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From Soil Remediation to Biofuel: Process Simulation of Bioethanol Production from *Arundo donax*

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A range of energy crops can be grown on marginal land (i.e. land that is not suitable for food crop production or contaminated site) to provide feedstocks for bioenergy, non-food products and biofuels. The food versus fuel debate had a significant negative impact in Europe on first generation biofuels production from food crops (i.e. wheat, rapeseed, etc). A new approach involving the use of marginal land for the production of lignocellulosic species for the production of bioethanol is now pursued in Italy and in many other countries, where the demand for high quality water resources, arable land, food and fossil fuels is rapidly growing. With an emerging "feed versus fuel debate" there is a pressing need to find options for the use of marginal lands and wastewaters or saline ground waters to produce second generation biofuel or bio paper crops. *Arundo donax* was selected as a potential crop for use in these areas, since it produces more cellulosic biomass and sequesters more contaminants, using less land and pesticides than any other alternative crops reported in the literature. The objective of this paper is to evaluate economically a simplified process for the production of second generation bioethanol from *A. donax*. Process calculations and economic analyses are performed using the software SuperPro Designer®.

1. Introduction

In the last years the use of renewable energy sources is significantly increased in many EU countries and it is expected to increase more in the next years (De Caprariis et al., 2013). In particular, a growing interest is toward the bioethanol use as energy source. It can be produced through two main pathways. In the first one, the so-called first generation bioethanol is produced by the alcoholic fermentation. This process uses as feedstock the "sweet juice" obtained from sugar-rich plants pressing, such as sugar cane, sugar beet, sweet sorghum. In the other process, second generation ethanol is produced via fermentation of the sugar originated by the enzymatic hydrolysis of cellulose and hemicellulose, which are the main constituents of plants. In the latter case, besides the reduction of CO_2 emission by over 80 % (Demirbas, 2008) with respect to fossil fuels, it is not expected any threat of food supplies with respect to crops for human or animal consumption. As a result of such advantages a strong enhancement in second generation bioethanol production is expected in the next future (Demirbas, 2008). One of most interesting alternatives seems the use of biomass obtained from a cycle of phytoremediation. In this case there are same additional positive aspects; the plants remove dangerous elements or compounds from soil or water and after these plants are used as a resource for the production of energy (Accardi et al., 2012). These biofuel feedstocks can be produced on marginal lands not suitable for cultivation for food and fodder (Giudicianni et al., 2014), including marginal lands or low nutrients areas, and even contaminated soils by human activities. *Arundo donax* is characterized by low nutrients demand, high resistance to pathogens and parasites, high water content and thermal stress resistance, and high capacity for growing in substrates with high salt concentration. These properties render the *A. donax* a culture that fits very inhospitable environments and therefore its cultivation is taking place even in marginal lands, all over the world (Asia, Southern Europe, North Africa and the Middle East). In addition *A. donax* has

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an unusual very high photosynthetic capacity, which results in important ecological benefits (Mirza et al., 2011). Furthermore its use as a phytoremediation system has been introduced in environmental studies because of the advantages of its environmental friendliness, cost effectiveness and the possibility of harvesting the plants for the extraction of absorbed contaminants, that cannot be easily biodegraded (Kos et al., 2003). *A. donax* is also suitable for the processes of biomass conversion leading to the production of ethanol because of its characteristics of moisture content and the ratio between holocellulosic and lignin. *A. donax* can be also used for the production of energy and fine chemicals (Shatalov et al., 2013) as bioethanol, 3 hydroxy butyrolactone, glycerol, xylitol, arabinose (Ribechini et al., 2012).

2. Process simulation

Operating and process parameters of typical bioethanol production plant are obtained from literature (Kwiatkowski et al., 2006). In this study a typical block diagram (Figure 1) is considered for the transformation of *A. donax* into bioethanol.

