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Water Management in Lignocellulosic Ethanol Production- a Case Study and Comparative Analysis from a Swedish Perspective

Rickard Fornell*[a], Karin Willquist[a], Anneli Petersson[a], Carl-Johan Franzén[b]

[a]SP Technical Research Institute of Sweden, Box 857, 50115, Borås, Sweden
[b]Chalmers University of Technology, 40296, Gothenburg, Sweden
Rickard. Fornell@sp.se

The project presented here has focused on studying the water balance in a wheat straw-based conceptual High Gravity (i.e. suspended solids in the bioreactors at above 20 %) lignocellulosic ethanol process using xylose-fermenting yeast, cultivated on the hydrolysate from the process. Based on an initial review of inhibitory substances in lignocellulosic ethanol production, different relevant inhibitors were selected to be included in the analysis of water flows in the process. Experimental analyses of compounds at different positions in the ethanol process were conducted, based on material extracted from the Biorefinery Demo Plant, in Örnsköldsvik, Sweden. The results from analyses were used in flowsheeting model development, which in turn was used in order to analyse the impact of recycling process streams in the conceptual ethanol process. The main result is a comparative analysis on energy efficiency and process economics between different recycling options for three different concepts (two High Gravity alternatives and one Low Gravity alternative with 10 % suspended solids). The results indicate the levels of inhibitory substances at different positions in the ethanol process, and connect this information with the opportunities for recycling and reducing water flow. It is shown that water is an important factor for the economic performance of the process, and that a higher solids content in the process gives better results due to lower investment costs. It is also shown that recycling process streams can have a strong effect on both energy performance (flash steam recycle) and economics (hydrolysate recycle).

1. Introduction

Lignocellulosic ethanol production is on the verge of commercialization, but still there are issues to be resolved for this process. Due to the recalcitrance of lignocellulosic raw materials a harsh pretreatment is most often needed, and this leads to the formation of inhibitory compounds that potentially exacerbate the performance of the following hydrolysis and fermentation reactions. The process is conventionally dilute (suspended solids around 10 %) in order for inhibitor concentrations to be kept low, and thus not deteriorate the performance of the bioreactors. This on the other hand leads to large flow rates, high fresh water demand, and increasing costs for waste water treatment. Due to the large flow of waste water the potential for integration with adjacent infrastructures, e.g. CHP plants, industrial plants, pulp mills, might be difficult even if it is shown that these types of integrations are beneficial from an energy perspective. Studies on so called High Gravity processes (with suspended solids at 20 % or more) have begun to increase. One example of a High Gravity concept is the so called Multifeed approach, developed at Chalmers University of Technology. This concept has the potential to reach very high suspended solids in the fermentor, whilst at the same time decreasing the effect of inhibitory compounds.

This paper focuses on the water management of lignocellulosic ethanol processes, and includes experimental analyses of compounds at different positions in an ethanol process using the Multifeed concept with on-site production of flocculating, xylose-fermenting yeast, and using flowsheet models in SuperPro Designer^{TM} for assessment of the potential for recycling of water in the Multifeed ethanol process. Finally a comparative

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analysis of energy and economics between three different conceptual ethanol production processes (Low Gravity, Multifeed, and “conventional” High Gravity fermentation) is included.
A review and mapping of inhibitory substances in ethanol production, (formation, degradation and level of inhibition at different stages of the process), and a water pinch analysis based on three different methods to investigate the applicability of this methodology to lignocellulosic biorefineries were also included in the project on which this paper is based. Due to page restrictions these topics are omitted from this paper, but will be included in a later publication by the authors.

2. Method

The analysis made in this paper is based on a conceptual lignocellulosic ethanol process. The pretreatment and bioreactor systems are based on data from lab and demo-plant studies, and the other parts of the process are based on literature references. A description of the base case process used in this study, i.e. the multifeed concept as designed in the flowsheeting software SuperPro Designer^{TM}, is presented below.

