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BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D2.4 - Report on Overall Side Stream Utilization

WP2 - Tasks 2.3 & 2.4

20.12.2023

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Abbreviations and acronyms

Acronym	Description
APEA	Aspen Process Economics Analyser
APR	Aqueous phase reforming
BL	Black liquour
CAPEX	Capital expenditure
FCOP	Fixed cost of production
HDO	Hydrodeoxygenation
HTL	Hydrothermal liquefaction
IHDO	Integrated hydrodeoxygenation
IHTL	Integrated hydrothermal liquefaction
IRR	Internal rate of return
ISBL	Inside battery limit (the core part of a chemical plant)
NPV	Net present value
NRTL	Non-random two-liquid activity coefficient model
OPEX	Operating expenses
OSBL	Outside batter limit (auxiliary system outside the core chemical plant)
PSA	Pressure swing adsorption
VCOP	Variable cost of production

Executive Summary

Overall side stream utilization in the integrated black liquor hydrothermal liquefaction (IHTL) concept was reviewed in this report. There are two side streams exiting from an integrated hydrodeoxygenation section (IHDO) of an IHTL plant: aqueous stream and off-gas stream. It is also possible to take out part of the off-gases already after the IHTL section. In the IHTL concept considered in this work, aqueous phase reforming (APR) is applied to produce hydrogen from oxygenated organic compounds in the aqueous stream from the IHDO. However, it was estimated that hydrogen production of APR is not enough to supply hydrogen for the IHDO process. Furthermore, due to low productivity of hydrogen and fast catalyst deactivation in APR, it is questionable whether an investment in an APR plant would be feasible. It was estimated that only 20 - 25 % of hydrogen demand of IHDO could be produced by APR with fresh catalyst in the start of the operation.

Regarding gas treatment of the off-gas stream from IHDO rich in hydrogen and hydrogen sulfide, three different cases were studied: separation of hydrogen and production of sulfuric acid (Case 1), sulfuric acid production without hydrogen separation (Case 2) and hydrogen separation and burning the non-condensable gases in a recovery boiler (Case 3). Process concept models were built in Aspen Plus simulation software to obtain mass and energy balances for the three cases. Furthermore, CAPEX and OPEX were estimated for three cases and the profitability of most promising cases 1 and 3 were assessed. It was discovered that profitability of Cases 1 and 3 is high. However, further studies are needed for scale up of these studied cases and to improve the accuracy of economic analysis.

Regarding overall side stream utilization, it is recommended to produce fresh hydrogen by water electrolysis and direct aqueous phase to waste water treatment. Furthermore, it is feasible purify hydrogen from off-gases and recycle it back to IHDO. It might be feasible as well to produce sulfuric acid from hydrogen sulfide in the off-gases. However, difference regarding profitability was not significant comparing the cases where sulfuric acid was produced after hydrogen separation or the rest off-gases were burned in the recovery boiler.

Keywords

Black liquor, Hydrothermal liquefaction, HTL, Transportation Fuels, Aviation, Shipping, Aqueous phase reforming, APR, Gas treatment, Sulphur, Sulphuric acid, Hydrogen, H_2

1 Introduction

The BL2F project has been focused on the developing an innovative technology that can convert black liquor (BL) into synthetic drop-in fuels in a plant integrated to a pulp mill. The process (Figure 1) involves conversion of wet BL into biocrude using a combination of salt-separation and hydrothermal liquefaction (HTL). This biocrude is then upgraded through a two-step hydrothermal hydrodeoxygenation (HDO) process to reduce the oxygen content of the resulting oil. To increase conversion efficiency, aqueous fractions from HTL and from the first integrated HDO step (IHDO) are valorised using aqueous phase reforming (APR) to produce H_2, which is utilized as a hydrogen supply for IHDO process. Furthermore, gaseous fraction formed in the IHTL and IHDO processes will be sent back to pulp mill for further treatment.

The objective of deliverable D2.4 was to report overall side stream concept comprising APR in Task 2.3 and gas treatment in Task 2.4. In Task 2.3, the aim was to investigate hydrogen production from IHDO aqueous streams via catalytic APR in laboratory scale. This task has been reported in detail in the report of deliverable D2.3.[1] In Task 2.4, the objective was to study the composition of gases exited from IHDO process as well as treatment of the gases at the pulp mill. The options for the gas treatment were the combustion in the odorous gas treatment at the pulp mill, hydrogen separation from the gas and sulfuric acid production of the gas. The different gas treatment alternatives were mainly studied in the Master's thesis of Mustafa Saad.[2]

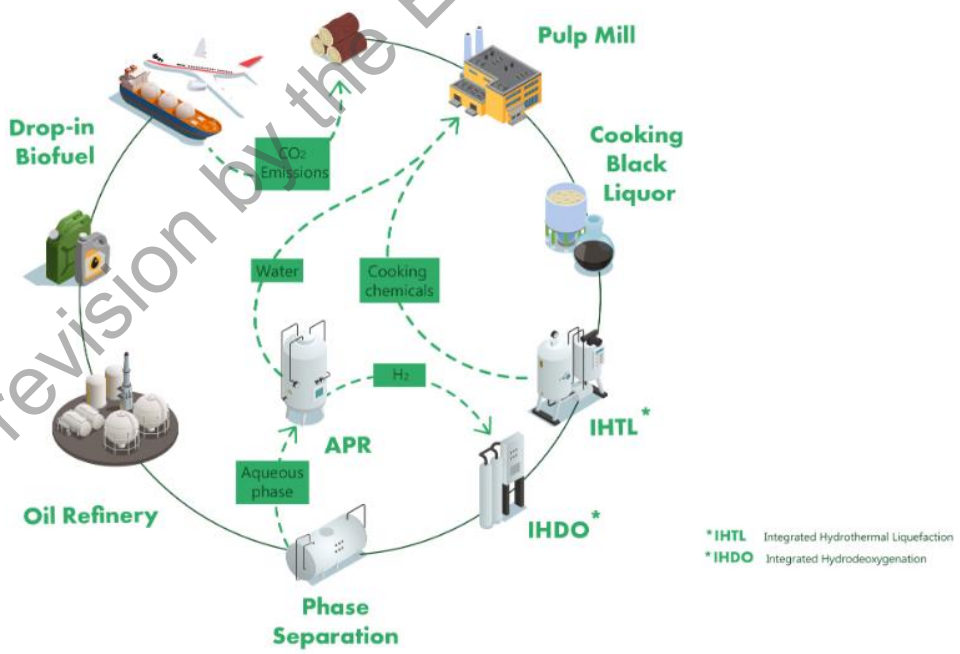

Figure 1. Concept overview for BL2F project.

