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# Energy Intensity of Two-Stage Fermentative Hydrogen Production from Biomass in a Plant Equipped with Fuel Cells for Power Supply

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A conceptual hydrogen production plant composed of a pretreatment unit for starchy raw material, a bioreactor for dark fermentation, a photobioreactor for photofermentation and gas upgrading & compression units is considered. In order to supply the plant with necessary heat and power, a part of the stream of raw gas is burned in a boiler and in addition some product gas is directed to fuel cells followed by a catalytic oxidant. Estimates are presented of the influence of product gas purity on the total energy demand in the plant rated 60 kg/h $H_2$ in the raw gas.

## 1. Introduction

Hydrogen can be sustainably produced by fermentation-based conversion of various kinds of biomass (Claassen et al., 2009) of which only starchy raw material is considered in the present paper. Initially, the raw material has to be pretreated with the aim to convert starch to glucose. In the main part of the $H_2$ plant, two-stage bacterial fermentation of glucose solution is employed. The fermentation process starts with the conversion of feedstock by thermophilic bacteria that produce $H_2$ together with carbon dioxide and acetic acid:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \quad (1)$$

The co-product acetic acid is a prime substrate for $H_2$ and $CO_2$ production in the subsequent photofermentation by phototrophic bacteria:

$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2 \quad (2)$$

Finally, the gaseous products are directed to a gas upgrading unit where $H_2$ is separated from $CO_2$.

In the present paper, the energy intensity of fermentative $H_2$ production in a small-capacity, stand-alone plant is estimated. The results of previous experimental research (Claassen et al., 2010) are accounted for in the calculations.

## 2. Flow sheet of the hydrogen plant

### 2.1 Biomass pretreatment

The pretreatment of potato-starch material (35 % wt. starch and 65 % wt. water) consists of three main process steps (Figure 1): enzymatic treatment, liquefaction and saccharification. In the first step the feedstock is mixed with water and enzymes are added. Then the mixture is heated up to about 100 °C and kept for several hours in the liquefaction step. After inactivation of enzymes the outlet stream is

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cooled down to about 60 °C. The liquefied mixture is subsequently fed to the saccharification reactor and enzymes are introduced to promote the conversion of starch to glucose. Next the enzymes contained in the outlet stream from the saccharification stage are inactivated, the outlet stream is heated up and pH correction takes place. Finally the raw glucose syrup is ready for feeding to the thermophilic bioreactor.