2.1 Design of the multifeed ethanol process

The studied ethanol process is based on wheat straw as feedstock (assumed capacity 212,000 metric tonnes dry substance/year). The straw is pretreated at 188 °C for 7 minutes using sulphuric acid as catalyst (0.2%). Direct steam (12.3 bar) is used. The Dry Substance is 24 % leaving the pretreatment system, i.e. after flashing the process flow to atmospheric pressure. After the pretreatment the liquid and solid fractions are separated in a filter press, and the solid fraction is sent to the bioreactors. The liquid fraction, here called the hydrolysate, is sent to the yeast propagation reactors, where yeast is cultivated on a mixture of hydrolysate and molasses. Yeast cells are then centrifuged and sent to the bioreactors, and the excess hydrolysate together with the water phase from the centrifuge are sent to the Waste Water Treatment Plant (WWTP). In the bioreactors enzymes are added for hydrolysis of the incoming slurry, and the pentoses and hexoses are fermented to ethanol. A detailed description of the bioreactor system can be found in (Wang et al, 2016). Data used for designing pretreatment and bioreactors where based on runs in the Biorefinery Demo Plant (BDP) in Örnsköldsvik, Sweden.
The remaining part of the process was designed based on information in the scientific literature, mainly from (Humbird et al., 2011). The WWTP was partly based on (Kumar and Murthy, 2011), and the cooling water and boiler systems water balances were partly based on information in (Ahmetovic et al., 2010). Vent gases from yeast cultivation and fermentation are sent to a water scrubber where ethanol and other organic components are returned to the process, and a fairly pure CO_2 gas stream is withdrawn from the process. After the bioreactors, the slurry, containing 5 % ethanol, is sent to a purification section where distillation columns and molecular sieves are used. The end product leaving this section has an ethanol concentration well above 99 %. The bottoms from distillation contain organic residues. This stream is separated in a filter press, and the lignin-rich solid fraction is sent to the steam boiler. The liquid fraction is sent to the WWTP. The first step in the WWTP is an anaerobic digestion reactor, and the second step is aerobic bio-oxidation.

2.2 Defining inhibitors and experimental analysis

Based on a literature review, inhibitory substances, i.e. Acetic acid, extractives, furfural and phenols (dissolved lignin) from pretreatment, and sulphur and sodium from chemicals addition, were included in the study. Samples for testing were extracted from trials at the Biorefinery Demo Plant in Örnsköldsvik, Sweden. Pretreatment flash steam condensate was analyzed for TOC, Total S and Furfural concentration. Pretreated hydrolysate liquid was analyzed for inorganic ions, Total S, Acetic acid, HMF, Furfural and sugars, and the spent water after the yeast cultivation and the SSF was analyzed for organic substances. Organic substances were analyzed by HPLC. Phenols and extractives could not be analysed, and instead literature data was used in the process model.

2.3 Process integration and techno-economic analysis

The process was subjected to a pinch analysis. Stream data was extracted from flowsheet models built in the software SuperPro Designer^{TM}, and a heat exchanger network that is practically feasible and near the minimum hot utility demand was constructed for each alternative. Individual ΔT was used for the different streams. The hot and cold utility demands resulting from the HEN construction were included in the SPD-model and the boiler/turbine system and the cooling water system were specified by iterating between the pinch analysis results and the (modified) computer model.
Three different alternatives were compared in this study. The base case was the multifeed concept, where ethanol is produced only from the solid fraction of the pretreated slurry. This was compared to a dilute, so called, Low Gravity (LG) ethanol process (alternative B), and a High Gravity (HG) ethanol process (alternative C). In alternatives B and C ethanol was produced from both liquid and solid fractions. In this comparison the conversions in the SSF were kept constant, in order to indicate the effects of varying ethanol conversion and

dry solids content in the process. The LG and HG-processes also had production of yeast on site, but not integrated with the process (i.e. hydrolysate was not used for yeast cultivation; instead molasses were used).

