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Guðmundur Gunnarsson
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Author Guðmundur Gunnarsson

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Publisher Innovation Center Iceland
Keldnaholt, 112 Reykjavik
E-mail: nmi@nmi.is
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Abstract

The Hellisheiði power plant near Reykjavik emits considerable quantities of non-condensable gas as other geothermal power plants in Iceland and elsewhere. Concentration of CO₂ in the gas is about 55% (by volume), that of H₂S about 25% and that of H₂ about 15- 17%. The remainder is mainly N₂ and O₂, originating from air which leaks into the vacuum system after the last turbine step. The geothermal power companies in Iceland (ON, Landsvirkjun and HS Orka) have now developed a process, Sulfix II, for the removal of most of the H₂S and part of the CO₂ from the gas of geothermal power plants. This process is based on washing the gas with water under pressure, resulting in an aqueous solution, containing H₂S and CO₂, which is injected into boreholes in the periphery of geothermal fields. The H₂S and CO₂ enters fissures and cracks at a depth of 600 – 2000 m, where they react with minerals in the rock to become permanently stored. In this report we describe how the H₂S removal capacity of the Sulfix process was doubled by some process modification. The gas from the Sulfix plant has higher H₂ content (35%) and lower H₂S content (1 – 4%) than the gas to Sulfix II. It is the main objective of this study to investigate if the gas can be used for the production of methane but production of hydrogen is also given some consideration. Microbial methanation was found to be the method best suited for methane production, mainly because it can tolerate some H₂S in the gas. Sometimes it is necessary to add electrolytic hydrogen to the gas to adjust the H₂/CO₂ ratio to 4, which is the ratio preferred for methanation. To make the gas suitable for methanation it may also be necessary to remove sulphur remaining in the gas, for example with a microbial desulphurisation method. In some case it is also necessary to remove N₂ and O₂ in the gas, for example with membranes. The possibility of using a second water washing step to remove H₂S and CO₂ and increase the H₂/CO₂ ratio was investigated. Four process alternatives for treating the gas so that it becomes suitable for methanation are described and the cost of methanation estimated. The cost of methane production in the four cases was found to be from 1,25 €/Nm³ methane to 1,8 €/Nm³. The least costly alternative involves microbial desulphurisation and membrane treatment resulting in gas with H₂/CO₂ =1. Electrolytic hydrogen is then added to adjust the H₂/CO₂ ratio to 4, resulting in methane production capacity of 263 Nm³/h, which is similar to the current production of methane in Iceland.

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1 Introduction

Geothermal power plants in Iceland emit considerable quantities of non-condensable gas. The components are mainly CO₂, H₂S and H₂, but their concentration can vary greatly between different power plants and boreholes. Until recently the non-condensable gas has been emitted to the atmosphere but because of new environmental regulations processes are now being developed to limit H₂S emission to the atmosphere. The geothermal power companies in Iceland, Landsvirkjun, Orka náttúrunnar (ON) and HS Orka, are now working together to find/develop cost effective methods to remove the H₂S from the geothermal gas and deposit it underground at the periphery of geothermal fields. Orka Náttúrunnar (ON) owns and operates a 300 MW geothermal power plant at Hellisheiði, in relations to this plant a pilot plant called Sulfix II is now being optimised in order to separate H₂S from the gas. The H₂S, and some of the CO₂, is dissolved in water in a water scrubber (absorption column) and pumped to boreholes in the periphery of the geothermal filed. This borehole is 2000 m deep and in the top of the boreholes is a 750 m long steel pipe, the remaining 1250 m to the bottom of the borehole consisting of bare rock. The water solution of H₂S and CO₂ exits the steel pipe at a depth of 750 m and continues its journey down the borehole, where it enters cracks and fissures to be distributed in the rock surrounding the borehole. There H₂S and CO₂ react with minerals in the rock to be permanently stored in the rock. The off gas from the Sulfix II treatment plant can contain 30 – 50 vol% H₂ and 30 – 60 vol% CO₂, depending on process conditions (flow rate of gas, flow rate of water to scrubber, pressure temperature of water etc.). In this report we summarise the results of recent experiments on optimisation of the water scrubber where the objective has been to maximise the quantity of H₂S removed from the gas. First we report shortly on the composition of gas to the scrubber and the fluctuation in gas composition that can be expected. Then recent tests on optimisation of the scrubber are described and finally some methods for further treatment of the gas from the scrubber are outlined, where the objective is to obtain gas the can be used for methane production. In this work we will assume that microbial methods are used for methanation. For methanation the H₂/CO₂ ratio should preferably be four and the content of inert gases (for example N₂) should be lower than 1% so that methane of sufficient quality for used in vehicles can be obtained. An advantage with the microbial methantion method is that the gas can contain some H₂S (up to 6000 ppmv and possibly higher) since the microorganisms can use H₂S as nutrient.

Four processes for the production of methane from of gas from the Hellisheiði power plant that has been treated in different ways are then described. In three of the cases it is assumed that electrolytic hydrogen is added to achieve the desired ratio H₂/CO₂ = 4. The manufacturing cost of methane is then estimated for the different cases.

Several references are made to earlier memos which have been written during the project, a complete list of these memos can be found in the Appendix.

The work described here has been carried out in cooperation with Orka Náttúrunnar (ON), Landsvirkjun and HS Orka. The project was financed by the above companies and Georg (Geothermal Research Group) as project 15-06-2015 and by Orkusjóður under grant no. 2015030029-2015.

Many of the simulation described in this report were carried out by Magnús Þór Árnasson from Mannvit, which provides engineering services. He also supplied the cost estimates for water washing and flashing.

2 Gas to scrubber

Gas to the scrubber is obtained from turbines 1 – 4 in the power plant. The composition of gas to the scrubber in the period June 2014 to June 2015 is shown in Figure 1.

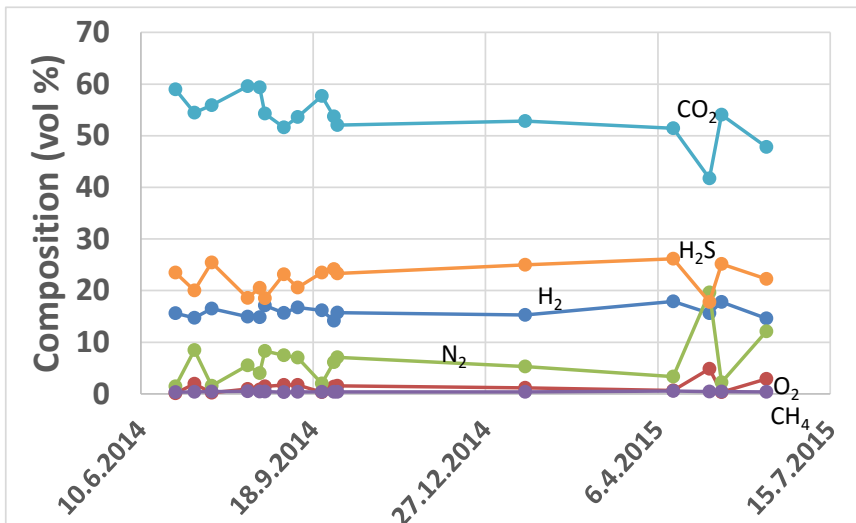


Figure 1. Composition of gas (dry) to scrubber in the period June 2014 – June 2015 (data from ON).

Figure 1 shows that there is some variability in the composition of the gas, especially large fluctuations in nitrogen (and oxygen) content are observed. This is largely due to different levels of leakage of air into the off gas system, whose pressure is below that of atmospheric pressure in the exit from the last turbine step. Leakage is partly through shaft seals.

Another reason for the variability of composition of the gas is that the geothermal fluid from different boreholes contains gas of different composition. The same boreholes are not always used to supply geothermal fluid to the power plant.

In the beginning of June 2015 the composition of the gas to the scrubber was measured more frequently and the nitrogen content was found to be low because of limited leakage of air into the system, see Figure 2, but a few days later the concentration of N₂ increased to above 10 vol%.

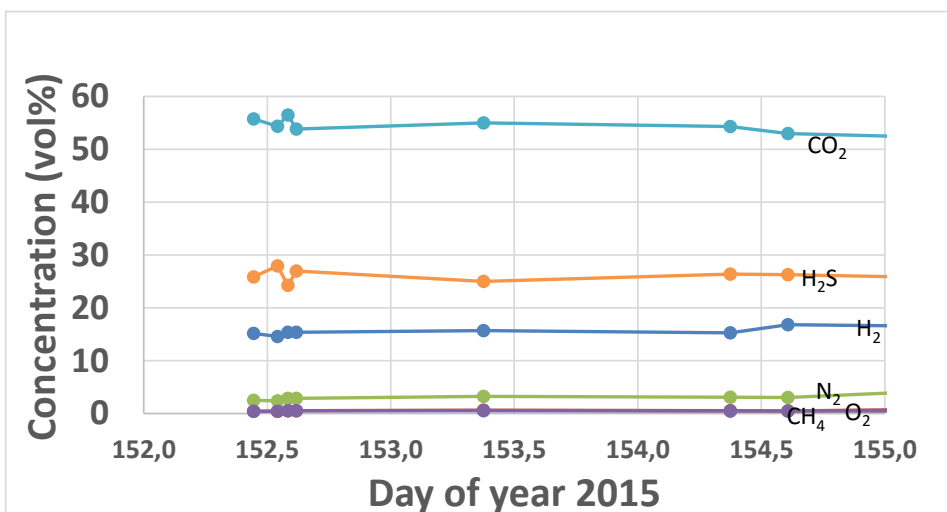


Figure 2. Composition of gas (dry) to scrubber from June 1 to June 3, 2015 (data from ON).