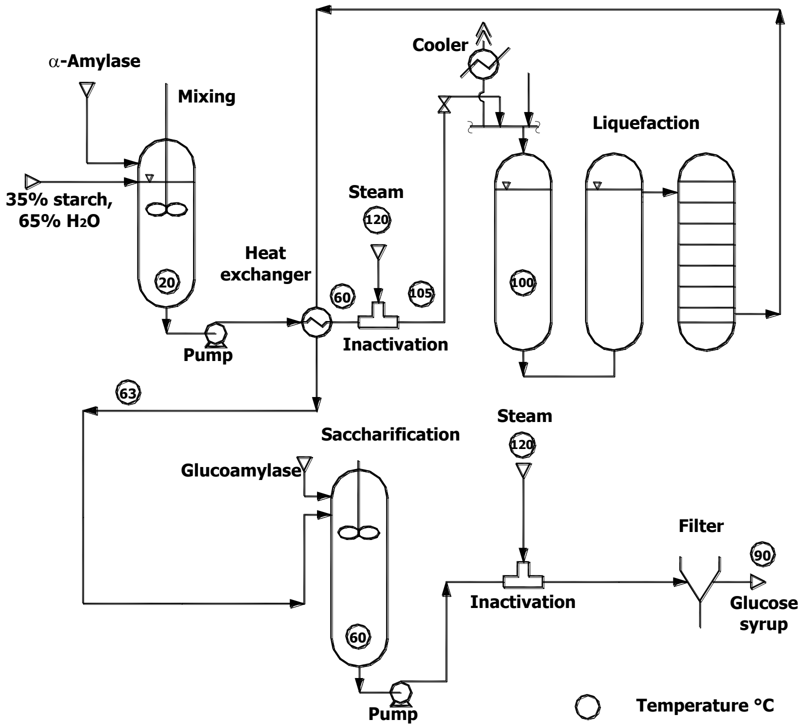

*Figure 1: Scheme of pretreatment of starch-containing raw material*

## 2.2 Thermophilic fermentation and photofermentation

Syrup obtained in the biomass pretreatment stage is diluted with water and then supplied to the thermophilic bioreactor (Figure 2). At a temperature level of about 70 °C the thermophilic bacteria convert sugar mainly into hydrogen, carbon dioxide and acetic acid (van Niel et al., 2002). To promote a high $H_2$ yield, the partial pressure of $H_2$ has to be maintained at a low level (bioreactor is operated under vacuum condition, approx. 50 kPa). The outflowing liquid from the first fermentation step contains organic acids and mainly acetic acid. The liquid is cooled down to 35 °C, diluted with water to the required concentration and supplied to the next bioreactor where photofermentation takes place at room temperature under influence of sunlight, yielding $H_2$ and $CO_2$ (Eroglu et al. , 2008; Gebicki et al., 2009). To compensate for reduced throughput of the photofermentation step at nightime or on cloudy days, a storage tank is provided before the photofermentor. The by-product of photofermentation is water mixed with non-fermentables. It might be re-used for the dilution of syrup supplied as feedstock to the thermophilic bioreactor.

The values of mass flowrates in the process are calculated starting from a simplified process model based on stoichiometric equations. An approximation of the real process is obtained by allowing for incomplete feedstock conversion. The conversion factors for both fermentation stages are assumed on the basis of experimental results: glucose to hydrogen 66 %; acetic acid to hydrogen 67 %.

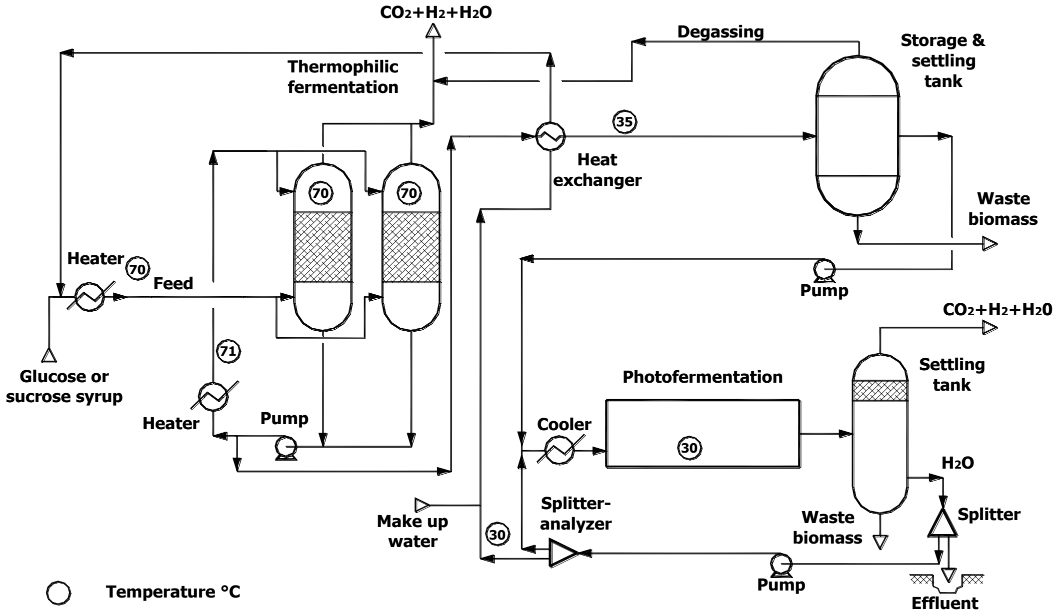

*Figure 2: Scheme of the fermentation stage including thermophilic fermentation and photofermentation.*

The operation of thermophilic fermentation is assumed to be continuous. However, as photofermentation is dependent on sunlight and therefore can only be operated intermittently, this process stage is assumed to run 12 h/d.

