

Purification of a syngas stream for the production of hydrogen for fuel cells standards

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Abstract

Climate change is a topic of increasing relevance in the last years, and the focus on new energy resources is fundamental in order to tackle it. Hydrogen has been defined as a promising candidate to replace fossil fuels in many areas, and its use is increasing at a rapid pace. Cortus Energy, a startup based in Sweden, designs biomass gasification plants, with a patented technology named WoodRoll®. This technology delivers a clean syngas which can be further upgraded to hydrogen for industrial and commercial use. This thesis has the objective of studying the purification of a syngas stream, produced through pyrolysis and subsequent gasification of biomass, in order to power a fuel cell system.

The possible purification systems are analyzed in the State of the art section, and from the analysis of all the possibilities, the PSA – Pressure Swing Adsorption – is selected as the setup that best suits the technical specifications and setup of WoodRoll®, coupled with a Water-gas shift reaction. The concept of adsorption on solids is reported and a theoretical and mathematical background is given on the phenomena of adsorption and the different theories that model it. An outlook on fuel cells and their current technological state is presented.

The possible setups are described together with the simulation run on the theoretical system; the simulations consider the variation of the cycle time, the gas composition and the adsorbent. The results are explained and commented in Chapter 5, together with a cost estimation of the unit and its P&ID.

1. Introduction

In recent years, the use of hydrogen has had an important increment: the increase in hydrogen production is due mainly to petrochemical processes such as biodiesel production and hydrocracking. In fact, most of the production of hydrogen is made on-site in chemical plants in order to have a feedstock to use in different reactions. Hydrogen is currently produced mainly through natural gas reforming and coal gasification [1], as they are well-established technology that can treat large productions. Hydrogen can be as well produced by biomass gasification. Biomass gasification has been predicted to be one of the cheapest ways of producing hydrogen in the future and has the strong advantage of being carbon neutral [2].

The use of hydrogen as an energy source has been strongly limited by multiple factors, among which the most determining were the availability of other

cheap feedstocks and the fact that it is a difficult material to handle. It has an extremely high heating value (around 142 MJ/kg) that makes it a high-quality fuel mass-wise; on the other hand, it has a low density and it has a wide flammability interval. In recent years, the fuel cells technology has expanded greatly thanks to the reduction of their manufacturing cost, and they have been applied in areas such as backup power.

This thesis has the objective of studying the purification of a syngas stream, produced through the WoodRoll technology in order to power a stationary fuel cell system. More precisely, the system could be fed with a side stream of clean syngas with the nominal flow-rate of 6 Nm³/h; the scope of this thesis is to identify a practical solution for the task of purifying the gas and power a fuel cell and define the reactors and subsystems needed to do it.

This study has been performed at Cortus Energy, a company based in Sweden that designs biomass

gasification plants. The particular feature of Cortus Energy's process is that it uses a patented technology named WoodRoll, that produces a clean gas composed mainly of hydrogen and carbon monoxide, that can be further upgraded to hydrogen for industrial and commercial use.

2. State of the art

The use of adsorption cycles has been common for a few decades since the process is far less energy intensive in comparison to purification through distillation: in the second case, a great amount of electricity has to be spent in order to cool the gas down to a level in which it can change phase. There are two different systems that use a similar principle to work: they are the PSA – Pressure Swing Adsorption – and the TSA – Temperature Swing Adsorption. They work on the principle that states that, by changing the partial pressure of a gas on an adsorbent material, the quantity that this material can adsorb will vary as well. Since there is no availability of waste heat and the unit is considerably bigger, PSA has been chosen as the preferred system for the case of WoodRoll.

Different theories have been developed in order to properly describe the phenomenon of adsorption: it is relevant, to have a close prediction, to know how the adsorption takes place. This is dependent on the number of layers of adsorbate that can build on the surface, and on the geometry of the adsorbent. An adsorbent is usually targeting a particular molecule, in other words, it will adsorb a greater quantity of a molecule rather than others. The main categories of adsorbents are the activated carbons, the molecular sieves, and the zeolites.

