Conceptual design of a process for hydrogen production from waste biomass and its storage in form of liquid ammonia

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Abstract

In this work we present the simulation of a plant for the exploitation of renewable hydrogen (e.g. from biomass gasification) with production of renewable ammonia as hydrogen vector and energy storage medium. The simulation and sizing of all unit operations were performed with Aspen Plus® as software. Vegetable biomass is used as raw material for hydrogen production, more specifically pine sawdust.

The hydrogen production process is based on a gasification reactor at high temperature (700-800 °C), in the presence of a gasifying agent such as air or steam. At the outlet, a solid residue (ash) and a certain amount of gas, which mainly contains H_2, CH_4, CO and some impurities (e.g. sulphur or chlorine compounds) are obtained. Subsequently this gas stream is purified and treated in a series of reactors in order to maximize the hydrogen yield. In fact, after the removal of the sulphur compounds through an absorption column with MEA (to avoid poisoning of the catalytic processes), 3 reactors are arranged in series: Methane Steam Reforming (MSR), High temperature Water-Gas Shift (HT-WGS), Low temperature Water-Gas Shift (LT-WGS).

In the first MSR reactor, the methane present reacts at 1000 °C in presence of steam and a nickel-based catalyst, in order to obtain mainly H_2, CO and CO_2. Subsequently two steps of WGS are present to convert most of the CO into H_2 and CO_2. Also these reactions are carried out in the presence of a catalyst and with an excess of water.

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All the oxygenated compounds must be carefully eliminated: the remaining traces of CO are methanated while CO_2 is removed by a basic scrubbing with MEA (35 wt%) inside an absorption column. The Haber-Bosch synthesis of ammonia was carried out at 200 bar and in a temperature range between 300 and 400 °C, using two catalysts: Fe (wustite) and Ru/C. In conclusion, from an hourly flow rate of 1000 kg of dry biomass and 600 kg of nitrogen, 550 kg of NH_3 at 98.8 wt% were obtained, demonstrating the proof of concept of this newly designed process for the production of hydrogen from renewable waste biomass and its transformation into a liquid hydrogen vector to be easily transported and stored.

1 - Introduction

Many options have been proposed to store energy form intermittent energy sources. Chemical storage presents a unique feature: flexibility. Ammonia has been recently presented as a zero-carbon molecule that can provide the required energy storage medium for renewable sources[1,2]. It can be stored under mild conditions (i.e. refrigerated at −33 °C at atmospheric pressure or at 0.8−1.0 MPa at atmospheric temperature), thus making it a versatile, easy to store hydrogen vector. Moreover, liquid ammonia has a greater volumetric hydrogen density than liquid hydrogen itself (i.e. liquid hydrogen at 20 K stores approximately 70 kg of H_2/m^3, while liquid ammonia at 300 K and 1.0 MPa stores 106 kg of H_2/m^3), so that the immediate implementation of an "ammonia economy" can better support the transition to the futuristic "hydrogen economy".

Hydrogen is the most abundant element on earth, but it can be found rarely in its pure form. Practically, this fact means that in order to produce hydrogen, it needs to be extracted from other sources. Of course, this extraction process needs energy, but hydrogen can be produced or extracted using virtually any primary source of energy, be it fossil or renewable. Hydrogen can be produced using diverse resources including fossil fuels, such as natural gas and coal, biomass, non-food crops, nuclear energy and renewable energy sources, such as wind, solar, geothermal and hydroelectric power to split water. This diversity of potential supply sources is the most important reason why hydrogen is such a promising energy carrier.

Biomass gasification is a mature technology pathway that uses a controlled process involving heat, steam and oxygen to convert biomass to hydrogen and other products, without combustion. Because growing biomass removes carbon dioxide from the
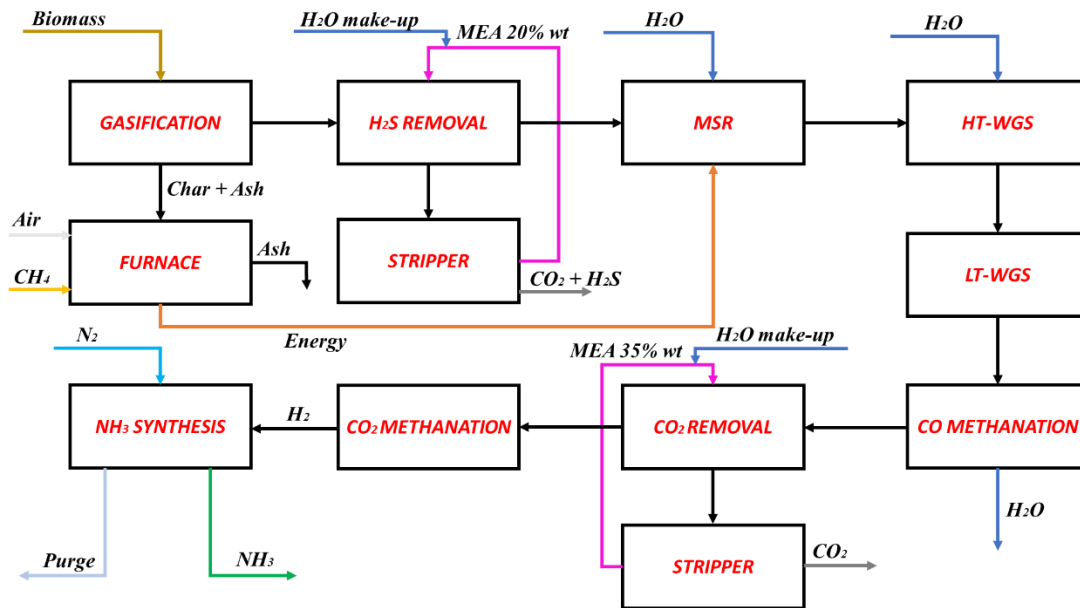
atmosphere, the net carbon emissions of this method is low, especially if coupled with carbon capture, utilization or storage in the long term. Biomass is a renewable organic resource, includes agriculture crop residues (such as corn stover or wheat straw), forest residues, special crops grown specifically for energy use (such as switchgrass or willow trees), organic municipal solid waste and animal wastes. This renewable resource can be used to produce hydrogen, along with other by-products, by gasification [3–6].

Literature reports cases in which the biomass and char gasification have been deeply studied in different operating conditions. In this work only a biomass gasification is simulated but, differently from other articles, it is coupled with a complete purification section sized with a series of kinetic equations. In fact, as Nikoo et al. [7] often the biomass selected was assumed without impurities or the CO_2 scrubbing is simulated with equilibrium reactions [5]. Another important issue regards the operating pressure: a proper simulation of hydrogen production in industrial conditions at high pressure (e.g. 30 bar) is actually missing.

On the other hand, the ammonia synthesis is a fundamental process and it has been continuously studied in all its aspects: peculiarities of the reaction mechanism, in fact, makes different catalytic formulations have an appreciable impact on large size reactors, that benefit of any possible decrease of the operating pressure and temperature [3,8–10]. From a simulation point of view, in literature some simulated plants with hydrogen production from renewables coupled with ammonia synthesis are present [3]. The main problem, as mentioned before, is the partial sizing of the plant (e.g. many important steps such as purification of the synthesis gas) are modelled as equilibrium steps and often also the reactors are sized as stoichiometric or Gibbs reactors [11].

In this work we have simulated hydrogen production by gasification of pine sawdust biomass at 800 °C. The gasification step was coupled with purification columns and different reactors to improve the hydrogen yield and purity, as required by ammonia synthesis. Consequently, this product is mixed with nitrogen and used to produce ammonia in the Haber-Bosch process at 200 bar. A block diagram of the process is represented in Figure 1.

Fig. 1: Block diagram of the integrated process for biomass gasification and ammonia synthesis.

Biomass H₂O make-up MEA 20% wt H₂O H₂O

GASIFICATION H₂S REMOVAL MSR HT-WGS

Char + Ash

Air FURNACE Ash STRIPPER CO₂ + H₂S LT-WGS

CH₄

N₂ Energy H₂O make-up MEA 35% wt

NH₃ SYNTHESIS H₂ CO₂ METHANATION CO₂ REMOVAL CO METHANATION

Purge NH₃ STRIPPER CO₂ H₂O

2 – Models and methods

All the simulations have been carried out in Aspen Plus® (AspenTech Inc.) as process simulator, added with home developed Matlab codes and custom models.

A first point is the definition of the list of components, since we needed to specify the biomass and ash as non-conventional components from a thermodynamic and properties point of view. The system also includes ionic species (e.g. carbonates, sulphides and MonoEthanolAmine, MEA), used for the basic scrubbing of sulphides and CO_2. Therefore the selection of the thermodynamic packages should be carefully done and 3 different flowsheets sections have been defined to this aim: 1) Biomass treatment and syngas production; 2) Syngas purification; 3) NH_3 synthesis.

In the first section the thermodynamic model used is RK-Aspen. The model has been chosen according to [4], but to represent this section, all the models developed for apolar mixtures can be used. In fact, in all these blocks a gas mixture is present, composed principally of N_2, H_2, CO_2, CO, CH_4 and H_2O so it can be easily represented by several standard models.

The second section uses the *"ENRTL"* model and is used to represent the two purification sections present in the flowsheet, where ionic species are present. The model selected for this part must consider the presence of electrolytes and the ENRTL-RK model has been selected with the addition of the Henry constant. A series of Henry's constant for the components N_2, H_2, CO_2, CO, CH_4, O_2 have been created. This step is fundamental in order to represent an absorption column or a stripper column in fact, with these constants the

software can calculate the variation of concentration of a component in the double film (gas-liquid) section. The parameters to set the Henry constants for each components are collected in Table 1 [12].

Table 1: Parameters for the calculation of Henry's constants.

Components i j	A_{ij}	B_{ij}	C_{ij}	D_{ij}	T_{low}	T_{up}
H_2-H_2O	191.6	-6993.51	-26.312	0.0150431	274	339
O_2-H_2O	155.9	-7775.06	-18.397	-0.009444	274	348
CO_2-H_2O	91.34	-5875.96	-8.5982	-0.012493	293	1000
CO-H_2O	183.3	-8296.75	-23.337	0	273	353
CH_4-H_2O	195.3	-9111.67	-25.038	0.0001434	273	353
N_2-H_2O	176.5	-8432.77	-21.558	-0.008436	273	346
H_2S-H_2O	358.1	-13236.8	-55.055	0.059565	273	423
CO_2-MEA	20.31	-896.5	0	0	0	2000

The last part of the flowsheet regarding the ammonia synthesis loop, defined *"NH3-SYN"*, RKS-BM model has been selected, according to [13].

2.1 - Kinetics

The kinetics of the reactions have been set using the Langmuir Hinshelwood Hougen Watson (LHHW) or the power law formulations [14]. One reaction is Methane steam reforming (MSR) that converts methane is converted in a mixture of H_2 and CO and is carried out at ca. 1000 °C, in presence of steam and a nickel-based catalyst [14–16]. In literature there are a lot of different kinetic models, among which we selected an equation validated in our selected conditions [14], which sets a combination of 3 reversible reactions:

$CH_4 + H_2O \leftrightarrows CO + 3H_2$ *ΔH= +206.1 kJ/mol*   (R1)

$CO + H_2O \leftrightarrows CO_2 + H_2$ *ΔH= -40.6 kJ/mol*   (R2)

$CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$ *ΔH= +164 kJ/mol*   (R3)

The kinetic equations of each reactions are presented in LHHW form[14] (Table 2):

$$r_1 = \frac{\frac{k_1}{p_{H_2}^{2,5}}\left(p_{CH_4}\,p_{H_2O} - \frac{p_{H_2}^3\,p_{CO}}{K_{e,1}}\right)}{\left(1 + K_{CO}\,p_{CO} + K_{H_2}\,p_{H_2} + K_{CH_4}\,p_{CH_4} + K_{H_2O}\,{p_{H_2O}}/{p_{H_2}}\right)^2} \qquad (E1)$$

$$r_2 = \frac{\frac{k_2}{p_{H_2}}\left(p_{CO}\,p_{H_2O} - \frac{p_{H_2}\,p_{CO_2}}{K_{e,2}}\right)}{\left(1 + K_{CO}\,p_{CO} + K_{H_2}\,p_{H_2} + K_{CH_4}\,p_{CH_4} + K_{H_2O}\,{p_{H_2O}}/{p_{H_2}}\right)^2} \qquad (E2)$$

$$r_3 = \frac{\frac{k_3}{p_{H_2}^{3,5}}\left(p_{CH_4}\,p_{H_2O}^2 - \frac{p_{H_2}^4\,p_{CO_2}}{K_{e,3}}\right)}{\left(1 + K_{CO}\,p_{CO} + K_{H_2}\,p_{H_2} + K_{CH_4}\,p_{CH_4} + K_{H_2O}\,{p_{H_2O}}/{p_{H_2}}\right)^2} \qquad (E3)$$

where:

r = Rate of reaction (kmol / kg · h)

k_i = Kinetic factor

p_j = Partial pressure (bar)

K_j = Adsorption constants

$K_{e,\,i}$ = Equilibrium constants

j = Component index

i = Reaction number

Table 2: Kinetic parameters for the Methane Steam Reforming reaction.

	Pre-exp (kmol/kg*h*bar)	Ea (kJ/mol)	A	B
k_1	4.2248E+15	240.1		
k_2	1.955E+06	67.13		
k_3	1.02E+15	243.9		
$K_{e.1}$		223.075	30.114	-26830
$K_{e.2}$		-36583.36	-4.036	4400
$K_{e.3}$		186491.99	26.078	-22430
K_{CO}	8.23E-05	70.65	-9.41	-8.497
K_{H2}	6.12E-09	82.9	-18.9	-9.971
K_{CH4}	6.65E-04	38.28	-7.31	-4.604
K_{H2O}	1.77E+05	-88.68	12.08	10.666

Water-gas shift reaction

The water-gas shift reaction is an exothermic reaction used to treat a gas rich in CO with water in order to obtain H_2 and CO_2. It is a catalytic reaction and is conducted in a range of temperature between 400 and 180 °C [17].

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \Delta H= \text{-40.6 kJ/mol} \quad\quad\quad\quad\quad\quad \text{(R4)}$$
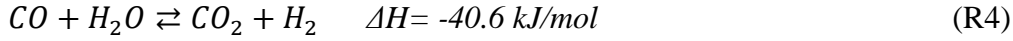
The water-gas shift is usually conducted in two steps with two different catalysts and temperatures[18]: high temperature (HT-WGS) and low temperature water-gas shift (LT-WGS). The former is carried out at 310 °C – 450 °C with the use of a Fe-Cr oxide-based catalyst, whereas the second in a range of between 180 °C – 250 °C with a mixture of ZnO, CuO and Cr_2O_3/Al_2O_3 at varying composition depending on the manufacturer [17,19].
The kinetic equation for HT-WGS is given in [20] il Power rate law formulation:

$$-r_{CO} = (\varphi \cdot k_0)\, e^{\left(-E_a/RT\right)}\, p_{CO}^n\, p_{H_2O}^m\, p_{CO_2}^p\, p_{H_2}^q \left(1 - \frac{p_{CO_2}\, p_{H_2}}{p_{CO}\, p_{H_2O}\, K_{eq}}\right) \quad\quad \text{(E4)}$$

where:

r = Rate of reaction (mol / g · s)

k_0 = Kinetic factor

φ = Pressure factor (0.6715)

Ea = Activation energy (kJ / mol)

R = Universal gas law constant (8.3144 J / mol · K)

T = Temperature (K)

p_i = Partial pressure (kPa)

K_{eq} = Equilibrium constants

i = Component index

Differently from the MSR, in this case we have to adjust the kinetic factor with a parameter (φ) that changes according to the operative pressure; the calculation of this factor is reported in [20].

$$\varphi = P^{\,0.5-P/250} \quad\quad for\ P < 30\ atm \quad\quad\quad\quad\quad\quad\quad\quad \text{(E5)}$$

$$\varphi = P^{\,0.5-P/500} \quad\quad for\ 30 \leq P \leq 55\ atm \quad\quad\quad\quad\quad\quad \text{(E6)}$$

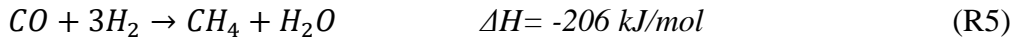In this way we can easily represent this reaction in a wide range of pressure and the kinetic parameters used are listed in Table 3.

Table 3: Kinetic parameters for the HT-WGS reaction.