This demonstrates that one has to assume that there is always some N₂ in the gas to the scrubber, possibly about 5 – 10%.

3 First water washing step

3.1 Water washing to remove H₂S

An absorption column (scrubber) for water washing of part of the gas from the Hellisheiði power plant was designed and constructed. In simulation of the absorption process it was assumed that the water to the absorption column is condensate water from the turbines that has been cooled to about 20 °C and flow rate under normal operation is 36 kg/s. The flow rate of water saturated gas is 0,40 kg/s at a pressure of 5 bara and temperature of about 40 – 50 °C. Assumed composition and flow rate of gas and the flow rate and composition of gas from the scrubber, according to simulations is shown, in Table 1 (Mannvit 2013).

Here it should be noted that in the simulations it was assumed that the gas to the scrubber contained 25 vol% H₂, which is 10% more than what is found in practice, see Figure 1 and Figure 2.

Table 1. Composition of flow rate of gas to Sulfix II, and the resulting flow rate of gas from Sulfix II and its composition according to simulations (Mannvit 2013).

	To Sulfix II		From Sulfix II	
	Flow rate (kg/s)	Composition (vol%)	Flow rate (kg/s)	Composition (vol%)
H ₂ S	0,11	25,0%	0,0023	1,1%
CO ₂	0,2757	48,4%	0,1186	43,8%
H ₂	0,0064	24,5%	0,0063	50,8%
N ₂	0,0056	1,5%	0,0056	3,2%
O ₂	0,0009	0,2%	0,0009	0,5%
CH ₄	0,0006	0,3%	0,0006	0,6%
Sum	0,3992	100,0%	0,1343	100,0%

Composition of the gas from the scrubber was monitored during 1 year from June 2014 to June 2015, see results in Figure 3. Comparison with Figure 1 shows that the bulk of the H₂S has been removed since the concentration of H₂S decreased from about 25 vol% in the inlet gas to the scrubber to 1 – 3% in the outlet gas from the scrubber. Some of the CO₂ is also absorbed, and the concentration of gases with limited solubility (H₂, N₂, CH₄) in water increases.

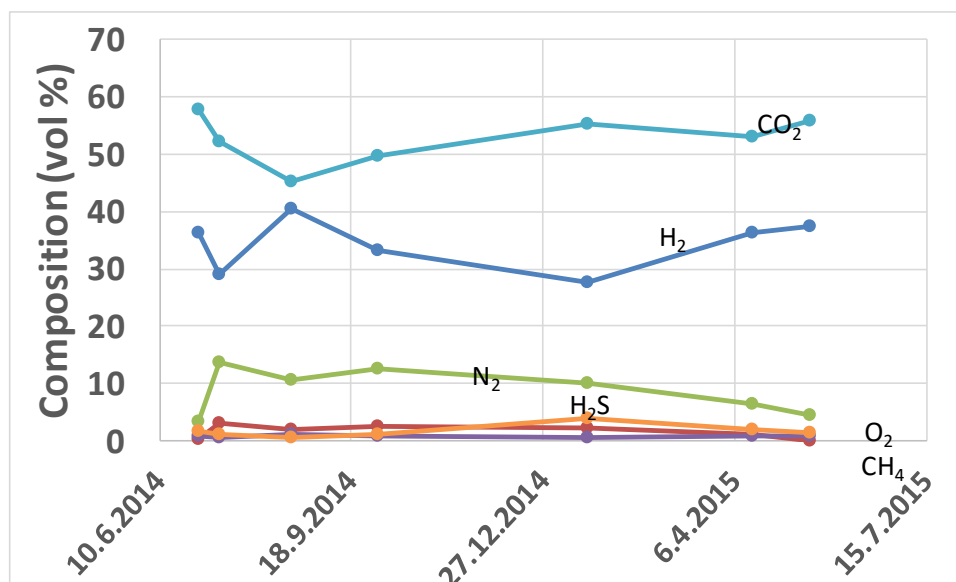


Figure 3. Composition of gas (dry) from water scrubber in the period June 2014 – June 2015.

The primary objective with the scrubber was to remove H_2S from the gas and pump the aqueous solution of H_2S (with some CO_2) underground, as described above. The Sulfix II plant was originally designed to treat only part of the gas from the power plant. Because of the success of H_2S removal with the scrubber the following question came up: Can the scrubber be used treat even more gas than previously assumed and in that way even increase the quantity of H_2S stored underground, and thus decrease further the quantity of H_2S released to the atmosphere?

The capacity to the scrubber was investigated in the beginning of June 2015 when the composition of the gas to the scrubber was as shown in Figure 2. Flow rate of water to the scrubber was varied between 10 and 60 l/s and the gas flow rate was kept constant at about 0,5 kg/s. Pressure in the scrubber was 5 bara. The results are shown in Figure 4.

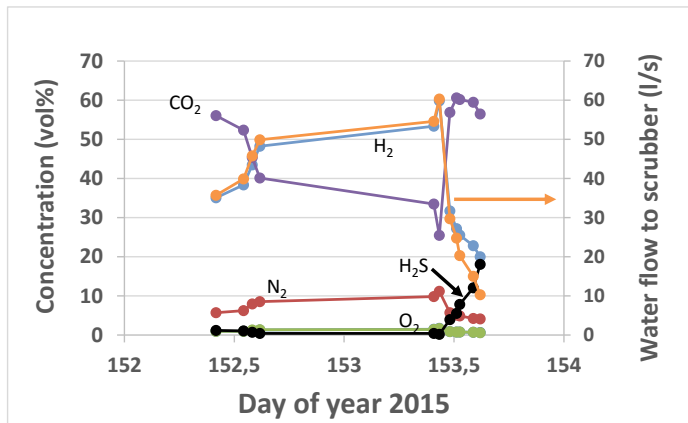


Figure 4. Results of capacity test of Sulfix II scrubber in beginning of June 2015, where the chemical composition of gas from scrubber is shown (Data from ON).

The results were compared with simulations of the scrubber under the experimental conditions, see comparison for H_2 , H_2S and CO_2 are shown in Figure 5 and Figure 6.

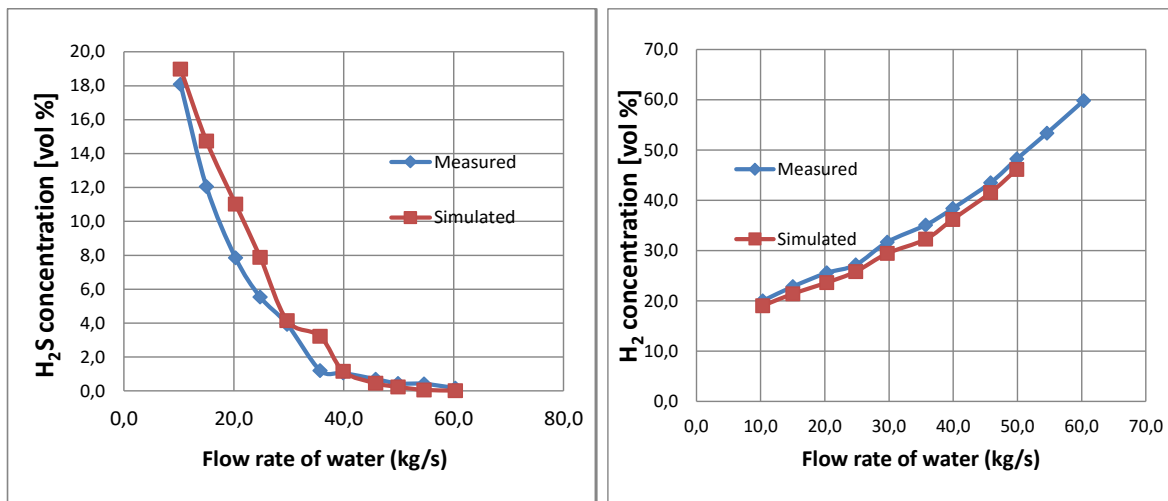


Figure 5. Concentration of H_2S and H_2 in gas from Sulfix II scrubber as function of flow rate of water to scrubber. Measured values and simulated values are shown (Magnús Þór Arnarson 2016).