### 2.3 Gas upgrading

The flow-sheet of gas upgrading stage where amine absorption is employed is shown in Figure 3 (Markowski et al. 2010). The gas mixture generated in thermophilic fermentation at 70 °C is rich in steam and has to be initially cooled down so that steam is condensed. The resulting two-phase mixture is supplied to a separation unit where water is separated from the gas which flows to a vacuum pump where the pressure is increased making it possible to mix the gas with that generated in the photofermentor. The combined gas stream is compressed by a blower to 120 kPa and subsequently fed to the absorber where absorption of $CO_2$ by active solvent takes place. The obtained high-purity hydrogen is evacuated from the absorber. The rich active solvent flows to the desorber operated at 200 kPa and 120 °C. The outflowing mixture of carbon dioxide and steam is evacuated from desorber. The lean active solvent obtained in the desorber is cooled down and recycled to the absorber.

## 3. Optimization of selected process parameters for minimum energy intensity of hydrogen production

In this study, in addition to the process stages described in Sections 2.1–2.3 above, the production system is assumed to include a compression unit in which the pressure of product gas is raised to 70 MPa. The energy demand in $H_2$ production is assumed to be covered by combined heat and power generation in a subsystem comprising:

- PEM fuel cells supplied with product gas,
- Catalytic oxidant supplied with waste gas and hot air discharged from fuel cells,
- Steam boiler supplied with raw gas obtained from fermentation.

Theoretically possible energy flows between CHP equipment and the different stages of $H_2$ production are illustrated in Figure 4 and will be considered in the determination of minimum energy demand. It should however be emphasized that in a real-life plant in which the process stages are optimally integrated, the arrangement of energy flows may differ from the theoretical one (Foglia et al., 2009).

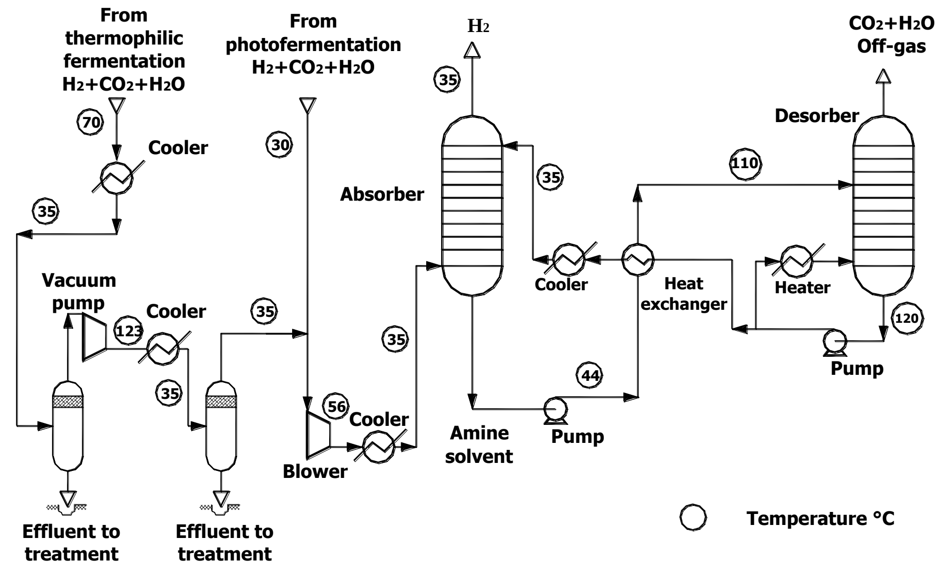

*Figure 3: Scheme of the gas upgrading stage with amine absorption method*

Using energy flow symbols indicated in Figure 4, the required heat and power flows can be expressed as follows:

