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Process Simulation of Biobutanol Production from Lignocellulosic Feedstocks

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A potential flowsheet to produce butanol production by conversion of a lignocellulosic biomass has been simulated by means of the software Aspen Plus®. The flowsheet has included upstream, fermentation, and downstream sections and the attention has been focused on the upstream section. The proposed process is characterized by an economic potential, three times the depreciation rate of the main fixed investment rate, as well as environmental benefits because it is a "clean energy source".

1. Introduction

The production of chemicals and fuels from renewable resources is among targets of the “white biotechnology”. The interest in the biotechnology route for these productions is due to several driving forces: the global warming, the increase of the crude oil price, and legislative restrictions regarding the use of non-renewable energy sources (Naik et al., 2010). A potential solution to the growing demand for fuels from renewable resources is the butanol produced according to the biotechnological route. Main issues that require further investigation are: i) the scouting of renewable resources to be bioconverted into butanol; ii) the selection of strains characterized by high solvent productivity; iii) the development bioreactor systems characterized by high specific productivity; iv) the development of downstream processing strategies for enhanced solvent recovery.
As regards renewable resources, the aim is to select feedstocks plentiful, inexpensive, and not edible (Qureshi and Blaschek, 2000; Kumar and Gayen, 2011; Raganati et al., 2013a). Lignocellulose is the most plentiful renewable resource on the planet, it is made of potential fermentable sugars, it is not useful as food resources, and it is quite cheap. Lignocellulosic materials are characterized by three components: cellulose, hemicelluloses, and lignin. An interesting classification of lignocellulosic feedstocks and their average compositions has been reported by Garrote et al. (1999).
As regards pre-treatment methods, Conde-Mejía et al. (2012) reported a spectrum of single steps typically adopted/suggested for lignocellulosic feedstocks: steam explosion, ammonia fiber explosion, irradiation, dilute acid hydrolysis, and organosolvent extraction.
Regarding to fermentation step, Clostridium strains are able to metabolize a wide range of carbohydrates - like glucose and lactose, pentoses and hexoses - and to produce butanol mixed with acetone and ethanol: the fermentation known as ABE, Acetone-Butanol-Ethanol (Jones and Woods, 1986). Studies carried out on ABE fermentation adopting feedstocks derived from lignocellulosic biomass – a potential inexpensive feedstocks - have reported the yield values and the solvent production rate for batch tests (Raganati et al.2012; Jurges et al., 2012). It is also known that the fermentation productivity may be strongly increased by process intensification as in biofilm packed bed reactors (Lee et al., 2008; Napoli et al., 2010; Raganati et al., 2013)
To achieve further optimization of the process is necessary to isolate the solvent from the fermentation medium. Studies available in the literature on solvent recovery are quite limited. Particularly interesting is the contribution from Liu et al (2004) regarding downstream process synthesis for biochemical production

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of ABE. They have proposed a list of optimal and near-optimal flowsheets with conventional operating units. Attempts to characterize the butanol recovery from the experimental point of view (Mariano et al., 2012; Rom et al., 2013) and from the techno-economic point of view (Napoli et al., 2012) are also reported in the literature.
To the author knowledge, just few studies are reported in the literature on the whole upstream process (Quintero et al., 2012; Qiao et al., 2013). The characterization of the process to produce butanol from the selected feedstock as well as the techno-economic assessment of the process are key issues to be developed in order to identify critical points to study in depth (Olivieri et al., 2013).
The present contribution reports results of a study aiming at investigating the techno-economic feasibility of butanol production from lignocellulosic biomass. The production process has been splitted into three sections: the upstream section, the fermentation section, and the butanol recovery section. Particular attention has been paid to the basic steps required for the upstream process. The upstream units have been analysed according the approximated cost-estimation methods integrated with the simulation software Aspen Plus®.

