feed	0.4	Simulation
Compression 1 stage	88	Simulation
Compression 2 stage	76	Simulation
Compression 3 stage	34	Simulation
Recycle expansion	-49	Simulation
Plasma reactor	1904	2020 kJ/mol ethylene [1]
Total	2498	kW
Specific energy demand	101,018	kJ/kg ethylene
	28	kWh/kg ethylene
Hot utility demand	181	kgH_2O/kg ethylene

2.4 *Profit margin*

Table S6. Profit margin of the one-step process as function of the electricity price.

Ethylene price USD/ton	Electricity price USD/MWh	Electricity cost USD/ton	Raw material cost USD/ton	Ethylene production cost USD/ton	Profit Margin USD/ton
1200	100	2806	546	3352	-2152
1200	50	1403	546	1949	-749
1200	25	702	546	1247	-47
1200	20	561	546	1107	93
1200	15	421	546	966	234
1200	10	281	546	826	374
1200	5	140	546	686	514

Ethylene production cost=Specific energy demand × electricity price + Specific gas demand × gas price
Specific gas demand=Volumetric shale gas feed/mass of ethylene produced
Profit margin=Ethylene price - ethylene production cost
Break-even electricity price=23 USD/MWh

3. Two-step process

3.1 Streams mass flow, composition, temperature and pressure conditions

The mass flow, composition, temperature and pressure conditions of all the streams involved in the two-step plasma-assisted ethylene production process are presented in Table S7.

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process.

Material		Dehydrated shale gas	Recycling	Plasma reactor feed	Reactor product	Water for washing column
Mole flow						
CO_2	kmol/hr	0.4	0.0	0.4	0.3	0.0
CO	kmol/hr	0.0	0.0	0.0	0.1	0.0
H_2	kmol/hr	0.0	40.4	40.4	50.4	0.0
CH_4	kmol/hr	9.8	28.3	38.1	29.8	0.0
C_2H_6	kmol/hr	1.9	0.0	1.9	1.3	0.0
C_2H_4	kmol/hr	0.0	0.1	0.1	4.2	0.0
C_2H_2	kmol/hr	0.0	0.0	0.0	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0	1.4	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0	551.7
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	16.0	0.0	16.0	12.8	0.0
CO	kg/hr	0.0	0.0	0.0	2.0	0.0
H_2	kg/hr	0.0	81.3	81.3	101.6	0.0
CH_4	kg/hr	157.3	453.8	611.1	477.7	0.0
C_2H_6	kg/hr	57.0	0.2	57.2	38.2	0.0
C_2H_4	kg/hr	0.0	3.2	3.2	117.5	0.0
C_2H_2	kg/hr	0.0	0.0	0.0	1.6	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	16.2	0.0
H_2O	kg/hr	0.0	0.0	0.0	0.0	9939.6
O_2	kg/hr	0.0	0.0	0.0	1.2	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	12.1	68.8	80.8	87.5	551.7
Mass Flows	kg/hr	230.3	538.6	768.9	768.9	9939.6
Volume Flow	cum/hr	279.7	948.2	1270.4	3388.9	10
Temperature	°C	25	-107	-84	200	25
Pressure	bar	1	1	1.1	1	1