2 Overall side stream concept

Optimized utilization of side streams is in a key role in biorefinery concepts. In this way both process economics as well as sustainability including carbon balance and energy efficiency can be improved. The BL2F concept is based on the integration with a Kraft pulp mill thus enabling utilization of the side streams at the pulp mill as well. The concept is on the other hand based on integration of IHTL and IHDO processes which means that all the streams produced at IHTL except the salts brine containing the cooking chemicals are led to IHDO and the main side streams, i.e. off-gases (gas fraction) and aqueous fraction are separated and taken out after IHDO. However, part of the off-gases can optionally be taken out already after IHTL. Gases are led to pulp mill for further treatments. The gas treatments studied in the project and considered in this report are:

- Separation of hydrogen from the gas stream and production of sulfuric acid from the rest of the gas after hydrogen separation
- Sulfuric acid production without hydrogen separation
- Separation of hydrogen and burning the non-condensable gases in recovery boiler

These three concepts were studied as a part of the project in the master's thesis of Mustafa Saad[2] and the main results of the thesis are reviewed in this report.

Aqueous fraction obtained from IHDO contains water soluble oxygenated organics and this stream is led to aqueous phase reforming to obtain hydrogen to be utilized in IHDO. If additional hydrogen is needed it will be produced by water electrolysis using green electricity. A flow diagram of side stream utilization is presented in

Figure 2.

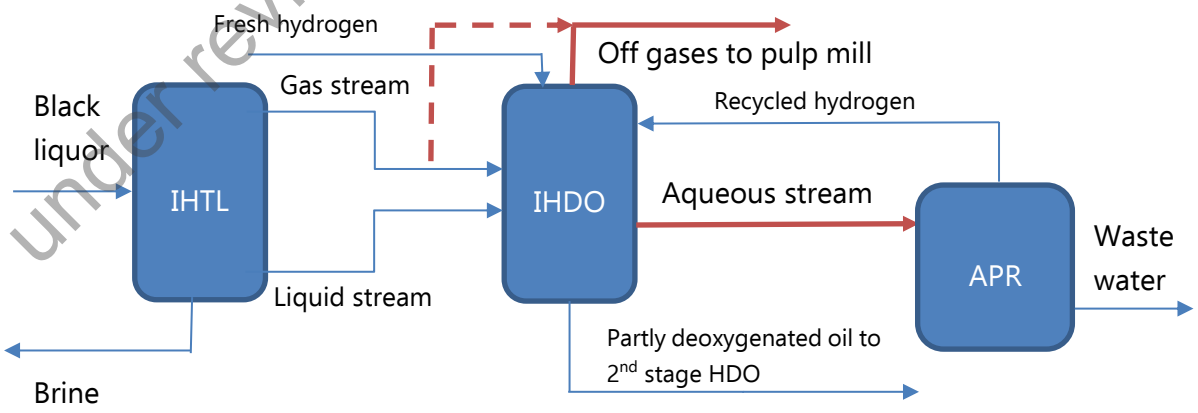

Figure 2. Flow diagram of side stream utilization (side streams in red color).

3 Aqueous phase reforming

Aqueous phase reforming (APR) is a catalytic technology where the aim is to split oxygenated hydrocarbons catalytically to hydrogen and carbon oxides in aqueous liquid phase. Compared to conventional gas phase reforming technologies energy consuming and expensive evaporation of water is avoided in APR. In BL2F, the aim has been to apply APR for the hydrogen production from aqueous fraction obtained from IHDO process. The experimental work of APR done in BL2F is reported in detail in D2.3 - Report on aqueous phase reforming concept.[1] Due to nature of feedstock, the aqueous phase in IHTL concept is rich in oxygenates with aromatic structures, especially phenolics. However, some aliphatic monohydric alcohols, especially methanol, were observed in the aqueous phase as well. A typical composition of the organics in an aqueous phase obtained from the HTL of black liquor is given in Figure 3.[3] It should be noted that phenolics and other aromatic oxygenates were not calibrated in the analysis and therefore not shown in Figure 3. However, the concentrations of phenolics can be estimated based on HTL study found the literature (Figure 4).[4] However, instead of BL the feedstock in this study was lignin rich fraction (LRF) from lignocellulosic ethanol production using poplar feedstock.

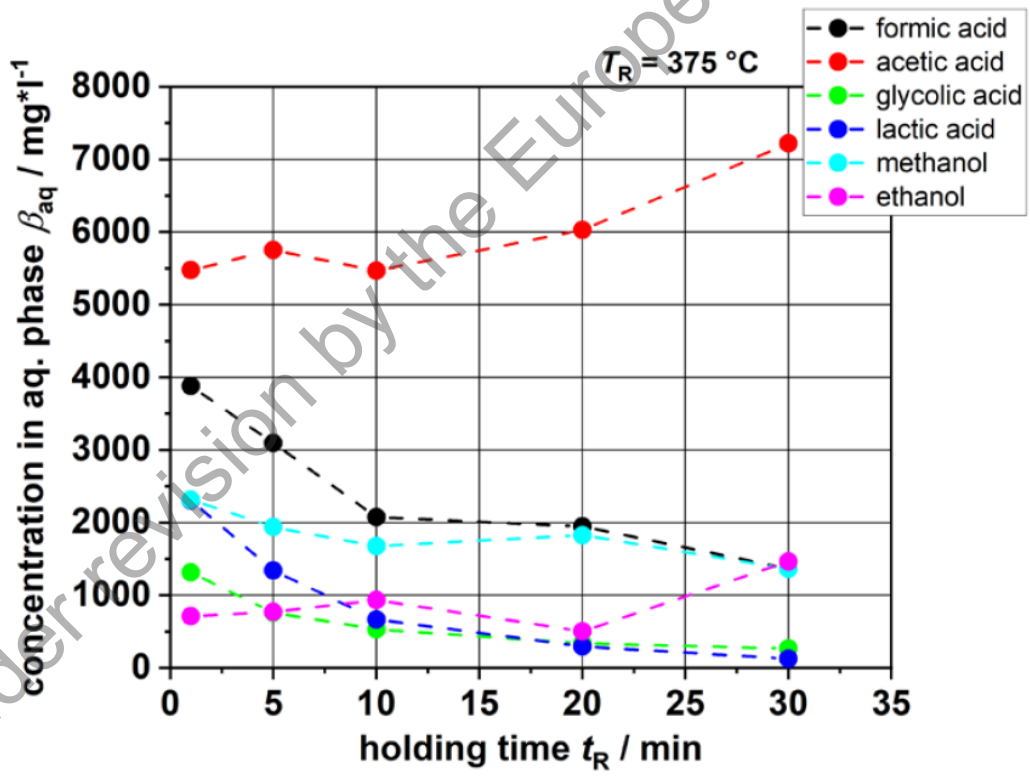

Figure 3. Typical composition of some organics in the aqueous phase from the HTL of black liquor.