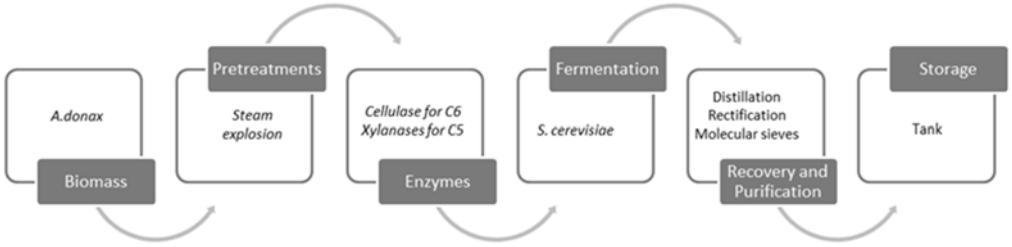

Figure 1: Block diagram of process for the production of bioethanol from A. donax

The simulation study is performed with the SuperPro Designer®, a modelling software, which is specially designed for processes, including biological components. In our simulation *A. donax* is chosen as the raw biomass in consequence of several advantages, both physiological and economic, such as its high yield (30-40 $t/ha^{-1}yr^{-1}$) and density (up to 40.000 plants ha^{-1}), the wide harvest time (from March to September), the low demand for fertilizer and herbicides. The assumed composition of *A. donax* is: holocellulose 55-65 % wt., protein 2-4 % wt., lignin 11-17 % wt., water 2-8 % wt., glucose 30-36 % wt., uronic acid 0.5-1.5 % wt., xylose 15-25 % wt., total carbon 35-45 %wt., hydrogen 5-8 % wt., oxygen 45-50 % wt., sulfur and nitrogen 1.5-5.5 % wt. (Pascoal Neto et al., 1997). The process flow-sheet (Figure 2, 3, 4, 5, 6) is laid out according to the data, which derive from the scientific literature (Junqueira et al., 2009). The process simulator estimates energy requirements and equipment parameters for the specified operating scenario. Volumes, composition and physical characteristics of input and output streams for each equipment item are identified according to the specific software database. The energy of each unit and the cost of raw materials are obtained from literature (Kwiatkowski et al., 2006).

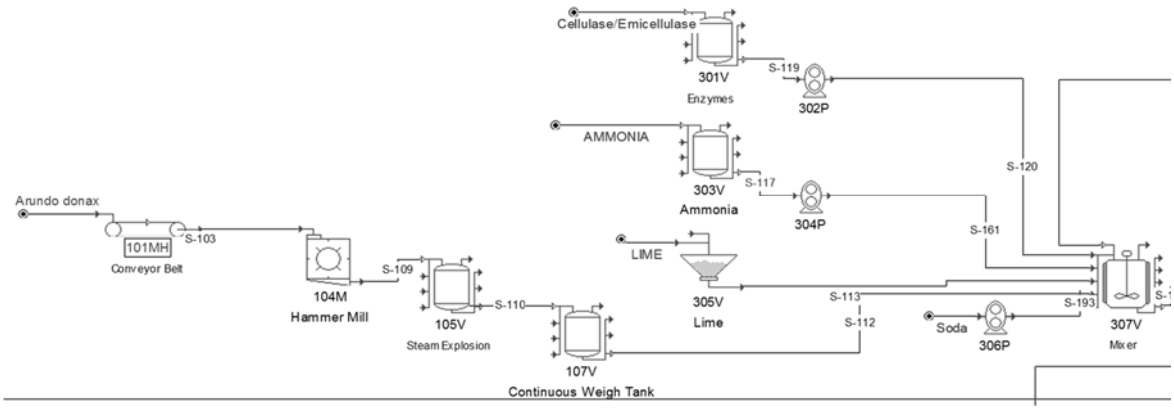

Figure 2: Pre-treatment phase with conveyor, hammer mill, steam explosion, continuos tank

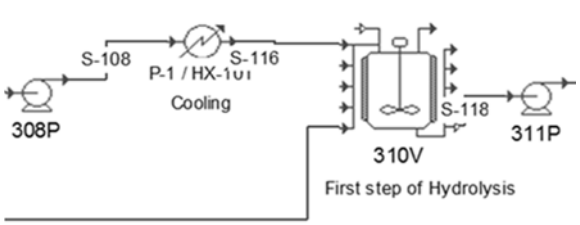

Figure 3: (first hydrolysis step) biomass from pre-treatment tank reaches a homogenization and before arriving in the first tank of hydrolysis it is cooled