	Pre-exp (mol/g*s*Pa)	Ea (kJ/mol)	A	B
$k_0 \cdot \varphi$	3.1043	88000		
K_{eq}		38061.66	-4.33	4577.8
	Exponent			
n	0.9			
m	0.31			
p	-0.156			
q	-0.05			

LT-WGS

The kinetic equation used is described in [19] with a LHHW expression.

$$r = (\varphi \cdot k) \; p_{CO} \, p_{H_2O} \left[\frac{1 - \frac{p_{CO_2} \, p_{H_2}}{p_{CO} \, p_{H_2O} \, K_{eq}}}{\left(1 + K_{CO} \, p_{CO} + K_{H_2O} \, p_{H_2O} + K_{CO_2} \, p_{CO_2} + K_{H_2} \, p_{H_2} \right)^2} \right] \quad \text{(E7)}$$

where:

r = Rate of reaction (mol/g · s)

k = Kinetic factor

φ = Pressure factor (4.33)

p_j = Partial pressure (Pa)

K_j = Adsorption constants

K_{eq} = Equilibrium constant

j = Component index

$\varphi = 0.86 + 0.14 \, P \qquad for \; P \leq 24.8 \; atm$ (E8) [17]

$\varphi = 4.33 \qquad\qquad\quad for \; P > 24.8 \; atm$ (E9) [17]

The kinetic parameters used are listed in Table 4.

Table 4: Kinetic parameters used for the LT-WGS reaction.

	Pre-exp (mol/g*s*Pa^2)	Ea (kJ/mol)	A	B
$k_0 \cdot \varphi$	0.066393	3.777		
K_{eq}		38061.66	-4.33	4577.8
K_{CO}	2.2	-843.91	0.788	101.5
K_{H2O}	0.4	-1316.17	-0.916	158.3
K_{CO2}	0.0047	22764	-5.36	-2737.9
K_{H2}	0.05	13270.61	-2.996	-1596.1

CO_x methanation

Carbon monoxide and dioxide methanation are useful reactions in order to remove traces of CO and CO_2 in a hydrogen rich stream[21–23]. In fact, part of the hydrogen can be used for these reactions in order to obtain methane that is an inert component for ammonia synthesis.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = \text{-206 kJ/mol} \qquad \text{(R5)}$$
$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \qquad \Delta H = \text{-164 kJ/mol} \qquad \text{(R6)}$$

These reactions are catalysed by a solid catalyst such as nickel on alumina in vapor phase at ca. 250 °C. In the end, the CO methanation is an irreversible reaction whereas the methanation CO_2 is reversible.

CO methanation in accordance to our conditions is described in [23]. The kinetic equation proposed is LHHV type (Table 5):

$$r_{CH_4} = \frac{k_{CH_2} \, K_{CO} \, K_{H_2}^2 \, p_{CO}^{0,5} \, p_{H_2}}{\left(1 + K_{CO} \, p_{CO}^{0,5} + K_{H_2} \, p_{H_2}^{0,5}\right)^3} \qquad \text{(E10)}$$

where:

r = Rate of reaction (kmol / kg $\cdot$ s)

k_{CH_2} = Kinetic factor

p_j = Partial pressure (bar)

K_j = Adsorption constants

j = Component index

Table 5: Kinetic parameters for the methanation reaction

	Pre-exp (mol/g*s*bar)	Ea (kJ/mol)	A	B
K_{CO2}	1.333E+06	103		
K_{CO}	5.80E-04	-42	-7.452	5.051
K_{H2}	1.600E-02	-16	-4.135	1.924

For Carbon dioxide methanation the model proposed by Falbo et al.[21], can be used to represent this reaction as a LHHV model (Table 6):

$$r_{CO_2} = \frac{k}{1+ K_{H_2O} \, p_{H_2O}} \left(p_{CO_2}^n \, p_{H_2}^{4n} - \frac{p_{CH_4}^n \, p_{H_2O}^{2n}}{(K_{eq})^n} \right) \qquad \text{(E11)}$$

where:

r = Rate of reaction $(kmol/kg \cdot s)$

k = Kinetic factor

p_j = Partial pressure (atm)

K_j = Adsorption constants
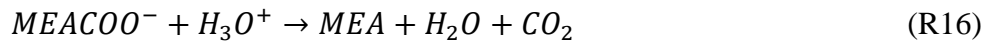
K_{eq} = Equilibrium constant

j = Component index

Table 6: Kinetic parameters for CO_2 methanation

	Pre-exp (mol/g*s*atm)	Ea (kJ/mol)	A	B	C	D
k	9.543E+01	75.3				
K_{eq}		38061.66	-5.046	-2631	1.246	-4.104E04
K_1	9.100E-01		-0.094	0	0	0
α	0.91	1/atm				
n	0.152					

NH₃ synthesis

Ammonia is synthesised through a catalytic reaction occurring at 300 - 400 °C and in a pressure range between 150 and 200 bar according to the type of catalyst[13].

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \quad \Delta H = -62.76 \; kJ/mol \qquad \text{(R7)}$$
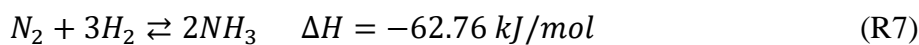
The most common catalyst are based on iron but new types of catalysts have been progressively developed to overcome it limits. In a previous work we have already optimised a multibed configuration based on Fe (from wustite precursor) + Ru/C[13,24]. In our cases we have paired an iron catalyst and a ruthenium on graphite catalyst in order to increase the yield of ammonia. We must define 2 different kinetic equations for each catalytic system, the LHHV models reported in [13] are used for this simulation (Table 7):

- *Fe catalyst (from wustite):*

$$r_1 = k \left[\left(K_{eq}\right)^2 \ p_{N_2} \left(\frac{p_{H_2}^{2.25}}{p_{NH_3}^{1.5}}\right) - \left(\frac{p_{NH_3}^{0.5}}{p_{H_2}^{0.75}}\right) \right] \qquad (E12)$$

- *Ru/C catalyst:*

$$r_2 = k \ \frac{\left[p_{N_2}^{0.5} \left(\frac{p_{H_2}^{0.375}}{p_{NH_3}^{0.25}}\right) - \frac{1}{K_{eq}} \left(\frac{p_{NH_3}^{0.75}}{p_{H_2}^{1.125}}\right) \right]}{1 + K_{H_2} \ p_{H_2}^{0.3} + K_{NH_3} \ p_{NH_3}^{0.2}} \qquad (E13)$$

where:

r = Rate of reaction (kmol$/$kg $\cdot$ s)

k = Kinetic factor

p_j = Partial pressure (atm)

K_j = Adsorption constants
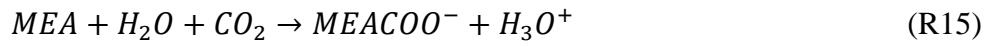
K_{eq} = Equilibrium constant

j = Component index

Table 7: Kinetic parameters for the Ammonia synthesis reaction.

	Pre-exp (mol/g*s*atm)	Ea (kJ/mol)	A	B	C	D
k_0	7.47E+08	45				
$K_{eq, term\ 1}$			-7.8	9218	-5.42	0.00078
$K_{eq, term\ 2}$			2.88	0	0	0

	Pre-exp (mol/g*s*atm)	Ea (kJ/mol)	A	B	C	D
k_0	426	23				
$K_{eq, term\ 1}$			-7.19	0	0	0
$K_{eq, term\ 2}$			-1.876	-4609	2.69	0.000127
K_{H2}			-10.3	4529	0	0

K_{NH3}	-6.48	3523	0	0

Absorption and Stripping reactions

Using only equilibrium reactions we would by far undersize the separation columns [12].

$$MEA^+ + H_2O \rightleftarrows MEA + H_3O^+ \qquad \text{(R8)}$$

$$2H_2O \rightleftarrows OH^- + H_3O^+ \qquad \text{(R9)}$$

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \qquad \text{(R10)}$$

$$H_2S + H_2O \rightleftarrows HS^- + H_3O^+ \qquad \text{(R11)}$$

$$HS^- + H_2O \rightleftarrows S^{2-} + H_3O^+ \qquad \text{(R12)}$$

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad \text{(R13)}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \qquad \text{(R14)}$$

$$MEA + H_2O + CO_2 \rightarrow MEACOO^- + H_3O^+ \qquad \text{(R15)}$$

$$MEACOO^- + H_3O^+ \rightarrow MEA + H_2O + CO_2 \qquad \text{(R16)}$$

Here we have listed all the reactions that we have to insert: the first 5 reactions are defined as equilibrium reactions whereas the other 4, as kinetic reactions. The kinetic reactions are expressed as in power rate law form and in Table 8, we report all the kinetic parameters

Table 8: Kinetic parameters reactions occurring in absorbers and strippers.

	K	Ea (cal/mol)
R.6	1.33e+17	13249
R.7	6.63E+16	25656
R.8	3.02E+14	9855.8
R.9 (ABS)	5.52E+23	16518
R.9 (STRIP)	6.50E+27	22782

3 - Flowsheet layout

Starting from the hydrogen production section, from a solid hydrogen vector the process includes raw material gasification (e.g. carbon or biomass), sulphur compound removal, MSR, WGS and CO_x removal [25,11] (Fig. 1). The raw material selected is the pine sawdust, a type of biomass that can be gasified mainly in fluidised bed reactors with production of H_2, CO_2, CO, CH_4, char and ash[4,26]. This operation is carried out at ca. 800 °C with air or steam as gasifying agent. First the biomass thermally decomposes and releases a certain quantity of the so called *"volatile matter"* (VM) and a solid residue remains. This solid residue is composed by ash and char; the latter, defined as *"fixed carbon"*, can be gasified again in order to maximize the yield of volatile matter.

These transformations occur practically in the same reactor, but to replicate them in Aspen Plus$^{®}$ we were obliged to simulate the gasification vessel as a combination of more reactors. A first stoichiometric reactor was necessary to transform the biomass (non-conventional component) into its conventional component (C, H_2, O_2, N_2, S), plus ash (non-conventional component). After a solid separator is placed to separate the VM from the solid residue and the gas phase is sent to a Gibbs reactor where C, H_2, O_2, N_2, S were transformed in a gas mixture composed of H_2, CO_2, CO, CH_4, H_2S and then, this stream was recombined with the solid material and sent to another section in which CSTR reactors simulate the char gasification[4,7,27]. In this preliminary study the latter is not computed and char was assimilated to C and used as fuel to support the methane steam reforming.

After the gasification a purification section is present to remove sulphur-containing compounds that can poison all the subsequent catalysts. The purification section is composed of an absorption column to wash the gases with an alkanolamine, combined with a stripper to recycle the solvent. Then, the methane present in the gas mixture, undergoes steam reforming at 1000 °C in presence of a catalyst in order to convert methane to further hydrogen and carbon monoxide. The water-gas shift section follows, in which the CO reacts with steam at 350-180 °C, respectively in the HT and LT steps. This would leave a CO residual concentration < 1 % wt[18]. The last traces of CO will be removed employing the catalytic CO-methanation reaction. At this point, a second purification section is present in order to remove ca. 90 % wt of the CO_2 whereas the remaining is removed by methanation. With these passages, we have a hydrogen stream extremely pure, with ca. 0 % wt of CO and CO_2 and traces of water. This last impurity can be easily removed during the

compression stage, required to increase the pressure up to the operative condition of the ammonia synthesis loop (200 bar). The compression is done through a multi-stage compressor alternated with a refrigeration system; in this way, decreasing the temperature between one compressor and the other one, we can separate liquid water with a flash unit and we can decrease the total duty. At the end, we will obtain a stream of pressurized H_2 with a water concentration around 50-100 ppm.

After, the pressurized H_2 is mixed with nitrogen in order to obtain a mixture of $H_2 + N_2$ with a molar ratio equal to 3:1. The stream obtained, is sent to the NH_3 synthesis section: this part of the flowsheet is composed by six reactors in series (representing 6 catalyst layers) with the first four filled with iron catalyst whereas the last two, with Ru/C. This layout has been inherited by the work of[13], but in general, in the ammonia synthesis we must always put a series of reactors with intercooler to allow adiabatic operation in the catalyst layer and efficient heat removal to follow favourable thermodynamic pathways. Indeed, the reaction is exothermic and, an increase of temperature reduces the ammonia yield.

The refrigeration of the outlet stream of the reactor, can be carried out by a heat exchanger but, we can also decrease the temperature by mixing the outlet with fresh feed. In these ways, the feeds temperatures of each reactors (catalytic bed) are always reduced to ca. 350-400 °C. After the last reactor, a separation of liquid ammonia is introduced whereas the incondensables, containing mainly H_2, N_2 and CH_4 are recycled back to the first catalyst bed. Before it can be recycled, a split unit is needed to purge a certain percentage of gas in order to avoid an accumulation of inerts. After the purge, the remaining gas is compressed again at 200 bar (to compensate the pressure drop) and recycled.

4 – Equipment and flowsheet specifications

The flowrate of dry biomass was set at 1000 kg/h, 25 °C, 1 bar and, according to [28], as example of an industrial medium scale plant. For pine sawdust the ultimate and proximate analysis (dry basis) were retrieved from the literature (Table 9), where the sulfanal datum refers to the sulphur percentage for each category [7].

Table 9: Ultimate, Proximate and sulphur content analysis of pine sawdust.

	Ultanal		*Proxanal*		*Sulfanal*	
ASH	0.55	Moisture	0	Pyritic	0.19
C	50.54	FC	17.16	Sulfate	0.19
O	41.11	VM	82.29	Organic	0.19
H	7.08	ASH	0.55		
N	0.15				
S	0.57				

Initially the biomass reacts in an isothermal stoichiometric reactor *"DECOMP"*, in order to transform it in a stream composed by its elemental species (C, H_2, O_2, N_2, S) with a mass fraction based on the ultimate analysis (Figure 2). The subsequent block "SEP" is present to separate the solid material (Char + Ash) from the gas phase (Volatile Matter). On Aspen Plus, the solid separation can be performed of course in a cyclone block but in this case we do not know the particle size distribution of the biomass. Therefore, this separator is specified in order to obtain all the hydrogen, oxygen, nitrogen and sulphur as gas phase, whereas the carbon is split between the solid and gas phase. The percentage of split is defined by the proximate analysis, in this way, we will obtain a solid stream composed of fixed carbon (char) + ash and a vapour stream.

The vapor stream feeds a Gibbs reactor called *"GASI"* at 800 °C and 1 bar with the calculation of both chemical and phase equilibriums. This block transforms the elemental compounds in a new gas mixture composed mainly of H_2, CO_2, CO, CH_4, H_2S by minimizing the Gibbs free energy of the system. The only care we must have, concerns the nitrogen that must be selected as an inert material since it can lead to ammonia formation while minimising the Gibbs free energy (obeying only to thermodynamic constraints). The outflowing stream is cooled at 45°C and sent to the first purification section.

**Figure 2:** Biomass gasification section.
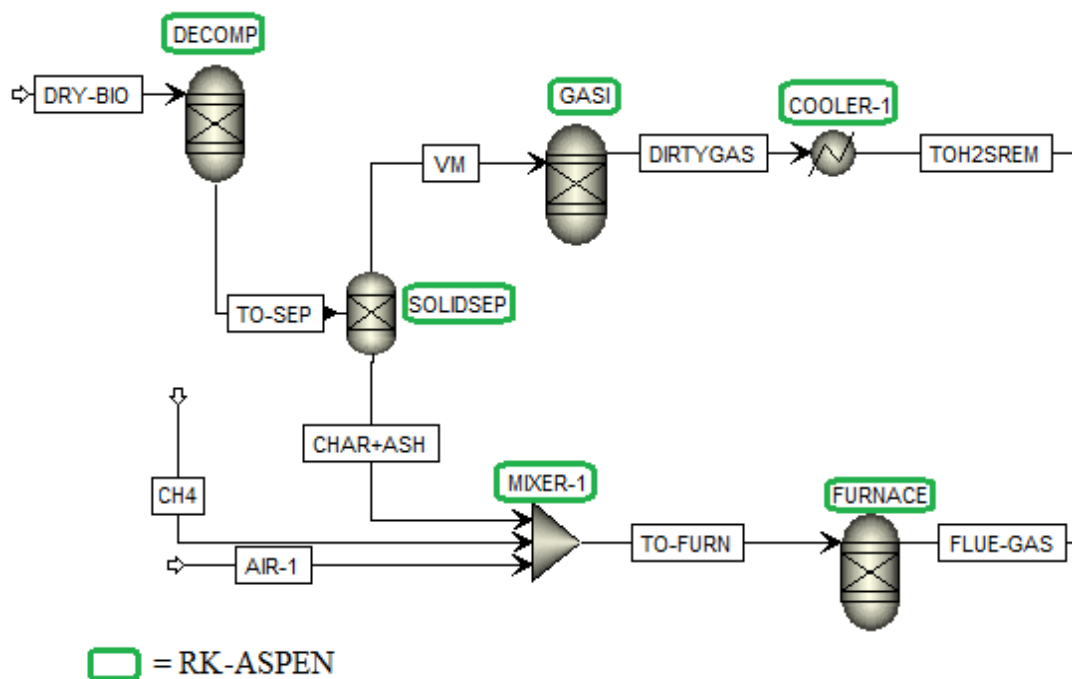
		VM	DIRTYGAS	TO-FURN	FLUE-GAS
Temperature	*°C*	800	800	137.60	1671.92
Pressure	*bar*	1	1	1	1
Mass Flows	*kg/hr*	907.77	907.77	4506.09	4506.09
Mole Flows	*kmol/hr*	83.06	51.56	164.08	156.89

The solid material instead, will be used as a fuel to feed the MSR. To simulate this, char and ash are mixed with air and methane and then sent to the *"FURNACE"*. This is an adiabatic Gibbs reactor that operates at 1 bar. Inside we will have the combustion of methane and carbon, generating a flue gas at elevated temperature (1672 °C).