According to the modality adsorption takes place, the correlation between the amount of gas adsorbed and the pressure gives a plot. These types of diagrams are named "isotherms" and correlate the partial pressure of a gas to the amount of gas adsorbed on the solid. There are six main types of isotherms that have been categorized by Brunauer [3]. The isotherms define the different types of adsorption that occur on surfaces. Isotherms have different shapes, connected to the number of layers and to the adsorption mechanisms. The curve can be similar to a logarithm curve, but can sometimes have steps, or other particular shapes. The basic theory has been anticipated by Henry in the XVIII century with the law on gas adsorption on water and is true for the low pressures.

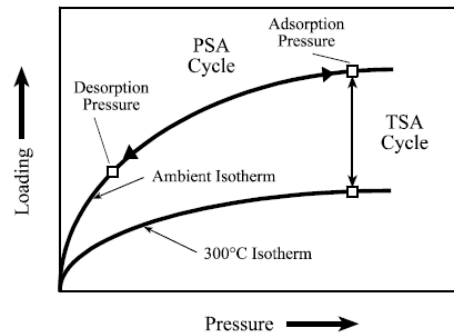


Figure 1. Working scheme of PSA and TSA

By changing the temperature, the isotherm changes as well according to a Van't Hoff equation; as a general rule, by increasing the temperature, the material will adsorb less gas. This fact is unfavorable in the case of cycles, as the adsorption of a molecule on a surface results in the emission of heat.

In Figure 1 are reported the two adsorption cycles: the PSA uses the concept of cyclically changing the pressure in order to achieve the separation, while the TSA swings the temperature. In general, PSA is more used as it is less energy intensive, but TSA is used in case of presence of waste heat to be used.

Once purified, the hydrogen can be used in a fuel cell. A fuel cell is an electrochemical system that is using the oxidation of hydrogen in order to generate electricity. The difference with a standard chemical reaction is in the fact that a fuel cell generates directly a flux of electrons, without having the loss in efficiency that comes from the transformation of the reaction energy in heat. A fuel cell has usually an efficiency around 50% on the fuel; in the case of a combined heat and power solution, the total efficiency can reach 90%. Fuel cells require being fed with high-quality fuels because their electrodes are composed by precious catalysts - such as platinum - that would get irretrievably poisoned by the presence of a high concentration of CO. The catalyst is a fundamental component of the fuel cell as it allows to split the molecules of fuel into atoms, and then allowing them to be recombined. The fuel cells that have been considered for the setup have a good resistance to carbon monoxide and can stand up to 25 ppm of CO. Fuel cell vehicles require a very high gas purity, with a maximum amount of CO of 0.2 ppm.

3. Simulation of the system

The unit has been simulated through the solution of a system of partial differential equations that model the phenomenon of adsorption. The system has been modeled with a basic Skarström cycle, consisting of four phases of pressurization, adsorption, blowdown, and purge. The unit consists of two adsorption columns: the phases are timed in order to always have a column that can receive the feed. While one column is in adsorption phase, the other column is in regeneration phase, and when a column is in pressurization, the other one is in blowdown.

The adsorption column has been divided in slabs, each one with the same characteristics and the condition of being perfectly mixed. The radial effects of molecular and thermal diffusion have not been considered in the simulation. The thermal dependence of adsorption on temperature has not been considered too. The solution has been implemented using forward Euler method for the integration, and the adsorption on the materials has been described with the Linear Driving Force model.

Two important parameters to describe adsorption are the concentration of the gas phase C and the amount of gas phase on the solid adsorbent q , mutually dependent.

