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Fermentative Hydrogen Production: Influence of Application of Mesophilic and Thermophilic Bacteria on Mass and Energy Balances

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Fermentation of biomass residues and second generation biomasses is a possible way to enable a sustainable production of hydrogen. The HYVOLUTION-project investigates the production of hydrogen by a 2-stage fermentation process of biomass. It consists of a dark fermentation step of sugars to produce hydrogen, CO_2 and organic acids followed by a photo-heterotrophic fermentation, in which all intermediates are converted to more hydrogen and CO_2. This work compares the use of mesophilic and thermophilic bacteria in the dark fermentation step, analyzing the effects on the overall process. Based on experimental results, simulation models developed with Aspen Plus V7.1® are used to calculate the mass- and energy balances of the process. Results show that dark fermentation at mesophilic conditions requires a higher amount of feedstocks but almost no heat input as well as smaller equipment. However, better economic performance is assumed for the thermophilic operation of the dark fermentation step.

1. Introduction

The future "hydrogen economy" must be environmentally sustainable. Hydrogen, however, is currently produced almost just from fossil fuels (CH_4 reforming and carbon gasification). Without carbon capture and sequestration (CCS), a hydrogen production facility based on fossil fuels would produce comparable CO_2 emissions as the use of fossil fuels in conventional combustion engines.

A possible way to enable a sustainable production of hydrogen is the fermentation of biomass residues and second generation biomasses. Advantages connected to fermentative hydrogen production are mainly the local integration, due to possible adaptation to different types of feedstock, the use of effluents as fertilizers, and the reduction of economic and environmental impact of fuel transport. The HYVOLUTION-project investigates the biological production of hydrogen from biomass in a 2-stage fermentation process. The proposed process consists of a dark fermentation step of sugars to produce hydrogen, CO_2 and organic acids followed by a photo-heterotrophic fermentation, in which the organic acids are converted to further hydrogen and CO_2 (Claassen and de Vrije, 2006).

In this work, operation of dark fermentation with mesophilic and thermophilic bacteria is compared to identify is the most promising dark fermentation organism and analyzing the effects on the following process steps in terms of mass and energy balances.

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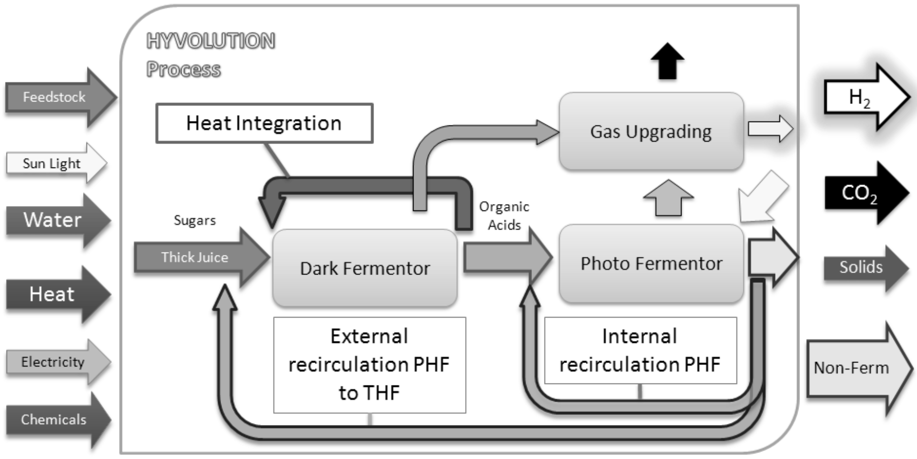

Figure 1: Scheme of HYVOLUTION process for Thick Juice.

2. Process Description

For the calculations, processes based on Thick Juice have been due to available results experimental results from Hyvolution-project for thermophilic operation of the dark fermentation step and reported results in literature for mesophilic fermentation. The assumed composition of Thick Juice is summarized in Table 1. Thick juice is a food biomass, but is chosen due to the good data basis for both process options. However, previous results (Wukovits et al, 2010) showed that molasses, which is an important by-product/residue of sugar production, performed almost as good as thick juice.

The analyzed process is divided in three main steps: dark fermentation, photo-(heterotrophic) fermentation and gas upgrading (Fig. 1). Main parameters of the process steps are reported in Table 2.

