Environmental, Energetic and Economic Evaluation of Implementing a Supercritical Fluid-Based Nanocellulose Production Process in a Sugarcane Biorefinery

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Nanocellulose, which is a disintegration product of plant cellulose, has recently come to public attention because of its great mechanical properties combined with renewability and biodegradability. From an environmental point-of-view, nanocellulose has shown potential for applications in drinking water filtration, catalytic degradation of organic pollutants, etc. Nanocellulose prepared from renewable and biodegradable lignocellulosic materials is only considered green and environment-friendly when its obtaining method is also environmentally friendly. Thus, this procedure should be done by means of an eco-friendly multistep procedure. Towards this direction in this study, nanocelulose production that uses supercritical fluid-based processes for cellulose separation, e.g. supercritical CO_2 explosion or organosolv assisted by CO_2, were compared with conventional steam explosion and organosolv processes in terms of environmental, energetic and economic aspects using commercial simulator Aspen Plus. In addition, the implementation of nanocelulose production as part of an ethanol production process from lignocellulosic materials was also investigated. The results showed that the production of nanocellulose from the lignocellulosic residue of the ethanol production through enzymatic hydrolysis is very promising. On the other hand, this more economically attractive process design was when explosion-based methods (i.g. SO_2-catalized steam explosion and supercritical CO_2 explosion) were used during cellulose separation step. It was determined that over 95% of the energy needs for cellulose disintegration during nanocellulose production process come from heating requirements. However, it was also found that this latter step can be self sufficient in terms of energy usage when the undisintegrated cellulose is used as fuel into an energy generation system. It was estimated that a combined heat and power boiler can produce a heat surplus of 365 kWh, which can be redirected to the lignocellulosic biomass fractionation, enzymatic hydrolysis and/or ethanol production processes, thus reducing the overall energy requirement. In terms of environmental aspects, three environmental indicators were examined. The CO_2 emissions per kg of nanocellulose produced was found to be acceptable as it is, but the chemicals/water usage should be re-examined, as their requirements were deemed higher than the desirable.

1. Introduction

Man has been using cellulose-based materials for millennia in a wide range of applications, and continues to do so today. It is the most plentiful natural, renewable biopolymer on Earth, and is found at some level in most living organisms. The yearly production is estimated to be in excess of 75 gigatons (Habibi et al., 2012).
Recently, there has been a movement to integrate cellulosic material into polymer composites. Macro-scale cellulose is not very compatible with the hydrophobic polymer matrix and is prone to form aggregates during processing among other complications. This greatly reduces the potential for macro-scale cellulose to be used as reinforcement in polymer composites. However, cellulose has a hierarchical structure and the "building blocks" of macro-scale cellulose are much more compatible with polymer matrices. These "building blocks"

discussed in this study are known as nanocellulose, although it goes by several other names in literature: cellulose nanocrystal, nanocrystalline cellulose, nanowhiskers, whiskers, rod like cellulose, and microcrystals (Brinchi et al., 2013).

Nanocellulose are characterized by a high aspect ratio between length and width. Their widths typically fall in the range of 2-20 nm and their lengths from 100 nm to several micrometers. The chemical properties of nanocellulose are also very desirable. Examples of these desirable chemical properties are easily modifiable surface properties (e.g. addition of chemical compounds or drugs) due to reactive –OH side groups and a high surface area. Finally, with the movement to greener technology, nanocellulose are highly desirable as it is biodegradable, renewable, sustainable, abundant, and highly biocompatible (Brinchi et al., 2013).

Outside of polymer composites, there are some other uses for nanocellulose being developed. Applications are currently in development for enzyme immobilization, antimicrobial and medical applications, use as a catalyst, biosensors and bio-imaging, and drug delivery. From an environmental point-of-view, nanocellulose has shown potential for several applications (Lam et al., 2012). Unfortunately, there is currently very low commercial availability of nanocellulose, due to the time consuming production process, low yield, and high production costs (Brinchi et al., 2013). In this context, in this study, the economic, energetic, and environmental perspectives of implementing nanocellulose production as part of the ethanol production process were investigated. This was done with an additional goal of investigating the valorization of the residual cellulose leftover after enzymatic hydrolysis in the production of ethanol by means of alternative lignocellulosic fractionation processes, such as the supercritical fluid-based ones.

2. Process description

The ethanol/nanocellulose production process evaluated can be broken up into three major subdivisions: Lignocellulosic fractionation and enzymatic hydrolysis, ethanol production and production of nanocellulose from enzymatic hydrolysis residual material.