The equations used to describe the systems are describing the conservation of mass, the kinetics of adsorption and the amount of adsorbate that can be charged on the adsorbent. Equation 1 is presenting the conservation of a component on a slab; the equation considers the porosity of the adsorbent ε , the density of the solid ρ_s and the velocity u . The system is described according to the dimensional variables time t and space in the column z .

$$\frac{\partial C_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \rho_s \frac{\partial q_i}{\partial t} + \frac{\partial(uC)}{\partial z} = 0 \quad (1)$$

Equation 2 is describing the Linear Driving Force model, thus the model used in the simulations. The use of this equation is simplifying the complex adsorption mechanisms otherwise described by systems of equations more laborious to solve [4]. k_{ldf} is the linear driving force constant, regulating the adsorption kinetics; it is usually calculated through experiments.

$$\frac{\partial q_i}{\partial t} = k_{ldf}(q_{sat} - q_i) \quad (2)$$

Equation 3 is used to calculate the maximum quantity of adsorbate that can be charged on the

adsorbate, as a function of pressure. The two parameters used, q_{max} and b , are specific for the interaction between the adsorbent and the adsorbate and can be found experimentally.

$$q_{sat} = \frac{q_{max,i}bp}{1 + bp} \quad (3)$$

Two different configurations have been tested; the difference between them is the way the gas is treated. In one configuration, named "single pass", the stream of syngas is treated through every reactor, one after another, in a linear setup. In the second configuration, named "double pass", a double stage treatment has been implemented: the off-gas of a first PSA is treated through a water-gas shift reaction and then purified through a second PSA.

The two systems are represented with Process Flow Diagrams in Figure 2 and Figure 3.

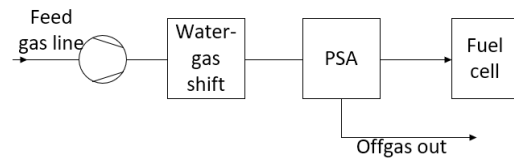


Figure 2. Process flow diagram of the single-pass system

The reason why a second configuration is developed is the higher yield that the water-gas shift reaction has in this case and the possibility of producing gases with different compositions.

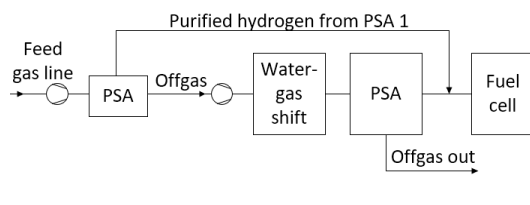


Figure 3. Process flow diagram of the double-pass system

The simulations have been carried out by varying the most important parameters of the system, which are:

- The composition of the gas
- The type of adsorbent
- The cycle time

The compositions of the tested gas are reported in Tables 2 and 3 [5].

- **Table 1.** Composition of the raw gas

Component	% molar
H ₂	59.1
CO ₂	11.0
CO	27.9
CH ₄	2.0

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- **Table 2.** Composition of the gas previously treated with WGS

Component	% molar
H ₂	67.7
CO ₂	29.8
CO	0.9
CH ₄	1.6

The composition of the raw gas has been measured in the test plant after the gas cleaning unit [6], while the composition of the gas after the water-gas shift reaction has been calculated in a thesis previously completed at Cortus [5].

Two different adsorbents have been selected, namely an activated carbon and a carbon molecular sieve that has been used in similar experiments.

The parameters of the two materials are reported in Table 1.

Table 3. Langmuir parameters of the adsorbents

Molecule	Activated Carbon Norit R1 Extra		Carbon Molecular Sieve Carbotech CMS H2 55/2	
	n_{max} (mmol/g _{ads})	b (1/Pa)	n_{max} (mmol/g _{ads})	b (1/Pa)
CO ₂	12.5	1.74	6.5	0.4
CH ₄	7.41	1.35	4	0.4
H ₂	2.87	0.31	0.5	0.6
CO	5.76	1.74	3	0.6
N ₂	5.49	0.6	2.5	0.6

The activated carbon was chosen according to a study that simulated a similar system [7], while the parameters of the Carbon molecular sieve were reported in a brochure by the manufacturer Carbotech.