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		**Water for washing column after the pump**	**Washing tower bottom product**	**Washing tower top product**	**1-stage compression outlet stream**	**Cooling of 1-stage compression outlet stream**
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.3	0.3	0.3
CO	kmol/hr	0.0	0.0	0.1	0.1	0.1
H_2	kmol/hr	0.0	0.0	50.4	50.4	50.4
CH_4	kmol/hr	0.0	0.0	29.8	29.8	29.8
C_2H_6	kmol/hr	0.0	0.0	1.3	1.3	1.3
C_2H_4	kmol/hr	0.0	0.0	4.2	4.2	4.2
C_2H_2	kmol/hr	0.0	0.0	0.1	0.1	0.1
CARBON	kmol/hr	0.0	1.4	0.0	0.0	0.0
H_2O	kmol/hr	551.7	549.4	2.3	2.3	2.3
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	12.8	12.8	12.8
CO	kg/hr	0.0	0.0	2.0	2.0	2.0
H_2	kg/hr	0.0	0.0	101.6	101.6	101.6
CH_4	kg/hr	0.0	0.0	477.7	477.7	477.7
C_2H_6	kg/hr	0.0	0.0	38.2	38.2	38.2
C_2H_4	kg/hr	0.0	0.0	117.5	117.5	117.5
C_2H_2	kg/hr	0.0	0.0	1.6	1.6	1.6
CARBO-01	kg/hr	0.0	16.2	0.0	0.0	0.0
H_2O	kg/hr	9939.6	9897.7	41.9	41.9	41.9
O_2	kg/hr	0.0	0.0	1.2	1.2	1.2
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	551.7	550.8	88.4	88.4	88.4
Mass Flows	kg/hr	9939.6	9913.9	794.5	794.5	794.5
Volume Flow	cum/hr	10.0	10.0	2192.6	1192.9	899.0
Temperature	°C	25	27	25	116	25
Pressure	bar	1	1	1	2.4	2.4

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		**1-stage flush drum bottom product**	**1-stage flush drum top product**	**2-stage compression outlet stream**	**Cooling of 2-stage compression outlet stream**	**2-stage flush drum bottom product**
Mole flow						
CO_2	kmol/hr	0.0	0.3	0.3	0.3	0.0
CO	kmol/hr	0.0	0.1	0.1	0.1	0.0
H_2	kmol/hr	0.0	50.4	50.4	50.4	0.0
CH_4	kmol/hr	0.0	29.8	29.8	29.8	0.0
C_2H_6	kmol/hr	0.0	1.3	1.3	1.3	0.0
C_2H_4	kmol/hr	0.0	4.2	4.2	4.2	0.0
C_2H_2	kmol/hr	0.0	0.1	0.1	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	1.4	1.0	1.0	1.0	0.5
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	12.8	12.8	12.8	0.0
CO	kg/hr	0.0	2.0	2.0	2.0	0.0
H_2	kg/hr	0.0	101.6	101.6	101.6	0.0
CH_4	kg/hr	0.0	477.7	477.7	477.7	0.0
C_2H_6	kg/hr	0.0	38.2	38.2	38.2	0.0
C_2H_4	kg/hr	0.0	117.5	117.5	117.5	0.0
C_2H_2	kg/hr	0.0	1.6	1.6	1.6	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	24.6	17.2	17.2	17.2	9.6
O_2	kg/hr	0.0	1.2	1.2	1.2	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	1.4	87.1	87.1	87.1	0.5
Mass Flows	kg/hr	24.6	769.9	769.9	769.9	9.6
Volume Flow	cum/hr	0.0	898.9	513.2	389.7	0.0
Temperature	°C	25	25	116	25	25
Pressure	bar	2.4	2.4	5.5	5.5	5.5

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		2-stage flush drum top product	3-stage compression outlet stream	Cooling of 3-stage compression outlet stream	3-stage flush drum bottom product	3-stage flush drum top product
Mole flow						
CO_2	kmol/hr	0.3	0.3	0.3	0.0	0.3
CO	kmol/hr	0.1	0.1	0.1	0.0	0.1
H_2	kmol/hr	50.4	50.4	50.4	0.0	50.4
CH_4	kmol/hr	29.8	29.8	29.8	0.0	29.8
C_2H_6	kmol/hr	1.3	1.3	1.3	0.0	1.3
C_2H_4	kmol/hr	4.2	4.2	4.2	0.0	4.2
C_2H_2	kmol/hr	0.1	0.1	0.1	0.0	0.1
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.4	0.4	0.4	0.2	0.2
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	12.8	12.8	12.8	0.0	12.8
CO	kg/hr	2.0	2.0	2.0	0.0	2.0
H_2	kg/hr	101.6	101.6	101.6	0.0	101.6
CH_4	kg/hr	477.7	477.7	477.7	0.0	477.7
C_2H_6	kg/hr	38.2	38.2	38.2	0.0	38.2
C_2H_4	kg/hr	117.5	117.5	117.5	0.0	117.5
C_2H_2	kg/hr	1.6	1.6	1.6	0.0	1.6
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	7.6	7.6	7.6	4.2	3.4
O_2	kg/hr	1.2	1.2	1.2	0.0	1.2
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	86.5	86.5	86.5	0.2	86.3
Mass Flows	kg/hr	760.3	760.3	760.3	4.2	756.1
Volume Flow	cum/hr	389.7	218.2	164.3	0.0	164.3
Temperature	°C	25	120	25	25	25
Pressure	bar	5.5	13	13	13	13