$$QT= Q_P + Q_{Po} + Q_B + Q_{Bo} + Q_U + Q_{Uo} \tag{3}$$

$$PT = P_P + P_B + P_U + P_C \tag{4}$$

Heat generated in the oxidant depends on $H_2$ energy discharged from fuel cells and can expressed as:

$$Q_{Po}+Q_{Bo}+Q_{Uo}= PT\cdot(1/\eta_{FC} - 1)\cdot \eta_O \tag{5}$$

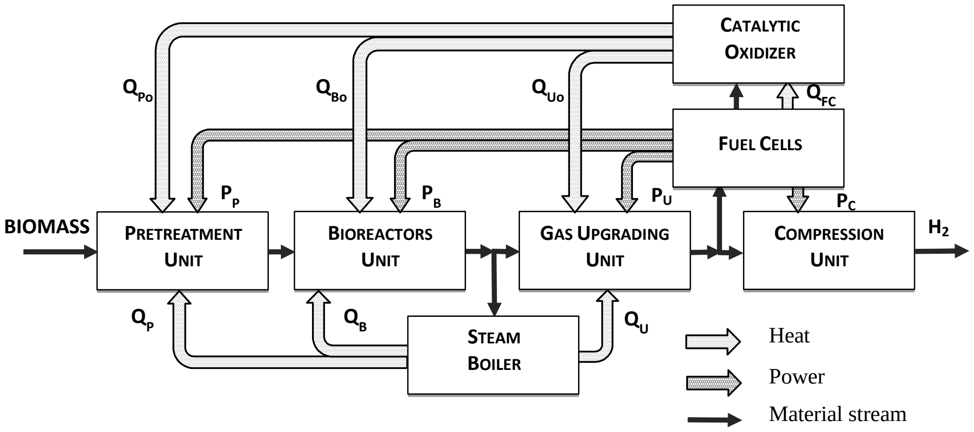

*Figure 4: Scheme of possible energy flows in the hydrogen production system*

To complement equations (3)–(5), the total demand for $H_2$ energy in the production system can be expressed as:

$$PE=(Q_P+Q_B+Q_U)/\eta_G+(Q_{Po}+Q_{Bo}+Q_{Uo})/\eta_O+PT \tag{6}$$

At known values of process parameters indicated in Figures 1–3, the energy demand in thermophilic fermentation depends mainly on glucose concentration before thermophilic fermentation $C_g$, energy demand in photofermentation – on acetic acid concentration before photofermentation $C_a$, and energy demand in gas upgrading – on $CO_2$ volume fraction in the product gas $C_c$. Consequently, the total demand for $H_2$ energy can be considered as a function of variables $C_g$, $C_a$, $C_c$.

Conditions for minimum total energy demand were studied assuming:

- combined $H_2$ output of both fermentation stages 60 kg/h (equivalent $H_2$ energy output 2000 kW);
- glucose concentration before thermophilic fermentation, in g/L, $5 \leq C_g \leq 50$;
- acetic acid concentration before photofermentation, in mmol/L, $40 \leq C_a \leq 100$;
- $CO_2$ volume fraction in the product gas $0.03 \leq C_c \leq 0.32$;
- boiler efficiency $\eta_G = 0.90$, oxidant efficiency: 0.95;
- PEM fuel cell efficiency as a function of $CO_2$ volume fraction in the $H_2$ -rich feed gas, Table 1.

The results of the study indicate that in order to minimize the energy demand, the concentrations of glucose and acetic acid should always be maintained at their upper limits. The influence of $CO_2$ volume fraction in the product gas on the minimum total energy demand is illustrated in Figure 5.

