Integration of a Biomass-to-Hydrogen Process in an Oil Refinery

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In this article, the substitution of a fossil fuel-based hydrogen (H_2) production unit with a biomass-based process in a large European refinery is studied. Pinch Analysis is performed and several cases are evaluated in terms of energy and CO_2 balances. Integration opportunities yield an increase of the energy efficiency from 70 to 79 %. In addition to H_2, a maximum of 77 t/h of HP steam or 21.8 MW of electricity can be exported to the refinery. Maximum potential for reduction of CO_2 emissions amounts to 758 kt/y and is found when H_2 and electricity are coproduced.

1. Introduction

As a consequence of increasing sulphur content of crude oil supplies, steady increase in diesel demand and harsher environmental specifications for fuels, hydrogen and energy demands are rising in European refineries (CONCAWE, 2012). To overcome hydrogen deficits, many refineries have, or will invest in dedicated hydrogen production units (HPU) producing hydrogen through steam reforming of light hydrocarbons, e.g. methane. These trends lead inevitably to increased carbon dioxide (CO_2) emissions from the refinery (Reinaud, 2005) since both demands are covered by additional fossil fuel. However, alternative hydrogen production routes exist: electrolysis and thermal dissociation use water as feedstock while several processes rely on biomass. From a sustainability point of view, electrolysis may prove an interesting pathway if renewable-based electricity is used. Unless combined with large scale electricity storage, availability issues arise. Thermal dissociation by means of nuclear or solar energy is also a source of environmental and technological concerns. Among biomass-based processes, production of hydrogen from biomass gasification combines high efficiency with the use of renewable feedstock, which could reduce both dependence on fossil feedstock and emissions of fossil CO_2 (Dincer and Zamfirescu, 2012).

In this work, the substitution of an existing, fossil fuel based HPU with a process based on thermal steam gasification of woody biomass (indicated in the following by the acronym BioH2) is studied. The focus is put on opportunities for heat integration and energy and CO_2 balances depending on the degree of substitution of the fossil fuel based process with the biomass based one.

2. Case study

2.1 Oil refinery and hydrogen production unit (HPU)

The refinery studied in this work has a capacity of 11.4 Mt crude oil/y (220,000 bpd). The facility is able to process 100 % Russian Export Blend crude oil, one of the world's sourest blends. This imposes heavy processing of the feedstock to produce market grade products, both in desulfurization and upgrading aspects. As a consequence, hydrogen demand in the refinery is high and H_2 produced in

catalytic reforming (approx. 5 t/h) does not cover the whole demand: 7.4 t/h need to be produced in a dedicated HPU. Fuel gas-fired boilers produce a total of 77.4 t/h of HP steam (39 bar, 390 °C) in the refinery. In an ongoing energy analysis performed by Chalmers Industriteknik, a large amount of excess heat available from the refinery is shown. In particular, a total of 114.7 MW is available from the different units at temperatures over 150 °C.

The HPU relies on commercial, well-established operations: steam reforming of desulfurized hydrocarbons, followed by shift reaction and hydrogen purification via Pressure Swing Adsorption (PSA). The unit can accommodate naphtha and butane as feedstock, both pure or as mixtures of varying proportions. For CO_2 and energy balances, a pure butane feed is assumed in this work. Data from the refinery show that with a yield of 0.3 t H_2/t butane, a butane feed of 24.3 t/h is needed to produce 7.4 t/h of H_2. Thanks to heat recovery inside the process, data show that the HPU is self-sufficient in terms of steam and even exports 25 t/h of HP steam to other units in the refinery.