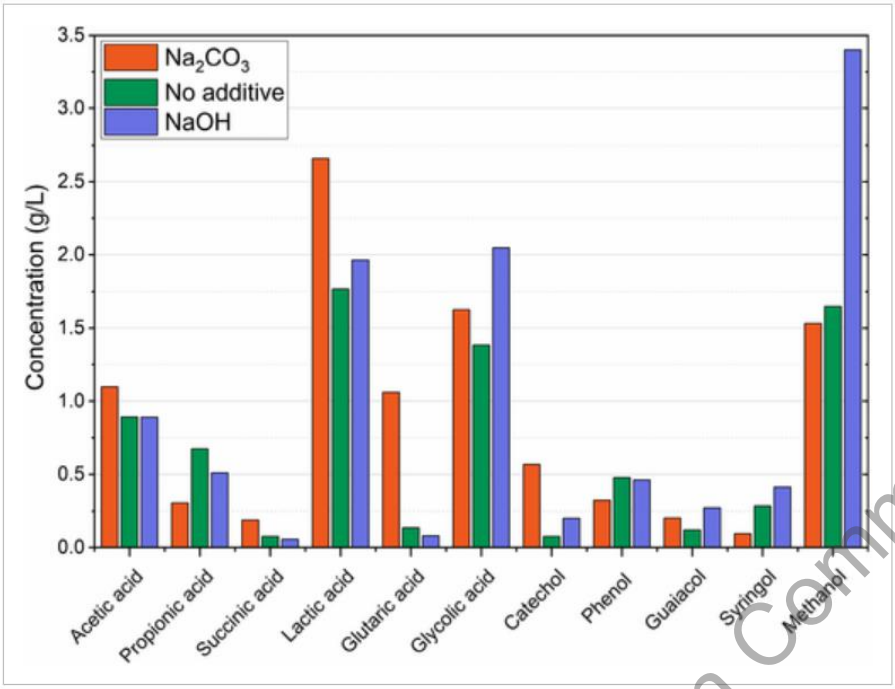

Figure 4. Composition of organics in the aqueous phase in HTL of LRF in lignocellulosic ethanol production using poplar feedstock.[4]

Based on the experimental work done in the project, stability of the catalysts developed and tested in the project still needs to be improved. Furthermore, low conversions of phenolics to hydrogen (< 5 %) being present in the aqueous streams studied were observed. This means at least that APR cannot cover the whole hydrogen demand for IHDO. It was estimated based on the observed concentration of oxygenates in aqueous stream (aliphatic alcohols and ketones ~2 wt-% and phenolics ~0.3 %) and hydrogen yields (aliphatic alcohols and ketones ~ 30 % and phenolics ~ 1 %) that in the beginning of lifetime of the catalyst, APR could supply 20-25 % of the hydrogen demand of IHDO. The maximum percentage of hydrogen supply for IHDO with full conversion all oxygenates dissolved in aqueous stream would be ~ 90 %. It has been planned to cover the rest of the demand by green hydrogen produced by water electrolysis. However, especially short catalyst lifetime and relative low hydrogen yields in APR question the economic feasibility of an APR plant for hydrogen production as a part of the IHTL concept.

4 Gas treatment

The focus of the gas treatment was to treat the off-gases obtained from IHDO. However, the gases from IHTL are also led to IHDO wherein hydrogen is added to the reactor and some carbon oxides are formed. Optionally, off-gases formed in IHTL can be taken out already after the IHTL. Since there is a need for hydrogen excess in hydrotreatment processes, hydrogen can be assumed to be the main component in the gases purged from the IHDO even in the case where a part of the off gases is recycled back IHDO without purification in order to improve hydrogen utilization.

The targets of the gas treatment are twofold. On the one hand, treatment of odorous gases and on the other hand improving the overall economics of the process by separating and utilizing of some components from the off-gas stream.

4.1 Gas composition

As explained above, the main component in the off-gases from the IHDO is hydrogen. In addition to hydrogen, the gas contains carbon oxides formed in the IHDO and light sulfur compounds formed both in IHTL and IHDO. A typical composition of the gas stream is given in Table 1. The composition is based on IHDO batch experiments done at VTT using HTL biocrude obtained from Tampere University. Furthermore, since H_2S was not analysed in these experiments, H_2S concentration was assumed to be 2 mol-% based on the litterature.[2]

Table 1. Typical composition of gas stream from IHDO. H_2S concentration estimated based on the literature.[2]

Compound	Mol-%
CO_2	0.4
Ethylene	0.01
Ethane	0.03
H_2	95.0
O_2	0.6
N_2	1.9
H_2S	2.0

4.2 Gas treatment at pulp mill

The base case to treat the gases in BL2F concept is to send the gases to the odorous gas treatment at pulp mill integrated to the IHTL plant. In practice, this will mean burning them in the recovery boiler or in a separate odorous gas boiler. However, it would be beneficial to utilize the sulphur in the gases for sulfuric acid production and hydrogen for pure hydrogen production to be used e.g. for IHDO. Three different cases were determined to be studied (see Chapter 2) and these cases are introduced in Chapters 4.2.2 – Chapters 4.2.4. Finally, these cases will be compared in Chapter 4.2.5 based on the techno-economic assessment performed as a part of Mustafa Saad Master's thesis.[2]

4.2.1 Methodology of concept studies

The first step to investigate the three studied concepts was to develop the flow diagrams for three cases. It was assumed that the off-gas stream from IHDO unit is 5000 kg/hr with the composition given in Table 2 with temperature 400 °C and pressure 10 bar(a). Information on the configuration of sulfuric acid plant and hydrogen separation technologies were obtained

from the literature. For sulfuric acid production, technology described by Valmet was assumed.[5] Regarding hydrogen separation, different technologies were compared in the thesis of Mustafa Saad[Error! Bookmark not defined.] and pressure swing adsorption process (PSA) was chosen for the concept studies.

As a second step, the flowsheets of all three concept were built in Aspen Plus software and these cases were simulated assuming steady state. However, no detailed model was constructed for PSA i.e. simple split fraction for hydrogen was assumed. Aspen Plus version 11 was applied for the simulations. Electrolyte NRTL was used as a thermodynamic method being capable to be used to simulate sulfuric acid plants. However, for non-condensable components, Henry's law was used to estimate the liquid phase solubilities. More detailed information on the specification of Aspen Plus models can be found in the Master's thesis of Mustafa Saad.[2]

Finally, techno-economic assessment was performed for the three studied cases. Aspen Process Economic Analysed (APEA) was mainly applied to estimate to the capital costs of the plants based on concepts of Cases 1-3. However, since PSA was not modelled in detail in Aspen Plus, the information regarding capital cost was based on the literature to obtain estimates for the main equipment of PSA and combined in the Cases 1 and 3 with other main equipment costs obtained from Aspen Plus. APEA in Aspen Plus 11 used data from 2018 with Chemical Engineering Plant Cost Index (CEPCI) 603.1. This was scaled to CEPCI value of 2022 being 833.1.[6] Based on the purchased costs of main equipment following equation (1) was used to calculate ISBL fixed capital cost of a plant:[7]

$$C = \sum_{i=1}^{i=M} C_{E,i,A}\left[(1+f_p) + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)/f_m\right] \quad \textbf{(1)}$$

where

$C_{E,I,A}$ purchased equipment cost of i in alloy (other than carbon steel)

M is total number of equipment

f_p is installation factor for piping

f_{er} is installation factor for equipment erection

f_{el} is installation factor for electrical work

f_i is installation factor for instrumentation and process control

f_c is installation factor for civil engineering

f_s is installation factor for structures and building

f_l is installation factor for lagging, insulation and paint

f_m is material factor (purchased cost of another metal alloy/purchased cost of carbon steel)

Following values were used for these factors in this study (Table 2). Furthermore, stainless steel AISI 304/316 was assumed as the material with material factor 1.3.