*Table 1: Fuel cell efficiency as a function of $CO_2$ volume fraction in $H_2$-rich feed gas (Schumacher and Modigell, 2007; efficiency at 0.35 $CO_2$ vol. estimated by the present authors)*

| $CO_2$ vol. fraction | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 | 0.06 | 0.07 | 0.08 | 0.10 | 0.12 | 0.35 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Efficiency | 0.498 | 0.496 | 0.494 | 0.492 | 0.490 | 0.488 | 0.486 | 0.484 | 0.480 | 0.471 | 0.420 |

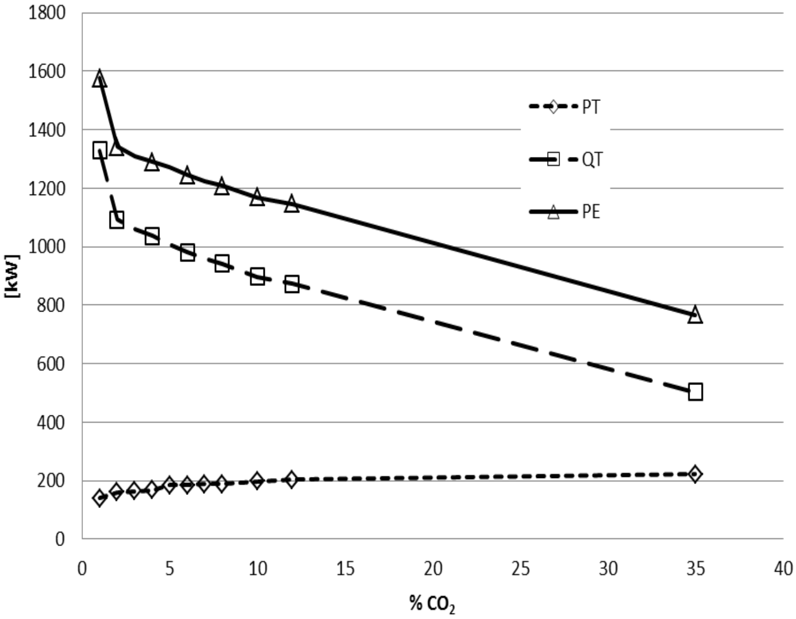

*Figure 5: Estimated power (PT), heat (QT) and total energy (PE) demand in the $H_2$ production system at $C_g$=50 g/L and $C_a$=100 mmol/L*

## 4. Concluding remarks

At $CO_2$ volume fraction in the product gas below 0.20, the total energy demand in fermentative $H_2$ production in a stand-alone plant considered in Section 2 above is equivalent to more than 50% of the energy value of produced $H_2$. The main reason for that is a high heat demand in the amine-absorpton based gas upgrading unit. The total energy demand could be only slightly reduced by applying high-temperature fuel cells rather than PEM fuel cells considered in the present paper. To avoid high energy costs, opportunities should explored for producing $H_2$ in add-on plants placed in industries where waste biomass for use as a feedstock could be available along with waste heat for use in the gas upgrading unit.

## Symbols

$C_g$ – glucose concentration [g/L]
$C_a$ – acetic acid concentration [mmol/L]
$C_c$ – $CO_2$ volume fraction in the product gas [-]
$P_P$ – power supplied to the biomass pretreatment unit [kW]
$P_B$ – power supplied to the two fermentation stages [kW]
$P_U$ – power supplied to the gas upgrading unit [kW]
$P_C$ – power supplied to the compression unit [kW]
PT – total power supplied to the $H_2$ production units [kW]
$Q_P$, $Q_{Po}$ – heat flows supplied from the boiler and oxidant to the biomass pretreatment unit [kW]
$Q_B$, $Q_{Bo}$ – heat flows supplied from the boiler and oxidant to the two fermentation stages [kW]
$Q_U$, $Q_{Uo}$ – heat flows supplied from the boiler and oxidant to the gas upgrading unit [kW]
QT – total heat flow supplied to the $H_2$ production units [kW]
PE – total demand for $H_2$ energy in the production plant [kW]
$\eta_G$ – boiler efficiency [-]
$\eta_O$ – oxidant efficiency [-]

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