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		4-stage compression outlet stream	Cooling of 4-stage compression outlet stream	4-stage flush drum bottom product	4-stage flush drum top product	5-stage compression outlet stream
Mole flow						
CO_2	kmol/hr	0.3	0.3	0.0	0.3	0.3
CO	kmol/hr	0.1	0.1	0.0	0.1	0.1
H_2	kmol/hr	50.4	50.4	0.0	50.4	50.4
CH_4	kmol/hr	29.8	29.8	0.0	29.8	29.8
C_2H_6	kmol/hr	1.3	1.3	0.0	1.3	1.3
C_2H_4	kmol/hr	4.2	4.2	0.0	4.2	4.2
C_2H_2	kmol/hr	0.1	0.1	0.0	0.1	0.1
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.2	0.2	0.1	0.1	0.1
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	12.8	12.8	0.0	12.8	12.8
CO	kg/hr	2.0	2.0	0.0	2.0	2.0
H_2	kg/hr	101.6	101.6	0.0	101.6	101.6
CH_4	kg/hr	477.7	477.7	0.0	477.7	477.7
C_2H_6	kg/hr	38.2	38.2	0.0	38.2	38.2
C_2H_4	kg/hr	117.5	117.5	0.0	117.5	117.5
C_2H_2	kg/hr	1.6	1.6	0.0	1.6	1.6
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	3.4	3.4	1.7	1.6	1.6
O_2	kg/hr	1.2	1.2	0.0	1.2	1.2
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	86.3	86.3	0.1	86.2	86.2
Mass Flows	kg/hr	756.1	756.1	1.7	754.3	754.3
Volume Flow	cum/hr	94.0	71.0	0.0	71.0	69.5
Temperature	°C	117	25	25	25	28
Pressure	bar	30	30	30	30	31

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		**Caustic tower (22%wt) NaOH solution**	**Caustic tower bottom product**	**Caustic tower top product**	**Cooling of caustic tower top product**	**Demethanizer top product**
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2	kmol/hr	0.0	0.0	50.4	50.4	50.4
CH_4	kmol/hr	0.0	0.0	29.8	29.8	29.8
C_2H_6	kmol/hr	0.0	0.0	1.3	1.3	0.0
C_2H_4	kmol/hr	0.0	0.0	4.2	4.2	0.1
C_2H_2	kmol/hr	0.0	0.0	0.1	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	5.1	5.5	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.7	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.3	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.1	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2	kg/hr	0.0	0.0	101.6	101.6	101.6
CH_4	kg/hr	0.0	0.0	477.7	477.7	477.7
C_2H_6	kg/hr	0.0	0.0	38.2	38.2	0.2
C_2H_4	kg/hr	0.0	0.0	117.5	117.5	3.4
C_2H_2	kg/hr	0.0	0.0	1.6	1.6	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	92.7	99.6	0.0	0.0	0.0
O_2	kg/hr	0.0	1.2	0.0	0.0	0.0
NaOH	kg/hr	26.1	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	30.8	0.0	0.0	0.0
HCOONa	kg/hr	0.0	4.9	0.0	0.0	0.0
Mole Flows	kmol/hr	5.8	5.9	85.7	85.7	80.3
Mass Flows	kg/hr	118.8	136.5	736.7	736.7	583.0
Volume Flow	cum/hr	0.09	0.1	69.2	32.5	28.9
Temperature	°C	25	28	28.4	-115	-125
Pressure	bar	31	31	31	31	31