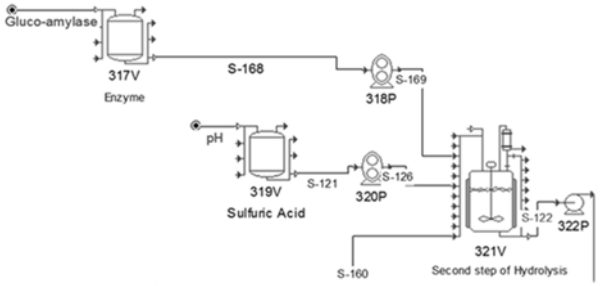

Figure 4: (second hydrolysis step) biomass makes contact with a second set of enzymes. and chemicals (i.e. ammonia, lime) for the continuation of the hydrolysis to obtain maximum yields of monomers of sugars

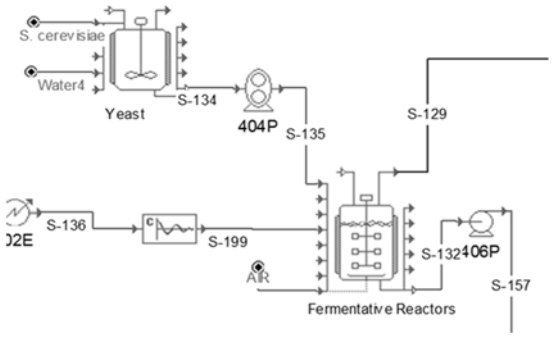

Figure 5: propagation and fermentation phase. During these two phase before it increases the concentration of the yeast under aerobic conditions and subsequently is passed to the fermentation in anaerobic conditions

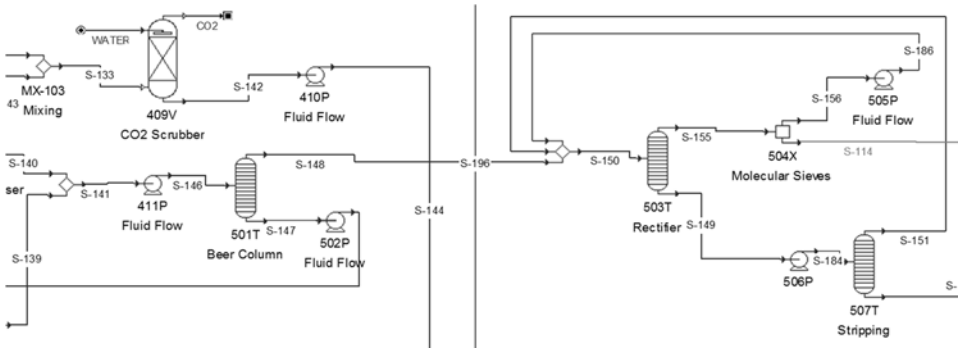

Figure 6: step of separation and purification of ethanol which achieves a purity of over 99%

2.1 Pretreatment, hydrolysis and fermentation

Main parameters and characteristics of the process are reported in Table 1 and Table 2. In the enzymatic hydrolysis the lignocellulose conversion occurs by using enzymes, which are able to depolymerize lignocellulosic biomass. After milling and steam explosion pretreatment (Figure 2), chemical hydrolysis and enzymatic hydrolysis (Figure 3, 4) are conducted at mild conditions: pH is about 4.8 and the temperature is between 45 and 50 °C, which are optimal conditions for the enzymes (Bin et al 2011). The main advantage of enzymatic hydrolysis over chemical hydrolysis is that it does not cause corrosion and offers greater safety during the operational phases of the process compared to biorefinery plant with acid pre-treatment. Nowadays

the major bottleneck in lignocellulosic ethanol production is the cost of the enzymes. Hence, the development of a cocktail of enzymes such as cellulases, hemicellulases and other accessory enzymes is required for complete hydrolysis. The plant configuration choice involves the use of two bioreactors for the enzymatic hydrolysis. In the first bioreactor (Figure 3) the hydrolysis of the fraction of the biomass, containing the C6 sugars, occurs by cellulases. These enzymes are classified in glycolic hydrolase families based on their sequence homology and hydrophobic cluster analysis (i.e. endo-glucanase, exo-glucanase, β-glucossidase). In the second bioreactor (Figure 4) there are the enzymes for the hydrolysis of the other major components of lignocellulosic biomass: the xylans (C5), which is the main carbohydrate present in hemicelluloses. Hydrolysis of xylan is carried out by a group of enzymes that are called xylanases. Removal of xylan from lignocelluloses using xylanases increases the accessibility of cellulose to enzymatic hydrolysis. Xylan does not form tightly packed crystalline structures like cellulose and is more susceptible to enzymatic hydrolysis. The complete hydrolysis of xylan requires the action of multiple xylanases with overlapping specificities and action. The saccharide components are the feedstock for the following fermentation unit. When high-solids loadings (15 % wt.) are used, enzymatic hydrolysis potentially offers many advantages with respect to the conversion achieved at low or moderate solids loadings, because higher sugar and ethanol concentrations are obtained at lower capital and operating costs (Modenhbach et al., 2013). In this study three different enzymes (cellulase, hemicellulase and gluco-amylase) are considered. The following propagation and fermentation stages (Figure 5), using *S. cerevisiae*, starts at the end of the second hydrolysis step; a fermentative reactor of 12,000 m^3 and hydrolysis reactor volume of 8 m^3 are considered. A residence time of 48 h at 30 °C, with 2.5 g/L of *S. cerevisiae* is assumed for the fermentation unit.