2. Materials and Process description

Biomass composition depends on the lignocellulosic culture adopted. An exhaustive review on the biomass composition has been reported by Kumar et al. (2009). A first classification of lignocellulosic cultures is hardwood and softwood. Within each class the concentration of hemicellulose, cellulose and lignin range over a quite limited interval. The average composition of the biomass adopted in the present study is: lignin 20%, cellulose 44%, and hemicellulose 36%.
Figure 1 shows a synoptic diagram with the main steps adopted for the investigated process. They are: the comminution of the biomass; the steam explosion with the release of cellulose, hemicellulose, and lignin; hydrolysis of the cellulose and hemicellulose, hexoses and pentoses as products; lignin harvesting; sugars fermentation; and butanol recovery.
The units adopted to produce butanol from lignocellulosic biomass are reported in Figure 2.
Biomass comminution has been simulated by a train of chipping/milling units able to reduce the size of the softwood from the field-harvesting size to those (S2 stream) optimal for successive operations.
The steam explosion operation (SE) has been adopted to pre-treat the comminuted biomass. A saturated steam stream (Steam in Figure 2) at 160°C has been adopted. The steam is vented as stream V1.
The suspension of exploded biomass (S3 stream) is sent to a two-step hydrolysis process. The HCl stream L2 is mixed with the suspension S3 to provide the first acid hydrolysis. The hydrolyzed sugars are recovered mainly into the liquid stream L3 and the suspension rich in cellulose and lignin S4 is mixed with the enzyme rich stream L4 to provide the second enzymatic hydrolysis. The suspension S6 rich in lignin is separated from the liquid stream L5 rich in hydrolyzed sugars. The liquid stream L3 rich in a mixture of pentoses and hesosse produced from the hydrolysis of the hemicellulose is neutralized: the stream L3 is mixed with the stream L4, an aqueous solution of NaOH at 0.4 M. The streams rich in pentoses L6 and that rich in hexoses L5 are mixed to be sent at the fermentation section.

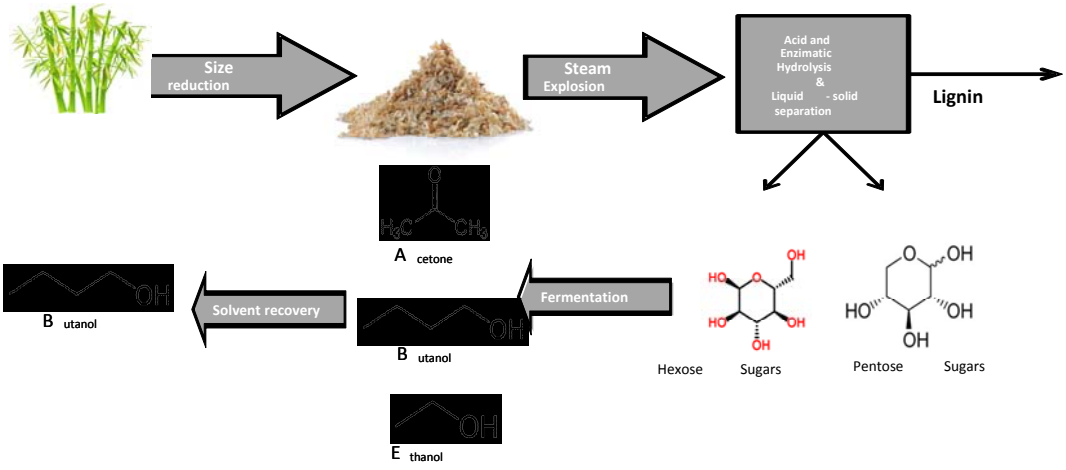

Figure 1: Synoptic diagram of the butanol production form lignocellulosic biomass. Main steps of the upstream process