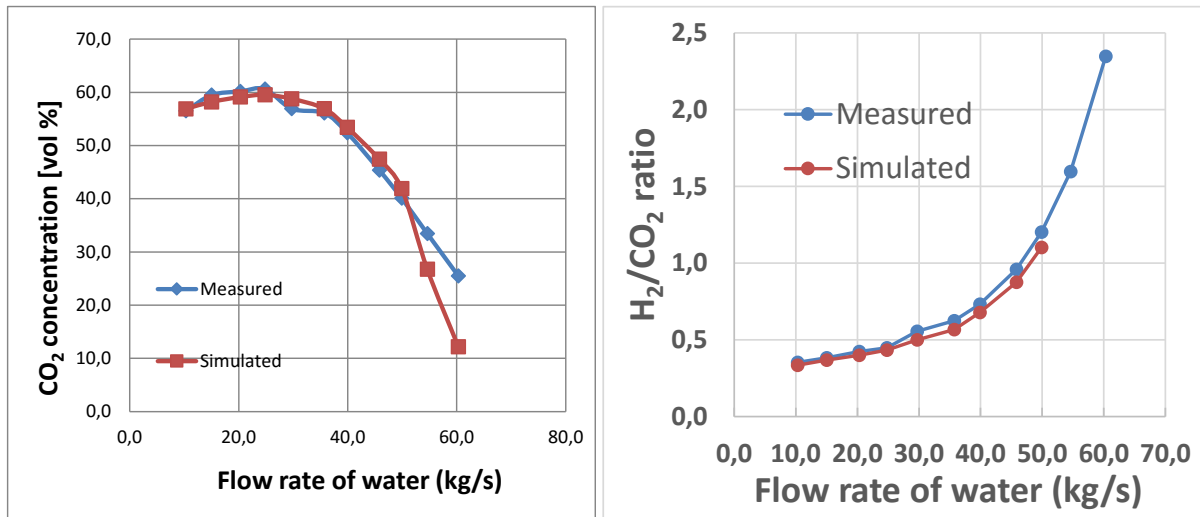


Figure 6. Concentration of CO₂ in gas from Sulfix II scrubber as function of flow rate of water to scrubber. Measured values and simulated values are shown (Magnús Þór Arnarson 2016).

When the water flow rate increases, at constant gas flow rate, the ratio of H₂/CO₂ in the gas from the scrubber increases, see Figure 6. For production of methane this ratio should be 4. This may possibly be achieved by more extensive water washing of the gas than described above. Simultaneously the H₂S in the gas would be reduced to below 2000 ppmv.

The capacity of the Sulfix II plant for increased removal of H₂S has been simulated under the process conditions shown in Table 2 (Magnús Þór Arnarson 2016). The results are shown in Table 3

Table 2. Process conditions for increased capacity Sulfix II plant.

Flow rate of water to scrubber	50 kg/s
Temperature of water to scrubber	15 °C
Pressure of water to scrubber	10,0 bara
Flow rate of gas to scrubber	0,83 kg/s
Temperature of gas to scrubber	40 °C
Pressure of gas to scrubber	6,0 bar

Table 3. Composition and flow rate of gas to increased capacity Sulfix II, and the resulting flow rate of gas from increased capacity Sulfix II and its composition according to simulation (Magnús Þór Arnarson 2016)

	To increased capacity Sulfix II, T=40°C		From increased capacity Sulfix II, T=15°C	
	Flow rate (kg/s)	Composition (vol%)	Flow rate (kg/s)	Composition (vol%)
H ₂ S	0,2073	24,2%	0,0045	1,3%
CO ₂	0,5616	50,7%	0,2320	53,5%
H ₂	0,0073	14,3%	0,0072	36,1%
N ₂	0,0185	2,6%	0,0183	6,6%
O ₂	0,0036	0,4%	0,0035	1,1%
CH ₄	0,0017	0,4%	0,0016	1,0%
H ₂ O	0,0327	7,2%	0,0005	0,3%
Sum	0,8000	100%	0,2676	100%

To achieve the conditions shown in Table 2 a new compressor with increased pressure and gas flow rate needs to be installed, as well as new heat exchangers for water to the scrubber. Some modifications in the internals of the adsorption column are also needed.

Comparison of Table 1 and Table 3 shows that by the above modification it is possible to increase the capacity of the Sulfix II column to remove H₂S by about 100%. However, here it should be pointed out that experience tells us that the H₂S removal capacity of scrubber is overestimated, it is likely that the H₂S flow rate from the scrubber is larger than that shown in Table 3, which may result in gas flow rate and composition as shown in Table 4. It is also likely that the flow rate of N₂ and O₂ will be higher than shown in Table 3

Table 4. Likely flow rate and composition of gas from increased capacity Sulfix II plant.

	Flow rate (kg/s)	Composition (vol%)
H ₂ S	0,0113	3,3%
CO ₂	0,2256	51,5%
H ₂	0,0072	36,1%
N ₂	0,0184	6,6%
O ₂	0,0035	1,1%
CH ₄	0,0017	1,0%
H ₂ O	0,0005	0,3%
Sum	0,2682	100,0%

If methane was produced from the gas from increased capacity Sulfix II (see composition in Table 4), the methane would contain about 13 vol% N₂, which is too high for application as fuel for vehicles. Preferably most of the N₂, O₂ and H₂S should be removed before methane synthesis.

3.2 Recovery of carbon dioxide from solution from first washing step

The solution from the scrubber is at a pressure of 6 bara and 15 °C and contains the CO₂ and H₂S scrubbed from the gas. The solution is now injected in the periphery of the geothermal field, where the dissolved gas react with minerals in the rock, as described in the introduction.

By heating this solution to 85°C under pressure and flashing at 6 bar it is possible to recover some of the CO₂ dissolved in the solution, as well as part of the H₂S. The quantity of CO₂ and H₂S that can be recovered in this way has been simulated, see results in Table 4.

Here it was assumed that the composition of gas from Sulfix II is as shown in Table 4.

Table 5. Flow rate of gas to and from increased capacity Sulfix II and flow rate of gas obtained from flashing solution from Sulfix II at 85°C and 6 bara.

	Gas to Sulfix II (kg/h)	Gas from Sulfix II (kg/h)	Gas from flashing (kg/h)
Hydrogen Sulfide	746,3	16,2	290,5
Carbon Dioxide	2021,8	835,2	720,4
Hydrogen	26,3	25,92	0,4
Oxygen	13,0	12,6	0,4
Nitrogen	66,6	65,88	0,7
Methane	6,1	5,76	0,0
Water	117,7	1,8	47,5

It should be noted that gas from flashing contains very small quantities of N_2 and O_2 . The H_2S content is however very high, which would require H_2S removal (about 2500 t/year) if the CO_2 is to be used for methane production or in greenhouses. A disadvantage of this approach is that H_2S injected is reduced from about 6400 tonnes per year to about 3200 tonnes per year.

4 Second water washing step

4.1 Water washing to remove H₂S

The gas from the enhanced capacity Suffix II plant contains several percent H₂S, see Table 3. This can be decreased further in a second washing step in a 0.8 m diameter washing column with a packing height of 6 m. The capacity of the second washing step has been simulated for different flow rates of water at 15 °C to the scrubber, which is operated at 5 bara. The results shown that when the water flow rate is 18 l/s, it is possible to decrease the concentration of H₂S in the gas to below 1 mol%, see Figure 7.

The second washing step also removes some of the CO₂, which for water flow rate of 18 l/s results in removal of 38% of the CO₂, see Table 6. In the second washing step the ratio H₂/CO₂ has increased from 0,7 to 1,1 but the concentration of nitrogen and oxygen has also increased. To make the gas suitable for methane synthesis it is preferable to remove more CO₂ and most of the nitrogen and oxygen. This can be achieved with membranes as described below.

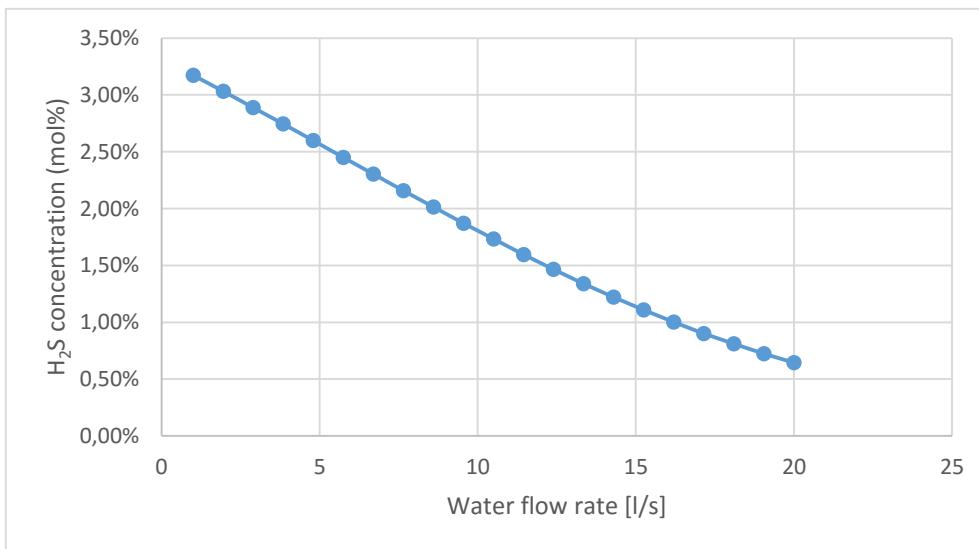


Figure 7. Concentration of H₂S in gas from second washing step in a scrubber operated at 5 bara and 15°C for different flow rates of water to the scrubber (Magnús Þór Arnarson 2016).