Table 2. Values of factors used in Equation (1).

Item	Process type - Fluids
Purchase cost	C_e
f_p	0.8
f_{er}	0.3
f_{el}	0.2
f_i	0.3
f_c	0.3
f_s	0.2
f_l	0.1

Based on the ISBL fixed capital cost, total fixed capital cost was calculated as follows (Equation 2):[7]

Total capital cost = ISBL capital cost + OSBL capital cost (40 % of ISBL) + Engineering cost (10 % of ISBL + OSBL) + contingency (10 % of ISBL + OSBL) + working capital (15 % of ISBL + OSBL) **(2)**

For the calculation of total cost of production, following equation was used:[7]

Total cost of production = variable cost of production (VCOP) + fixed cost of production (FCOP) – total annual capital charge **(3)**

where VCOP is calculated as follows:

VCOP = Raw materials costs (RM) + Utilities costs (UTS) – By-product revenues (BP) **(4)**

Raw material costs include raw materials related to the production of desired product. Fixed cost of production includes labour, maintenance, overhead costs and insurances and taxes. Utilities costs include use of utilities for the production such as electricity, cooling water, steam etc. By-product revenues comprise incomes from the sales of by-products or secondary

products. Total annual capital charge is calculated based on total annual capital charge ratio depending on the interest rate and the time period studied.

Finally based on the CAPEX and OPEX economic analysis is performed including net present value (NPV) and internal rate of return (IRR) calculations. NPV and IRR are calculated as follows:[7]

$$\mathrm{NPV} = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \quad \textbf{(5)}$$

where

CF_n is cash flow in year n

t is project life in the years

I is interest rate

$$\sum_{n=1}^{n=t} \frac{CF_n}{(1+i')^n} = 0 \quad \textbf{(6)}$$

where

i' is IRR (or discounted cash flow rate of return).

More information on the methodology of techno-economic assessment can be found in the Master's thesis of Mustafa Saad.[2]

4.2.2 Case 1: Separation of hydrogen and production of sulfuric acid

In the Case 1, hydrogen is first separated by a PSA unit from the gas stream from IHDO and the rest of the gas is directed to a sulfuric acid plant. In the sulfuric acid plant, H_2S is first burned to SO_2 and SO_2 is then oxidized catalytically in fixed bed reactors to SO_3. SO_3 is finally absorbed in the water to obtain sulfuric acid. Some electricity is generated from the steam generated by the exothermic reactions. The waste gas stream will be directed to the recovery boiler. A flow diagram of Case 1 is given in Figure 5.

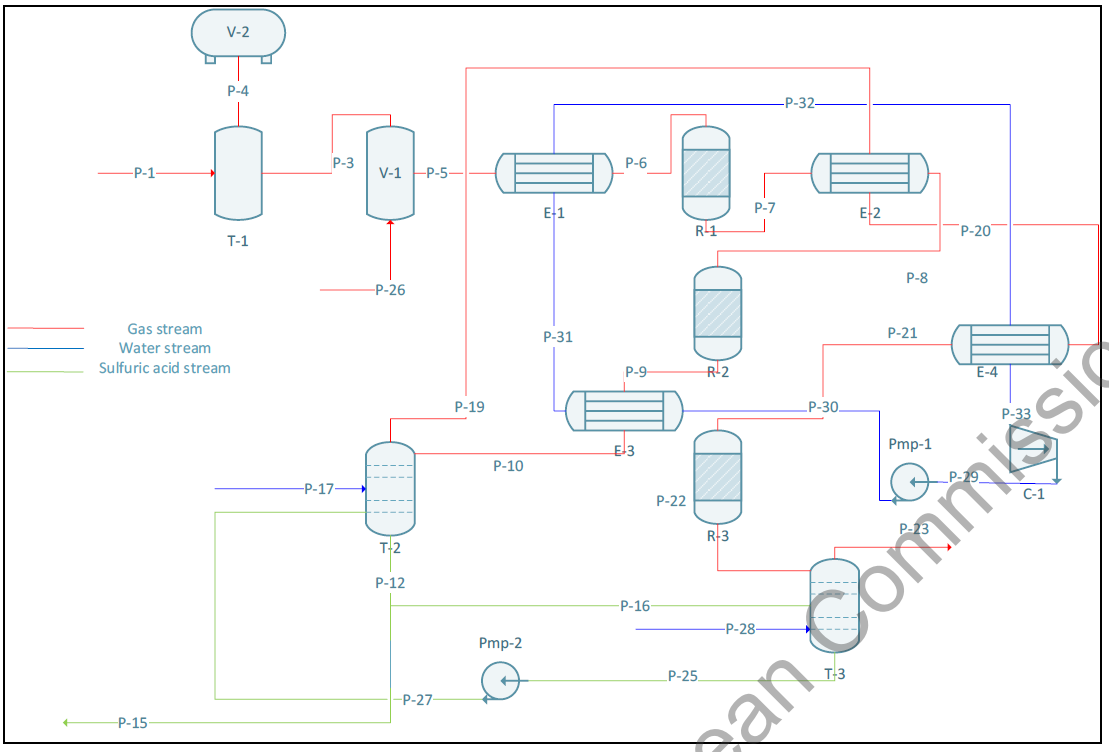

Figure 5. Flow diagram of Case 1.[2]

Gas flow from IHDO is first directed to T-1 which describes the PSA unit for the separation of hydrogen from the gas stream. Purified hydrogen is collected to the vessel V-2 and the rest of the gas stream is directed together with air (P-26) to a furnace described by V-1 to burn H_2S to SO_2. Temperature of this stream after the furnace is 1106 °C and the stream will be cooled down by heat exchanger E-1 before the reactors R-1 – R-2 to oxidize SO_2 to SO_3. After R-2 the gas stream is cooled down to 300 °C before feeding to absorption tower T-2 where SO_3 is absorbed in the water to produce sulfuric acid. The gas with some unreacted SO_2 will continue to through heat exchangers to reactor R-3 where rest of the SO_2 is oxidized to SO_3. The stream from the reactor is directed to another adsorption tower where SO_3 reacts with injected water to sulfuric acid. In the cooling water circulation, there is turbine C-2 installed to generate some electricity from the steam formed in heat exchangers E-1, E-3 and E-4. The waste gas stream P-23 will be sent to recovery boiler.

Aspen Plus flowsheet of Case 1 is given in Figure 6 with temperature (°C) and pressure (bar(a)) labels of the flows.