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		Demethanizer bottom product	PSA outlet stream-H2 removal	PSA outlet stream to be recycled	Heated PSA outlet stream prior to recycling	Recycling stream after the expansion
Mole flow						
CO_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2	kmol/hr	0.0	7.9	42.5	42.5	42.5
CH_4	kmol/hr	0.0	0.0	29.8	29.8	29.8
C_2H_6	kmol/hr	1.3	0.0	0.0	0.0	0.0
C_2H_4	kmol/hr	4.1	0.0	0.1	0.1	0.1
C_2H_2	kmol/hr	0.1	0.0	0.0	0.0	0.0
CARBON	kmol/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0	0.0
Mass flow						
CO_2	kg/hr	0.0	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2	kg/hr	0.0	16.0	85.6	85.6	85.6
CH_4	kg/hr	0.0	0.0	477.7	477.7	477.7
C_2H_6	kg/hr	38.0	0.0	0.2	0.2	0.2
C_2H_4	kg/hr	114.0	0.0	3.4	3.4	3.4
C_2H_2	kg/hr	1.6	0.0	0.0	0.0	0.0
CARBO-01	kg/hr	0.0	0.0	0.0	0.0	0.0
H_2O	kg/hr	0.0	0.0	0.0	0.0	0.0
O_2	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	5.4	7.9	72.4	72.4	72.4
Mass Flows	kg/hr	153.7	16.0	567.0	567.0	567.0
Volume Flow	cum/hr	0.4	3.2	24.9	57.9	998.1
Temperature	°C	-8	-125	-125	25	-107
Pressure	bar	31	31	31	31	1

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		Purge stream	Deethanizer feed	Deethanizer bottom product	Deethanizer top product
Mole flow					
CO_2	kmol/hr	0.0	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0	0.0
H_2	kmol/hr	2.1	0.0	0.0	0.0
CH_4	kmol/hr	1.5	0.0	0.0	0.0
C_2H_6	kmol/hr	0.0	1.3	0.9	0.3
C_2H_4	kmol/hr	0.0	4.1	0.0	4.1
C_2H_2	kmol/hr	0.0	0.1	0.0	0.1
CARBON	kmol/hr	0.0	0.0	0.0	0.0
H_2O	kmol/hr	0.0	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0	0.0
Mass flow					
CO_2	kg/hr	0.0	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0	0.0
H_2	kg/hr	4.3	0.0	0.0	0.0
CH_4	kg/hr	23.9	0.0	0.0	0.0
C_2H_6	kg/hr	0.0	38.0	27.7	10.3
C_2H_4	kg/hr	0.2	114.0	0.0	114.0
C_2H_2	kg/hr	0.0	1.6	0.2	1.4
CARBO-01	kg/hr	0.0	0.0	0.0	0.0
H_2O	kg/hr	0.0	0.0	0.0	0.0
O_2	kg/hr	0.0	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0	0.0
Mole Flows	kmol/hr	3.6	5.4	0.9	4.5
Mass Flows	kg/hr	28.3	153.7	28.0	125.7
Volume Flow	cum/hr	50	1.8	0.1	4.5
Temperature	°C	-107	-35	-18	-37
Pressure	bar	1	15	15	15

Table S7. Streams mass flow, composition, temperature and pressure conditions; two-step process (continued).