2.1 Lignocellulosic biomass fractionation and enzymatic hydrolysis
The effect of four different lignocellulosic fractionation (pretreatments) processes was explored in this study.

SO$_2$-catalized steam explosion
In the SO$_2$-catalized steam explosion, milled feedstock is soaked at room temperature in a 2% w/w SO$_2$ solution for 30 minutes. Then it is sent to the steam explosion tank, where it is heated to 190 °C and held at that temperature for 5 minutes before being exploded. Cellulose retention is 95.9%. In the enzymatic hydrolysis process, the slurry of pretreated feedstock (2% weight in solid), water and enzymes travels through several reactors over 24 hours at 50 °C. The enzymes are cellulase (15 filter paper units (FPU) per gram of biomass, 65 FPU/g of enzyme activity) and β-glucosidase (0.9 Internation Units (IU) per gram biomass, 17 IU/g of enzyme activity). Following this process, only 30.8% of the cellulose inputted to this process remains unconverted to glucose (Carrasco et al., 2010).

Supercritical CO$_2$ explosion
In the supercritical CO$_2$ explosion, milled feedstock is mixed with water to create a slurry with 60% moisture content. Then, that slurry is heated to 200 °C and 276 bar in a CO$_2$ atmosphere. It is held there for 30 minutes before being exploded. In the enzymatic hydrolysis, the pretreated feedstock is added to a citrate buffer (0.05M sodium citrate and 0.05 M citric acid) with 0.05 grams of sodium azide per liter until the feedstock is 5% WIS. Enzymes activities of 0.92 FPU/ml, 0.76 β-glucosidase IU/ml, and 0.35 xylanase enzyme units (U)/ml. The temperature of the slurry is then raised to 50 °C and stirred at 200 rpm (unfortunately, no processing time is provided). Following enzymatic hydrolysis, only 23% of the cellulose inputted to the pretreatment remains unconverted to glucose (Srinivasan and Ju, 2012).

Organosolv fractionation
In the organosolv fractionation process, the milled feedstock is cooked in an H$_2$SO$_4$-ethanol aqueous solution at 180 °C for 60 minutes. The concentration of ethanol is 50% v/v and the concentration of the H$_2$SO$_4$ is 1.25% w/w dry feedstock. In the hydrolysis portion, the pretreated feedstock (2% cellulose w/v concentration) is combined in a solution of 50 mM acetate buffer (pH 4.8), 0.004% tetracycline, Celluclast (20 FPU/g cellulose), and Novozym 188 (40 IU/g cellulose). The solution then incubates at 45 °C and 150 rpm for 48 hours. Following the enzymatic hydrolysis, only 15% of the cellulose inputted to the pretreatment remains unconverted to glucose (Pan et al., 2006).

Supercritical CO$_2$ organosolv fractionation
In supercritical CO$_2$, 10 g of the milled feedstock is combined with 50 mL of a 1-butanol/water mixture (1-butanol concentration 90%) in a pressure reactor. The reactor is closed and pumped full of CO$_2$ to a pressure of 70 bar. It is then heated to 150 °C and pressurized to 230 bar, and held at that point for 45 minutes. After

that time, it is depressurized and washed with a 1% sodium hydroxide solution and water until it is pH neutral. The yield of the cellulose is 74.4% of the input by weight (Pasquini et al., 2005).

Pasquini et al. (2005) did not perform an enzymatic hydrolysis process following their pretreatment, so no specific data for a corresponding enzymatic hydrolysis is available. Therefore, the enzymatic hydrolysis yield of Srinivasan and Ju (2012) experiment was used, as their pretreatment process most closely matches that of Pasquini et al. (2005). Hence, we assumed that following enzymatic hydrolysis, only 3.4% of the cellulose inputted to the enzymatic hydrolysis process remains unconverted to glucose.

2.2 Ethanol production

For our purposes, the only relevant data on the production of the ethanol is the conversion efficiency of the fermentation process. This value is sourced from the paper of García et al. (2013) and is equal to 95%.

2.3 Production of nanocellulose from the enzymatic hydrolysis residual material

The nanocellulose production process is divided in acid hydrolysis centrifugation, dialysis, sonication and drying steps.

In the acidic hydrolysis process, the enzymatic hydrolysis residual material is hydrolyzed at 45 °C for 30 minutes with vigorous, constant stirring in an aqueous solution of 20 mL of H_2SO_4 (concentration 64%) per gram of treated feedstock. The yield of this process is 65% of the weight of the treated feedstock introduced to this process (Dos Santos et al., 2013).