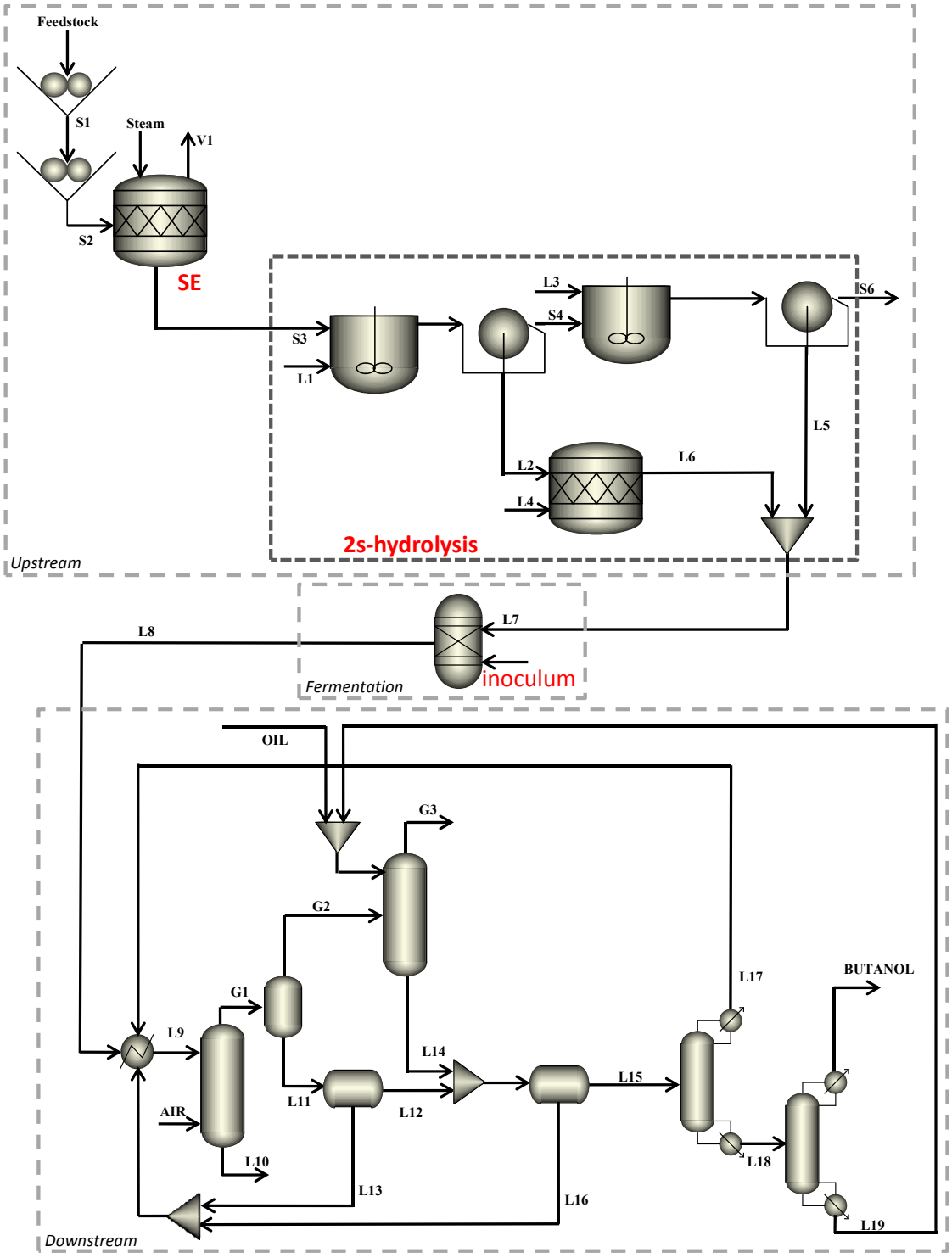

Figure 2: Flowsheet of the investigated butanol process from lignocellulosic biomass. SE) Steam explosion; 2s-hydrolysis) two-step hydrolysis section; Downstream) details in Napoli et al. (2012).

Main assumptions regarding the composition of the solution produced from the upstream section are: i) L6 stream is a solution of glucose, mannose, arabinose, and xylose; ii) products from the partial conversion of the lignin (e.g. phenolic compounds, vanillin, ferulic acid) and from hemicelluloses and cellulose (e.g. furfural and HMF) are absent.

The fermentation unit consists of a biofilm packed bed reactor (Napoli et al., 2010). *Clostridium acetobutylicum* has been selected as the actor of the ABE fermentation because it is able to convert

hexoses and pentoses typically released during the hydrolysis of cellulose and hemicellulose (Raganati et al., 2012).
Details on the recovery and concentration of butanol from the fermentation broth are reported in Napoli et al. (2012).
The cheeping and the milling units have been designed assuming Hardgrove Grindability index value 77 according to Green and Perry (2008).
The filtration unit used to harvest solids has been designed assuming a solid concentration of about 2 kg/m^3. The area of a vacuum continuous filter has been estimated assuming the pressure drop across the filter 70 kPa and the specific cake resistance $2 \cdot 10^6$ m/kg.
Reactors adopted for the acid and the enzymatic hydrolysis have been designed adopting the kinetics reported in Liu et al. (2012). The volume of the reactors has been assessed.
The volume of the biofilm reactor has been assessed by setting: i) the sugar conversion at 90%; ii) butanol and ABE yields assessed by Raganati et al. (2012); iii) specific butanol productivity was set at 4.5 g/L h (Napoli et al., 2010).
The flowsheet in Figure 2 has been simulated and sized by means of Aspen Plus®.