Table 6. Composition of gas from second washing step in a scrubber operated with water flow rate of 18 l/s and 5 bara.

	Flow rate (kg/s)	Composition (vol%)
H ₂ S	0,0022	0,8%
CO ₂	0,1406	41,4%
H ₂	0,0072	46,2%
N ₂	0,0183	8,5%
O ₂	0,0035	1,4%
CH ₄	0,0016	1,3%
H ₂ O	0,0005	0,3%
Sum	0,1739	100%

4.2 Second washing step to adjust H₂/CO₂ ratio

In the second washing step described above the objective was primarily to reduce H₂S content of the gas which resulted in removal of some of the CO₂ and in an increase in H₂/CO₂ ratio from 0,7 to 1,1. For

methane synthesis this ratio should be higher, preferably 4, when the gas enters the methanation reactor. The possibility of using water washing to increase the H_2/CO_2 ratio values to higher than 1.1 was investigated by performing simulations at different scrubbers pressures (5 – 8 bara) and water flow rates assuming that the water temperature was 20 °C, and that the flow rate and composition of gas to the scrubber was as shown in Table 4. In this case the column diameter was 1 m and the packing height 6 m.

The H_2/CO_2 ratio for different pressures and flow rates is shown in Figure 8. For comparison it can be mentioned that the flow rate of water to the enhanced capacity Sulfix II plant is 50 kg/s, see Table 2.

The results in Figure 8 indicate that the results of the water washing step is very sensitive to slight changes water flow rate to scrubber, especially when the scrubber is operated at high pressure and high water flow rate to scrubber.

If water washing is sufficient to increase H_2/CO_2 ratio to just above 4, then gas will contain about 12% N_2 and 2% CO_2 . This is too high for methane synthesis since the nitrogen content in the methane gas will become very high, or 41%. Therefore, before methane synthesis the gas needs to be treated further, possibly with membranes or PSA (pressure swing adsorption).

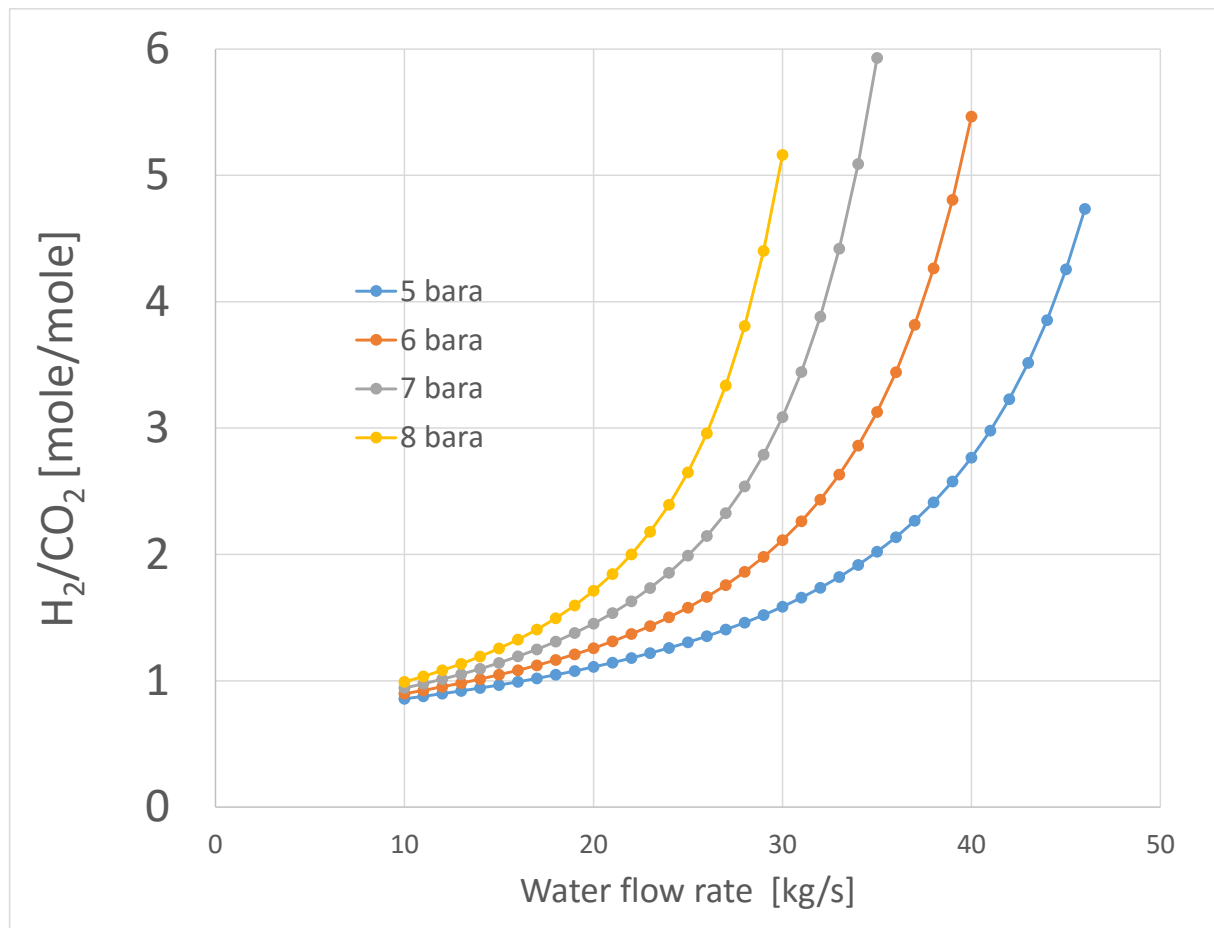


Figure 8. H_2/CO_2 ratio in gas from second washing step for different water flow rates in scrubber operated at different pressures.

Composition of gas from the from the second washing step in a scrubber operated at 8 bara and different water flow rates is shown in

Table 7.

Table 7. Composition of gas (mol%) from the from the second washing step in a scrubber operated at 8 bara and different water flow rates. Also shown is the flow rate of gas from the scrubber and the H₂/CO₂ ratio in the gas.

Water flow rate (kg/s)	17	20	23	26	29
Hydrogen Sulfide	0,23%	0,10%	0,04%	0,02%	0,0056%
Carbon Dioxide	36,2%	31,8%	26,9%	21,3%	15,41%
Hydrogen	50,9%	54,5%	58,6%	63,1%	67,85%
Oxygen	1,6%	1,7%	1,8%	1,9%	2,06%
Nitrogen	9,3%	10,0%	10,8%	11,6%	12,46%
Methane	1,4%	1,5%	1,7%	1,8%	1,92%
Water	0,3%	0,3%	0,3%	0,3%	0,29%
Sum	100,0%	100,0%	100,0%	100,0%	100,0%
Gas flow rate (kmol/h)	25,2	23,4	21,6	20,2	18,7
Gas flow rate (kg/h)	513,7	439,6	367,9	299,2	236,7
H ₂ /CO ₂	1,41	1,71	2,18	2,96	4,40

4.3 Recovery of carbon dioxide from scrubber solution

Water solution from scrubbing the gas from Sulfix contains mainly the carbon dioxide and hydrogen sulphide washed from the gas. Carbon dioxide can be partially recovered by flashing the pressurised solution from the scrubber at 1 bara. Composition of the gas obtained by flashing has been simulated for different water flow rates to the scrubber, when the scrubber is operated at 8 bara, see results in Table 8.

Table 8. Composition of gas (mol%) obtained by flashing at 1 bara solution from the second washing step in a scrubber operated at 8 bara and different water flow rates to scrubber. Also shown is the flow rate of gas from the scrubber.