Material		**Purifier feed**	**Purifier bottom product**	**Purifier top product**
Mole flow				
CO_2	kmol/hr	0.0	0.0	0.0
CO	kmol/hr	0.0	0.0	0.0
H_2	kmol/hr	0.0	0.0	0.0
CH_4	kmol/hr	0.0	0.0	0.0
C_2H_6	kmol/hr	0.3	0.3	0.0
C_2H_4	kmol/hr	4.1	0.2	3.9
C_2H_2	kmol/hr	0.1	0.1	0.0
CARBON	kmol/hr	0.0	0.0	0.0
H_2O	kmol/hr	0.0	0.0	0.0
O_2	kmol/hr	0.0	0.0	0.0
NaOH	kmol/hr	0.0	0.0	0.0
NaOH(aq)/22%wt	kmol/hr	0.0	0.0	0.0
Na_2CO_3	kmol/hr	0.0	0.0	0.0
HCOONa	kmol/hr	0.0	0.0	0.0
Mass flow				
CO_2	kg/hr	0.0	0.0	0.0
CO	kg/hr	0.0	0.0	0.0
H_2	kg/hr	0.0	0.0	0.0
CH_4	kg/hr	0.0	0.0	0.0
C_2H_6	kg/hr	10.3	10.3	0.0
C_2H_4	kg/hr	114.0	4.6	109.4
C_2H_2	kg/hr	1.4	1.4	0.1
CARBO-01	kg/hr	0.0	0.0	0.0
H_2O	kg/hr	0.0	0.0	0.0
O_2	kg/hr	0.0	0.0	0.0
NaOH	kg/hr	0.0	0.0	0.0
NaOH(aq)/22%wt	kg/hr	0.0	0.0	0.0
Na_2CO_3	kg/hr	0.0	0.0	0.0
HCOONa	kg/hr	0.0	0.0	0.0
Mole Flows	kmol/hr	4.5	0.6	3.9
Mass Flows	kg/hr	125.7	16.2	109.5
Volume Flow	cum/hr	75.1	0.0	53.2
Temperature	°C	-67	-96	-104
Pressure	bar	1	1	1

3.2 Heat integration

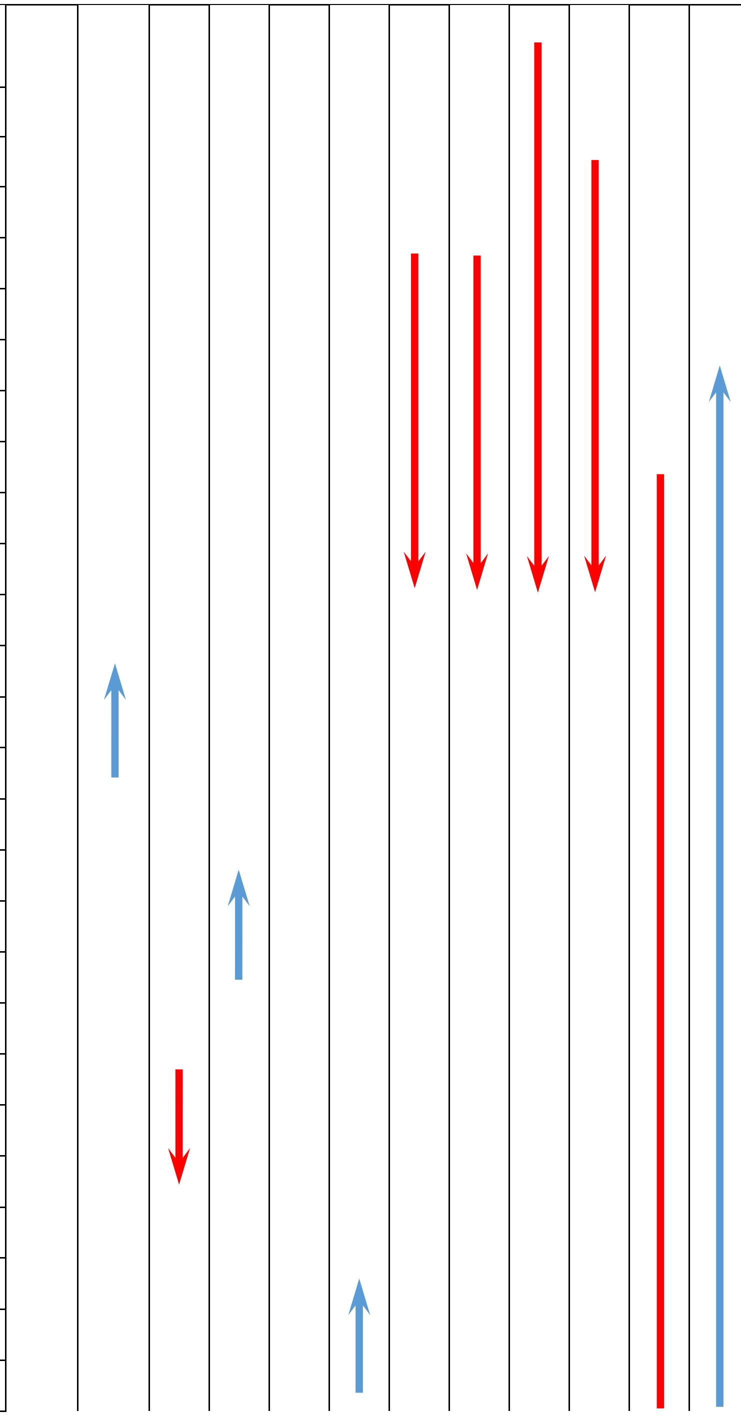
Eight hot and four cold process streams can be integrated to reduce the external hot and cold utility demand. The supplied and targeted temperatures, the temperature intervals and the energy content of these streams are presented in Table S8.