The absorption section is a mandatory unit to remove all the sulphur compounds before the methane steam reforming (MSR). The removal of acid gases such as CO_2 or H_2S, is carried out in packed columns with aqueous solutions of different amine or alkanolamine; in this work, the monoethanolamine (MEA) has been selected for the scrubber. This section of the flowsheet is depicted in Figure 3.

Figure 3: Sulphur removal section.
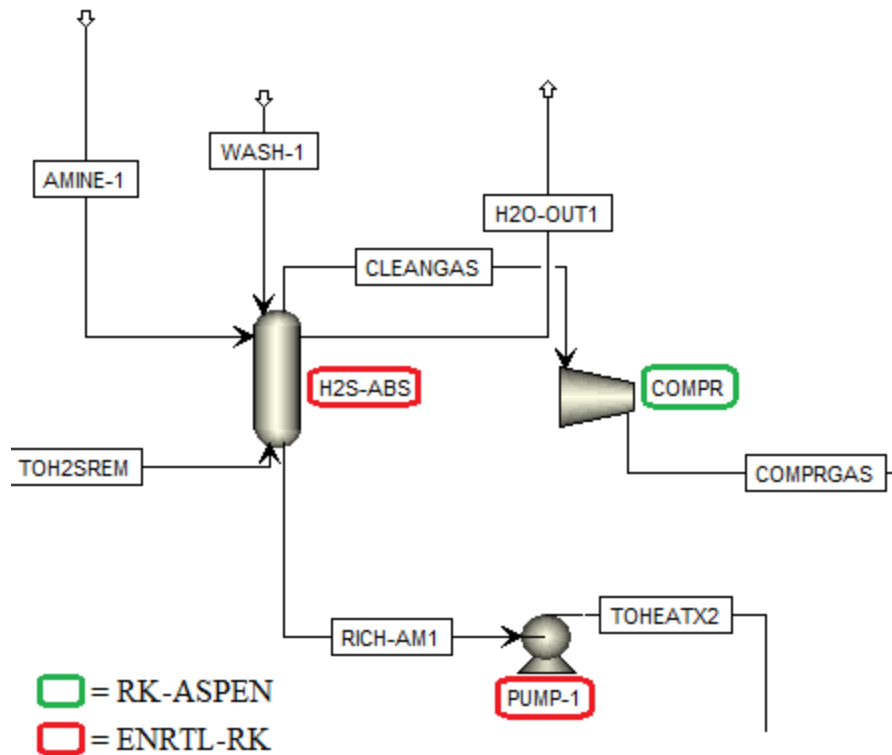
		AMINE-1	TOH2SREM	CLEANGAS	RICH-AM1	COMPRGAS
Temperature	*°C*	45	45	28.52	20.42	591.65
Pressure	*bar*	2	1	1	1	30
Mass Flows	*kg/hr*	500	907.77	936.91	480.87	936.91
Mole Flows	*kmol/hr*	23.84	51.56	53.37	22.57	53.37

H2SABS (RadFrac)

1. Calculation type: Rate-Based

2. 40 stages

3. Top Pressure: 1 bar

4. Reaction: Reaction ID *"ABS"* for all stages

5. Packing Type: MELLAPAC® 250Y

6. Diameter: 0.35 m

7. Height: 5 m

8. Wash Section Height: 0.5 m

9. Wash Section Diameter: 0.3 m

10. Flow model: mixed

11. Film resistance options: Discretize for liquid film (5 points); consider film for vapor film

Mass Fractions	AMINE-1	TOH2SREM	CLEANGAS	RICH-AM1	COMPRGAS
H_2	0	0.037	0.035	5.48E-07	0.035
CO_2	0	2.24E-03	1.11E-03	6.76E-10	1.11E-03
CO	0	0.79	0.76	0.00	7.65E-01
CH_4	0	0.16	0.16	0.00	1.58E-01
N_2	0	1.65E-03	1.60E-03	2.12E-08	1.60E-03
H_2S	0	0.007	1.34E-07	5.02E-07	0
H_2O	0.80	5.41E-04	0.039	0.78	3.91E-02
MEA	0.20	0	2.03E-05	0.18	2.03E-05
MEA^+	4.33E-04	0	0	0.026	0
HS^-	0	0	0	0.012	0
S^{2-}	0	0	0	7.44E-05	0
OH^-	1.19E-04	0	0	7.15E-06	0
H_3O^+	3.65E-14	0	0	4.90E-13	0
HCO_3^-	0	0	0	2.28E-05	0
CO_3^{2-}	0	0	0	1.40E-04	0
$MEACOO^-$	0	0	0	4.60E-03	0

WASH-1 (Stream)		
Temperature	45	°C
Pressure	2	bar
Flow-rate	50	kg/hr
Mass Frac		
H_2O		1

AMINE-1 (Stream)		
Temperature	45	°C
Pressure	2	bar
Flow-rate	500	kg/hr
Mass Frac		
H_2O		0.8
MEA		0.2

According to [12], the temperature was set to 45 °C and the pressure 2 bar. In order to eliminate both CO_2 and H_2S, mixtures with 20%-25% in weight of MEA are used; whereas for the elimination of CO_2 solutions with higher concentration in MEA 30%-35% are used [29].

After getting preliminary estimates with equilibrium calculations, we have turned to a rate based column, specifying the internals and relative transfer coefficients.

The size of the packing and the solvent flowrate were optimised till the stream *"CLEANGAS"* reached less than 10 ppm sulphur content. Column height and solvent

flowrate are inversely proportional, so, we must find a compromise between these two parameters. After setting height and flowrate, the diameter of the column was modified checking the effect on the *Hydraulic Plots* (HP), which allow to monitor the flow rates of liquid and vapor in the column.

In top of the column a washing section with water is also added to remove the traces of MEA that can be drag. To simulate this part, we add a feed of water with a mass flowrate equal to one tenth of the *"AMINE-1"* mass flowrate and this flux of water exits the column as a *"Side Product"*.

This stream is then sent to a compressor with an outlet pressure specified at 30 bar.

In order to recycle the amine solvent, a stripping unit is added, so that the stream *"RICH-AM1"* is pumped at the operative pressure of the stripper equal to 1.8 bar (Figure 4).

Figure 4: Sulphide stripping section.
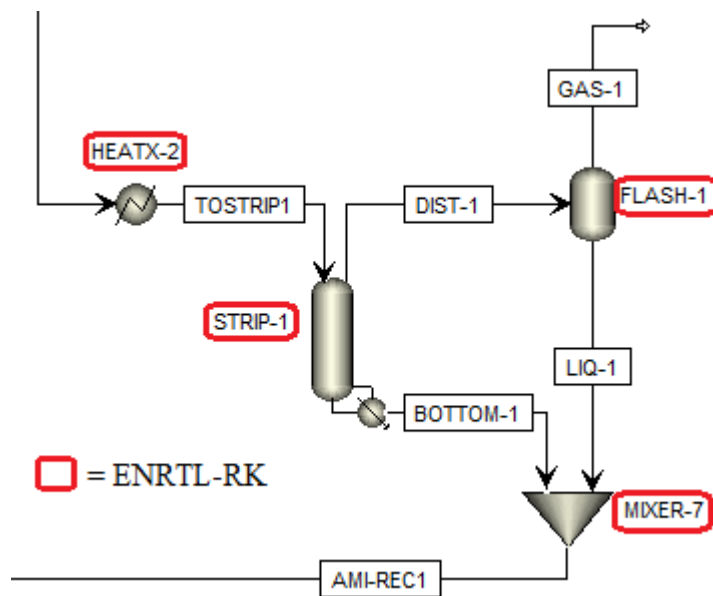
		TOSTRIP-1	BOTTOM-1	DIST-1	GAS-1	LIQ-1	AMI-REC1
Temperature	°C	86	119.6941186	118.57	35.00	35.00	130.82
Pressure	bar	1.8	1.8	1.8	1.8	1.8	1.8
Mass Flows	kg/hr	480.87	388.99	91.88	1.58	90.30	479.29
Mole Flows	kmol/hr	22.57	17.58	5.00	0.05	4.95	22.53

Mass Fractions	TOSTRIP-1	BOTTOM-1	DIST-1	GAS-1	LIQ-1	AMI-REC1 (app. mass frac)
H_2	5.79E-06	0	2.61E-05	2.87E-03	8.57E-08	1.78E-09
CO_2	7.8E-08	4.23E-07	1.79E-03	0.14	1.38E-04	1.50E-03
CO	1.1E-05	0	5.14E-05	5.64E-03	1.86E-07	5.39E-08
CH_4	6.1E-06	0	2.74E-05	3.00E-03	1.39E-07	2.30E-08
N_2	1.6E-08	0	7.29E-08	8.02E-06	1.82E-10	0
H_2S	4.7E-06	7.67E-06	0.012	0.82	2.63E-03	9.99E-04
H_2O	0.92	0.90	0.98	0.03	0.99	0.78
MEA	0.06	8.42E-02	0.00269675	1.155E-09	8.12E-06	0.21
MEA^+	8.94E-03	7.43E-03	0	0	2.71E-03	0
HS^-	7.83E-03	6.57E-03	0	0	2.29E-03	0
S^{2-}	4.025E-05	2.68E-05	0	0	7.36E-09	0
OH^-	1.132E-05	1.79E-05	0	0	2.84E-09	0
H_3O^+	3.141E-11	8.17E-11	0	0	5.03E-09	0
HCO_3^-	5.236E-05	5.92E-05	0	0	4.19E-04	0
CO_3^{2-}	1.676E-05	6.87E-06	0	0	3.27E-07	0
$MEACOO^-$	9.30E-04	7.07E-04	0	0	2.42E-06	0

STRIP-1 (RadFrac)

1. Calculation type: Rate-Based
2. 40 stages
3. Reboiler: Kettle
4. Distillate rate: 5 kmol/h
5. Top Pressure: 1.8 bar
6. Reaction: Reaction ID *"STRIP"* for all stages
7. Packing Type: MELLAPAC® 250Y
8. Diameter: 0.17 m
9. Height: 5 m
10. Flow model: mixed
11. Film resistance options: Discretize for liquid film (5 points); consider film for vapor film

The first block is a heat exchanger to increase the temperature of *"RICH-AM1"* to 85 °C. Then this stream is connected to the *"STRIP-1"* column. Also in this case, the block is *"RadFrac"* but now we have a Kettle reboiler. The path to size this stripper is the same reported previously for the absorption column, with a few modifications. The main difference is the presence of a reboiler and, for this reason, we have to specify a distillate molar rate inserting the sum of H_2S and CO_2 flowrate present in the stream *"RICH-AM1"*. Of course, the kinetics reactions to insert will be those related to the stripper (*"STIRP"*). The distillate stream *"DIST-1"* is sent to a flash unit where is cooled and here, we can separate the *"GAS-1"* stream containing mainly CO_2 and H_2S and liquid water as *"LIQ-1"*. The amine outlet is recycled back to the absorber column with a make-up of only water. The gas stream cleaned and compressed it is sent to the MSR section after mixing with steam and heating to the operative temperature (1000°C). A multitube reactor with external heating (from the Furnace) is envisioned[30] (Figure 5).

Figure 5: Steam Reforming of Methane SMR section.
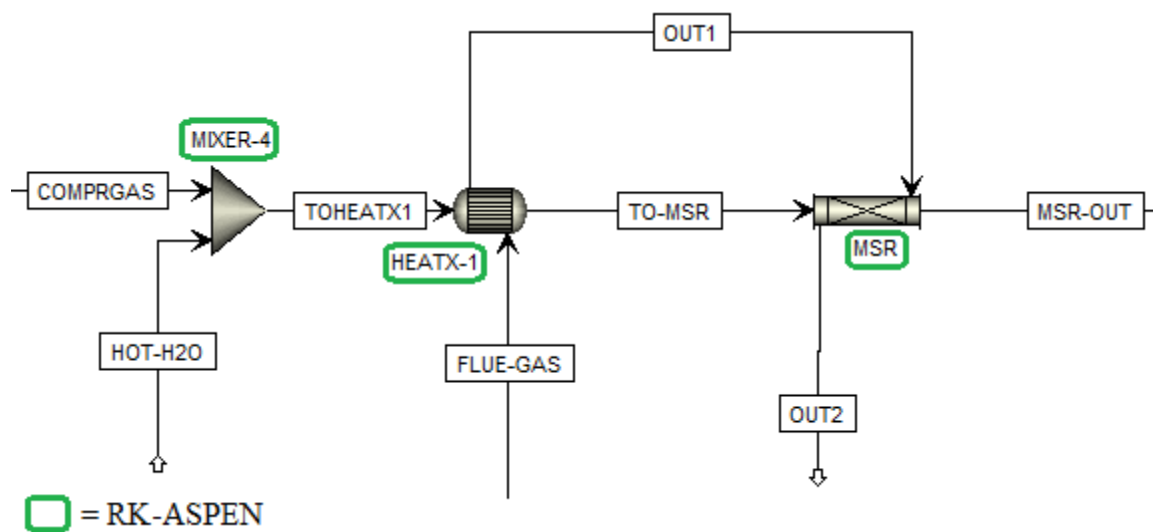
		TOHEATX-1	TO-MSR	FLUE-GAS	OUT-1	MSR-OUT	OUT2
Temperature	°C	418.16	1000	1671.92	1301.90	966.37	1087.91
Pressure	bar	30	30	1	1	29.96	1
Mass Flows	kg/h	1729.58	1729.58	4511.59	4511.59	1729.58	4511.59
Mole Flows	kmol/h	97.37	97.37	156.89	156.89	112.52	156.89

Mass Fractions	TOHEATX-1	TO-MSR	FLUE-GAS	OUT-1	MSR-OUT	OUT2
H_2	0.17	0.17	8.43E-05	8.43E-05	0.43	8.43E-05
CO_2	2.42E-04	2.42E-04	0.09	0.089	0.08	8.94E-02
CO	0.26	0.26	3.65E-04	3.65E-04	0.21	3.65E-04
CH_4	0.09	0.09	1.748E-22	0	0.01	1.75E-22
N_2	5.50E-04	5.50E-04	0.78	0.78	4.76E-04	0.78
H_2O	0.47	4.73E-01	0.09	0.087	0.26	0.09

HOT-H_2O (Stream)		
Vapour fraction	1	
Pressure	30	*bar*
Flow-rate	44	*kmol/h*
Mass Frac		
H_2O	1	

HEATX-1 (HeatX)

1. Model fidelity: Shortcut
2. Flow direction: Cocurrent
3. Calculation mode: Design
4. Cold stream outlet temperature: 1000 °C
5. Outlet pressure: 0 bar

MSR (RPlug)

1. Reactor type: Cocurrent thermal fluid
2. Heat transfer coefficient (thermal fluid-process stream): 100 W/m^{2}K
3. Multitube reactor: 100 tubes
4. Length: 1 m
5. Diameter: 4.6511 cm
6. Reaction: *"MSR"*
7. Pressure process stream: 0 bar
8. Frictional correlation to calculate process stream pressure drop: Ergun
9. Catalyst: 15.2% Ni supported on Mg spinel
10. Density: 2355 kg/m^3
11. Catalyst geometry: 6 mm; ring shaped (0.5769)
12. Loading: 2 kg
13. Bed Voidage: 0.5

When the catalyst quantity is optimised to achieve the desired methane conversions, the reactor length and diameter according to the catalyst density and then the pressure drop is evaluated.