Water flow rate (kg/s)	17	20	23	26	29
Hydrogen Sulfide	7,76%	6,84%	6,07%	5,45%	4,96%
Carbon Dioxide	87,83%	88,70%	89,43%	89,99%	90,38%
Hydrogen	1,62%	1,65%	1,69%	1,73%	1,81%
Oxygen	0,09%	0,09%	0,09%	0,09%	0,10%
Nitrogen	0,26%	0,26%	0,27%	0,28%	0,29%
Methane	0,09%	0,09%	0,09%	0,10%	0,10%
Water	2,36%	2,36%	2,36%	2,36%	2,36%
Sum	100,0%	100,0%	100,0%	100,0%	100,0%
Gas flow rate (kmol/h)	8,28	9,72	11,16	12,24	13,35
Gas flow rate (kg/h)	350,6	407,9	463,3	515,5	561,6

It is noteworthy that the gas from flashing has a high content of CO₂ and very low content of N₂ and O₂. After H₂S removal, for example by the Thiopaq process, this gas is suitable for methane production as described below in Chapter 5.3.

It can also be pointed out that after H₂S removal the gas is probably of sufficient purity for use in greenhouses for algae production and for production of food grade CO₂.

5 Production of methane

5.1 Methane from gas from Sulfix II

According to Table 4 likely composition of gas from Sulfix II is 6.6% N₂, 51.5% CO₂ and 36.1% H₂. By adding electrolytic hydrogen to this gas it is possible to adjust the ratio H₂/CO₂ to 4, which is suitable for methane synthesis. Unfortunately, the resulting methane will contain about 13 % N₂ which makes it unsuitable for use as fuel for vehicles. Removal of H₂S would also be needed. Here we explore the possibility of producing vehicle grade methane with the process described in Figure 9. The first step in this process could be removal of H₂S with the Thiopaq process (see memo 5) resulting in gas with very low H₂S content (<100 ppmv). About 350 tonnes of H₂S would be removed by the Thiopaq process each year. Other processes for removal of H₂S could also be applied. The H₂S removal step is necessary before the membrane treatment in the next step since there is possibility of precipitation of S which may clog the membranes if the concentration is too high. The gas from the Thiopaq process is then compressed to about 10 bara and heated to 60°C and subjected to membrane treatment to remove most of the N₂ and O₂ (see memo 4). About 39% of the CO₂ and 10% of the H₂ is lost with the retentate that does not go through the membrane. The gas going through the membrane, the permeate, will be enriched in H₂, see Table 9. The permeate is then mixed with H₂ from electrolysis (before or after compression to 9 bara) and sent to the microbial methanation reactor which is operated at 9 bara. Here it assumed that the reactor is run with a slight excess of H₂ so that the H₂ content in the methane produced is 2% of the methane content. The gas from the methanation reactor is then purified, mainly by drying, resulting in gas of the composition shown in Table 9.

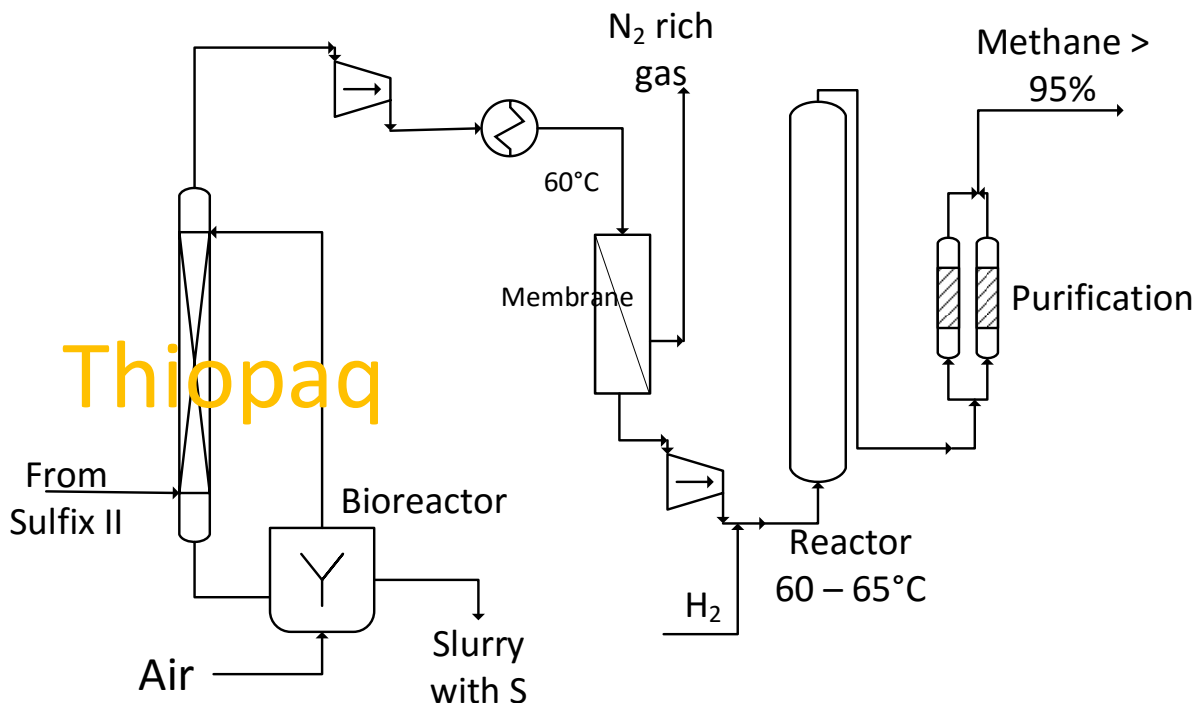


Figure 9. Process for production of methane from gas from Sulfix II.

For production of the electrolytic hydrogen needed for methane production about 3.5 MW of electric power is needed. For comparison it can be mentioned that if the gas had not contained any hydrogen, then 4.7 MW would have been needed for production of methane from the CO₂ flow equivalent to that of the retentate.

Table 9. Composition of gas to and from membrane and composition of methane after purification.

	Feed gas to membrane		Gas from membrane			Methane after purification	
	Composition (mol%)	Flow rate (kmol/h)	Retentate Composition (mol%)	Permeate Composition (mol%)	Flow rate (kmol/h)	Composition (mol%)	Flow rate (kmol/h)
Hydrogen Sulfide	0,01%	0,003	0,01%	0,006%	0,0015	0,00%	0
Carbon Dioxide	53,29%	18,45	63,3%	48,4%	11,25	0,00%	0
Hydrogen	37,34%	12,93	11,4%	50,0%	11,63	1,92%	0,23
Oxygen	1,14%	0,396	3,14%	0,17%	0,040	0,00%	0,00
Nitrogen	6,84%	2,369	18,8%	1,02%	0,237	2,02%	0,24
Methane	1,07%	0,371	2,94%	0,16%	0,037	96,1%	11,29
Water	0,30%	0,104	0,46%	0,22%	0,0522	0,00%	0
	100,0%	34,621	100,0%	100,0%	23,257	100,0%	11,75

The quantity of methane that can be produced in this way is about 250 Nm³/h or about 2 million Nm³/year, which is similar to the current methane production in Iceland. The Wobbe index of the gas obtained is 45,5 MJ/Sm³ which meet the requirement of the draft CEN standard for use of methane as vehicle fuel.

5.2 Methane from water washed gas from Sulfix II

By water washing gas from Sulfix II in a second water washing step it is possible to obtain gas with high H₂/CO₂ ratio (see

Table 7), which is more suitable for methane production than gas with low H_2/CO_2 ratio, as for example obtained after first water washing step (see Table 3). But unfortunately the gas contain high levels of N_2 which would result in methane with high N_2 content which is unsuitable for use as fuel for vehicles. Below we explore the possibility of applying membranes to remove N_2 and O_2 rom the gas from the second water washing step so that is becomes suitable for methane production.

If gas of the composition shown in

Table 7 is subjected to same membrane treatment described in Chapter 5.1 then the composition of the permeate from the membrane will become as shown in Table 10.

Table 10. Estimated composition of gas after membrane treatment of gas of composition shown in

Table 7.

Water flow rate (kg/s)	17	20	23	26	29
Hydrogen Sulfide	0,16%	0,07%	0,03%	0,01%	0,00%
Carbon Dioxide	31,8%	27,7%	23,2%	18,2%	13,0%
Hydrogen	66,0%	70,1%	74,6%	79,5%	84,5%
Oxygen	0,22%	0,24%	0,25%	0,27%	0,28%
Nitrogen	1,3%	1,4%	1,5%	1,6%	1,7%
Methane	0,2%	0,2%	0,2%	0,2%	0,3%
Water	0,2%	0,2%	0,2%	0,2%	0,2%
Sum	100,0%	100,0%	100,0%	100,0%	100,0%
H ₂ /CO ₂	2,07	2,53	3,22	4,37	6,50
Flow rate kmol/h	17,5	16,4	15,3	14,4	13,5

Interpolation of data in Table 10 show that for water flow rate to scrubber of 25 kg/s it is possible to obtain gas with H₂/CO₂ ratio of 4, which is suitable for methane production without any addition of hydrogen. For water flow rates to scrubber of 25 kg/s or higher the H₂/CO₂ ratio is higher than 4 which makes it possible to produce methane without any addition of electrolytic hydrogen to the gas. For water flow rates to scrubber lower than 25 kg/s the H₂/CO₂ ratio is lower than 4 which makes it necessary to add electrolytic hydrogen to the gas if it is to be used for methane production.