Table S8. Process streams available for heat integration in the two-step plasma-assisted ethylene production process.

Streams	No/Type	Actual temperature		Interval temperature		CP_M	ΔH	Total demand
		°C		°C		kW/°C	kW	kW
		T_{sup}	T_{targ}	T_{sup}	T_{targ}			
T-203/Condenser	1/Hot	-92	-125	-97	-130	5.1	-173	448 (Hot utility)
T-203/Reboiler	2/Cold	-8	-7	-3	-2	112.0	160	
T-204/Condenser	3/Hot	-37	-38	-42	-43	44.8	-63	
T-204/ Reboiler	4/Cold	-18	-17	-13	-12	56.2	71	
T-205/Condenser	5/Hot	-104	-105	-109	-110	145.0	-116	
T-205/Reboiler	6/Cold	-97	-96	-92	-91	225.2	113	
HEX-201	7/Hot	116	25	111	20	1.0	-92	-797 (Cold Utility)
HEX-202	8/Hot	116	25	111	20	0.9	-81	
HEX-203	9/Hot	120	25	115	20	0.8	-80	
HEX-204	10/Hot	117	25	112	20	0.8	-77	
HEX-205	11/Hot	28	-115	23	-120	0.8	-114	
HEX-212	12/Cold	-125	25	-120	30	0.7	104	

The process streams heat balances and the problem table algorithm involved in the pinch analysis for the two-process are presented in Table S9. Hot utility of 12.4 kW should be added to balance the heat cascade. The pinch temperature is at -92°C.

Table S9. Heat balances for the temperature intervals and problem table algorithm of the two-step process.

Temperature °C	Streams overlapping	ΔT °C	ΣCPm kW/°C	ΔH kW	S/D[1]	Unb C.[2] kW	B C.[3] kW
115							Add: 12.4
		3	-0.8	-2.5	Surplus		
112						2.5	15.0
		1	-1.7	-1.7	Surplus		
111						4.2	16.6
		81	-3.6	-289.6	Surplus		
30						293.8	306.3
		7	-2.9	-20.2	Surplus		
23						314.0	326.4
		3	-3.7	-11.0	Surplus		
20						325.0	337.4
		22	-0.1	-2.2	Surplus		
-2						327.2	339.6
		1	111.9	111.9	Deficit		
-3						215.3	227.7
		9	-0.1	-0.9	Surplus		
-12						216.2	228.6
		1	56.1	56.1	Deficit		
-13						160.1	172.5
		29	-0.1	-2.9	Surplus		
-42						163.0	175.4
		1	-44.9	-44.9	Surplus		
-43						207.9	220.3
		48	-0.1	-4.8	Surplus		
-91						212.7	225.1
		1	225.1	225.1	Deficit		
-92						-12.4	0.0