3. Results and Discussion

The water balance for the base case process without recirculation of water is shown in Figure 2. The steam and cooling water demands were based on results from the energy pinch analysis, and other water flows were based on either data from the Biorefinery Demo Plant or from the literature.

The minimum water demand in the process, according to Figure 1, is approximately 17 kg/s H_2O, or 3 kg/kg DS feedstock. The losses in this case were the evaporation and drift from the cooling tower and water in the solid fraction sent to the boiler. Compared to previous studies on water minimization in ethanol processes, it has been estimated that for corn to ethanol process the minimum water demand is as low as 0.7 kg/kg DS feedstock (Ahmetovic et al., 2010) for an optimized water network. The differences in results are mainly due to the difference in process design between lignocellulosic wheat straw-based and corn-based processes.

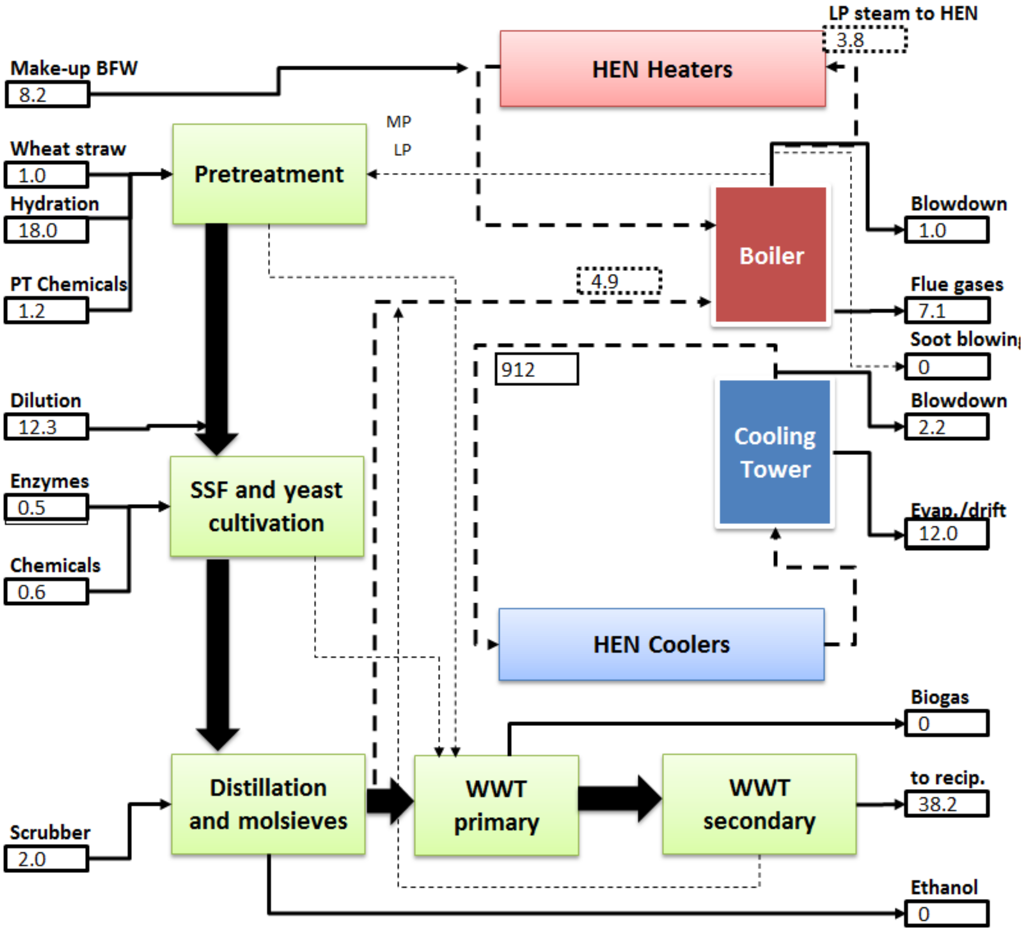

Figure 2. Water flowrates (kg/s H_2O) in the base case multifeed ethanol process (w/o recycling).