2.2 Biomass-to-hydrogen process (BioH$_2$)

As opposed to the HPU process above, which is well established and widely used, H_2 production through biomass gasification is still at research stage although well documented in the literature(Williams et al., 2007). The main technological issues are related to gasification and gas cleaning as the produced gas contains a non-negligible amount of tars (heavier, condensable hydrocarbons) that need to be removed prior to further processing. The BioH$_2$ process considered was modelled and simulated in ASPEN Plus(AspenTech, 2010). We considered indirect, atmospheric steam gasification of forest residues wood chips followed by gas cleaning, steam reforming, dual shift and PSA for H_2 purification, see Figure 1. Air drying prior to the gasifier was modelled according to(Holmberg and Ahtila, 2005). The gasifier was modelled considering thermodynamic equilibrium of H_2, CO, CO_2, and H_2O and correlation factors for methane and tars yields. Results were validated against experimental data mainly from the FICFB gasifier in Güssing, Austria(Hofbauer and Rauch, 2000; He et al., 2012). Heat is provided to the gasification zone by char combustion. The remaining parts of the process, from syngas cooling to PSA purification, were modelled using data from Hamelinck and Faaij (2002) and Johansson et al. (2012).
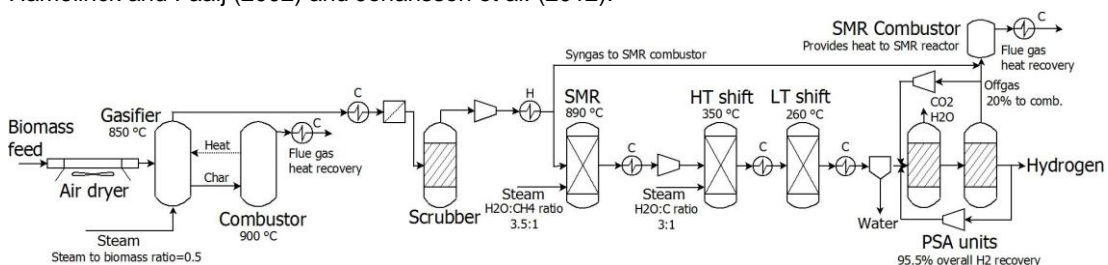

Figure 1: Flowsheet of the biomass-to-H$_2$ process, as simulated in ASPEN Plus

As a result of process simulation, a hydrogen yield of 0.1 ton of H_2 per ton of dry biomass was obtained, which corresponds to a H_2 efficiency of 67 % (MW H_2/MW dry biomass, HHV basis). The total process steam demand amounts to 11.6 t_{steam}/t_{H2}.

3. Methodology

To estimate theoretical energy and CO_2 balances of the processes, we use a targeting methodology whereby maximum heat recovery opportunities are investigated. The synthetic routes for hydrogen production are based on several process steps requiring heating and cooling at various temperature intervals. To avoid dealing with detailed process design and to focus on maximum performances of the investigated systems, maximum heat recovery between such heat sources and sinks was estimated by means of Pinch Analysis tools (Kemp, 2007; Klemes et al., 2010). The so-called Grand Composite Curve (GCC) is used here to represent aggregated heat demand and availability versus temperature level of the process. In addition we used a foreground/background graphical analysis to estimate the possible integration of an additional heat recovery steam cycle. Accordingly, the steam cycle GCC is

plotted against the process GCC and the maximum heat integration potential (i.e. the maximum steam cycle net power generation) is found when at least one pinch point is activated between the process and the steam cycle(Marechal and Kalitventzeff, 1996; Kemp, 2007). The refinery stream data including that of today's HPU were used. A set of the most relevant thermal streams of the BioH2 process was built from results of ASPEN simulations.

Gradual substitution of the HPU with the BioH$_2$ process was studied in order to detect potential interactions and interesting scenarios at partial substitution. Substitution percentages given in the following refer to the proportion of H$_2$ produced in the BioH$_2$ process. To discuss results we refer to "H$_2$ island" as the system based partially on HPU and partially on the BioH$_2$ process. As 25 t/h of HP steam are also currently generated in the HPU, this was considered as a required side-production. Any potential additional steam generation and export is referred to later as "export steam", see Figure 2.
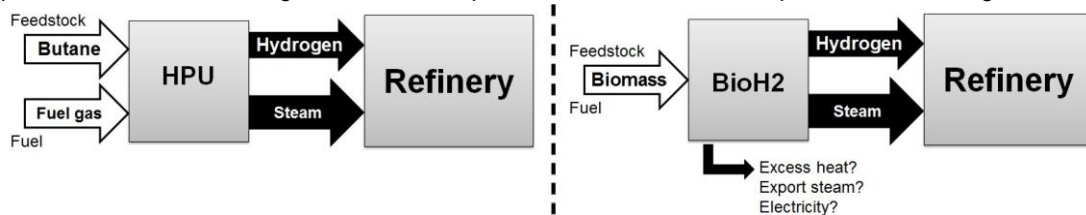

Figure 2: refinery with existing HPU (left); with biomass-to-hydrogen process (right)