													5	-0.1	-0.5	Surplus		
-97																	-11.9	0.5
													12	-5.2	-62.9	Surplus		
-109																	51.0	63.4
													1	-150.3	-150.3	Surplus		
-110																	201.3	213.7
													10	-5.2	-52.5	Surplus		
-120																	253.7	266.2
													10	-5.1	-51.5	Surplus		
-130																	305.2	317.6
	1	2	3	4	5	6	7	8	9	10	11	12						

[1]S/D = Surplus/Deficit

[2]Unb C. = Unbalanced cascade

[3]B C. = Balanced cascade

3.3 Electric power and energy requirements

Table S10. Electric power demand distribution over the different process steps involved in the two-step process.

Electricity demand	**kW**	**Source**
CH_4 compress/Cooling	467	Simulation
CH_4 expansion/Cooling	-127	Simulation
CH_4 feed	7	Simulation
Water feed	2	Simulation
Compression 1 stage	88	Simulation
Compression 2 stage	92	Simulation
Compression 3 stage	96	Simulation
Compression 4 stage	87	Simulation
Compression 5 stage	3	Simulation
Recycle expansion	-79	Simulation
Plasma reactor	1910	1642 kJ/mol ethylene [2]
Total	2545	kW
Specific energy demand	836,69	kJ/kg ethylene
	23	kWh/kg ethylene
Hot utility demand	-	kgH_2O/kg ethylene

3.4 Profit margin

Table S11. Profit margin of the two-step process as function of the electricity price.

Ethylene price USD/ton	Electricity price USD/MWh	Electricity cost USD/ton	Raw material cost USD/ton	Ethylene production cost USD/ton	Profit Margin USD/kg
1200	100	2324	383	2707	-1507
1200	50	1162	383	1545	-345
1200	25	581	383	964	236
1200	20	465	383	848	352
1200	15	349	383	732	468
1200	10	232	383	616	584
1200	5	116	383	499	701

Ethylene production cost=Specific energy demand × electricity price + Specific gas demand × gas price
Specific gas demand=(Volumetric shale gas feed/mass of ethylene produced)
Profit margin=Ethylene price - ethylene production cost
Break-even electricity price=35 USD/MWh

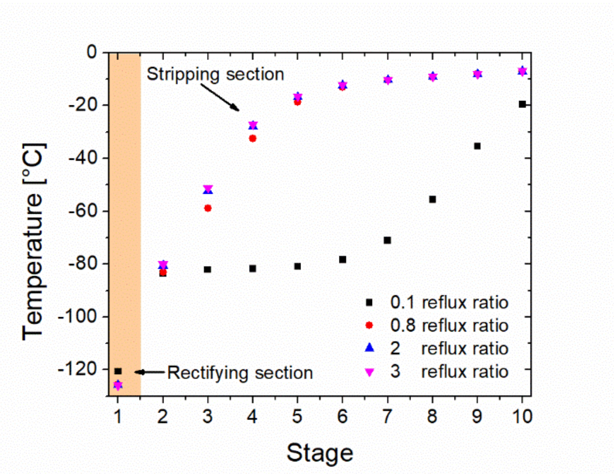


Figure S1. One-step demethanizer temperature profiles at reflux ratios of 0.1, 0.8, 2 and 3. The column temperature profile remains practically constant for reflux ratios >0.8.

References

1. Scapinello, M.; Delikonstantis, E.; Stefanidis, G.D. Direct methane-to-ethylene conversion in a nanosecond pulsed discharge. *Fuel* **2018**, *222*, 705–710.
2. Delikonstantis, E.; Scapinello, M.; Stefanidis, G.D. Low energy cost conversion of methane to ethylene in a hybrid plasma-catalytic reactor system. *Fuel Process. Technol.* **2018**, *176*, 33–42.