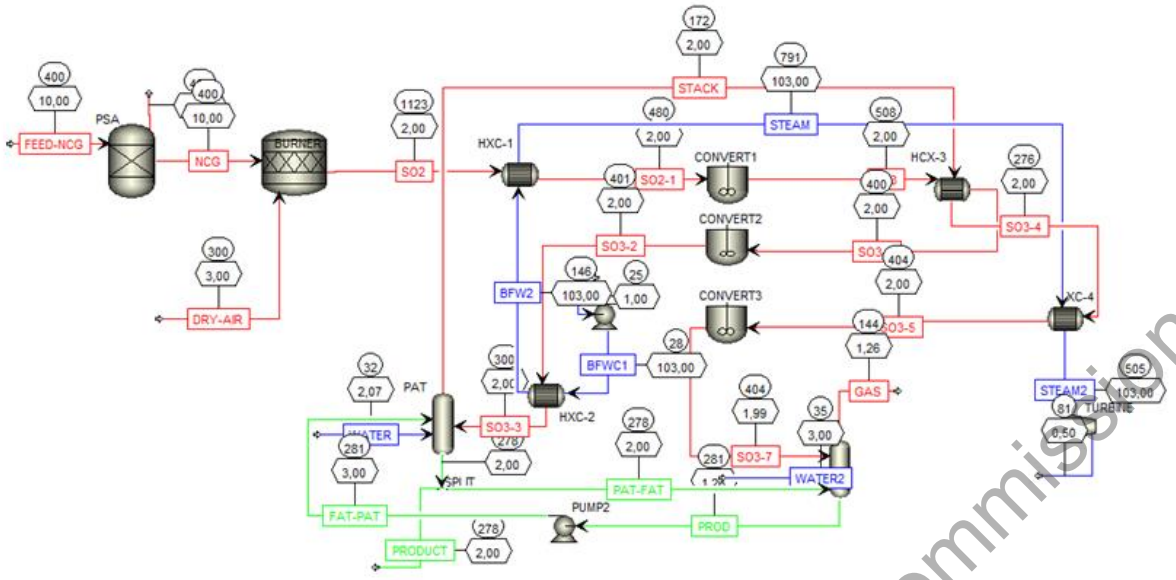

Figure 6. Aspen Plus flowsheet of the Case 1.[2]

The mass flows of the main streams in the flowsheet are given in Table 3.

Table 3. Main streams of the Case 1 flowsheet.[2]

	Component	Stream	Unit	Value
Feed	Non-Condensable gasses	P-1	tonne/hr	5
	Dry air	P-26	tonne/hr	65
	Water for 1st Absorption column	P-17	tonne/hr	6
	Water for 2nd Absorption column	P-28	tonne/hr	8
	Water Steam for Heat exchanger	P-29	tonne/hr	14.6
Total			**tonne/hr**	**98.6**
Product	sulphuric acid	P-15	tonne/hr	2.91
	steam production	P-33	tonne/hr	14.6
	Hydrogen	P-4	tonne/hr	2.31
Waste	exhaust gas	P-23	tonne/hr	78.78
Total			**tonne/hr**	**98.6**

4.2.3 Case 2: Sulfuric acid production without hydrogen separation

In the Case 2, sulfuric acid is produced in the similar sulfuric acid plant as in the Case 1 but without hydrogen separation prior to the sulfuric acid plant. Some electricity is produced from the steam generated by the exothermic reactions. Hydrogen is burned as well in the sulfuric acid plant. The flow diagram of Case 2 is given in Figure 7.

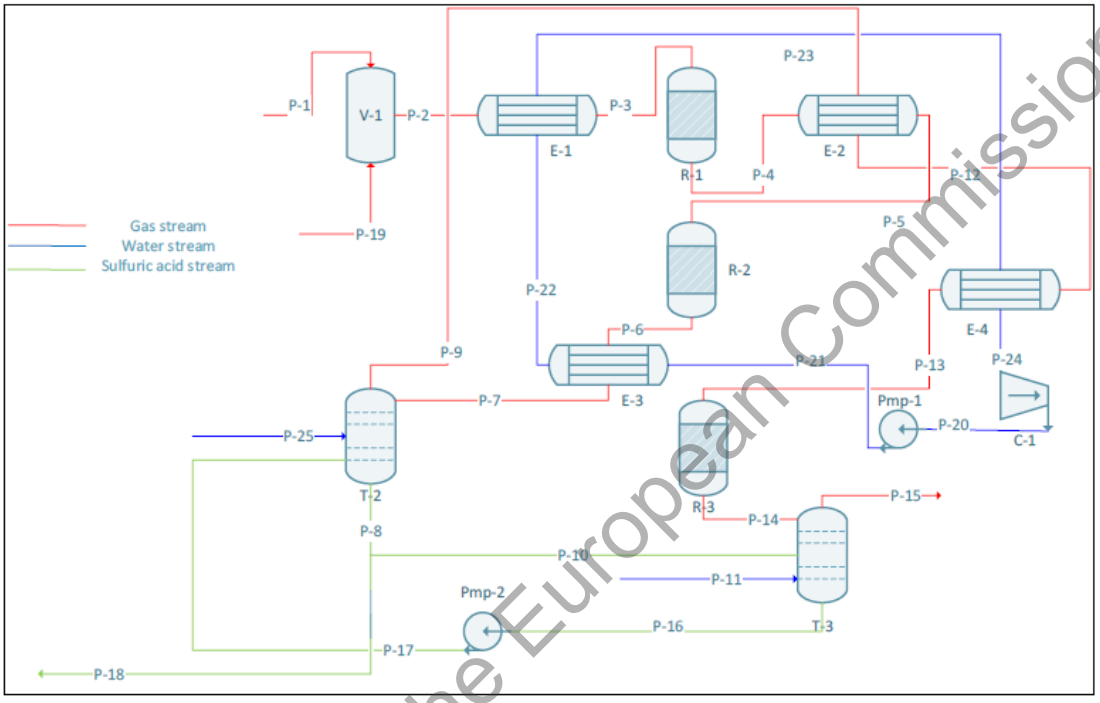

Figure 7. Flowsheet of the Case 2.[2]

The flow diagram of Case 2 corresponds flow diagram of Case 1 except there is no PSA unit in the beginning of the process. Aspen Plus simulation flowsheet with temperature and pressure information of the flows is given in Figure 8 and the main streams as mass flows in Table 4.