In Table 11, the composition of methane that can be produced from the membrane treated gas is shown. It is assumed that electrolytic hydrogen is added if H₂/CO₂ is lower than 4. The gas that can be obtained when water flow rate to scrubber is 25 kg/s has Wobbe index of 42 kJ/Sm³, which is just sufficient according to the requirements of the draft CEN standard. It would be preferable to obtain gas with higher Wobbe index, but that would require the addition of electrolytic hydrogen to gas of lower H₂/CO₂ ratio than 4 before methanation. I could also come into consideration to add a small quantity of propane to increase the Wobbe index.

The production capacity of methane with no hydrogen addition to gas obtained from scrubber with water flow rate of 25 kg/s would be about 65 Nm³/h, or about 0.55 million Nm³/year, or about fourth of the current methane production in Iceland.

The above results indicate that it is possible to start production of methane from geothermal gas at the Hellisheiði power plant, without any addition of electrolytic hydrogen, see Figure 10. This would enable of production capacity of 65 Nm³/h of methane of sufficient quality for use in vehicles, when flow rate of water to second water washing step is 25 kg/s. Production capacity of methane can be increased by lowering the water flow rate to the scrubber and adding electrolytic hydrogen to the gas from the second scrubber to adjust the H₂/CO₂ ratio to 4. If for example the water flow rate to the scrubber is lowered to 17 kg/s, then the production capacity of methane can be increased from 65 to 125 Nm³/h by adding hydrogen from a 1.1 MW electrolyser, see Table 11. This would however ever require that the methantator be designed for this capacity, at least.

Table 11. Composition of methane that can be produced from gas from second washing step after membrane treatment. Also shown is the flow rate of added electrolytic hydrogen (if needed), the power for water electrolysis (if needed), methane production capacity and Wobbe index of gas obtained.

Water flow rate (kg/s)	17	20	23	26	29
Hydrogen Sulfide	0,00%	0,00%	0,00%	0,00%	0,00%
Carbon Dioxide	0,00%	0,00%	0,00%	0,00%	0,00%
Hydrogen	1,88%	1,87%	1,84%	1,80%	1,74%
Oxygen	0,00%	0,00%	0,00%	0,00%	0,00%

Nitrogen	3,98%	4,81%	6,05%	8,04%	11,50%
Methane	94,14%	93,32%	92,11%	90,16%	86,76%
Water	0,00%	0,00%	0,00%	0,00%	0,00%
Sum	100,0%	100,0%	100,0%	100,0%	100,0%
H ₂ to be added (kmol(h))	10,83	6,78	2,83	none	none
Power for electrolysis (MW)	1,12	0,70	0,29	none	none
Methane production (Nm ³ /h)	125	102	79	59	39
Wobbe index of gas (MJ/Sm ³)	44,20	43,7	42,9	41,7	39,7

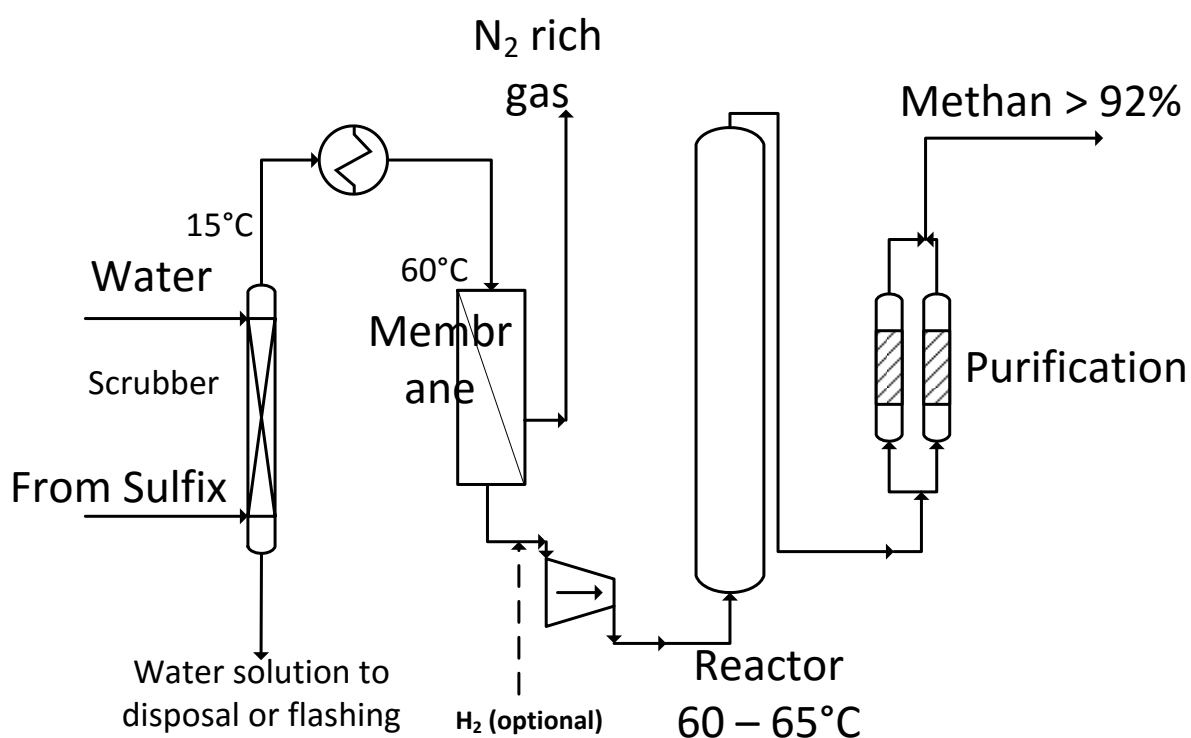


Figure 10. Process from production of methane from gas from Sulfix based on water washing of gas, membrane treatment and microbial methanation. H₂ can be added for increased methane production.

5.3 Methane from CO₂ recovered by flashing scrubber solution

As described in chapter 4.3 it is possible by flashing the scrubber solution from the second washing step to obtain gas with high CO₂ content and low N₂ and O₂ content. However the gas can contain 5 – 8 % H₂S which should preferably be removed before methanation. Here it is assumed that the Thiopaq method is for H₂S removal and that electrolytic hydrogen is added to obtain the right ratio of H₂/CO₂ for methanation, see Figure 11. The quantity of H₂S to be removed, the production capacity of methane and the power needed for water electrolysis is shown in Table 12. The methane gas obtained will in each case contain about 97.8% CH₄, 1.9% H₂ and only 0.3% N₂ and its Wobbe index will be 46.6 MJ/Sm³, which is more than sufficient according to the draft CEN specification.

Table 12. Quantity of methane that can be produced from gas obtained by flashing solution from second water washing step, for different flow rates of water to the scrubber in the second water washing step. Also shown is the H₂S that needs to be removed from the gas and the power needed for hydrogen production.

Water flow rate (kg/s)	17	20	23	26	29
H ₂ S to be removed (t/year)	192	199	202	199	198

CH ₄ that can be produced (Nm ³ /h)	162	192	222	245	269
CH ₄ that can be produced (million Nm ³ /year)	1,42	1,68	1,95	2,15	2,35
Power for water electrolysis (MW)	2,98	3,53	4,09	4,51	4,94

If we assume that water flow to the scrubber is 25 kg/s then it is possible to produce about 245 Nm³/h or about 2 million Nm³/year.

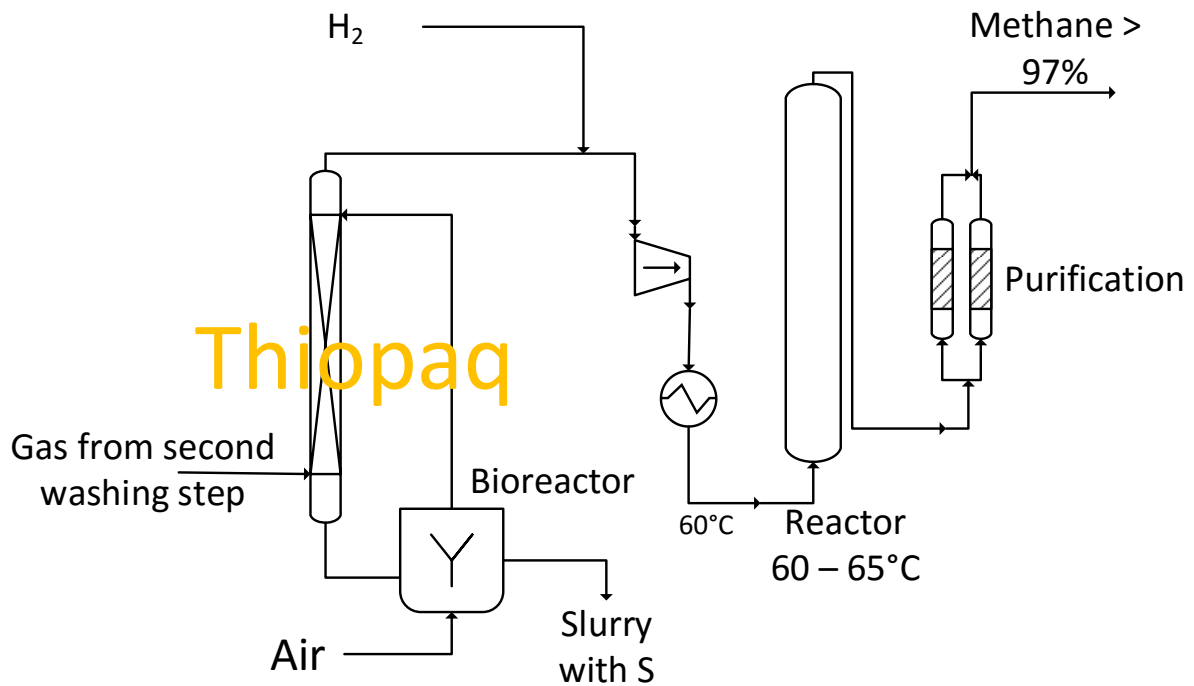


Figure 11. Process for production of methane from gas obtained from flashing liquid from second water washing step.