Table 1: Main parameters used in the simulation for the pretreatment step

Unit ID	Description	Detail	Energy demand (kWh)
101MH	Belt Conveyor	10 m	1,383.36
104M	Hammer Mill	Size/Capacity 46 ton/h	2,513.09
105V	Steam Explosion	200 m^3 – 200 °C - 9 atm - 7 min (residence time)	3,724.86
107V	Receiver Tank	74 m^3 – 2 h (residence time)	883.37

Table 2: Main parameters used in the simulation for the biochemical conversion

Unit ID	Description	Detail	Energy demand (kWh)
305V	Lime	4 m^3 – 25 °C	0.76
303V	Ammonia	8 m^3	1.28
301V	Enzymes	12 m^3 – pH 5	0.94
107V	Receiver Tank	74 m^3	1.28
307V	Mixer	54 m^3 – 30 % solids	361
310V	First Hydrolysis Step	180 m^3 – 70 °C – 4 d (residence time)	11,565.94
319V	Acid	18 m^3	0.77
317V	Enzyme	17 m^3 – density 1.5 g/L	1.4
321V	Second Hydrolysis Step	90 m^3 – 60 °C – 2 d (residence time)	9,453.23

Although several studies deal with the combined approach of *S. cerevisiae* and *Zymomonas mobilis* and the use of genetically modified microbial strains to increase the yields of ethanol (Szambelan et al., 2004), in the present simulation the use of *S. cerevisiae* as microorganism fermenter is only considered.

2.2 Separation and purification of ethanol

After the processes of fermentation, the fermentation broth is recovered and sent to a degasser drum in order to flash off the vapor (Figure 6). The gaseous stream is primarily constituted by ethanol, water and traces of carbon dioxide. The ethanol and water vapors are subsequently condensed and recombined with the liquid stream prior to distillation. Any uncondensed vapor is collected in the beer column, which captures about 56 % of the ethanol produced during fermentation. This is assumed as a continuous process, which is performed in a 100 m^3 column. The outlet from the bottom of the distillation column contains a considerable amount of water and non-fermentable material such as protein, oil, fibers, and residual substances, which are unconsumed during the fermentation. Ethanol recovery from the distillate of beer column is subsequently accomplished by the combined action of the rectifier (120 m^3 - 2 atm - ethanol 89 %), the stripper (4 m^3 – 1.5 atm - ethanol 98 %), and the molecular sieves (cycle duration of 24 h - ethanol 99.6 %). Over 99 % of the ethanol is recovered at the top of the rectifier as distillate. The remaining bottom product is fed to the stripping

column in order to remove additional water, while the distillate from stripping column is recycled to the rectifier. A molecular sieve adsorption column, packed with microporous beads, is used to reduce water percentage in the recovered bioethanol.

3. Results and discussion

The simulation is performed on the basis of 330 working days per years. Starting from about 350,000 t/y of *A. donax*, the production of about 70,000 t/y of bioethanol was obtained requiring 10,000 ha of cultivated land. Results indicate a production cost for bioethanol of about 0.80 $/kg.Table 3 reports the costs of the process as a percentage of the various items: the cost of utilities appears to be the predominant one, but possible operations for energy recovery from the combustion of solid residues are not considered in this work. In fact, the solid wastes generated in the process can be used for energy supplying in the pre-treatment step, or even submitted to a further treatment unit in order to recover high added value products.