The centrifugation process is a process in which the post-hydrolysis slurry is inundated with water (10-fold) to stop any further reactions. Then, it is centrifuged for 10 minutes at 7000 rpm to separate the cellulosic structures from the rest of the slurry. This process is repeated once (Dos Santos et al., 2013).

In the dialysis process, the precipitate from centrifugation is allowed to dialyze in tap water for approximately four days, until the pH was neutral The quantity of water was not specified, but we assume it is 10-fold as in the cessation of acid hydrolysis (Dos Santos et al., 2013).

Sonification is the last step of the nanocellulose extraction process, and it entails sonicating the neutralized dialysis mixture for 10 minutes at a frequency of 24kHz and a power of 4000 W (Dos Santos et al., 2013).

No specific data was available for the particulars surrounding the drying of the nanocellulose, so we proposed that a certain percentage of the water would be drained away by gravity, and then the remaining water would be removed via hot circulating air. The weight percentage of the nanocellulose at each of these points is assumed to be similar to that of cellulose used in paper manufacturing: 50% following draining and 95% following air drying (Ghosh, 2011).

3. Methodology

3.1 Economic analysis

In order to determine the most economically viable pretreatment method, a mass balance was performed. The assumption is made that the process parameters defined in the laboratory production scale are also relevant on a plant-sized scale. A representative cellulose content that generally is present in sugarcane bagasse was used in the simulations. Following the mass balance, the valorization ratio for each pretreatment method can be assessed. This indicator shows which pretreatment creates the greatest valorization of the feedstock when nanocellulose production is also considered. Only the cost of the feedstock was considered in this calculation. The Eq(1) below is what will be used to calculate the economic potential of each pretreatment method for production of ethanol in combination with nanocellulose. Feedstock, nanocellulose and Ethanol prices considered were $40.00/ton and $2,210.00 /ton, $0.71/L, respectively.

$$Valorization\ ratio = \frac{value\ of\ output\ products\ (US\$)}{cost\ of\ feedstock\ (US\$)} \tag{1}$$

3.2 Energetic analysis

The energy requirement of SO_2-catalyzed steam explosion pretreatment and the following enzymatic hydrolysis was assumed to be 0.083 kWh per kg of feedstock, considering as feedstock sugarcane (Ensinas et al., 2013). The energetic requirements of the nanocellulose production process (acid hydrolysis centrifugation, dialysis, sonication and drying) was obtained using Aspen Plus software (Figure 1).

3.3 Environmental analysis

Using the data from the nanocellulose production mass balance, some environmentally critical indicators were assessed. The amount of reagent, water, and CO_2 emissions per kilogram of nanocellulose produced were assessed.
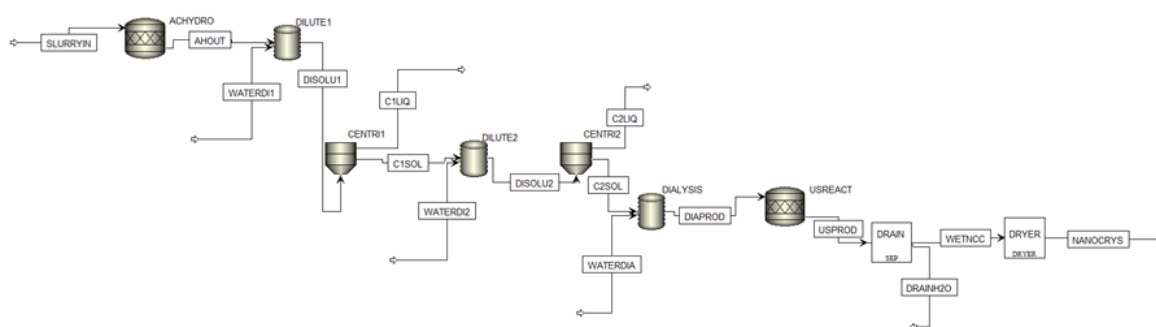
Figure 1: Aspen Plus flowsheet of the nanocellulose production process.

4. Results and discussion

4.1 Economic evaluation of the ethanol and nanocellulose co-production

The mass balances for each pretreatment method are presented in Table 1. These mass balances were performed assuming that the cellulose content of the sugarcane bagasse does not affect the outcome of the process. Additionally, they were performed using a 35% cellulose content w/w of the dry feedstock material. It was assumed that the moisture content of the feedstock material was 50% w/w.