The stream exiting the MSR reactor is mixed again with water and is sent to the water-gas shift reactors (Figure 6).

Figure 6: Scheme of the water gas shift section.
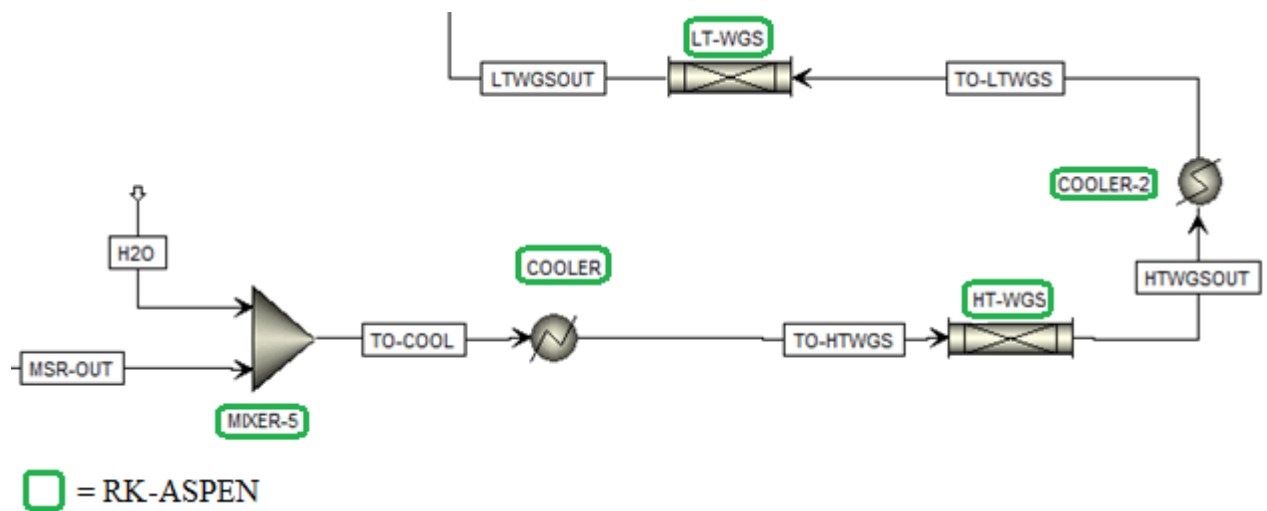
		TO-HTWGS	HTWGSOUT	TO-LTWGS	LTWGSOUT
Temperature	°C	400	504.65	190	240.65
Pressure	bar	29.96	28.95	28.95	28.17
Mass Flows	kg/h	2540.27	2540.27	2540.27	2540.27
Mole Flows	kmol/h	157.52	157.52	157.52	157.52

Mass Fractions	TO-HTWGS	HTWGSOUT	TO-LTWGS	LTWGSOUT
H_2	0.31	0.41	4.09E-01	4.56E-01
CO_2	5.84E-02	1.61E-01	0.16	0.207
CO	0.15	0.05	4.99E-02	3.63E-03
CH_4	1.05E-02	1.05E-02	1.05E-02	1.05E-02
N_2	3.40E-04	3.40E-04	3.40E-04	3.40E-04
H_2O	0.47	3.69E-01	0.37	0.323

| H₂O (Stream)		
Temperature	20	°C
Pressure	30	bar
Flow-rate	45	kmol/h
Mass Frac		
H_2O		1

HT-WGS (RPlug)

1. Reactor type: Adiabatic reactor
2. Length: 0.6 m
3. Diameter: 0.138 cm
4. Reaction: *"HT-WGS"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: 89 mol% Fe_2O_3, 11 mol% Cr_2O_3
8. Density: 2476 kg/m^3
9. Catalyst geometry: 8 mm; sphere (1)
10. Loading: 10 kg
11. Bed Voidage: 0.55

LT-WGS (RPlug)

1. Reactor type: Adiabatic reactor
2. Length: 0.3 m
3. Diameter: 0.103 cm
4. Reaction: *"LT-WGS"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: 32.7 % CuO, 47 % ZnO, 11 mol% Al_2O_3
8. Density: 1000 kg/m^3
9. Catalyst geometry: 8 mm; sphere (1)
10. Loading: 1 kg
11. Bed Voidage: 0.6

The stream is cooled to 400 °C before the *"HT-WGS"* reactor and to 190 °C before the *"LT-WGS"* reactor. The WGS reactors are both monotube and the final conversion of CO

is around 98 %. In the stream *"LTWGSOUT"* there is present a quantity of CO less than 0.5 % wt and this residual CO is then methanated in the *"CO-MET"* block (Figure 7).

Figure 7: Scheme of the CO methanation block.
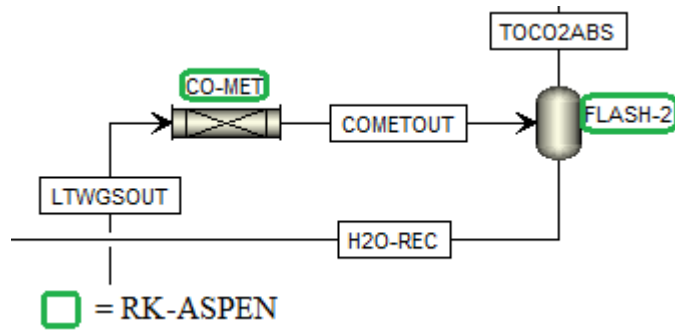
		LTWGSOUT	*COMETOUT*	*H2O-REC*	*TOCO2ABS*
Temperature	*°C*	241	262.54	45	45
Pressure	*bar*	28.17	27.37	27.37	27.37
Mass Flows	*kg/h*	2540.27	2540.31	921.89	1618.41
Mole Flows	*kmol/h*	157.52	156.38	51.13	105.25

Mass Fractions	*LTWGSOUT*	*COMETOUT*	*H2O-REC*	*TOCO2ABS*
H_2	0.46	0.45	2.99E-06	6.65E-01
CO_2	0.21	0.21	5.52E-04	0.31
CO	3.63E-03	0	0	0
CH_4	0.011	0.014	5.25E-07	0.021
N_2	3.40E-04	3.42E-04	1.23E-09	5.09E-04
H_2O	0.32	0.33	0.999	3.30E-03

	CO-MET (RPlug)

1. Reactor type: Adiabatic reactor
2. Length: 0.5 m
3. Diameter: 0.1483 cm
4. Reaction: *"CO-MET"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: 18 % Ni on Al_2O_3
8. Density: 1274 kg/m^3
9. Catalyst geometry: 7 mm; sphere (1)
10. Loading: 5.5 kg
11. Bed Voidage: 0.5

Also in this case, we have a monotube reactor sized in the same way as before and then a flash unit decreases the temperature to 45 °C (P= 0 bar) and eliminates all the excess of water.

This operation prepares the mixture for the carbon dioxide removal in the absorption column with an aqueous solution of MEA 35 % wt (Figure 8).

Figure 8: Scheme of the CO_2 removal section by scrubbing and methanation.
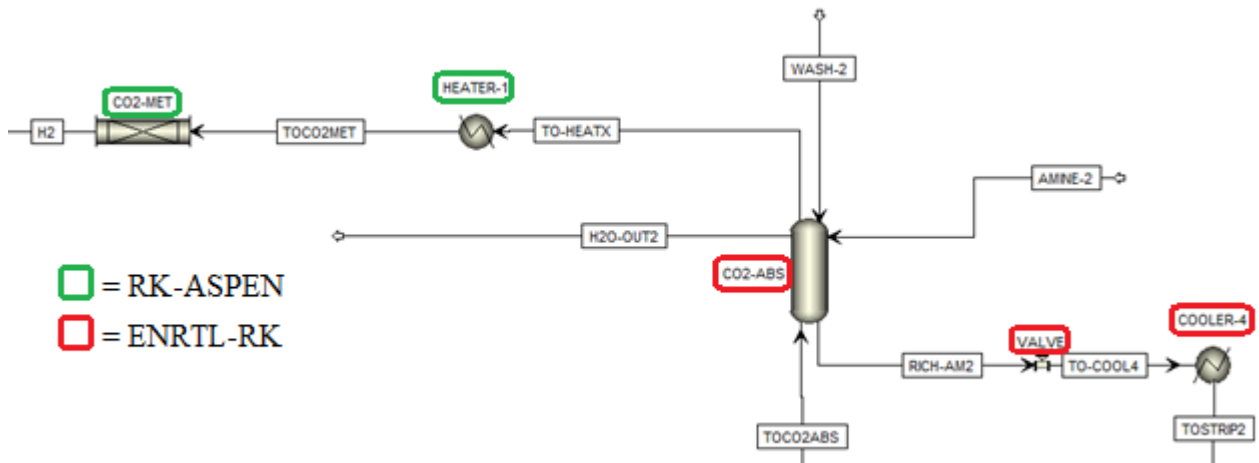
		TOCO2ABS	AMINE-2	TOHEAT	RICH-AMI2	TOCO2MET	H2
Temperature	°C	45	45	45	105	250	250
Pressure	bar	27.37	28	27	27	27	26.55
Mass Flows	kg/h	1618.41	12450	183.82	14084.59	183.82	183.82
Mole Flows	kmol/h	105.25	506.72	71.61	519.09	71.61	71.47

Mass Fractions	TOCO2ABS	AMINE-2	TOHEAT	RICH-AMI2	TOCO2MET	H2
H_2	0.09	0	7.57E-01	1.43E-04	0.9638	0.9618
CO_2	0.89	1.27E-08	1.69E-02	4.70E-04	9.87E-04	0
CO	1.14E-05	0	5.41E-05	5.64E-03	0	0
CH_4	2.21E-02	0	0.19	3.31E-05	3.08E-02	3.18E-02
N_2	9.27E-04	0	0	0	7.41E-04	7.43E-04
H_2S	7.66E-08	0	4.77E-11	1.87E-09	0	0
H_2O	3.86E-03	6.30E-01	2.59E-02	5.56E-01	3.69E-03	5.68E-03
MEA	5.47E-07	0.29	2.96E-05	2.94E-02	0	0
MEA^+	0	0.03	0	1.68E-01	0	0
HS^-	0	0	0	6.70E-09	0	0
S^{2-}	0	0	0	2.73E-11	0	0
OH^-	0	6.87E-06	0	4.18E-07	0	0
H_3O^+	0	7.05E-13	0	1.124E-09	0	0
HCO_3^-	0	1.52E-04	0	0.05	0	0
CO_3^{2-}	0	2.79E-04	0	8.12E-04	0	0
$MEACOO^-$	0	0.05	0	0.19	0	0

CO2ABS (RadFrac)

1. Calculation type: Rate-Based
2. 40 stages
3. Top Pressure: 27 bar
4. Reaction: Reaction ID *"ABS"* for all stages
5. Packing Type: MELLAPAC® 250Y
6. Diameter: 0.36 m
7. Height: 12 m
8. Wash Section Height: 1.2 m
9. Wash Section Diameter: 0.18 m
10. Flow model: mixed
11. Film resistance options: Discretize for liquid film (5 points); consider film for vapor film

	WASH-2 (Stream)		
Temperature	45	°C	
Pressure	28	bar	
Flow-rate	1200	kg/h	
Mass Frac			
H_2O		1	

	AMINE-2 (Stream)		
Temperature	45	°C	
Pressure	28	bar	
Flow-rate	12450	kg/h	
Mass Frac			
H_2O		0.63	
MEA		0.35	
CO_2		0.02	

This absorption column is sized in the same way as the column *"H2SREM"*, but this one is intended for CO_2 capture and operates at 27 bar. The remaining part will be methanated and we have to remove the maximum amount of CO_2 possible with the column absorption in order to have a significant hydrogen consumption and methane production. In this simulation the amount of CO_2 removed is equal to 99,8 % and the remaining part is methanated in an isothermal tubular reactor at 250 °C, called *"CO2-MET"*. After the scrubber, the *"RICH-AM2"* stream, is depressurized with a valve at 1.8 bar and then cooled to 85 °C with *"COOLER-4"*. These operations are useful to prepare the stream before to send it in stripping section for the regeneration (Figure 9).

Figure 9: Amine regeneration unit.
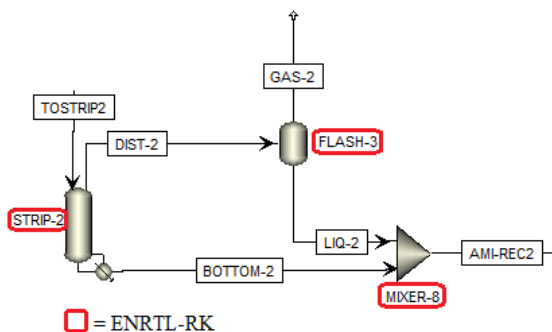
		TO-STRIP2	BOTTOM-2	DIST-2	LIQ-2	GAS-2	AMI-REC2
Temperature	°C	80	127.01	116.51	80	80	110.64
Pressure	bar	1.8	1.8	1.8	1.8	1.8	1.8
Mass Flows	kg/h	14084.59	7782.05	6302.13	4632.20	1669.94	12414.24
Mole Flows	kmol/h	520.44	252.65	300	253.14	46.12	505.71

Mass Fractions	TO-STRIP2	BOTTOM-2	DIST-2	LIQ-2	GAS-2	AMI-REC2 (app. mass frac)
H_2	1.43E-04	0	3.21E-04	7.18E-08	1.21E-03	2.68E-08
CO_2	3.67E-03	4.67E-06	0.24	7.08E-04	0.87	0.0187
CO	0	0	0	0	0	6.66E-09
CH_4	0	0	7.40E-05	1.79E-08	2.79E-04	1.08E-10
N_2	9.04E-07	0	2.02E-06	2.89E-10	7.62E-06	0
H_2S	1.49E-09	3.48E-13	1.94E-08	2.29E-10	6.97E-08	6.11E-10
H_2O	0.56	4.22E-01	7.56E-01	9.78E-01	0.13	0.63
MEA	0.02	4.84E-01	8.41E-03	9.39E-04	2.68E-06	0.35
MEA^+	0.16	3.56E-02	0	9.95E-03	0	0
HS^-	7.07E-09	2.08E-10	0	1.02E-09	0	0
S^{2-}	3.15E-11	4.77E-13	0	8.82E-14	0	0
OH^-	4.02E-07	6.95E-06	0	8.77E-08	0	0
H_3O^+	4.68E-10	1.55E-11	0	1.70E-09	0	0
HCO_3^-	3.52E-02	5.68E-04	0	9.03E-03	0	0
CO_3^{2-}	1.58E-03	3.97E-05	0	2.64E-05	0	0
$MEACOO^-$	0.21	5.85E-02	0	1.20E-03	0	0

STRIP-2 (RadFrac)

1. Calculation type: Rate-Based
2. 40 stages
3. Reboiler: Kettle
4. Distillate rate: 300 kmol/h
5. Top Pressure: 1.8 bar
6. Reaction: Reaction ID *"STRIP"* for all stages
7. Packing Type: MELLAPAC® 250Y
8. Diameter: 0.96 m
9. Height: 7 m
10. Flow model: mixed
11. Film resistance options: Discretize for liquid film (5 points); consider film for vapor film

The stream *"H2"* exiting the *"CO2-MET"* reactor, is compressed to 200 bar through 3 compressors (Figure 10). This part of the flowsheet is also responsible of the elimination of water, the last oxygenated compound in the gas mixture. This is possible during the

refrigeration between two compressors. Before starting the compression, the temperature is decreased at 50 °C and the water is separated through *"FLASH-4"*.

Figure 10: Compressors and water separation.
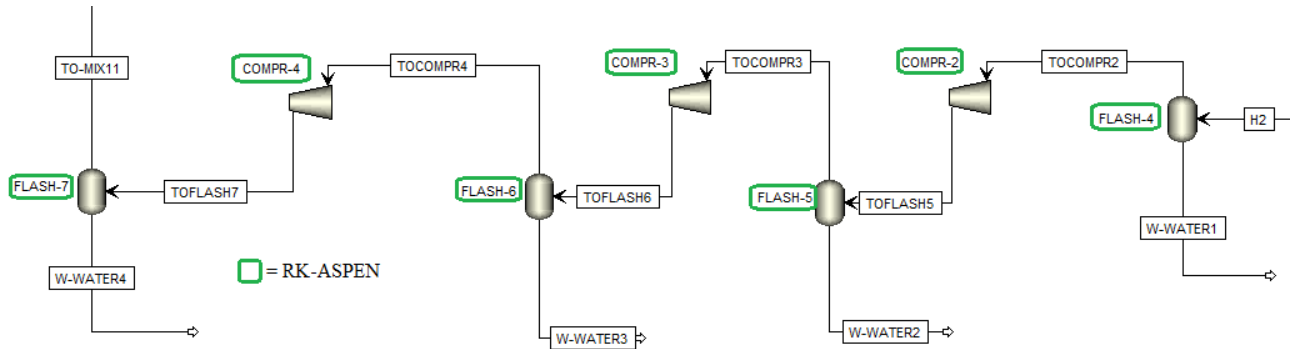
In this simulation, has been decided to use 3 compressors with the same compression ratio (1.98) alternated to flash units with a decreasing temperature (from 50 °C of *"FLASH-4"* to 5 °C *"FLASH-7"*). After the compression, the gas phase *"TO-MIX11"* exiting the last flash unit is a stream of extremely pure hydrogen with a water content largely lower than the limit of poisoning.