4. Energy balances, cases studied

4.1 Pinch Analysis

The GCC of the current HPU is given in Figure 3a. When building this curve, heating of the pre-reformer and reformer feeds and heat of the reforming reaction were not included as heat sinks. For technical reasons, heat at this temperature level is provided via fuel gas firing in a furnace and heat exchange with other streams is not a viable solution. Therefore these streams were made unavailable for process internal heat recovery. For consistency issues, this implies that energy released in the furnace is not included as heat source in the curve either. Figure 3a shows no hot utility demand, which means that apart from 29.4 MW of fuel gas fired in the reforming furnace, all energy demand in the process is covered by internal heat recovery.
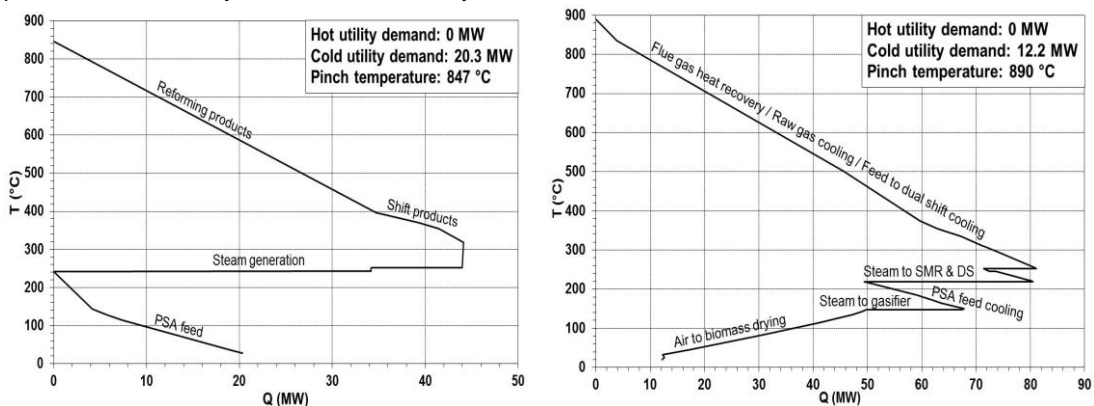

Figure 3: a) GCC of the HPU b) GCC of the BioH$_2$ process

The GCC for the BioH$_2$ process is presented in Figure 3b. Energy balance shows that the BioH$_2$ process is self-sufficient in terms of heat and steam generation. Biomass is used both as feedstock for hydrogen production and fuel for heat and steam generation. We observe therefore that there is no need for external fuel supply. Figure 3b also shows an excess of heat of 12.2 MW.

4.2 Substitution effects, cases studied

Figure 4 presents energy and CO_2 consequences of substituting the HPU with the $BioH_2$ process under the assumption of maximum heat recovery within the H_2 island. It is apparent that CO_2 emissions decrease linearly with increasing degree of substitution. The main contribution in emissions reduction is from avoided butane demand as feedstock for H_2 production. Up to 35 % substitution, there is enough excess heat in the HPU to cover biomass drying, which means that energy available from the $BioH_2$ increases with its size. At 35 % substitution, excess heat from the HPU and energy demand for drying exactly match, yielding a maximum of excess heat that can be exported from the H_2 island. When the share of biomass-based H_2 is further raised, an increasing amount of energy is taken from the $BioH_2$ process for biomass drying, which in turn reduces excess heat available from the H_2 island.
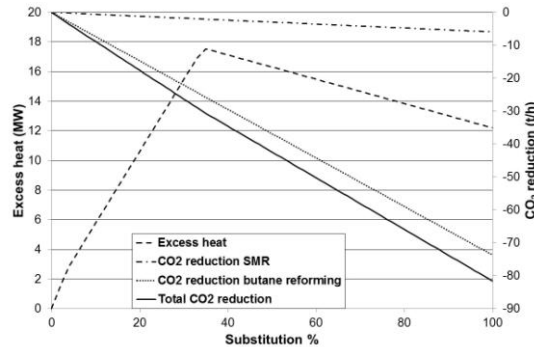

Figure 4: Substitution effects

Starting from these preliminary results, several possible process configurations are discussed in the following and compared in terms of steam export, electricity generation potentials and reduction of CO_2 emissions. In particular, Figure 3b shows large exergy losses in the $BioH_2$ process, due to the large temperature differences between hot and cold streams. We therefore considered investigating also the case of "external drying" to make such exergy pocket available for HP steam production or for combined heat and power purposes. Indeed, it was verified that even in the case of total substitution, enough excess heat is available from other refinery units to cover biomass drying.