As is visible in Table 1, the feedstock requirement increases with the amount of ethanol produced. Because of the cellulose to glucose conversion efficiency of the different pretreatment-enzymatic hydrolysis combination is more or less efficient for each combination and because these calculations were done on the basis of producing a constant amount of nanocellulose, more feedstock was required to produce the same amount of nanocellulose when the cellulose to conversion efficiency increased. In other words, when the pretreatment allows the enzymatic hydrolysis process to more effectively convert cellulose to glucose for ethanol fermentation, there is less available cellulose for nanocellulose production.

Table 1 also indicates the numerical reduction in nanocellulose production when a fixed quantity of feedstock of 1 t is fed into the pretreatment process. It is shown that the nanocellulose production is over 10 times higher for SO_2-catalyzed steam explosion when compared to CO_2 supercritical organosolv fractionation. This difference is reflected in the required feedstock values. The multiplicative difference between the two feedstock requirements is also over 10 times. It is important to note that the difference in nanocellulose production comes only from the difference in pretreatment and enzymatic hydrolysis methods, as the nanocellulose production method employed in these calculations, and hence the nanocellulose production method yield, is the same for every case.

Table 1: Amount of ethanol produced and required feedstock for each pretreatment method

Pretreatment Method	Nanocellulose (t)	Ethanol (L)	Feedstock required (t)	Nanocellulose (kg) per t of feedstock	Ethanol (L) per t of feedstock
SO_2 steam explosion	100	210,429	2,976	33.60	70.71
CO_2 explosion	100	295,510	3,822	26.16	77.32
Organosolv fractionation	100	499,854	5,861	17.06	85.28
CO_2 organosolv	100	3,389,586	34,661	2.89	97.79

After reviewing this mass balance data, the data indicated that if the goal is to maximize the production of nanocellulose in comparison to the amount of ethanol produced, explosion-based methods (i.g. SO_2-catalized steam explosion and supercritical CO_2 explosion) should be used as the pre-treatment method. However, if the goal is to maximize the production of ethanol and produce nanocellulose as a side business, the best method to use is CO_2 supercritical organosolv fractionation.

Following, the valorization ratio for each pretreatment method is also presented. As is visible in Table 2, the valorization ratio decreases as the production of ethanol increases. Because ethanol is not as valuable a product as nanocellulose, the larger valorization ratio, or the greater return on investment, occurs when the ratio between the quantity of nanocellulose and the quantity of ethanol produced is higher. For this reason, when producing nanocellulose and ethanol, the best pretreatment method for return on investment is not necessarily the one that most efficiently converts cellulose to glucose. Valorization ratio information is also interesting for biorefineries that are currently producing only ethanol and are thinking of upgrading their

pretreatment method. Instead, they may consider including nanocellulose production in their biorefinery, as it is increasing the return on investment more quickly than increasing ethanol production efficiency. This is obviously not the case when only ethanol is being produced. In that case, the highest valorization ratio would belong to the process that can create the most ethanol from the feedstock. Therefore, there may exist interest in the mid-level valorization ratios for those plants that have a primary goal of producing ethanol.

Based on the data presented in Table 2, we can take the following conclusion: if the goal of the biorefinery is to maximize the return on investment, explosion-based methods (i.g. SO_2-catalized steam explosion and supercritical CO_2 explosion) are the best pretreatment methods to use because they maximizes the ratio between the quantity of nanocellulose produced and the quantity of ethanol produced.

Table 2: Value of products and feedstock, and the valorization ratio for each pretreatment method

Pretreatment Method	Nanocellulose (US$)	Ethanol (US$)	Feedstock (US$)	Valorization ratio
SO_2 steam Explosion	221,000	149,404	119,052	3.11
CO_2 Explosion	221,000	209,670	152,890	2.82
Organosolv fractionation	221,000	354,896	234,432	2.46
CO_2 organosolv	221,000	2,406,605	1,386,427	1.90

4.2 Energetic evaluation of the ethanol and nanocellulose co-production

The first step in determining the energy consumption of nanocellulose production (excluding all processes before acid hydrolysis) is to model the production system in Aspen Plus software. The results showed that 95% of the required power comes from the heating processes. The energy required for the mechanical processes pales in comparison. There is however, the possibility of reducing the heat load of the acid hydrolysis process. It was assumed that the input stream to the acid hydrolysis heating process was at room temperature. But, since the addition of H_2SO_4 to water is an exothermic process, to point of being dangerous if added too quickly, a large portion of this required heat could probably be obtained just from adding the H_2SO_4 in close timing with the commencement of acid hydrolysis.