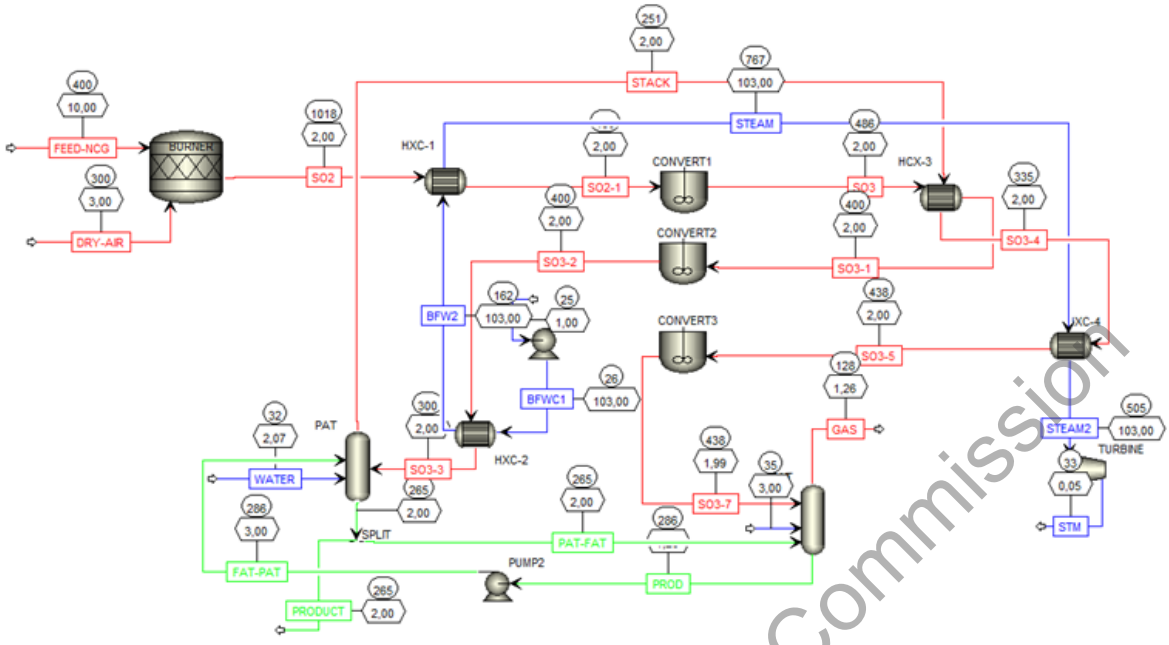

Figure 8. Aspen Plus flowsheet of Case 2.[2]

Table 4. Main flows of Case 2 flowsheet.[2]

	Component	Stream	Unit	Value
Feed	Non-Condensable gasses	P-1	tonne/hr	5
	Dry air	P-19	tonne/hr	400
	Water for 1st Absorption column	P-25	tonne/hr	6
	Water for 2nd Absorption column	P-11	tonne/hr	60
	Water Steam for Heat exchanger	P-20	tonne/hr	80
Total			**tonne/hr**	**551**
Product	sulphuric acid	P-18	tonne/hr	2,92
	steam production	P-24	tonne/hr	80
Waste	exhaust gas	P-15	tonne/hr	468
Total			**tonne/hr**	**551**

4.2.4 Case 3: Hydrogen separation and burning the non-condensable gases in a recovery boiler

In Case 3, hydrogen is separated in a PSA unit and the rest of the gas stream is then sent to recovery boiler. Opposite to other cases, recovery boiler was also modelled in Case 3. Flow diagram of Case 3 presented in Figure 9.

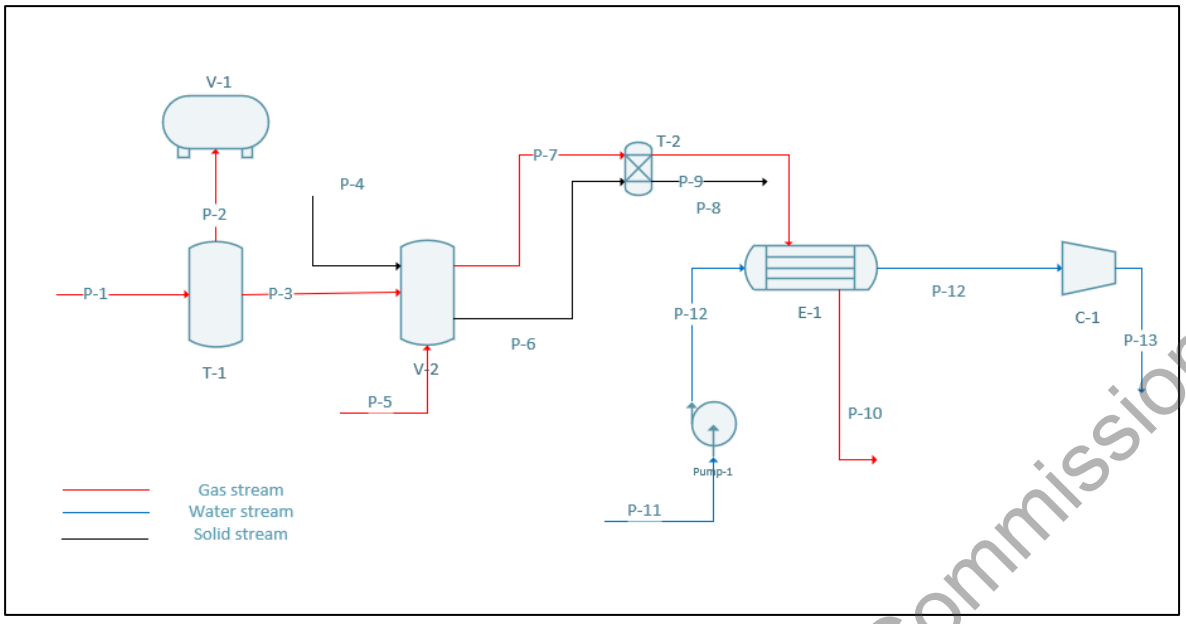

Figure 9. Flow diagram of Case 3.[2]

In case 3, gas stream from IHDO is first fed to PSA unit described by T-1 as in the Case 1. From T-1 the gas stream from which hydrogen is separated, is directed to recover boiler located at a pulp mill (existing plant). The gases are burner in the recovery boiler together with black liquor (P-4). Air is fed as well to the recovery boiler and the boiler modelled as a Gibbs reactor is operating at temperature 1196 °C. To separate green liquor from the gases there is a separator after the recovery boiler (T-2). Gases are led to heat exchanger E-1 where heat is recovered from the flue gases. Steam is generated as well in this heat exchanger to produce electricity in the turbine C-1. Aspen Plus simulation flowsheet is presented in Figure 10 and the main streams as mass flows in Table 5.

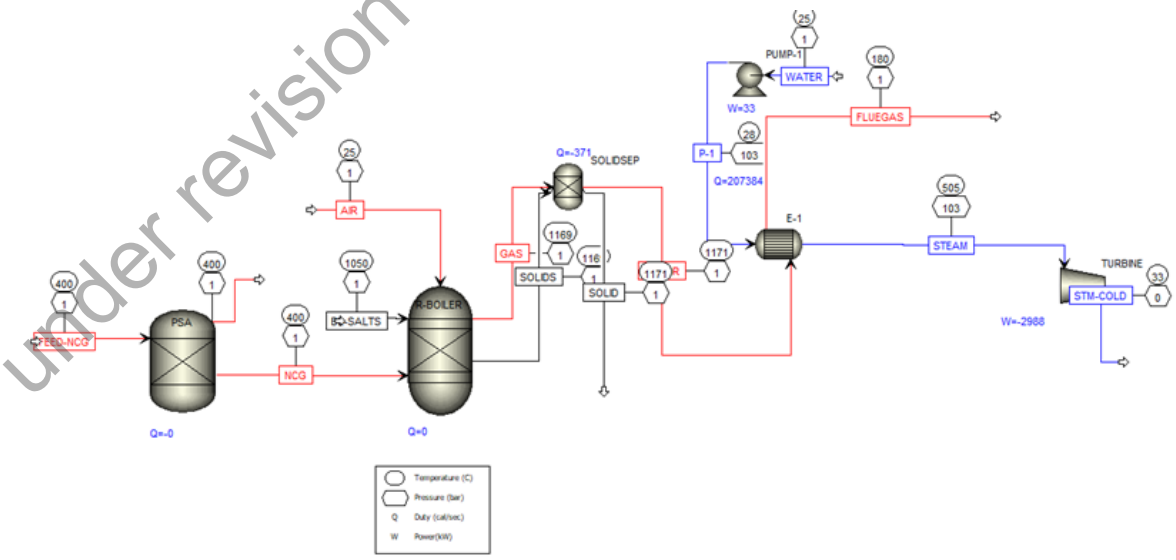

Figure 10. Case 3 Aspen Plus simulation flowsheet.[2]