At this point, this H_2 is mixed with N_2 at 200 bar, in a molar ratio 3:1. All the ammonia synthesis loop, was treated with the thermodynamic model RKS-BM (Figure 11).

Figure 11: Ammonia synthesis loop.
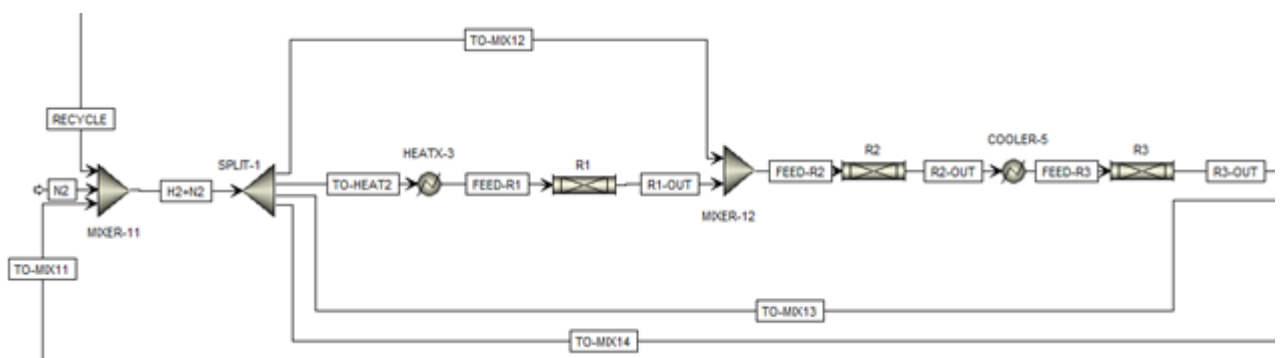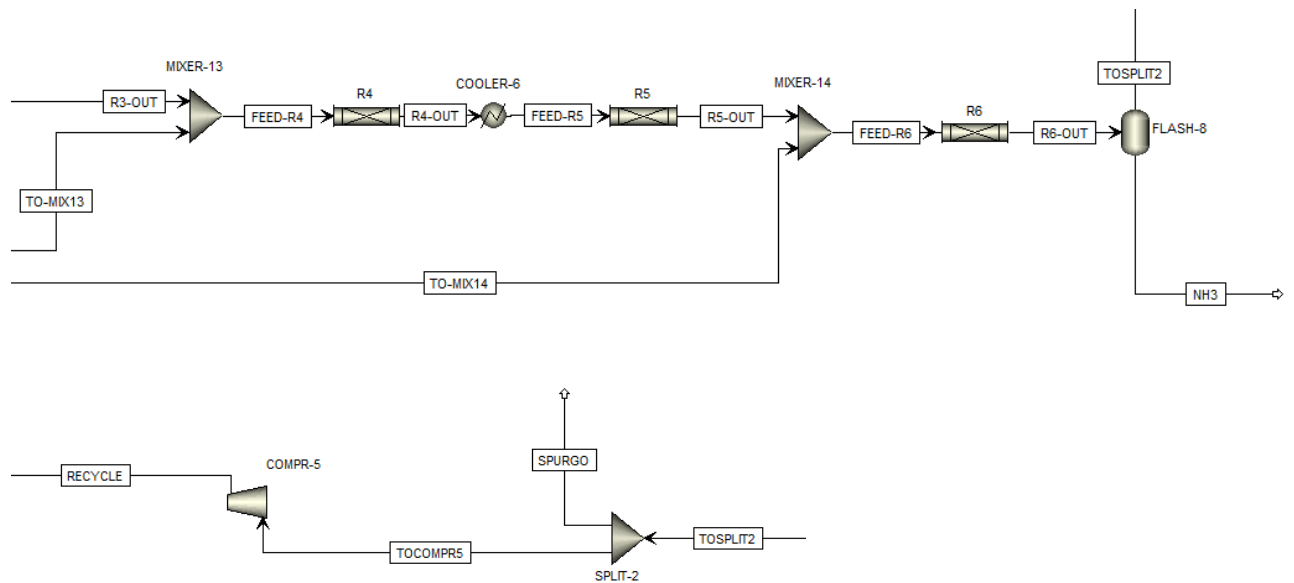
R1 (RPlug)

1. Reactor type: Isothermal reactor
2. Length: 1 m
3. Diameter: 0.1724 cm
4. Reaction: *"NH3-FE"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: Fe
8. Density: 3000 kg/m^3
9. Catalyst geometry: 6 mm; sphere (1)
10. Loading: 35 kg
11. Bed Voidage: 0.5

R2 (RPlug)

1. Reactor type: Isothermal reactor
2. Length: 2 m
3. Diameter: 0.206 cm
4. Reaction: *"NH3-FE"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: Fe

8. Density: 3000 kg/m^3

9. Catalyst geometry: 6 mm; sphere (1)

10. Loading: 100 kg

11. Bed Voidage: 0.5

R3 (RPlug)

1. Reactor type: Isothermal reactor

2. Length: 2.5 m

3. Diameter: 0.31923 cm

4. Reaction: *"NH3-FE"*

5. Pressure process stream: 0 bar

6. Frictional correlation to calculate process stream pressure drop: Ergun

7. Catalyst: Fe

8. Density: 3000 kg/m^3

9. Catalyst geometry: 6 mm; sphere (1)

10. Loading: 300 kg

11. Bed Voidage: 0.5

R4 (RPlug)

1. Reactor type: Isothermal reactor

2. Length: 4.5 m

3. Diameter: 0.5321 cm

4. Reaction: *"NH3-FE"*

5. Pressure process stream: 0 bar

6. Frictional correlation to calculate process stream pressure drop: Ergun

7. Catalyst: Fe

8. Density: 3000 kg/m^3

9. Catalyst geometry: 6 mm; sphere (1)

10. Loading: 1500 kg

11. Bed Voidage: 0.5

R5 (RPlug)

1. Reactor type: Isothermal reactor
2. Length: 2.5 m
3. Diameter: 1.018 cm
4. Reaction: *"NH3-RU"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: Ru/C
8. Density: 590 kg/m^3
9. Catalyst geometry: 6 mm; sphere (1)
10. Loading: 600 kg
11. Bed Voidage: 0.5

R6 (RPlug)

1. Reactor type: Isothermal reactor
2. Length: 4 m
3. Diameter: 1.039 cm
4. Reaction: *"NH3-RU"*
5. Pressure process stream: 0 bar
6. Frictional correlation to calculate process stream pressure drop: Ergun
7. Catalyst: Ru/C
8. Density: 590 kg/m^3
9. Catalyst geometry: 6 mm; sphere (1)
10. Loading: 1000 kg
11. Bed Voidage: 0.5

SPLIT-1 (FSplit)

Stream:	Split fraction:
TO-HEAT2	0.491043
TO-MIX1 2	0.129911
TO-MIX1 3	0.195198
TO-MIX1 4	

		H2 + N2	RECYCLE	R1		R2	
				IN	OUT	IN	OUT
Temperature	°C	3.00	0.00	400.00	541.96	428.32	506.09
Pressure	bar	200.00	200.00	200.00	199.97	199.97	199.93
Mass Flows	kg/h	816.93	622.37	706.76	706.76	893.74	893.74
Mole Flows	kmol/h	93.92	66.14	78.60	72.10	92.90	88.47

		R3		R4		R5		R6	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT
Temperature	°C	400.00	463.08	349.37	449.75	340.00	405.78	327.17	402.09
Pressure	bar	199.93	199.92	199.92	199.91	199.91	199.91	199.91	199.91
Mass Flows	kg/h	893.74	893.74	1174.57	1174.57	1174.57	1174.57	1439.32	1439.32
Mole Flows	kmol/h	88.47	84.94	116.17	108.82	108.82	104.09	133.53	126.95

The layout provides a split unit to separate the feed in 4 new streams that will be used later as fresh feed to decrease the reactor temperature, to simulate the quench feed option.

At the end of the series of reactors, a separation unit is placed "FLASH-8" and here a cryogenic separation at 0 °C occur. As liquid stream we obtain ammonia 98 % wt and, as gas phase, a stream rich in H_2, N_2 with a low quantity of residual ammonia. Before recycling, this stream is sent to a *"SPLIT-2"* block, in which a certain quantity is purged. This operation is mandatory to avoid inert accumulation (mainly methane). The split fraction for *"SPURGO"* is specified in order to obtain a total flowrate containing the same kg/h of CH_4 formed in the previous steps.

The value of purge defines also the amount of the recycle: with a low amount of purge, the recycle flowrate is big and this leads to an oversizing of the reactors due to the high amount of inert; viceversa, if we are purging a lot of gases this leads to high loses in term of H_2 and N_2. So, a compromise must be reached.

5 - Results

5.1 – Production and purification of the ammonia synthesis gas

The compositions and main fetures of the simulated streams are reported in the following Tables.

Table 10: Results of the streams flowrates, conditions and compositions expressed in mass fractions.

		VM	DIRTYGAS	OUT-GASIFIER	H2S REMOVAL	
					IN	OUT
Temperature	°C	800.00	800.00	800.00	45.00	28.52
Pressure	bar	1.00	1.00	1.00	1.00	1.00
Mass Flows	kg/h	907.77	907.77	907.77	907.77	936.91
Mole Flows	kmol/h	83.06	51.56	51.56	51.56	53.37

Mass Fractions	VM	DIRTYGAS	OUT-GASIFIER	H2S REMOVAL	
				IN	OUT
H_2	0.078	0.037	0.0365	0.0365	0.0354
O_2	0.45	0	0	0	0
CO_2	0	2.24E-03	0.0022	0.0022	0.0011
CO	0	0.79	0.7891	0.7891	0.7646
CH_4	0	0.16	0.1632	0.1632	0.1582
C	0.46	0	0	0	0
N_2	1.65E-03	1.65E-03	0.0017	0.0017	0.0016
S	6.28E-03	0	0	0	0
H_2S	0	6.67E-03	0.0067	0.0067	1.34E-07
H_2O	0	5.41E-04	0.0005	0.0005	0.0391

		MSR		HT-WGS		LT-WGS		CO-MET	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT
Temperature	°C	1000.00	966.37	400.00	504.65	190.00	240.65	240.65	262.54
Pressure	bar	30.00	39.96	29.96	28.95	28.95	28.17	28.17	27.37
Mass Flows	kg/h	1729.58	1729.58	2540.27	2540.27	2540.27	2540.27	2540.27	2540.31
Mole Flows	kmol/h	97.37	112.52	157.52	157.52	157.52	157.52	157.52	156.38

Mass Fractions	MSR		HT-WGS		LT-WGS		CO-MET	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT
H_2	0.0192	0.0563	0.0384	0.0512	0.0512	0.0569	0.0569	0.0556
CO_2	0.0006	0.2339	0.1593	0.4387	0.4387	0.5649	0.5649	0.5649
CO	0.4142	0.3884	0.2644	0.0866	0.0866	0.0063	0.0063	0
CH_4	0.0857	0.0154	0.0105	0.0105	0.0105	0.0105	0.0105	0.0141
N_2	0.0009	0.0009	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006
H_2S	7.23E-08	7.23E-08	4.92E-08	4.92E-08	4.92E-08	4.92E-08	4.92E-08	4.92E-08
H_2O	0.4795	0.3051	0.5268	0.4125	0.4125	0.3608	0.3608	0.3649

		CO2 REMOVAL		CO2-MET		H2O REMOVAL		H2 + N2
		IN	OUT	IN	OUT	IN	OUT	
Temperature	°C	45.00	45.00	250.00	250.00	250.00	5.00	2.99
Pressure	bar	27.37	27.00	27.00	26.55	26.55	200.00	200.00
Mass Flows	kg/h	1618.41	183.82	183.82	183.82	183.82	176.58	816.93
Mole Flows	kmol/h	105.25	71.61	714.61	71.47	71.47	71.06	93.92

Mass Fractions	CO2 REMOVAL		CO2-MET		H2O REMOVAL		H2 + N2
	IN	OUT	IN	OUT	IN	OUT	
H_2	0.0872	0.7569	0.7569	0.7538	0.7538	0.7847	0.1696
CO_2	0.8858	0.0169	0.0169	0	0	0	0
CO	0	0	0	0	0	0	0
CH_4	0.0221	0.1922	0.1922	0.1983	0.1983	0.2065	0.0446
N_2	0.0009	0.0081	0.0081	0.0081	0.0081	0.0084	0.7857
H_2S	7.66E-08	0	0	0	0	0	0
H_2O	0.0039	0.0259	0.0259	0.0398	0.0398	3.91E-04	8.45E-05

All the carbon (C), the oxygen and sulphur, are completely consumed to produce mainly CO, CH_4 with a little consuption of hydrogen; whereas all the sulphur is converted in H_2S. In the MSR reactor (Figure 12), 82 % of methane was converted, with 60.2 % selectivity towards hydrogen and accordining with literature, it is in the industrial range of yield.

Figure 12: Conversion profiles along the resctors in the H_2 production and purification steps. a) MSR reactor; b) HT-WGS; c) LT-WGS; d) CO methanation and e) CO_2 methanation.

a)

b)

c)

LT-WGS

d)

CO-MET

e)