The first thing to notice about the results is that the energy consumption of nanocellulose production per kg of residual cellulose is almost 25 times higher than the energy consumption per kg of feedstock material. This is because more than half of the solid feedstock material is ineligible for conversion to nanocellulose (i.e. it is not cellulose), and because it is assumed that 50% of the feedstock mass is water. The next item of note is that nanocellulose production accounts for almost half of the total energy consumed per kg of feedstock. This means that nanocellulose production nearly doubles the total energy consumption of the system (a hypothetical sugarcane biorefinery that uses SO_2-catalyzed steam explosion during the biomass fractionation step currently producing only ethanol) (Ensinas et al., 2013).This is obviously a large amount for the total energy to increase by, but we think it is justifiable in that nanocellulose production adds much more value to the process than ethanol production, as previously demonstrated. Additionally, as the majority of the nanocellulose production energy consumption comes from heating needs, if these needs can be reduced (estimated at about 35%), the percentage of total energy consumption attributable to nanocellulose production drops to just over one-third of the total energy needs. Therefore, we find this energy consumption data to be acceptable.

Using the mass balance and energy consumption data, we were able to calculate the energy attainable by burning the cellulose that is not processed into nanocellulose during production. The Higher Heating Value (HHV) for cellulose used was 18.5 MJ/kg (Sheng and Azevedo, 2005). To determine the amount of electricity and steam that could be produced, it was assumed there is a Combined Heat and Power (CHP) boiler with 79.5% of the HHV being converted to steam (i.e. heat) and 6.9% of the HHV is converted to electricity.

One can see that after conversion in a CHP system, the residual cellulose can self-sustain the electrical requirements of the system, but it is not capable of auto sustainability in terms of the required heat energy. The benefit of having superfluous electrical energy is two-fold: First, no energy purchases are required to sustain production (cost benefit of $0.0705 per kWh). Second, the extra energy can be sold to the grid (cost benefit of $0.051 per kWh).

Because the CHP system does not produce enough heat to auto sustain the production of nanocellulose, heat (i.e. more fuel) would have to be imported. However, if the reduction in heat requirement levied in the last section due to the method by which H_2SO_4 is added to the acid hydrolysis bath, the total heat requirement is reduced to 1074 kWh. With this new heat requirement value, the CHP system now produces a heat surplus of 365 kWh. This is a benefit as the surplus heat can be redirected to the pretreatment, enzymatic hydrolysis, or ethanol production processes, thus reducing the required fuel for heating.

4.3 Environmental evaluation of the nanocellulose production

Using the mass balance data of nanocellulose production, it was determined that nanocellulose production requires 56.62 kg of H_2SO_4 (its only reagent) and 1282 L of H_2O per kg of nanocellulose produced. These values are quite high considering that H_2SO_4 is considered as hazardous and the ratio for ethanol production is 4 L of H_2O per L of ethanol, thus further experimental adjustments should be done considering theses aspects.

For the considered nanocellulose production process, the CO_2 emissions calculated are 0.87 kg of CO_2 per kg of nanocellulose produced. For production of natural gas, the CO_2 emissions per kWh are around 0.55 kg, and if we assume that all of the cellulose burned in the CHP is converted to electricity at a rate similar to a turbine designed specifically for electricity production (i.e. 35% of HHV), the CO_2 emissions per kWh are 0.96 kg. Obviously, this is higher, but because the growth of feedstock is capturing CO_2 in the atmosphere, the net CO_2 reduction is 0.74 kg of CO_2 per kg of nanocellulose produced. Therefore, although the emissions per kWh are greater for burning cellulose as compared to natural gas, the amount of net carbon capture is much higher. This result is considered quite good, and no further work is recommended on this portion of the process.

5. Conclusions

The implementation of a nanocellulose production process as part of the ethanol production process in a sugarcane biorefinery demonstrated to be very promising in terms of economic, energetic and environmental aspects. When considering a supercritical fluid-based lignocellulosic biomass fractionation process, such as supercritical CO_2 explosion and supercritical CO_2 organosolv fractionation, placed inside an alcoholic fermentation facility it should be pointed out that benefits can come from the recycle of the CO_2 produced as a by-product during fermentation, reducing overall CO_2 emissions, becoming these processes designs very promising in terms of environmental aspects. As it was demonstrated in this study supercritical CO_2 explosion presented intermediate and promising economical parameters, so this method should be further investigated.

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