The dark fermentation is an anaerobic fermentation step in which highly thermophilic or mesophilic bacteria can be employed. In this step, sugars are converted to hydrogen, CO_2 and organic acids, preferably acetic acid, with 95% of consumption. Both bacteria require high amounts of water to reach the low tolerated sugar concentration (10 g/L). In case of thermophilic bacteria, high amounts of heat are required to bring the fermentation broth to the necessary 70 °C and to keep it under vacuum conditions (0.5 bar) close to boiling conditions (Foglia et al., 2011).

The considered reactions involved in the fermentation of sucrose in the dark fermenter, besides the growth of bacterial biomass, are given in Eqs. 1-5:

$$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 8H_2 + 4CO_2 + 4CH_3COOH \quad (1)$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_3H_6O_3 \quad (2)$$

$$3C_{12}H_{22}O_{11} \rightarrow 4C_3H_6O_2 + 2CH_3COOH + 2CO_2 + 2H_2O \quad (3)$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4H_2 + 4CO_2 + 2C_4H_8O_2 \quad (4)$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CO_2 + 4CH_3CH_2OH \quad (5)$$

Table 1: Assumed composition for Thick Juice.

Components	Thick Juice
Dry matter (dm) (%wt)	71.5
Sucrose (%wt dm)	92.0
Ashes (sol. and insol.) (%wt dm)	5.6
Pectin (%wt dm)	2.4

The photo-heterotrophic fermentation step (PHF) is a light driven process, which converts the produced organic acids to hydrogen and CO_2. The reactor operates best around 30 °C and works at a substrate concentration of 40 mM, with a substrate consumption of 75 %.

Table 2: Basic settings for thermophilic fermentation (THF),mesophilic fermentation (MEF) and photo-heterotrophic fermentation (PHF).

Parameter	Value
Plant capacity	60 kg/h Hydrogen, 97% (vol)
Feedstock	Thick Juice
Thermophilic fermentation (THF)	
Sucrose consumption in THF	95 %
Temperature THF	70 °C
pH THF	6.5
Substrate concentration THF	10 g/L sugar
Sucrose conversion to acetic acid (Eq. 1)	75%
Sucrose conversion to lactic acid (Eq. 2)	5%
Mesophilic fermentation (MEF)	
Sucrose consumption in MEF	95 %
Temperature MEF	35 °C
pH THF	6.5
Substrate concentration MEF	10 g/L sugar
Sucrose conversion to acetic acid (Eq. 1)	18.4%
Sucrose conversion to propionic acid (Eq. 3)	5.6%
Sucrose conversion to butyric acid (Eq. 4)	29%
Sucrose conversion to ethanol (Eq. 5)	11%
Photo-heterotrophic fermentation (PHF)	
Organic acid consumption in PHF	75 %
Temperature PHF	30 °C
pH PHF	7.3
Substrate concentration PHF	40 mM organic acids (total)
Acetic acid conversion to hydrogen (THF, Eq. 6)	40% (Özgür and Eroglu, 2010)
Lactic acid conversion to hydrogen (THF, Eq. 7)	65% (He et al, 2006)
Mixed (MEF effluent mix) organic acid conversion to hydrogen (MEF, Eqs. 6, 8 and 9)	35%[1] (Uyar et al, 2009)

[1]Already considering a reduction of organic acid conversion of 20% caused by ethanol inhibition

The considered reactions involved in the photo fermentation process are the following (Eqs. 6-9):

$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2 \tag{6}$$

$$C_3H_6O_3 + 3H_2O \rightarrow 6H_2 + 3CO_2 \tag{7}$$

$$C_3H_6O_2 + 4H_2O \rightarrow 7H_2 + 3CO_2 \tag{8}$$

$$C_4H_8O_2 + 6H_2O \rightarrow 10H_2 + 4CO_2 \tag{9}$$

The composition of dark fermenter effluent is summarized in Table 3. The ethanol content arising during mesophilic operation causes a decrease of yields/conversion and productivities of about 20% compared to the absence of ethanol (Özgür et al., 2010).
The produced raw gas from the two fermentation steps contains hydrogen, carbon dioxide and water. To obtain pure hydrogen (assumed to be 97% per volume) the raw gas is processed in a dedicated vacuum swing adsorption (VSA) step.
Previous work showed that process integration is necessary to make the process energetically and ecologically feasible (Foglia et al., 2009; 2010a). Recirculation experiments at thermophilic conditions showed that reduction of 60% of dilution water required in the fermentation steps with process effluent doesn't sensibly affect the system in terms of yields and productivities.
To reduce the heat demand of the dark fermentation step, a heat exchanger is inserted to preheat the cold fermenter inlet with its warm outlet.