6 Business cases

6.1 Cases studied

Production cost of methane for the following case will be estimated.

- **Case 1:** Gas from Sulfix II is desulphurised with Thiopaq and treated with membranes as described in Chapter 5.1. Electrolytic hydrogen is added to adjust the H₂/CO₂ ratio to 4 and methane produced in the microbial methanation reactor.
- **Case 2:** Gas from Sulfix II I water washed with 25 kg/s of water and water washed gas treated with membranes to give gas suitable for methanation as described in Chapter 5.2.
- **Case 3:** Gas from Sulfix II I water washed with 17 kg/s of water and water washed gas treated with membranes to give gas with H₂/CO₂ ration of 2.07 and electrolytic hydrogen is added to adjust the H₂/CO₂ ratio to 4 and methane produced in the microbial methanation reactor, see Chapter 5.2.
- **Case 4:** Water from water washing of gas with 17 kg/s of is flashed to give CO₂ with about 5.7 vol% H₂S. Gas is desulphurised with Thiopaq, see Chapter 5.3, so that it can be used for methanation after electrolytic hydrogen has been added to adjust H₂/CO₂ ratio to 4.

The cost of manufacturing methane in the different cases shown above will be estimated below. The approach taken here is first to estimate the cost of electrolytic hydrogen needed and to calculate the cost of desulphurisation with Thiopaq. Electrolytic hydrogen and desulphurised gas will be considered as raw materials.

6.2 Estimation of manufacturing cost of methane

6.2.1 Production of electrolytic hydrogen for the different cases

The quantity of hydrogen that has to be produced for the different cases is shown in Table 13.

Table 13. Hydrogen production by electrolysis for the cases considered. Also shown is the number of electrolyzers needed, their operating rate, electric energy consumption and cost of electrolysis plants.

	Hydrogen produced (Nm ³ /h)	Number of electrolyzers	Operating rate of electrolyzers as percentage of full capacity	Electric energy consumption for electrolysis (kWh/Nm ³)	Cost of electrolysis plant (M€)
Case 1	754	2	78%	4,58	3,94
Case 2	none	none	none	none	none
Case 3	243	1	50%	4,36	2,13
Case 4	653	2	67%	4,49	3,94

Here we shall assume that hydrogen is produced by alkaline electrolysis of water in electrolyzers supplied by NEL Hydrogen (see memo 1). The largest electrolyser from NEL Hydrogen has a production capacity of 485 Nm³/h at full capacity. Electric energy consumption for hydrogen production (at atmospheric pressure) increases as activity of the electrodes in the electrolyzers deteriorates, from about 4,5 kWh/Nm³ to about 4.9 kWh/Nm³ in ten years, when electrodes and membranes are renewed. The average energy consumption is here assumed to be 4.7 kWh/Nm³ when the electrolyzers are operated at full capacity. The electrolyser in Table 13 does not need to be operated at full capacity, resulting in somewhat lower electric energy consumption as shown in Table 13.

The electrolysis plant is assumed to be directly connected to the power plant at Hellisheiði, to which it pays 30 €/MWh of electricity. Transmission fees are as for large customers connected to the Landets grid (<http://landsnet.is/english/transmissionandmarket/transmissiontariff/tariff/>), but with 40% rebate in transmission energy charge, transmission capacity charge and transmission delivery charge

With the above assumptions, the manufacturing cost of H₂ will be as shown in Table 14 for Case 1, Case 3 and Case 4. Here it is assumed that the weighted average cost of capital (WACC) is 6% and the lifetime 20 years.

Table 14. Manufacturing cost of hydrogen in Case 1, Case 3 and Case 4.

			Case 1	Case 3	Case 4	Unit
Operating hours/year	8.760					
Hydrogen production			754	243	652	Nm ³ /h
Hydrogen production			593	191	514	tonne/year
Electric energy consumption			4,88	4,66	4,79	kWh/Nm ³
Power for electrolysis			3,68	1,13	3,13	MW
Cost of electrolysis plant (CAPEX)			3,94	2,13	3,94	M€
Electricity costs						
Electric energy cost to energy producer	30	€/MWh	966.702	297.488	821.588	€/year
Transmission energy charge	0,9792	\$/MWh	28.264	8.698	24.022	€/year
Ancillary service charge	0,33	€/MWh	10.771	3.315	9.154	€/year
Transmission losses	0,69	€/MWh	22.227	6.840	18.890	€/year
Transmission capacity charge	33.237	\$/year	29.773	26.670	23.890	€/year
Transmission delivery charge	19.361	\$/MW/year	63.795	19.632	54.219	€/year
Other costs						
Maintenance	1,5%	of CAPEX	59.072	31.967	59.072	€/year
Insurance/Permits	1,5%	of CAPEX	59.072	31.967	59.072	€/year
Personnel	55.000	€/operator	55.000	55.000	55.000	€/year
Annualized Capital Cost						
	WACC	Lifetime (years)				
Electrolysis plant	6%	20	343.347	185.800	343.347	€/year
Total Manufacturing Cost						
			1.638.025	667.375	1.468.256	€/year
Manufacturing Cost/Unit H₂						
			0,248	0,314	0,257	€/Nm ³ H ₂
			2,759	3,489	2,857	€/kg H ₂
			82,8	104,7	85,7	€/MWh

The cost of the electrolysis plants shown in Table 13 includes the cost of compressors for compressing hydrogen from atmospheric pressure to 15 barg. The electric energy for compression and other equipment in the plant estimated to be 0,3 kWh/kg H₂.

In Case 1 and Case 4 the electricity cost is 34,6 €/MWh, whereas in Case 3 it is 36,6 €/MWh.

6.2.2 Cost of desulphurisation

In Case 1 and Case 4 it will be necessary to desulphurise the gas before methanation. Here we shall assume that the Thiopaq method is used for desulphurisation. The gas from desulphurisation will contain less than 25 ppmv of H₂S.

The quantity of gas that has to be treated and quantity of H₂S that has to be removed is shown in Table 15 together with the total cost of desulphurisation. Here it is assumed that the weighted average cost of capital is 6% and the lifetime 20 years.

Table 15. Gas to be desulphurised in Cases 1 and 4 and the total cost of H₂S removal.

	Gas to desulphurisation (kmol/h)	H ₂ S removed (kg/day)	Total cost of H ₂ S removal (€/year)
Case 1	35,8	0,972	309.192
Case 4	8,3	0,526	188.188

In Case 4 the gas from desulphurisation will be CO₂ of about 98% purity, the main impurity being H₂. The cost of desulphurisation can in this case be estimated to be 0,07 €/kg CO₂ (70 €/tonne). This CO₂ (with 25 ppmv H₂S) is probably of sufficient purity for use in green houses and for cultivation of algae. Further removal of H₂S can be achieved with the use of activated carbon. However, it should be emphasised that in order to produce CO₂ as described here it would be necessary to water wash the gas from Sulfix II as described in Case 3 above.

Cost of disposal of sulphur is not included in the cost estimate above, since it is assumed that the sulphur can be disposed of as a fertiliser at no cost.

6.2.3 Cost of membranes

Membrane treated of washed gas is needed in Case 1, 2 and 3, in Case 1 for treatment of gas from Sulfix II and in Cases 2 and 3 for treatment of water washed gas from second washing step. The primary objective with membrane treatment is to remove N₂ and O₂, but an additional benefit is increase in H₂/CO₂ ratio as described above.

The flow rate of gas to membranes and of permeate from membrane is shown in for Cases 1, 2 and 3, where the cost of membranes is also shown. The feed gas to membranes has to be heated to 65°C and the pressure of the feed gas is assumed to be 10 bara and that of the permeate 1 bara.