The following cases are further discussed:

Case A. 35 % substitution, internal drying, HP steam export;
Case B. 100 % substitution, internal drying, HP steam export;
Case C. 100 % substitution, external drying, HP steam export;
Case D. 100 % substitution, external drying, electricity export (generation through condensing turbine).

5. Results and discussion

Table 1 presents results for the studied configurations. The potential reduction of CO_2 emissions obtained by substituting the current fossil fuel based HPU with the BioH2 process was evaluated assuming: 1) that biomass is CO_2-neutral and 2) that every carbon atom in the butane and fuel gas feeds ultimately produces a molecule of CO_2. CO_2 balance is calculated according to Equation 1:

$$\Delta CO_2 = - \sum_{Feeds} (mass\,flow_{avoided}) \times (specific\,CO_2\,emission) \qquad (1)$$

When HP steam is exported, it is assumed that refinery fuel gas-fired boilers are offloaded by the corresponding load. For Case D, it is assumed that electricity produced in the condensing steam cycle replaces electricity from coal power plants with $\eta_{el}=0.43$. Emissions of 92 kg CO_2/GJ coal are assumed. Total efficiency is calculated according to Equation 2:

$$Total\,efficiency = \frac{\sum Energy\,in\,outputs\,(MW, HHV\,basis)}{\sum Energy\,in\,inputs\,(MW, HHV\,basis)} \qquad (2)$$

Table 1: Comparison of 4 cases and the current HPU. ΔCO_2 is also shown as a percentage of the refinery total annual CO_2 emissions (1.67 Mt in 2010).

Case	Biomass input		H_2 from HPU		H_2 from BioH$_2$		HP steam export		Electricity generation	H_2 efficiency	Total efficiency	ΔCO_2	
	MW	t/h	MW	t/h	MW	t/h	MW	t/h	MW	%	%	kt/y	%
HPU	0	0	291.5	7.4	0	0	0	0	0	80	80	0	0
A	152	29	189	4.8	102.5	2.6	17.5	27.4	0	75	79	-226	14
B	433	83	0	0	291.5	7.4	12.2	19	0	67	70	-629	38
C	433	83	0	0	291.5	7.4	49.4	77	0	67	79	-646	39
D	433	83	0	0	291.5	7.4	0	0	21.8	67	72	-758	45

All configurations with the BioH$_2$ process present efficiencies lower than that of the HPU. This is partly due to a H$_2$ yield higher in the HPU than in the BioH$_2$ process. The large energy demand of biomass drying also puts a penalty on the BioH$_2$ process. This effect is especially visible in Case B, where drying is performed with heat recovered from the BioH$_2$ process itself: this case has the lowest total efficiency with 70 %. In Case A, biomass drying energy demand and excess heat from the remaining HPU capacity come to a perfect match and 27.4 t/h of export HP steam can be produced.

Cases B to D all have 100 % substitution but total efficiencies between 70 and 79 % because of different ways to use the heat from the BioH$_2$ process. Cases B and C both export HP steam to the refinery, but results show an increase of total efficiency by 9 percentage points (from Case B to C) as a benefit of "external drying". It is apparent that using refinery excess heat for biomass drying opens the opportunity of using BioH$_2$ heat to generate HP steam which is highly beneficial. 77 t/h export steam can be produced in this latter case, which is almost equivalent to the total amount of HP steam produced in refinery boilers (77.4 t/h). Consequently, it would be possible to shut down these boilers.
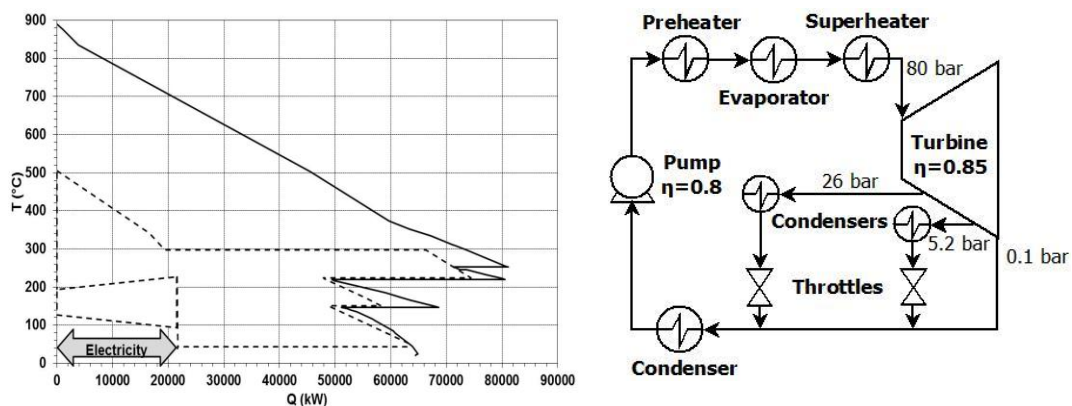