3. Process Simulation and Models

The process has been implemented in the flow sheeting program Aspen Plus® (V7.1, Aspen Technology, Inc., Burlington, USA, 2008) which was used to solve mass and energy balances. The physical properties of the components were obtained either from the Aspen Plus® component database, from literature or taken from NREL's databank on biomass components. The simulation models adopted for the mass and energy balances have been described in detail in previous works (Foglia et al, 2010a; 2011).
The involved electrolyte equilibrium was considered during simulation to calculate the pH of process streams, to obtain the correct carbon dioxide content of the raw gas stream, and to control the effects of recirculation on the osmolality of the fermentation broth. The thermodynamic model "ElecNRTL" was used to calculate the vapor-liquid equilibrium in all unit operations.

Table 3: Assumed composition of dark fermenter effluent.

Components	Thermophilic	Mesophilic
Acetate [g/L]	7.9	2.6
Lactate [g/L]	0.8	-
Propionate [g/L]	-	0.6
Butyrate [g/L]	-	2.7
Ethanol [g/L]	-	1.1

4. Results and Discussion

The process has been designed to produce 60 kg/h of pure hydrogen (97 % vol) equivalent to 2 MW thermal power.
A summary of the results for the two types of bacteria are shown in Table 4, reporting the most important parameters of the process, such as biomass consumption, dilution water demand and heat demand.
As expected from the usual low hydrogen yield in the dark fermentation step during mesophilic operation, the process option with mesophilic fermentation requires almost double the amount of feedstock compared to thermophilic operation of the dark fermenter to produce the same amount of hydrogen.
Since the substrate concentrations are fixed for both the cases, the total water demand is similar. However, higher sucrose demand in the mesophilic case requires more water in the dark fermentation step and less in the photo fermenter, since due to the higher water demand in the dark fermentation step the acids in the dark fermentor effluent (DFE) are already at lower concentration when entering the photo fermenter.
Connected to the water demand is the chemical demand,
The difference in heat demand for the two cases is caused by the temperature level in the dark fermentation step. Although, the introduction of a heat exchanger a large amount of heat can be recovered during thermophilic operation, strongly reducing the heat input necessary to warm up the fermenter inlet to 70 °C, the reduction of hydrogen partial pressure in the dark fermenter by vacuum stripping (0.5 bar) causes a high additional heat demand for the thermophilic fermentation. While during thermophilic fermentation at 70 °C and 0.5 bar considerable amount of water is evaporated and heat input is necessary to compensate the connected temperature drop, at 35 °C and 0.5 bar, evaporation of water is negligible.
Major advantage of mesophilic bacteria compared to thermophilic operation of the dark fermentation step are the around 10 times higher productivities considerably reducing the capital costs for the dark fermentation step. However, analyzing the major cost factors of the process (Ljunggren and Zacchi, 2010) better economic performance is assumed for thermophilic operation of the dark fermentation step, especially going towards feedstock options requiring pretreatment.

Table 4: Results for thermophilic fermentation (THF), mesophilic fermentation (MEF) and photo-heterotrophic fermentation (PHF).

Parameter	Units	Case	
Dark fermentation bacteria		Mesophilic	Thermophilic
Feedstock consumption	[kg/h]	2622	1270
Water demand dark fermentation	[t/h]	69.5	32.0
Water demand photo fermentation	[t/h]	16.6	75.3
Hydrogen production dark fermentation	[kmol/h]	13.1	14.9
Hydrogen production photo fermentation	[kmol/h]	20.5	18.4
Overall heat demand	[kW]	-	798

5. Conclusions and Outlook

The work gives an overview on heat and water demand of two-stage hydrogen fermentation processes applying different dark fermentation bacteria. Mesophilic bacteria require higher feedstock demand but lower heat input compared to thermophilic ones. Although showing lower productivities and therefore higher investment costs, thermophilic fermentation is still expected having a better economic performance, especially when going towards feedstock options requiring pretreatment.
Improvement of mass- and energy balances in terms of feedstock specific productivities and conversion to hydrogen together with a detailed economic analysis will provide better insight into advantages and disadvantages of mesophilic and thermophilic operation of dark fermentation during two-stage fermentative hydrogen production.

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