3. Economic assessment

The cost estimation for the conceptual design of the flowsheet dedicated to the production of butanol from lignocellulosic biomass has been carried out following the procedure proposed by Happel and Jordan (1975). The purchased cost for the main units of the flowsheet has been estimated in agreement with correlations reported in Peters et al. (2003). Data have been updated to 2011 by means of the index cost (Peters et al., 2003; Chemical Engineering, 2013).
Economic data have been integrated with those assessed for the train of units adopted for the recovery and concentration of butanol from the fermentation broth assessed by Napoli et al. (2012).
The overall process has been characterized in terms of economical potential (EP):

$$EP = \text{Product value} - \text{Raw Matl. Cost} \quad (1)$$

and of the yearly rate (L) of depreciation of the main fixed investment (I) required for the plant. L has been estimated as:

$$L = e I_F \quad (2)$$

where e is [1/yr] the yearly fractional depreciation rate, I_F the fixed investment of the system (Peters et al., 2003). The depreciation rate “e” has been assessed accordingly to the sinking fund method: e=i/[exp(in)-1], where n [yr] is the expected project life and i [1/yr] the rate of return of the firm. Tentative reference values of n=10, i=0.10 1/yr and e= 0.058 1/yr have been adopted for this preliminary economic assessment (Rudd and Watson, 1968).

4. Results

The structure of the flowsheet reported in Figure 2 allows to assess the investments for the units by focusing on the three subsections separately. According to this strategy the attention has been focused on the first two sub-sections: upstream and fermentation. Data from the assessments carried out by Napoli et al. (2012) have been adopted for the third sub-section (downstream).
The flowsheet has been simulated for a flow rate of butanol stream rate fed at the downstream section of set at 251 kg/h, according to the simulation carried out by Napoli et al. (2012).
Table 1 reports the results of the simulation of the milling/chipping process in terms of the size of “particles”. The size range of the biomass adopted (feedstock) has been set according to typical data available in the literature on softwood harvesting. Results particle distribution after the chipping step (S1 stream) and the milling step (S2 stream) are reported. The power required is 0.02 kWatt and 0.29 kWatt for chipping and milling steps, respectively.
The operation units dedicated to the hydrolysis have been sized in terms of volume. The reactor for the acid hydrolysis was 0.57 m^3, that for the enzymatic hydrolysis was 8.8 m^3.
The purchased cost for the main items adopted in both upstream and fermentation sub-sections of the flowsheet reported in Figure 2 are listed in the Table 2. Main values of the factors suggested by Happel and Jordan (1995) have been adopted for the items K through I.
The economical potential EP of the process for the proposed flowsheet is about 1,254 k€/yr assuming that cost of the raw materials is negligible: it is the butanol cost (0.6 €/kg) for the yearly production rate (2,100 t/yr).

Table 1: Particle size distribution of the feedstock and after simulation of both the chipping (S1) and milling (S2) steps.

Size [mm]	Feedstock	S1 stream	S2 stream
0-1	0%	0.7%	20%
1-1.6	0%	11%	80%
1.6-50	0%	9%	0%
50-100	0%	3%	0%
100-150	0%	76%	0%
150-2000	100%	0,3%	0%

Table 2: Fixed capital for major equipments of the upstream and fermentation sub-sections.

	Item			Material (k€)
A	Crusher 1 (chipping)			7.9
B	Crusher 2 (milling)			7.9
C	Steam Explosion unit			20.3
D	Hemicellulose hydrolysis unit			25.7
E	Filter 1 and Filter 2			116.6
F	Cellulose hydrolysis unit			60.0
G	Neutralization Unit			18.9
I	Fermentation			310.0
J	(sum of A to I)			638.2
		factor (*)		
K	Insulation	18.8%	of J	120.0
L	Piping	90.0%	of J	574.0
M	Foundation	10.0%	of J	63.8
N	Buildings	6.8%	of J	43.4
O	Structures	4.8%	of J	30.6
P	Fireproofing	5.6%	of J	35.7
Q	Electrical	11.3%	of J	72.1
R	Painting & cleanup	5.6%	of J	35.7
S	Sum of material and labor			1,610.0
T	Overheads	30.0%	of S	484.0
U	Total erected costs			2,100.0
V	Engineering fee	10.0%	of U	210.0
W	Contingency fee	10.0%	of U	210.0
	Total investment			**2,520.0**

(*) factors include both material and labor contributions

The depreciation rate of the main fixed investment (L) is about 420 k€/yr
The comparison between EP and L suggests that there is room for successive economic assessment. Additional data would be required to complete the analysis with exercise costs. An optimization of the overall process is required too.

5. Final remarks

A potential lignocellulosic flowsheet to produce butanol by conversion of a lignocellulosic biomass has been reported. It has been simulated by means of the simulation software Aspen Plus®. Set the butanol production rate at 251 kg/h, the comparison between the economical potential (1,254 k€/yr) and the depreciation rate of the main fixed investment (420 k€/yr) left room for the economic feasibility of the process.

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