The time of the cycle has varied between the intervals of 240 seconds for the short cycle and 1200 seconds for the long cycle. For the slow adsorption cycle, the pressurization and blowdown phase are 100 seconds long, while the adsorption and purge steps are 500 seconds long. For the fast adsorption cycle, the pressurization and the blowdown last for 20 seconds while the adsorption and purge steps last for 100 seconds.

The column has been hypothesized to be 1.5 meters long, with a diameter of 20 centimeters. The diameter of the column has to be adapted in order to be optimized for the fluid flow. If the setup is requiring a low Reynolds number, the diameter shall be increased because of the low velocity. The obtained optimal diameters were 22 centimeters for the slow cycle and 18 for the fast cycle.

Results

Eight possible setups have been simulated, by changing the aforementioned parameters. The plots of q and C have been obtained, and an example is reported in Figure 4. This graph shows the cyclical variation of the adsorbate concentration in the adsorbent over three cycles; the different gases are reported in different colors. Each gas is described by two Langmuir constants that define the shape of its isotherm, and by a Linear Driving Force constant that describes the kinetics of the adsorption. In Figures 4 to 6 are shown the data from one of the simulations, in particular, the simulation of a slow cycle on a non-treated gas, using Activated Carbon as an adsorbent.

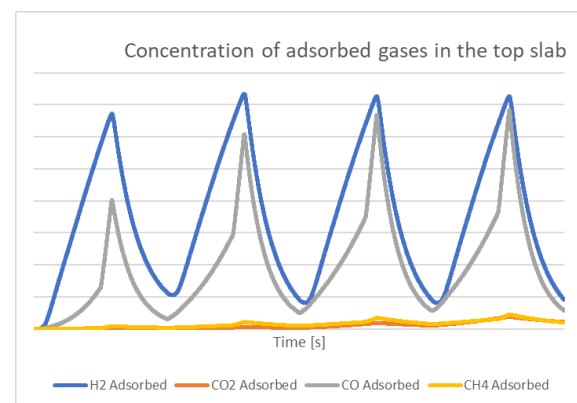
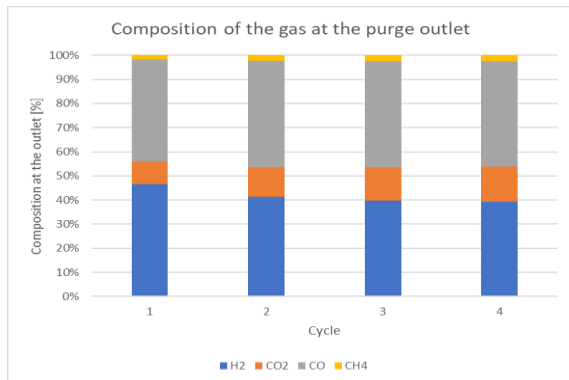
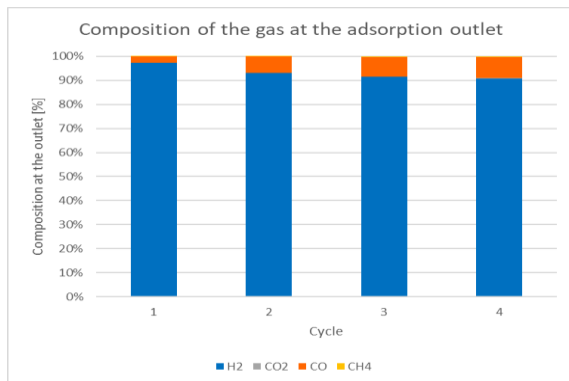


Figure 4. Pattern of the adsorbed material in the bottom slab of the column, first 4 cycles

Figures 5 and 6 show the composition of the gas at the outlet in the first four cycles of the simulation

previously mentioned. The composition at the purge is reflecting the gases desorbed during the purge phase and has thus a higher amount of CO and CO₂.