Table 5. Main flows of Case 3 flowsheet.[2]

	Component	**Stream**	Unit	Value
Feed	Non-Condensable gasses	P-1	tonne/hr	5
	Dry air	P-5	tonne/hr	20
	NA_2CO_3	P-4	tonne/hr	50
	Water for Heat exchanger (Steam system)	P-9	tonne/hr	9.245
Total			**tonne/hr**	**84.245**
Product	Hydrogen	P-2	tonne/hr	2.308
	steam production	P-10	tonne/hr	9.245
	Solids	P-6	tonne/hr	49.242
Waste	exhaust gas	P-8	tonne/hr	23.45
Total			**tonne/hr**	**84.245**

4.2.5 Comparison of the cases

The three cases were compared e.g. in the means of energy consumption as well as economic analysis. A comparison of energy consumption and generation in the three cases in presented in Table 6.

Table 6. Energy consumption and generation in Cases 1 - 3.[2]

Duties (MW)							Electricity generation (MW)		
Case 1									
E-1	E-2	E-3	E-4	Pump-1	Pump-2	**Total Duty**	C-1		
15,8	2,1	1,2	4,7	0,08	0,0003	**23,9**	3,5		
Case 2									
E-1	E-2	E-3	E-4	Pump-1	Pump-2	**Total Duty**	C-1		
74	12	11	13,99	0,3	0,0013	**111,3**	24		
Case 3									
E-1				Pump-1		**Total Duty**			
8,68				0,033		**8,7**	3		

As can be seen from the table, clearly highest electricity generation can be obtained in the Case 2 due to complete combustion of hydrogen. On the other hand, clearly highest duties are also needed for the Case 2.

Economic analysis started with the calculation of CAPEX for all three cases. Capital costs for Cases 1-3 are given in Table 7. As can be seen, CAPEX of Case 2 is clearly highest and CAPEX of Case 3 clearly lowest.

Table 7. Capital costs of Cases 1 - 3.[2]

Cost parameters	Basis (Towler, Sinnott 2021)	Case 1	Case 2	Case 3
ISBL capital cost. MM€		10.93	17.44	4.23
OSBL capital cost. MM€	40 % of ISBL	4.37	6.98	1.69
Engineering cost. MM€	10 % of (ISBL+OSBL)	1.53	2.44	0.59
Contingency. MM€	10 % of (ISBL+OSBL)	1.53	2.44	0.59
Working capital. MM€	15 % of (ISBL+OSBL)	2.30	3.66	0.89
Total fixed capital cost MM€		**18.36**	**29.30**	**7.11**

Gross margin calculations based on the revenues of main and by-products as well as raw material costs are presented in Table 8. Utilities and fixed costs as well as annualized capital cost are not included in the calculation of gross margin. Based on the gross margin calculations, the process of the Case 2 is not profitable. The main reason for this compared to other cases is the lack of revenues from hydrogen sales. Based on these calculations, economic analysis was continued only with Cases 1 and 3.

Table 8. Gross margin calculations.

Key Product and Revenue (REV)							
Key Product		Case 1		Case 2		Case 3	
Product	Price €/unit	Units/year	(k€/yr)	Units/year	(k€/yr)	Units/year	(k€/yr)
Sulfuric Acid (tonne)	200	23253	4650.69	23342	4668.45	-	-
Electricity (kWh)	0.04	28576000	1143.04	1.56e8	6236.00	24000000	960.00
Pure Hydrogen (kg)	3	18463360	55390,08	-	-	18463360	55390,08
Total Revenues (REV) (k€/yr)		**61183.81**		**10904.45**		**56350.08**	
Raw Materials (RM)							
Hydrogen (kg)	2	21720000	43440.00	21720000	43440.00	21720000	43440.00
Water (tones)	2.5	252258.88	633,17	1287399.2	3231.37	80800	202.00
Total Raw Materials (RM) (k€/yr)		**44073.17**		**46671.37**		**43645.20**	
Gross Margin (GM = REV + BP – RM)							
Gross Margin (k€/yr)		**17433**		**-34003**		**12907**	

As a next step total production cost was calculated including variable costs (raw materials and utilities), fixed costs and total annual capital charge. Summary of the calculations of total production cost can be found in Table 9. A detailed calculations of variable and fixed costs and annual capital charge can be found in the Master's thesis of Mustafa Saad.[2]

Table 9. Gross profit and total cost of production calculations summary.[2]

	Case 1 (k€/yr)	Case 3 (k€/yr)
Variable cost of production (VCOP)	43819.33	43461.99
Fixed cost of production (FCOP)	2642.00	1238.76
Cash cost of production = VCOP + FCOP	46461.33	44700.75
Total key product revenues (REV)	61183.81	56350.08
Gross profit = REV – (VCOP + FCOP)	14722.48	11649.33
Total cost of production = VCOP + FCOP – total annual capital charge	47934,89	45271,07

Finally, profitability calculations were performed for Cases 1 and 3 (Table 10). Both cases have excellent profitability with very short payback time, 1.4 and 0.7 years, respectively. Furthermore, IRR was high for both cases was high. NPV as a function of time is presented in Figure 11.

Table 10. Profitability analysis of Cases 1 and 3.[2]

	Unit	Case 1	Case 3
Average cash flow	MM€/yr	14.9	11.7
Simple payback period	Years	1.39	0.68
Return on investment (10 years)	%	52.81	108.49
Return on investment (15 years)	%	58.96	120.89
NPV 10 years	MM€/yr	28.2	29.1
NPV 15 years	MM€/yr	40.4	38.7
NPV 20 years	MM€/yr	46.6	43.6
IRR 10 years	%	49.7	89.9
IRR 15 years	%	51.5	90.4
IRR 20 years	%	51.7	90.4