CO_2-MET

38
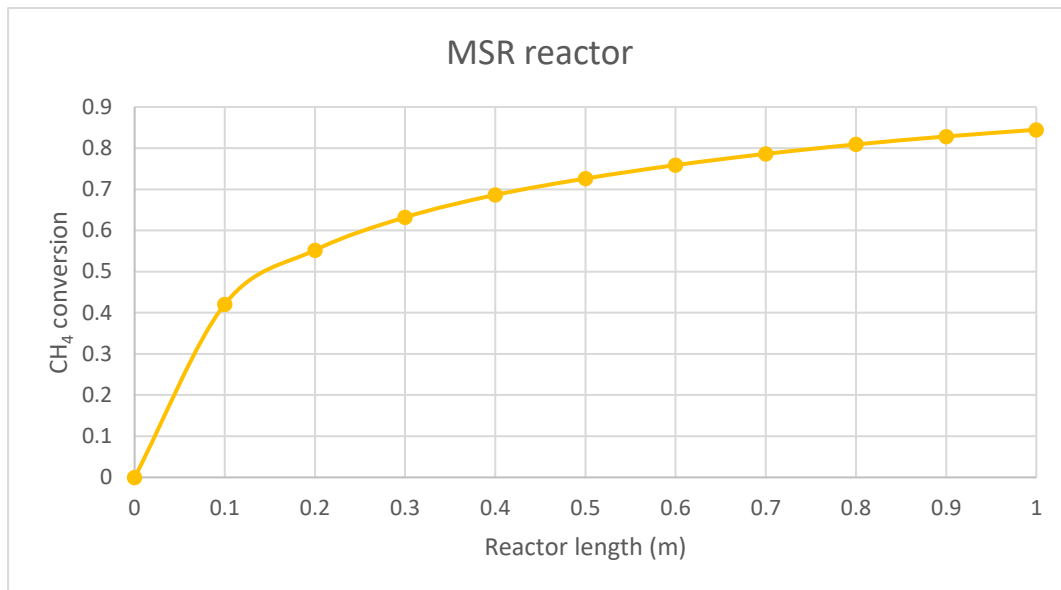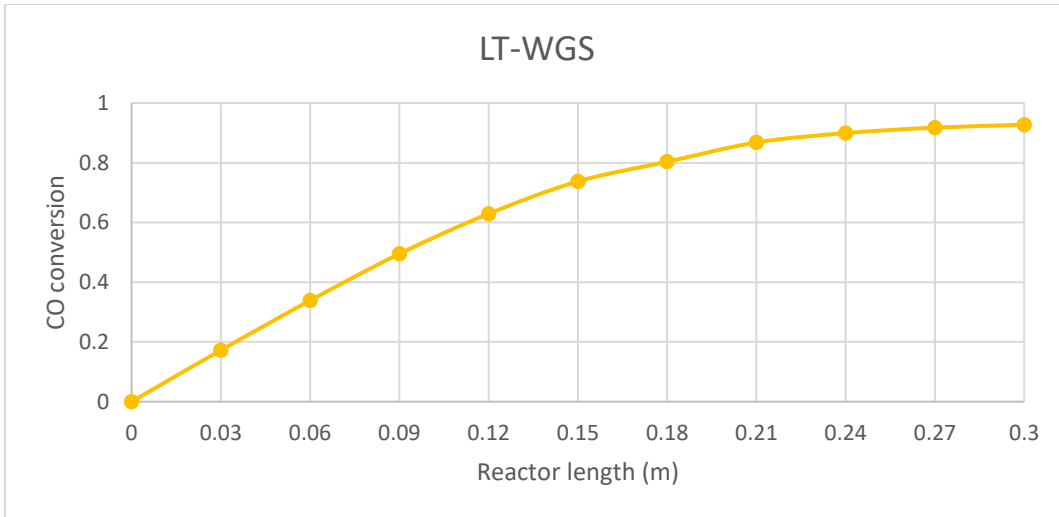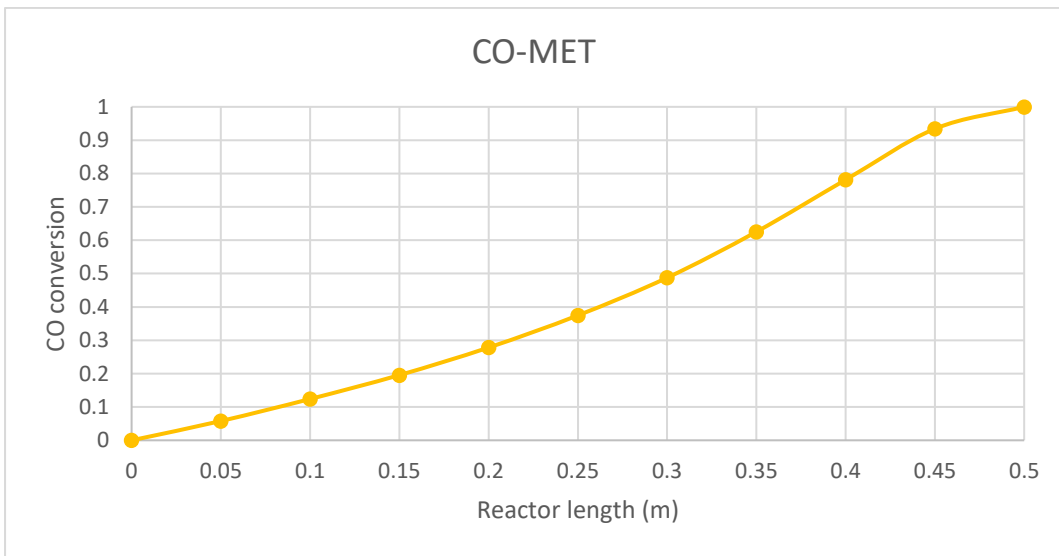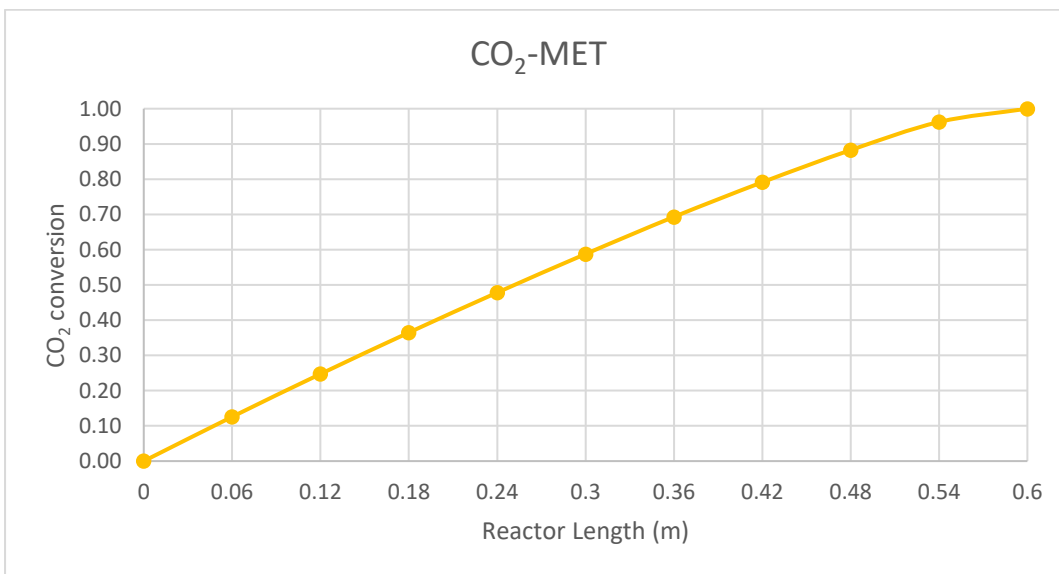
90 % of the total methane that remains in the syngas derives from this step. Attempts to push the conversion towards higher values faces a couple of drawbacks, such as difficulties to maintain the temperature along the reactor and an increasing ratio H_2O/CH_4. The first point is tricky because, with the same amount of catalyst if the temperature is maintained as close as possible to 1000 °C (or higher) a much greater conversion is obtained, with respect to an adiabatic reactor. This is regulated by the flue gas temperature and we can manage it, by changing the flowrate of *"AIR-1"* or methane that feeds the *"FURNACE"* reactor. The other factor is the molar ratio methane/water: ideally, based on our kinetics, the optimal ratio would be 1:3, but increasing values up to 1:5 increase significantly the conversion. In this simulation the ratio was therefore always set to 1:5.

In literature many articles [18,20] discuss the combination of the HT-WGS and LT-WGS. Generally, it is preferred to have a conversion higher than 60-70 % in the high temperature reactor in order to avoid an oversizing of the low temperature step. In this specific case the total conversion of CO is 97.6%, 67.2 % in the HT-WGS reactor.

As for the methane steam reforming, also in this case the CO/H_2O molar ratio plays a crucial role and it can change from 1:1 to 1:3. Also in this case, a higher amount of water pushes the conversion, so a ratio 1:3 was adopted.

Two methanation reactors accomplish the final hydrogen purification from CO_X. The former provides the complete elimination of CO and is placed after the LT-WGS reactor, whereas the latter is placed after the CO_2 scrubbing column. In both cases, we reach a complete consumption of CO_X. A significant issue with these reactors is the high exothermicity: when sizing an adiabatic reactor, too high outlet temperatures and instable thermal profile is observed. External cooling is a better option [22].

For what concerns the absorption and stripping columns, we have carefully examined all the hydraulic plots in order to understand if these columns were sized correctly. Indeed, absorption columns and strippers should ensure the removal of the solute by physical or chemical absorption, but to do so they should operate correctly from the hydrodynamic point of view. If the correct match between packing elements and flowrates is not net, very poor efficiency is found, imposing the need of column oversizing. Therefore, the flowrates (and the consequent costs estimations) determined considering only the equilibrium calculations are not fully meaningful if not accompanied by the verification that those values stand in a rate-based simulation.

As an example, the vapour or liquid flowrates inside the column (black dots) and an operative range of our column (blue lines) are compared in Figure 13. The packing stability
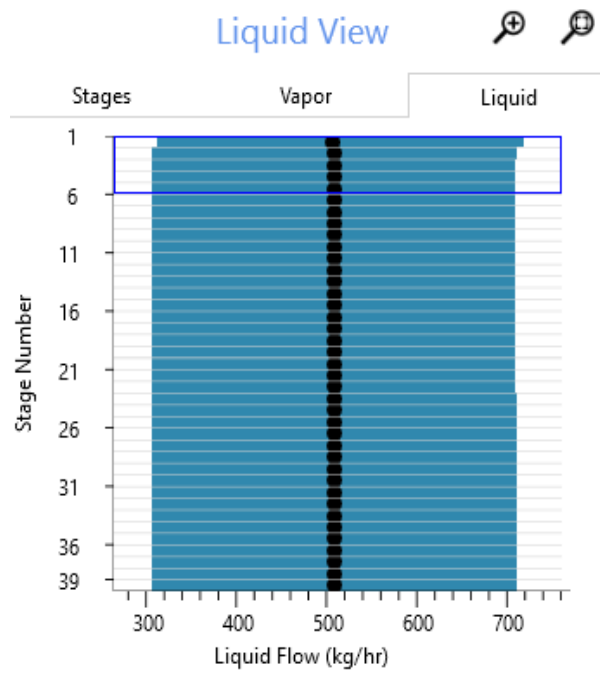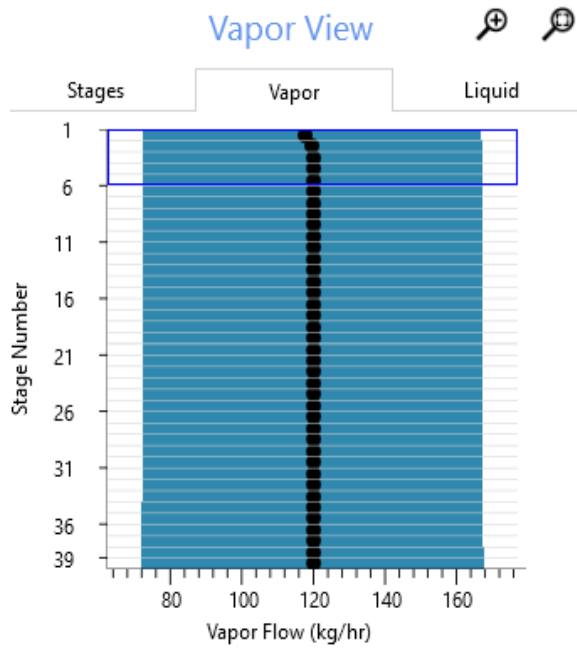
diagram shows the vapor flow versus liquid flow curves for various values of the fractional pressure drop per unit packed height. The operating limits are determined by the curve at the maximum allowable pressure drop and the minimum liquid flow rate per unit area.

Figure 13: Example of hydraulic plots for the gas and liquid phases. a) H_2S absorber; b) H_2S stripper; c) incorrect sizing CO_2 absorber; d) correct sizing CO_2 absorber
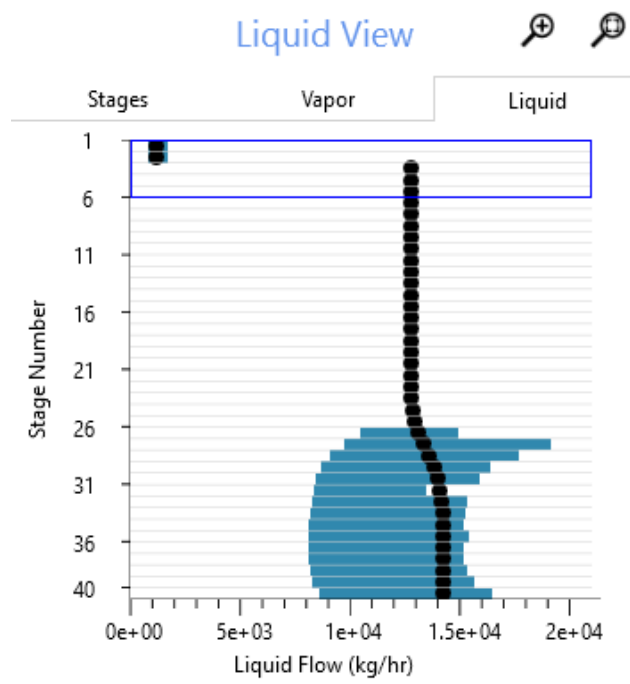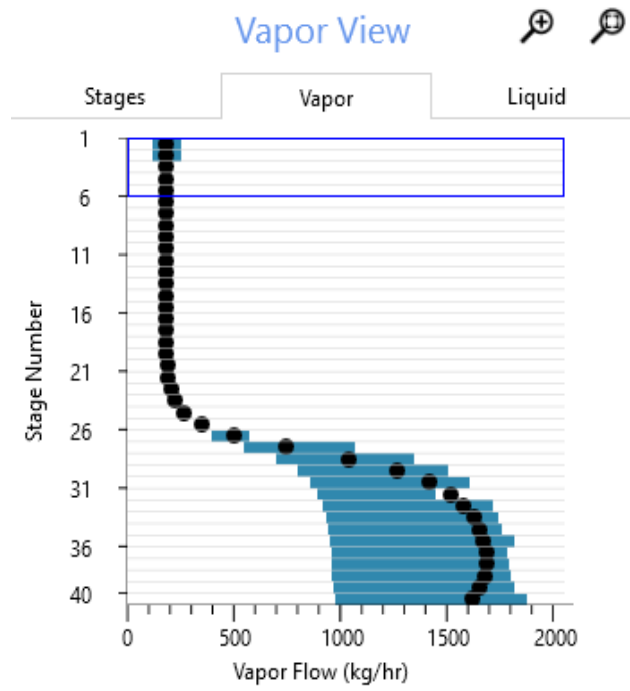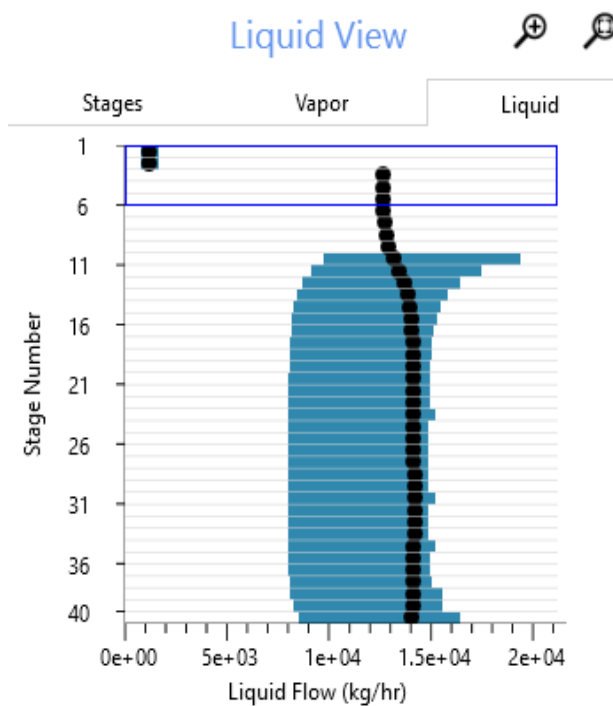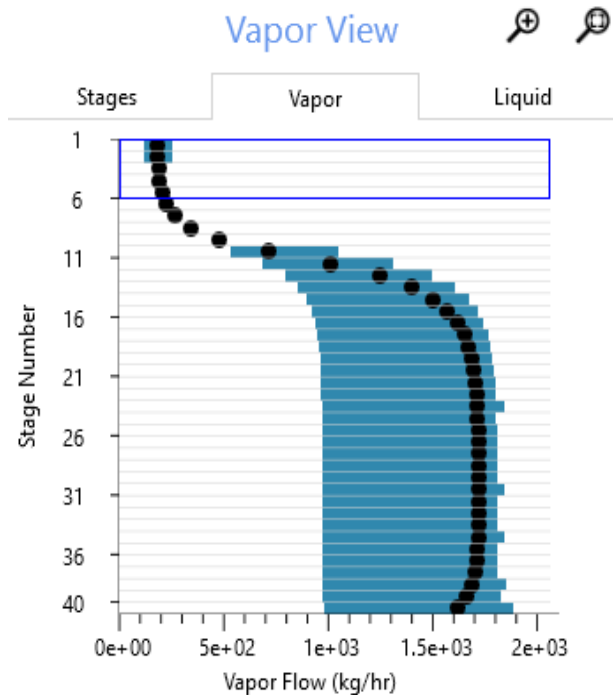
a)

Vapor View

Stages | Vapor | Liquid

Vapor Flow (kg/hr)

Stage Number

Liquid View

Stages | Vapor | Liquid

Liquid Flow (kg/hr)

Stage Number

b)

Vapor View

Stages | Vapor | Liquid

Stage Number vs Vapor Flow (kg/hr)

Liquid View

Stages | Vapor | Liquid

Stage Number vs Liquid Flow (kg/hr)

c)

Vapor View

Liquid View

d)