Figures 5, 6. Composition of the gas at the outlet of the phases of Adsorption and Purge

The simulations have been stopped once the quasi-steady state had been reached. The quasi-steady state has been reached after a number of cycles between 4 and 25, according to the different configurations. The results of the simulations are reported in Table 4. In the case the sum of the components is not equal to 100%, it is because of numerical approximations.

Table 4. Results of the simulations

Setting	Purity reached at QSS				Cycles before QSS
	H ₂	CO ₂	CO	CH ₄	
Raw gas, slow cycle, CMS	82.9	2.4	12.9	1.7	4
Raw gas, slow cycle, AC	89.9	0.7	8.7	0.6	11
Raw gas, fast cycle, CMS	73.0	5.9	19.7	1.4	21
Raw gas, fast cycle, AC	72.3	3.4	22.7	1.5	20

cycle, AC					
WGS, slow cycle, CMS	91.5	6.8	0.4	1.3	5
WGS, slow cycle and AC	96.3	2.9	0.3	0.5	16
WGS, fast cycle and CMS	80.1	17.7	0.6	1.6	7
WGS, fast cycle and AC	80.7	17.6	0.6	1.1	22

The use of the longer cycle is always overperforming the shorter. This is because the adsorbent has sufficient time in order to charge and discharge the adsorbate. On the other hand, in the short cycle, the adsorbent is never properly regenerated.

The Activated Carbon has an excellent performance towards CO₂, and achieves the best results in the case of a long adsorption cycle with the gas previously treated by a WGS reaction, obtaining a gas composed by 96.5% of H₂ and 0.3% of CO. The use of a gas previously treated with WGS makes the feed gas to the PSA simpler to handle, as the unwanted gas is mainly the only CO₂, while in the case of raw gas it is a mixture of CO and CO₂.

The use of gas previously treated with a Water-gas shift reaction helped to improve the selectivity of the adsorbent. Usually, each adsorbent is used to target especially one single gas; in this case, the use of activated carbon with carbon dioxide was perfectly suiting because of the high amount of CO₂ that can be charged on the adsorbent.

During the internship at Cortus, a Piping and Instrumentation Diagram – P&ID – has been produced and from it a budget estimation has been performed. The total cost of the unit, considering the projecting and installation costs, are about 2.1 million SEK in the configuration with a single pass, and about 3.1 million SEK in the case with a double stage.

Discussion

The simulations didn't show to reach the desired purity required for fuel cells applications. The reasons why the result was not as required by fuel cell purity are the simplifications of the real system, the limitations of the simulation program, and the use of a simple cycle that has not been

optimized for the particular composition of the gas produced by the WoodRoll®.

During the period spent at Cortus, multiple suppliers and research centers have been contacted and the feedback has been positive: by using an optimized cycle and good adsorbent materials, the specifics required by stationary and automotive fuel cells can be accomplished. This would require an optimization of the cycle and of the adsorbents.

Conclusions

Different possible setups for the system have been analyzed, and it has been selected to use a Pressure Swing Adsorption, possibly coupled with a Water-gas shift reaction. Simulations have been run on a Skarström cycle, by supposing a system consisting of two adsorption columns. Three main parameters have been varied: the cycle time, the composition of the gas and the adsorption material.

The use of a sufficient desorption time is fundamental to regenerate the adsorbent, and the

simulations with the shorter time show a clearly lower performance in comparison to the longer cycle. The use of Activated Carbon is extremely effective in the case of a high amount of carbon dioxide, such as in the case of gas previously treated with WGS.

The unit has a high capital cost, particularly because of the high purchase price of the main components and because of the complex control system. A cost-benefit analysis should be performed in order to assess the choice between a single-pass or a double-pass system.

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