Figure 5: a) Background/foreground curves. Solid line: BioH$_2$ process, dashed line: steam cycle. b) Process flow diagram of the heat recovery steam cycle

In Cases C and D, the same amount of heat is available from the BioH$_2$ process. Unlike Case C where this heat is used to export HP steam to the refinery, Case D emphasizes the opportunity of recovering such heat for electricity production through a heat recovery condensing steam cycle. This integration option is highlighted in Figure 5, where the steam cycle, shown in dashed lines, is represented as a foreground subset of thermal streams against the background set of streams belonging to the BioH$_2$ process. 21 MW of electricity can be generated in this case, giving a total efficiency of 72 %.

Since biomass is considered CO_2-neutral in this study, any fossil fuel saving results in a net reduction in fossil CO_2 emissions. This is confirmed by the results in Table 1 which show that the higher potentials for CO_2 emission reduction are obtained at total substitution. Benefiting from electricity production, case D presents the highest potential of all with CO_2 emissions reduced by 758 kt/y.

A biomass input of 433 MW is needed for total substitution of the HPU. At present, there is no example of gasifier of this size – whether circulating fluidized bed (direct or indirect) or entrained flow. Fluidized bed boilers are, however, commercially available at comparable scale, which suggests that future generations of gasifier could reach such sizes (Thunman, 2012). This scale issue could also be overcome by installing two or three units of smaller throughput.

6. Conclusion

In this paper, the substitution of an existing HPU with a biomass-based hydrogen production process was studied. Opportunities for heat integration were identified and allowed increasing total efficiency of the BioH$_2$ process from 70 % to 79 %. It was shown that the BioH$_2$ process could provide the refinery not only with hydrogen but also with HP steam or electricity. Combining biomass feedstock and heat recovery measures showed a potential to reduce CO$_2$ emissions by a maximum of 758 kt/y.

References

Aspentech, 2010, AspenOne Engineering v7.2.

Concawe, 2012, EU refinery energy systems and efficiency. Brussels: CONCAWE.

Dincer I., Zamfirescu C., 2012, Sustainable hydrogen production options and the role of IAHE. International Journal of Hydrogen Energy.

Hamelinck C.N., Faaij A.P.C., 2002, Future prospects for production of methanol and hydrogen from biomass. Journal of Power Sources, 111, 1-22.

He, J., Göransson, K., Söderlind, U., Zhang W., 2012, Simulation of biomass gasification in a dual fluidized bed gasifier. Biomass Conversion and Biorefinery, 2, 1-10.

Hofbauer H., Rauch R., 2000, Stoichiometric water consumption of steam gasification by the FICFB-gasification process. Progress in Thermochemical Biomass Conversion, September 2000.

Holmberg H., Ahtila P., 2005, Evaluation of energy efficiency in biofuel drying by means of energy and exergy analyses. Applied Thermal Engineering, 25, 3115-3128.

Johansson D., Franck P.T., Berntsson T., 2012, Hydrogen production from biomass gasification in the oil refining industry - A system analysis. Energy, 38, 212-227.

Kemp I.C., 2007, Pinch Analysis and Process Integration, a user guide on process integration for the efficient use of energy, Oxford, UK, Butterworth-Heinemann.

Klemes J., Friedler F., Bulatov I., Varbanov P., 2010, Sustainability in the Process Industry: Integration and Optimization (Green Manufacturing & Systems Engineering), McGraw-Hill Professional.

Marechal F., Kalitventzeff B., 1996, Targeting the minimum cost of energy requirements: A new graphical technique for evaluating the integration of utility systems. Computers and Chemical Engineering, 20, S225-S230.

Reinaud J., 2005, The European refinery industry under the EU emissions trading scheme. International Energy Agency.

Thunman, H. 2012-04-23 2012. RE: Personal communication.

Williams R., Parker N., Yang C., Ogden J., Jenkins B., 2007, H2 Production via Biomass gasification. Advanced Energy Pathways Project. Davis, Ca.: UC Davis, Institute of Transportation Studies.