Vapor View

Liquid View
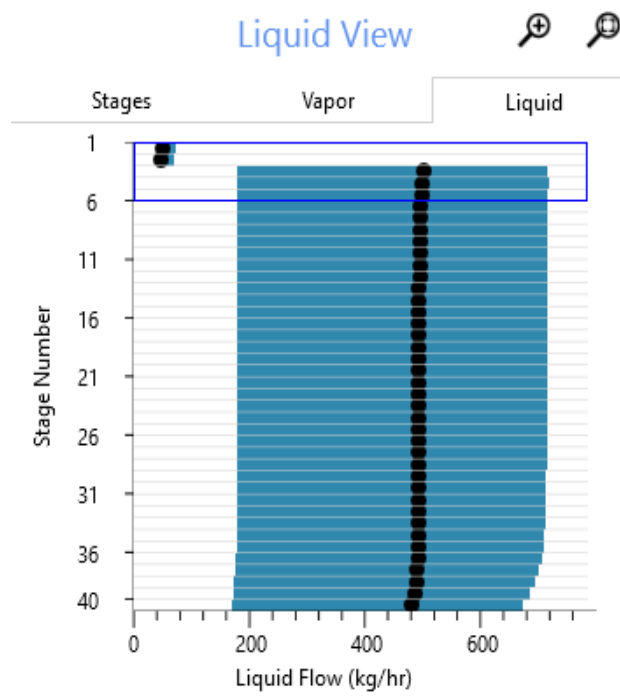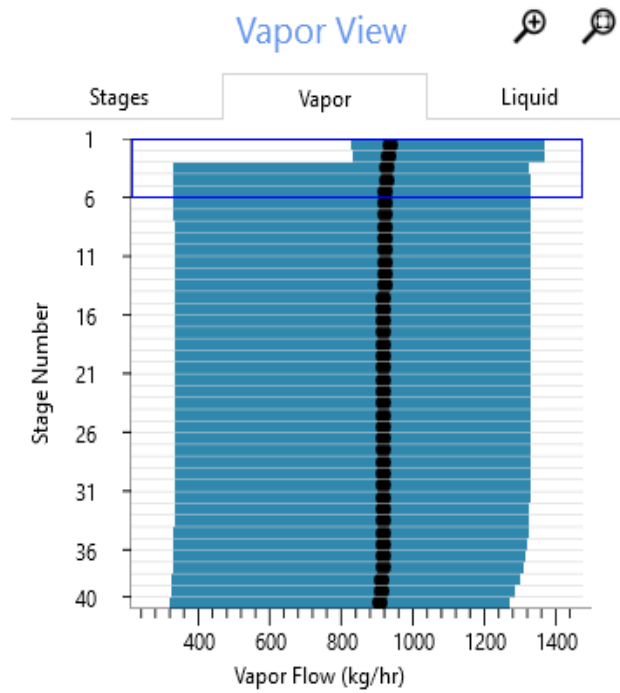
The first absorption column removes sulphur below 0.1 ppm. The subsequent stripper has been sized to reach a quantity of H_2S in the recycled solvent lower than 1 % wt. The sizing of these two columns was not critical. On the contrary, the second absorption column is designed to remove 32.6 kmol/h of CO_2 using a significant solvent flowrate. Initially, the CO_2 methanator was not planned, because through this absorption column few ppm of carbon dioxide could be reached. However, to achieve this performance, we needed a very

high liquid flow and this led to the flooding of the column. In fact, by looking to the hydraulic plots of Figure 13c, it is noted that only the last section of the column was correctly working. This type of sizing was not correct, and remained very critical for different selections of packings and combinations of flowrates. The only valid strategy to allow a reliable operation of the column was to decrease the liquid flowrate to reach a compromise between the amine flowrate, the CO_2 removal specification and the correct hydrodynamic regime in the column. Nevertheless, to comply with the stringent purity requirements for the ammonia synthesis syngas a CO_2 methanator was added, followed by the final CO_2 scrubbing.

In Figure 13d are reported the correct hydraulic plots of the CO_2 scrubber in which almost the totality of the column is working. The CO_2 mass fraction can be set as low as $8 \cdot 10^{-6}$ - 0.017 (up to 99.7 % removal) with small variations of the flowrate of the amine.

Figure 14 summarises the composition of the streams outflowing the main units of the plant.

Figure 14: Molar fraction of the streams of the hydrogen production and purification section.
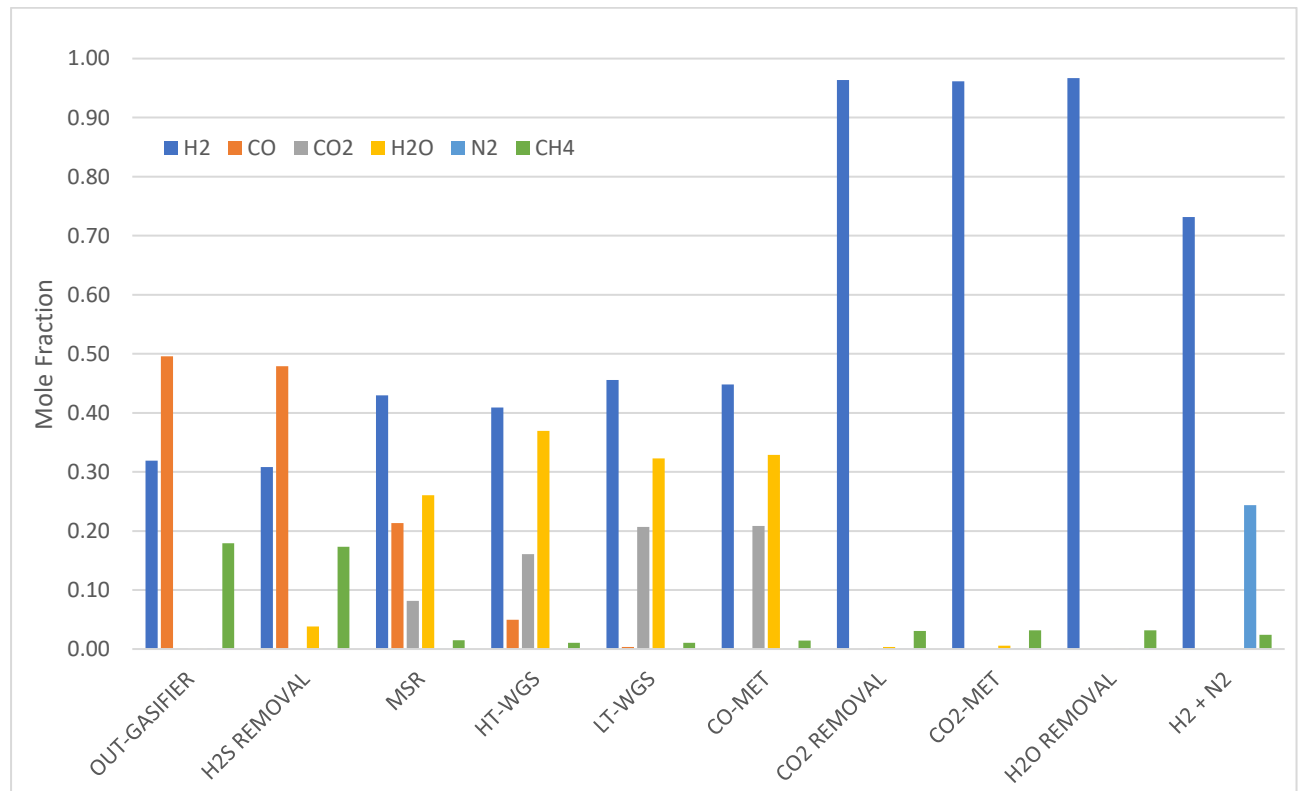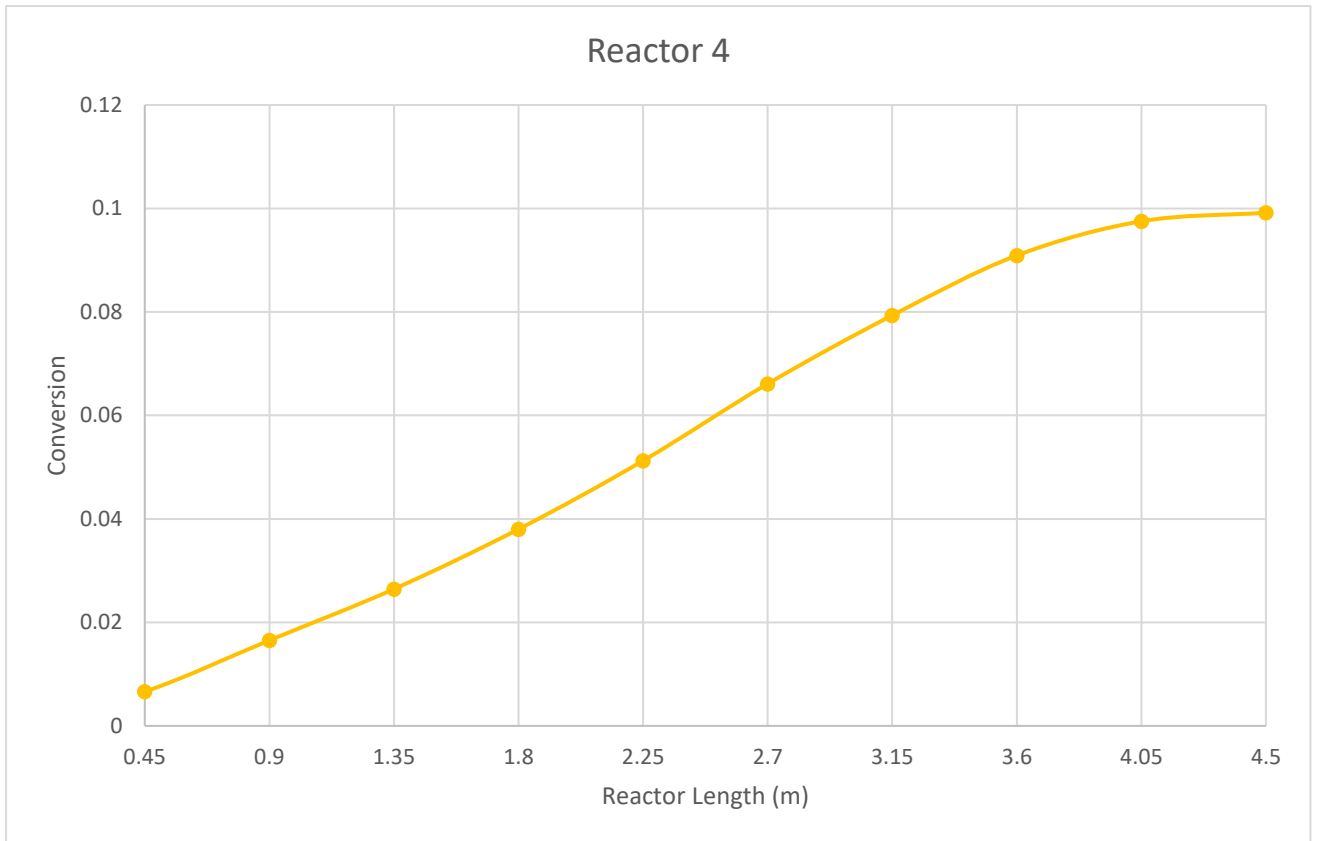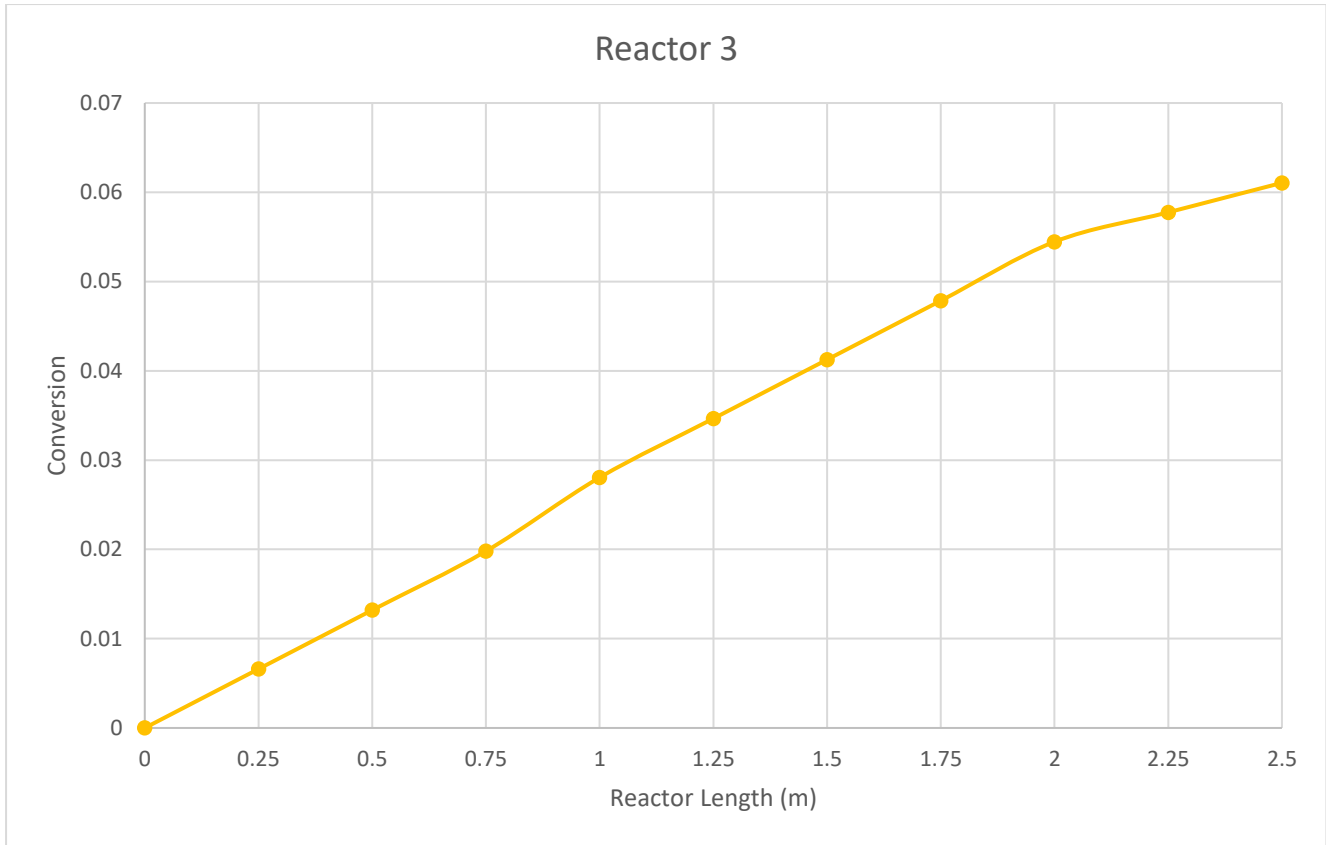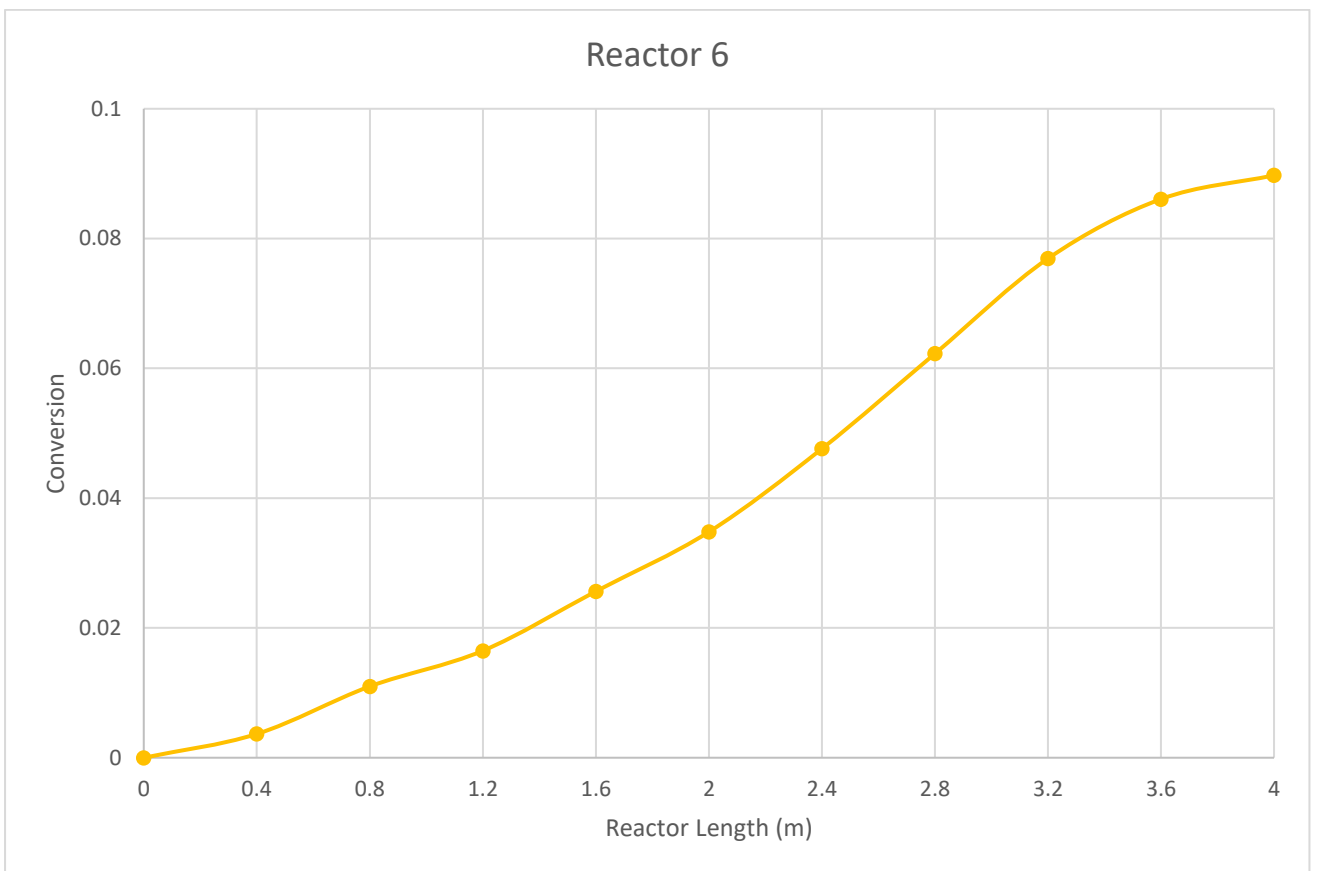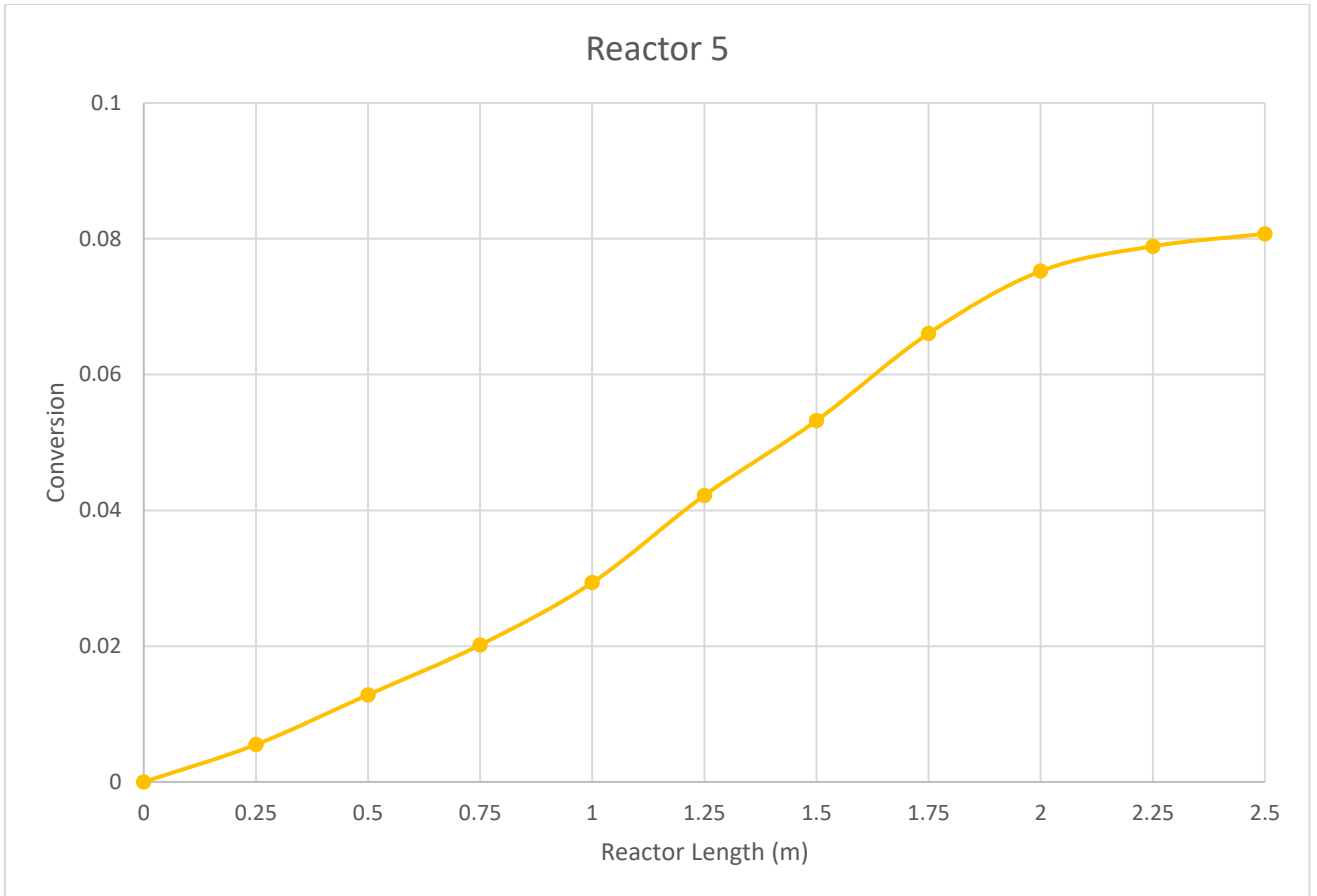