3.1 Inhibitory substances for recirculation alternatives

Table 1 is a summary of different inhibitory compounds at three different positions in the ethanol process, for the three different process alternatives (A = Multifeed, B = Low Gravity, C = High Gravity). All results in the table are from simulations made in SuperPro Designer. The concentrations of Na, S, acetic acid and furans in the simulations were validated by experimental analyses. Dissolved lignin and extractives could not be quantified experimentally in the project; the results are thus based on literature values.

Table 1: Potential inhibitors at different positions in the ethanol process, for the three alternatives.

A. Multifeed		1* Diss. Lignin *g/L*	2* Extractives *g/L*	3** Na+ *mg/L*	4 Sulphur *mg/L S*	5 Acetic acid *g/L*	6 Furans *g/L*
A.1	Feed SSF	1.3	3.2	21	277	1.8	0.8
Base Case	Feed Yeast Cult.	3.0	7.5	1101	644	4.1	1.8
	Feed AD	2.1	5.3	117	451	3.2	3.4
A.2	Feed SSF	1.3	3.4	22	278	2.0	2.0
Flash steam recycle in Pretreatment	Feed Yeast Cult.	3.1	7.7	1158	642	4.7	4.7
	Feed AD	2.5	6.1	136	508	3.7	3.7
A.3	Feed SSF	3.1	7.7	32	662	4.2	1.9
Recycle hydrolyzate to the SSF	Feed Yeast Cult.	3.0	7.5	1102	644	4.1	1.8
	Feed AD	2.7	6.8	167	581	4.2	4.7
A.4	Feed SSF	1.5	3.7	85	277	2.0	0.8
Recycle water from centrifuge to PT	Feed Yeast Cult.	3.4	8.5	1246	645	5.5	1.9
	Feed AD	2.3	5.7	119	431	3.5	3.7
B. Low Gravity-process							
B.1	Feed SSF	2.1	5.1	13	665	2.8	1.3
Base Case	Feed Yeast Cult.	-	-	-	-	-	-
	Feed AD	1.8	4.4	-	571	2.7	2.9
C. High Gravity-process							
C.1	Feed SSF	3.5	8.7	22	672	4.7	2.1
Base Case	Feed Yeast Cult.	-	-	-	-	-	-
	Feed AD	3	7.4		572	4.6	5.2
C.2	Feed SSF	3.5	8.8	22	671	5.3	5.4
Flash steam recycle in Pretreatment	Feed Yeast Cult.	-	-	-	-	-	-
	Feed AD	3.6	9.1	23	692	5.5	5.5

* Literature values. 5 % of lignin in feedstock is dissolved in pretreatment. 3.3% of dry feedstock is extractives.
** Na mainly from NaOH used for pH adjustments. No info for process alternatives B and C.
Based on data from the BDP runs, it is assumed that most of the NaOH is introduced prior to yeast cultivation.

Acetic acid and furans are the most relevant inhibitors according to Table 1. There is clear potential for accumulation of these compounds when recycling water streams. In process alternative C the concentration increased substantially compared to the base case. Both acetic acid and furans can be digested in a well-functioning process according to the Multifeed concept, which could be an important positive advantage for this alternative compared to the others.

3.2 Yields and flowrates for recirculation alternatives

Table 2 gives an indication of different product and water flows in the different process alternatives. As can be seen from the table, the water flow to the waste water treatment plant (WWTP) is higher for the Multifeed case than the other alternatives. This is due to the set maximum value of suspended solids to the bioreactors (at 185 g/L). This value leads to a necessity to dilute the feed stream with water in alternative A. More water and more hydrolysate is thus sent to the WWTP in this case, and the yield of ethanol is lower than the other alternatives. The lower yield of ethanol is to some degree compensated by the increased production of biogas. Alternative A.3, where hydrolysate is recycled to the bioreactors, becomes fairly similar to Alternative C, which thus indicates that there is flexibility in the process in terms of production. Focus could be on either ethanol or biogas.