Table 3: Costs summary

Cost Item	%
Utilities	52.83
Facility	24.92
Raw Materials	11.30
Labor-Dependent	10.95

Table 4: Units costs summary

Operation	%
Pre-treatment	59.43
Biochemical	24.05
Distillation	15.65
Common Support Systems	0.50
Co-product Processing	0.37

As regards the cost of the raw materials, assuming a cost of a single unit of rhizome for the cultivation of new land of 0.60-0.70 $/rhizome, and a density of about 10,000 - 15,000 rhizomes/ha, the production cost of one ton of standard chips of *A. donax* (45 % wt) does not exceed 18 $/t (Bartolini 2011). This value represents the best cost/benefit ratio in the market for biomass transformation and it could be further reduced in the next future up to below 10 $/t silage (about one-third the cost of corn silage) through advanced cultivation techniques (Bartolini 2011). In addition, since *A. donax* is a no-food species, the cultivation in heavy metals contaminated soils by human activities should be considered, thus coupling the polluted soils remediation with high value biomass production. In Table 4 the costs of each unit are reported, as percentage of the total cost of the process: as expected, the pre-treatment step results the major cost of the whole process.

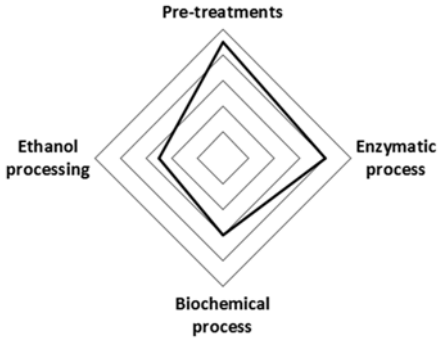

Figure 7: Performance of the costs of various process steps in an industrial plant for the production of bioethanol

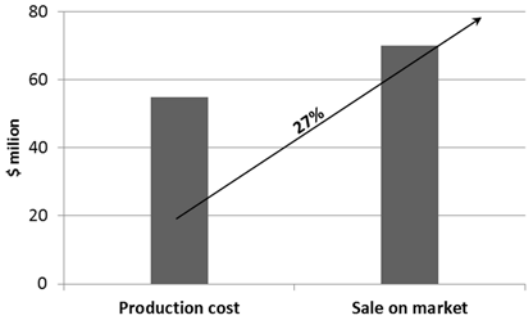

Figure 8: Production cost and sale on market

As mentioned above, our simulation does not take into account the recovery of energy (it can be obtained by the combustion of the biogas produced from biomasses), which could potentially satisfy all the energy requirement of the plant such as a II generation biorefinery (Kwiatkowski et al., 2006). Figure 7 shows the processes steps that require the greatest economic efforts due to two different aspects: energy and use of chemicals. The first step is the pre-treatment due to the large quantity of energy request. The process unit, that requires major costs of chemicals combined with higher energy costs for functionality, is hydrolysis with enzymatic processes. The total cost of electric energy consumed (12 GWh/y) by the process simulation is equal to 2 M$/y. Although the operating conditions of the process are conservative, the results of the simulation demonstrate the feasibility of a biotechnological plant, which produces bioethanol from *A. donax*.

From the simulation, the gain per year from the production of bioethanol, with respect to cost for power consumption, purchase of *A.donax*, f yeasts, enzymes and other chemical solvents is approximately 27 % (Figure 8).

4. Conclusions

In this study the implementation of biorefineries for the production of bio-ethanol is investigated by a technical and economical approach. The results of preliminary mass balances and kinetic study on an industrial plant, consisting on pre-treatment, hydrolysis, biological and recovery steps, show that the process blocks, that are economically expensive, are identified in the pre-treatment (8,5046.86 kWh consumable, assuming an average cost of energy in Europe of 237 $/MW) and in the use of enzyme cocktails for the hydrolysis (Sigma-Aldrich, 2014). The simulation also estimates a total cost of the process of about $ 25 milion The production costs related to the production of 80,000 t/y of bioethanol are estimated as about $ 56 million just considering the cost of raw materials (i.e. yeast, enzymes, biomass and chemical compounds), with a net profit, that is around 27 %/y (Figure 4). Adopting simple plant configurations, the price for the ethanol production is estimated at about 0.80 $/kg and it could potentially have a great market competitiveness compared to the use of oil or other fossil fuels. The supply chain of biomasses could also involve agricultural residues in order to ensure a continuous supplying of unused biomasses and low cost. This approach could be useful to understand the importance of the conversion of brownfield sites in the green economy, demonstrating the good yields of the process and profit, with easy process solutions.

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