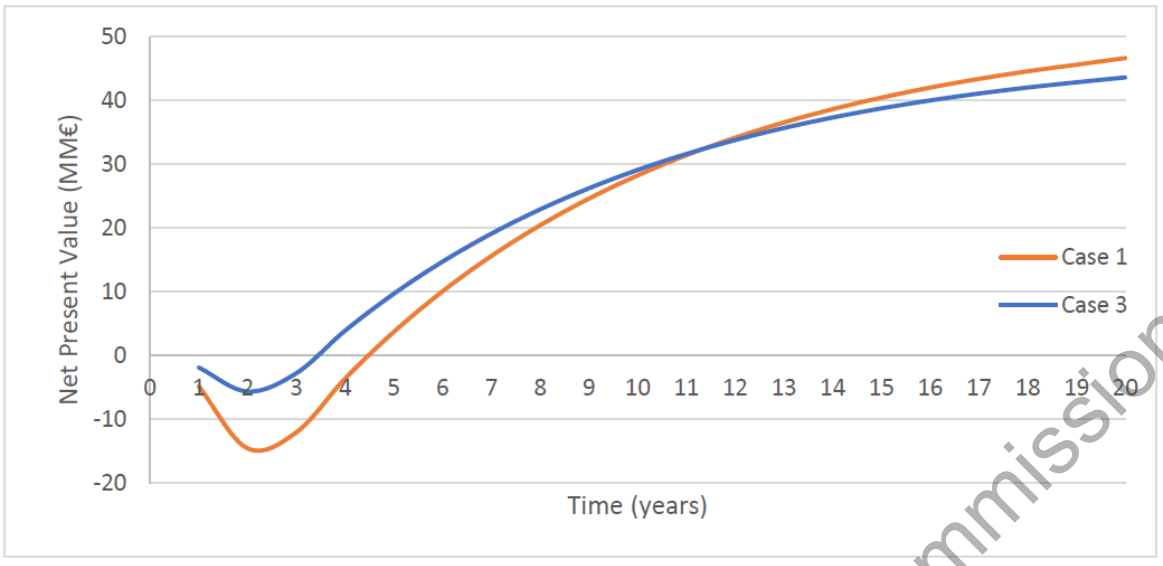

Figure 11. Net present value (NPV) of Cases 1 and 3 as a function of time.[2]

Due to lower CAPEX, Case 3 has higher initial NPV but after 12 years NPV of Case becomes higher due to higher gross profit. However, both cases show very positive profitability. Sensitivity of NPV in Cases 1 and 3 on different parameters such as hydrogen sulfide concentration in the gas stream, sulfuric acid price, electricity price and purified hydrogen sales price was studied as well and presented in the thesis of Mustafa Saad.[Error! Bookmark not defined.] The purified hydrogen price was observed to be the most sensitive parameter. NPV after 15 years as a function of hydrogen price (base case 3 EUR/kg) is presented in Figure 12.

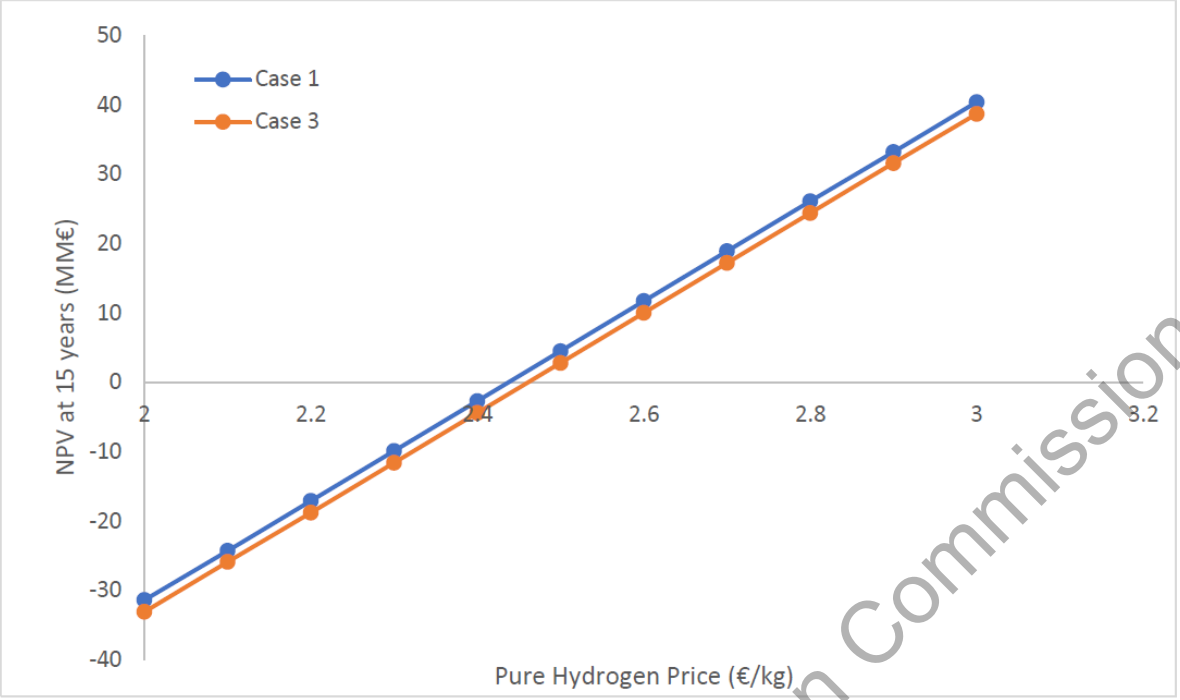

Figure 12. NPV after 15 years in the Cases 1 and 3 as a function of purified hydrogen price.[2]

As can be seen, NPV is very sensitive to the hydrogen price, only 0.3 EUR/kg change in the price will halve the NPV after 15 years.

5 Summary and Future Prospects

This report addresses the utilization of two side streams for the HTL plant: aqueous stream and off-gas stream from IHDO. Aqueous stream with some oxygenated organic compounds is treated by aqueous phase reforming (APR) to obtain hydrogen for the IHDO process. However, APR was mainly handled in the report of D2.3 and therefore APR was only shortly reviewed in this report. The main focus of this report was on the gas treatment. However, regarding APR, catalyst lifetime was concluded to be short and still need further development for the scale up the process to industrial scale. Furthermore, hydrogen production was concluded to be low covering only 20 -25 % of hydrogen demand for IHDO plant. One reason for this is the difficulties to reform phenols with aromatic structures being present in the aqueous stream.

To study different options for gas treatment, a master's thesis was done as a part of BL2F project, and the results of the thesis are summarized in this report. Three different cases were studied in the thesis including development of flow diagrams and Aspen Plus simulation models. Furthermore, economic analysis was performed for the all the cases. Case 2 showed negative revenues whereas Cases 1 and 3 turned out to be very profitable only with 1.4 and 0.7 years payback times, respectively. The main revenue is related to the sales of purified hydrogen and this was also the reason why Case 2 was not profitable since hydrogen was

burned at sulfuric acid plant in this case. On the other hand, net present value of Cases 1 and 3 seemed to be most sensitive to hydrogen price. It should be noted that in the case where gas treatment and IHDO plants are operated by the same actor i.e. hydrogen is used captively for IHDO (Cases 1 and 3) such profitability calculations based on hydrogen sales price might be unrealistic since hydrogen sales price determination can be irrelevant.

It is crucial for the profitability of IHTL concept that side streams can be utilized efficiently. However, regarding APR, it seems to be that catalyst lifetime is too short and hydrogen production is too low to make investment in such plant is feasible. This means that fresh hydrogen supply for IHDO should mainly based on green hydrogen produced by water electrolysis. Furthermore, hydroprocessing plants always require surplus hydrogen to be fed in the reactors and it seem to be feasible to circulate hydrogen back after purification in the PSA unit. It also seems to be feasible to produce sulfuric acid from hydrogen sulfide in the gas stream (Case 1). However, difference in the profitability of Cases 1 and 3 was minor (no sulfuric acid production in the Case 3) indicating that the main revenues were obtained from the purified hydrogen production. However, both concepts of APR and gas treatment require further development to produce information for scale up and to make profitability calculations more exact.

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