Table 2: feedstock and product rates and some process data for the different alternatives studied.

A.	Straw *t/y*	EtOH prod *m^3/y EtOH*	Biogas prod. *GWh/y CH4**	DS after PT *g/L*	WIS in SSF *g/L*	EtOH to dist. *g/L*	H2O to WWTP *m^3/m^3 EtOH*	*L/s*	BOD5 to WWTP *t O/dag*
A.1	212,000	51,698	141	240	185	49	24	41	89
A.2	212,000	51,914	140	240	185	49	20	35	89
A.3	212,000	60,583	97	240	185	49	14	28	55
A.4	212,000	51,508	141	240	185	49	22	37	89
B.									
B.1	212,000	62,897	110	160	110	36	22	46	65
C.									
C.1	212,000	62,897	100	270	182	59	12	25	58
C.2	212,000	62,897	98	270	183	59	10	20	58

* Lower heating value 13 MWh/t methane.

3.3 Energy and economy for recirculation alternatives

Table 3 shows the economics of the different process alternatives, focusing on parameters that differ between the different designs. Yeast propagation is designed in the same way in all alternatives, and only glucose and xylose are assumed to be carbon sources during cultivation. The CAPEX (capital expenditure) is based on (Humbird et al., 2011) and data from SuperPro Designer^{TM}. The demands and product rates are from the simulation models.

Table 3:Comparative economic assessment of different process alternatives.

A.	El. prod. *MW*	El. demand. *MW*	Steam demand *MW*	CAPEX *M€*	Revenues* *EtOH* *M€/y*	*Biogas* *M€/y*	*El.* *M€/y*	Diff. from A.1** *M€/y*	Diff. from A.1 *%*
A.1	11.7	3.9	25.2	178	42	16	4	-	-
A.2	13.7	3.9	17.5	173	42	16	5	1.6	4.5
A.3	12.2	4.0	25.0	167	49	11	4	3.7	10
A.4	11.7	3.9	25.1	176	42	16	4	0	0
B.									
B.1	8.9	5.3	42.5	222	51	12	2	-1.9	-5
C.									
C.1	12.8	3.5	23.6	156	51	11	5	7.8	21
C.2	14.3	3.5	16.3	149	51	11	5	9.5	26

*for an ethanol price at 800€/m3, a biogas price at 110€/MWh, and an electricity price at 60€/MWh).

** The difference in CAPEX/year (i = 10%, 20 years) + difference in revenues/year.

As indicated by the table, all alternatives generate a net surplus of electricity, and the steam demand can be covered by on site steam production. Recycling flash steam in the pretreatment section is the alternative that leads to the greatest effect on the steam demand (alternatives A.2 and C.2). The reason for this is that the flash steam is not needed as a heat source in a well-integrated process. CAPEX differs mainly due to the costs for the WWTP, which mainly is the cost for the Anaerobic Digestion. It can be deduced from Table 3 that, given the economic parameters used in this study, increased ethanol yield and decreased load to the WWTP are the two most important factors for increasing the profit margin. Table 3 also shows that there are substantial differences in both costs and revenues connected to the different alternative process designs and the type and degree of water recycle.

4. Conclusions

The study presented in this paper has indicated a few interesting points concerning water management in lignocellulosic ethanol production, for example:

- A high suspended solids concentration in the process will lead to lower cost, but not necessarily lower energy demand.

- Flash steam recycling in pretreatment leads to lower energy demand since it replaces live steam in the process. There might be risk for accumulation of furans and acetic acid, however.
- Hydrolyzate recycling to the bioreactors increases ethanol yield, which in the studied process alternatives and with the economic parameters in this study is the most important revenue. This will also lead to an accumulation of inhibitors, which needs to be addressed.

From the results of this study it is shown that a more detailed study on the variation in yield and accumulation of different inhibitors for different process alternatives would be interesting, and that optimized design of the waste water treatment plant and its effects on the process economics is important since costs connected with this plant might be high.

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