Table 16. Flow rate of gas to membrane units, and flow rate of permeate from membrane units and the estimated cost of installed membrane.

	Flow rate of gas to membrane (kmol/h)	Flow rate of permeate (kmol/h)	Cost of installed membranes (€)
Case 1	34,6	23,3	564 000
Case 2	25,2	17,5	327 000
Case 3	20,6	14,7	327 000

6.2.4 Cost of water washing

In Cases 2 and 3 the gas from Sulfix II will be water washed in a second water washing step, in Case 2 with 25 l/s of water and in Case 3 with 17 l/s. The same washing tower will be used in both cases and it is assumed that investment cost for water washing will be the same in these cases. The only difference will be in power of pumps needed for water. Total CAPEX for water washing is estimated to be about 2,38 million EUR, with an accuracy of -30% +50% (Magnús Þór Arnarson 2016).

6.2.5 Cost of flashing water from second washing step

In Case 4 the water from second water washing step (with 17 l/s of water to second water washing step) will be flashed from 8 bara to 1 bara, as described in Chapter 5.3. CAPEX for flashing is estimated to be about 0,55 million EUR, with an accuracy of -30% +50% (Magnús Þór Arnarson 2016).

6.2.6 Cost of methanators

Methanation will be carried out by microbial methanation in reactors of the type developed by Electrochaea (<http://www.electrochaea.com>). Methane production for the different cases is shown in Table 17.

Table 17. Methane production in cases 1 – 4. Also shown is the Wobbe Index of the gas obtained and estimated cost of the installed methanation system.

	Methane production (Nm ³ /h)	Wobbe index of methane (MJ/Sm ³)	Cost of methanation system (M€)
Case 1	263	45,50	3,5
Case 2	72	42,2	1,4
Case 3	132	44,20	2,1
Case 4	162	46,6	2,5

6.3 Manufacturing cost of methane

Manufacturing cost of methane in Cases 1 to 4 is shown in Tables

In calculating the annualised capital cost the weighted average cost of capital (WACC) is assumed to be 6% and the lifetime of methanator, membranes, water washing unit and flashing unit is 10 years. Electrolytic hydrogen and desulphurised gas are considered as raw materials as stated above.

Table 18. Manufacturing cost of methane for Case 1.

Methane capacity	263	Nm ³ /h CH ₄				
CPEX						
Water washing (€)	0					
Membranes (€)	564.337					
Methanation (€)	3.469.175					
	4.033.513					
Raw materials						
Hydrogen	754	Nm ³ H ₂ /h	0,248	€/Nm ³ H ₂	1.638.025	€
Desulphurised gas					309.192	€
Electricity	0,3	MW	34,6	€/MWh	90.929	€
Maintenace	3%	of CAPEX			121.005	€
Insurance and taxes	3%	of CAPEX			121.005	€
Operators	1	operator	55.000	€/operator	55.000	
Annualised capital cost	6%	in	10	years	548.025	€
Manufacturing cost					2.883.182	€
					1,25	€/Nm ³

Table 19. Manufacturing cost of methane for Case 2.

Methane capacity	72	Nm ³ /h CH ₄				
CPEX						
Water washing (€)	3.277.494					
Membranes (€)	392.349					
Methanation (€)	1.400.923					
	5.070.766					
Raw materials						
Hydrogen	0				0	€
Desulphurised gas					0	€
Electricity	0,3	MW	36,6	€/MWh	96.185	€
Maintenace	3%	of CAPEX			152.123	€
Insurance and taxes	3%	of CAPEX			152.123	€
Operators	1	operator	55.000	€/operator	55.000	
Annualised capital cost	6%	in	10	years	688.955	€
Manufacturing cost					1.144.385	€
					1,81	€/Nm ³

Table 20. Manufacturing cost of methane for Case 3.

Methane capacity	132	Nm ³ /h CH ₄				
CPEX						
Water washing (€)	3.277.494					
Membranes (€)	130.783					
Methanation (€)	2.144.905					
	5.553.181					
Raw materials						
Hydrogen	243	Nm ³ H ₂ /h	0,314	€/Nm ³ H ₂	667.375	€
Desulphurised gas					0	€
Electricity	0,3	MW	36,6	€/MWh	96.185	€
Maintenace	3%	of CAPEX			166.595	€
Insurance and taxes	3%	of CAPEX			166.595	€
Operators	1	operator	55.000	€/operator	55.000	
Annualised capital cost	6%	in	10	years	754.499	€
Manufacturing cost					1.906.250	€
					1,64	€/Nm ³

Table 21. Manufacturing cost of methane for Case 4.

Methane capacity	162	Nm ³ /h CH ₄				
CPEX						
Flashing (€)	549.520					
Membranes (€)	0					
Methanation (€)	2.470.136					
	3.019.656					
Raw materials						
Hydrogen	653	Nm ³ H ₂ /h	0,257	€/Nm ³ H ₂	1.468.256	€
Desulphurised gas					188.188	€
Electricity	0,3	MW	34,8	€/MWh	91.454	€
Maintenace	3%	of CAPEX			90.590	€
Insurance and taxes	3%	of CAPEX			90.590	€
Operators	1	operator	55.000	€/operator	55.000	
Annualised capital cost	6%	in	10	years	410.275	€
Manufacturing cost					2.394.352	€
					1,69	€/Nm ³

The results in Table 18 to Table 21 are summarised in Table 22. In June 2016 the prices of methane at pumping stations in Iceland was about 118 ISK/Nm³ without VAT or 0,83 €/Nm³. The lowest manufacturing cost was found for Case 1, where no water washing was used. The high cost in Cases 2 and 3 can mainly be traced to the high CAPEX of water washing and in Case 4 to the high cost of hydrogen.

Table 22. Manufacturing cost of methane for the different cases.

	Case 1	Case 2	Case 3	Case 4
Methane production (Nm ³ /h)	263	72	132	162
Methane manufacturing cost (€/Nm ³)	1,25	1,81	1,64	1,69

7 Discussion

The high cost of methane production found here illustrates that it is important to minimise the cost of gas treatment before methanation and to lower the cost of hydrogen. Cost of gas treatment is high because of the high H₂S content and because of inert gases like N₂ and O₂. Lower cost methane can probably be produced near geothermal power plants with low content of H₂S and inert gases. Another source of relatively pure CO₂ could be CO₂ obtained from processed landfill gas or gas from anaerobic digestion plants.

Lower cost hydrogen is also necessary to lower the cost of methane. This can possibly be achieved by participating in the regulating power market as described in in Jacobs thesis (Jacobs 2016) and memos 7 and 8. This would however require large flexibility in the methane production which would increase CAPEX for a methanation plant.

Case 1 gave the lowest cost methane or 1,25€/Nm³ or about 126 €/MWh. This can be compared to the price of biofuels in Europe in June 2016, which were about 95 €/MWh for biodiesel (fatty acid methyl ester) and 76 €/MWh for ethanol. Significant increases in price of biofuels are therefore required to make production of methane with the methods described here attractive. However, it should be pointed out the lower cost methane could be produced if the methane production capacity could be increased and if the cost of processing CO₂ containing gas was low. It could also be interesting to study of the biological methanation process can tolerate up to 1 – 4% H₂S. This might lower the total manufacturing cost.

8 References

- Jacobs, J. (2016). Economic Modeling of Cost Effective Hydrogen Production From Water Electrolysis by Utilizing Iceland's Regulating Power Market. MS, Reykjavik University.
- Magnús Þór Arnarson (2016). Estimation of CAPEX for water washing and flashing
- Magnús Þór Arnarson (2016). Flow sheet for increased capacity Sulfix II plant.
- Magnús Þór Arnarson (2016). Simulation of H₂S removal of gas from Sulfix II.
- Magnús Þór Arnarson (2016). Simulations of capacity test of Sulfix II scrubber.
- Mannvít (2013). OR - Hellisheiði power plant. Flow sheet for Sulfix, Phase II.

Appendix - List of Memos

Memo 1. Production of hydrogen with water electrolysis.

Memo 2. Liquefaction of methane with Sterling Cryogenerators.

Memo 3. Specification of methane for automotive applications.

Memo 4. Upgrading of gas from Sulfix II with membranes.

Memo 5. Removal of H₂S from geothermal gas with the Thiopaq process.

Memo 6. Status of technology for microbial methanation.

Memo 7. Water electrolyzers and frequency stabilisation of the electrical power grid.

Memo 8. Er hægt að lækka kostnað við framleiðslu vetnis með rafgreiningu með því að taka þátt í markaði Landsnets fyrir reglunarorku 29.3.16.

Memo 9. Er hægt að telja eldsneyti sem framleitt er úr kolsýru og rafgreiningarvetni tvöfalt eða jafnvel fjórfalt.

Memo 10. Market for methane.

Memo 11. Purification of geothermal hydrogen with PSA.

Memo 12. Removal of H₂S from geothermal gas with activated carbon.