5.2 - Ammonia synthesis loop

45

The conversion plots for all the reactors which represent the 6 catalyst beds are reported in Figure 15. With this synthesis loop we were able to obtain 550 kg/h of NH_3 at 98.8 % wt purity.

Figure 15: Hydrogen conversion plots across the six catalyst beds.

Reactor 3

Reactor 4

Reactor 5

Reactor 6

48
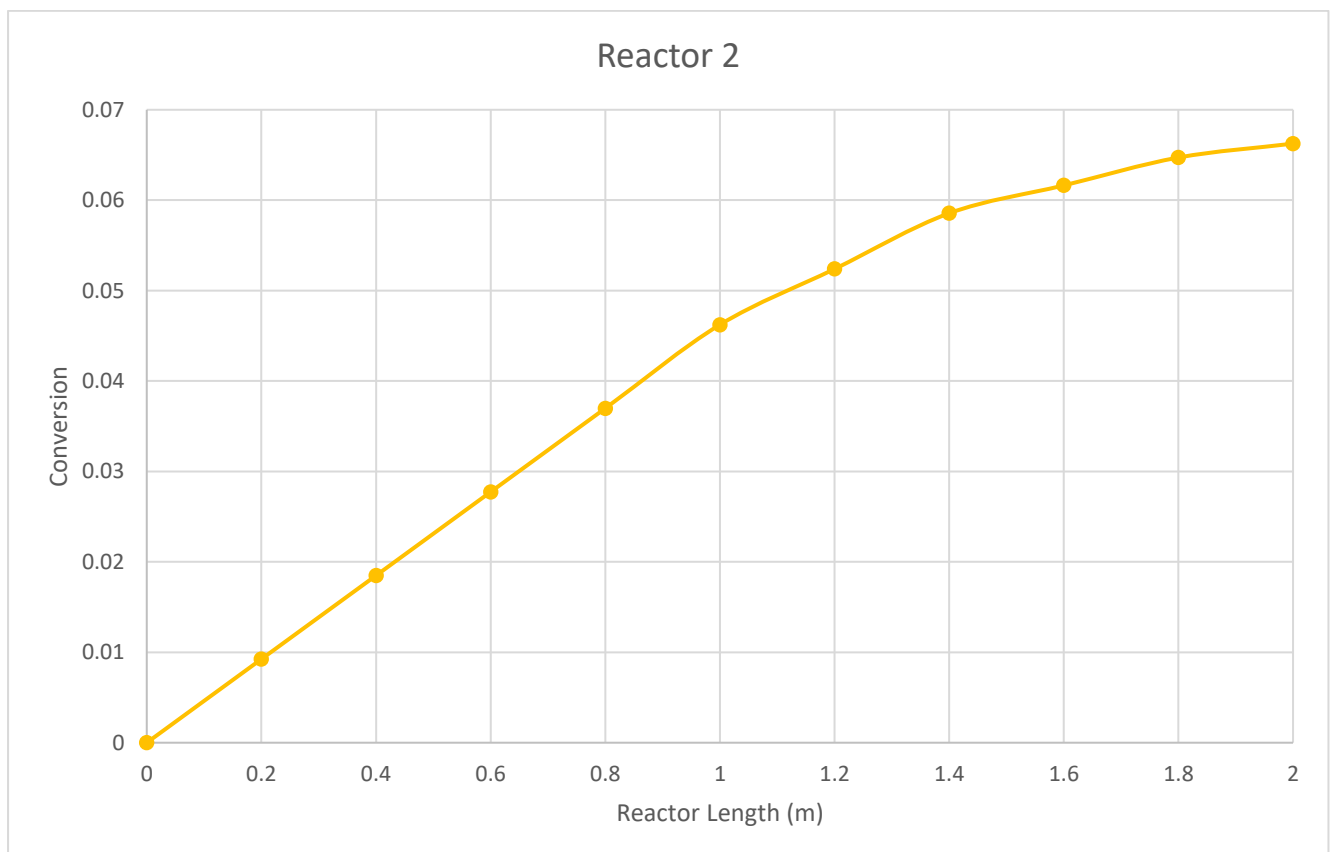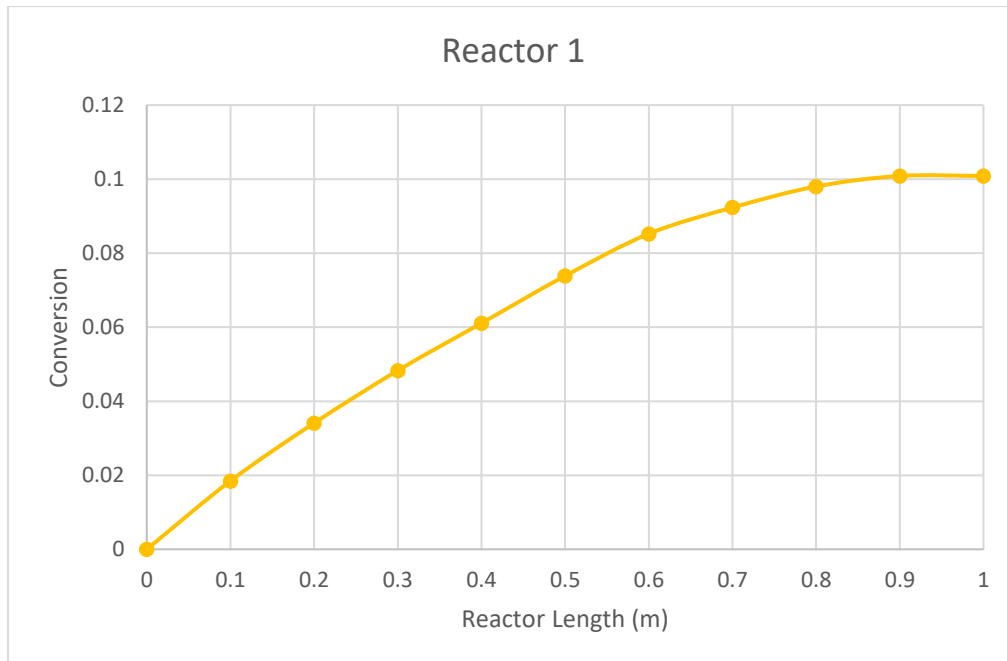
The streams specifications and compositions are summarised in Table 11.

Table 11: Streams specifications and compositions for the ammonia synthesis loop.

		H2 + N2	RECYCLE	R1		R2		R3	
				IN	OUT	IN	OUT	IN	OUT
Temperature	*°C*	3.00	0.00	400.00	541.96	428.32	506.09	400.00	463.08
Pressure	*bar*	200.00	200.00	200.00	199.97	199.97	199.93	199.93	199.92
Mass Flows	*kg/h*	816.93	622.34	706.74	706.74	893.72	893.72	893.72	893.72
Mole Flows	*kmol/h*	93.92	66.13	78.59	72.10	92.89	88.47	88.47	84.93

		R4		R5		R6		AMMONIA	SPURGO
		IN	OUT	IN	OUT	IN	OUT		
Temperature	*°C*	349.37	449.75	340.00	405.78	327.17	402.09	0.00	0.00
Pressure	*bar*	199.92	199.91	199.91	199.91	199.91	199.91	199.91	199.91
Mass Flows	*kg/h*	1174.53	1174.53	1174.53	1174.53	1439.27	1439.27	550.16	266.73
Mole Flows	*kmol/h*	116.16	108.81	108.81	104.09	133.53	126.94	32.46	28.34

Mass Fractions	H2 + N2	RECYCLE	R1		R2		R3	
			IN	OUT	IN	OUT	IN	OUT
H_2	0.1696	0.1425	0.1579	0.1301	0.1359	0.1209	0.1209	0.1090
N_2	0.7857	0.6600	0.7313	0.6026	0.6295	0.5602	0.5602	0.5048
CH_4	0.0446	0.1193	0.0769	0.0769	0.0769	0.0769	0.0769	0.0769
H_2O	8.70E-05	2.65E-09	4.94E-05	4.94E-05	4.94E-05	4.94E-05	4.94E-05	4.94E-05
NH_3	0	0.0783	0.0339	0.1903	0.1576	0.2419	0.2419	0.3093

Mass Fractions	R4		R5		R6		AMMONIA	SPURGO
	IN	OUT	IN	OUT	IN	OUT		
H_2	0.1207	0.1017	0.1017	0.0896	0.1021	0.0883	0.0008	0.1425
N_2	0.5590	0.4713	0.4713	0.4150	0.4731	0.4090	0.0035	0.6600
CH_4	0.0769	0.0769	0.0769	0.0769	0.0769	0.0769	0.0084	0.01193
H_2O	4.94E-05	4.94E-05	4.94E-05	4.94E-05	4.94E-05	4.94E-05	0.0001292	2.65E-09
NH_3	0.2434	0.3500	0.3500	0.4185	0.3478	0.4257	0.9871	0.0783

The purge is set to eliminate all the methane that is fed to the loop. In the stream $H_2 + N_2$ 36.44 kg/h of CH_4 are present and in the splitter 31.82 kg/h are purged so, the 87.32 % wt of CH_4 is eliminated whereas the remaining 4.62 kg/h are condensated and collected in the stream *"AMMONIA"*.

Overall, from a 1000 kg/h of dry pine sawdust biomass and 640 kg/h of nitrogen, with this plant one can obtain 550 kg/h of ammonia 98.8 % wt.

6 - Conclusions

The simulation of a hydrogen production process from pine sawdust gasification is here proposed as example of green hydrogen production. This unit has been successfully coupled with an ammonia synthesis loop in a fully integrated plant.

Before the simulation, an extensive work has been done in order to suitably represent the properties and the reactivity of biomass during the gasification, considering that unconventional components are included in the process and that different types of mixtures are present, each of them requiring its own thermodynamic package.

MSR, HT-WGS and LT-WGS reactors were designed in order to maximise the hydrogen yield and careful hydrogen purification was considered to cope with the stringent purity specifications of the ammonia synthesis loop. All these unit operations were designed according to specific kinetic equations in order to obtain a reliable sizing, selected and validated under similar operating conditions. Also absorbers and strippers were designed according to rate-based algorithms. This is specifically important and almost never found in the literature. Indeed, most reports include equilibrium calculations, but the flowrates or sizing details reported in such cases may be fully unreliable. Indeed, if it is not properly verified that in a real column such flowrates can properly match with a given packing or tray type, a severe underestimation of the working conditions can be concluded, estimating as feasible what is not practically achievable.

Concerning the CO_2 scrubbing, for instance, the sizing and convergence of this block was very difficult and at last feasible only by decreasing the CO_2 to be absorbed thanks to the addition of a CO_2 methanation unit.

About the ammonia synthesis loop, it has been developed in a previous work and here adapted and merged with the renewable hydrogen production section.

It is important to consider that in this flowsheet we are potentially underestimating the hydrogen production since we are not considering the option of char gasification.

Overall this green ammonia synthesis plant, based on hydrogen production from biomass gasification, is able to deliver 500 kg/h of ammonia, to be used as hydrogen vector.

Acknowledgements

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