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Production of Butanol and Other High Valued Chemicals Using Ethanol as Feedstock Integrated to a First and Second Generation Sugarcane Distillery

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Production of chemicals and second generation ethanol from lignocellulosic material integrated to first generation sugarcane biorefineries presents potential for industrial implementation, since significant part of the infrastructure may be shared between both first and second generation plants. Additionally, chemicals from renewable resources have attracted increasing attention, mainly for their market prices (usually higher than commodities as biofuels) and potential for replacing oil-based products used as feedstock in the chemical industry.
The production of chemicals through the alcoholchemistry route uses catalysts to convert ethanol into desired products according to catalysts activity and selectivity. One of the possibilities in the alcoholchemistry route is to use ethanol to produce n-butanol that can be sold as feedstock for the chemical industry and as drop-in biofuel for gasoline powered engines. Due to catalyst selectivity, this process generates also other chemicals, which can be purified to be sold as feedstock for the chemical industry. Previous studies have pointed out that the use of ethanol in a biorefinery to produce n-butanol presents good economic and environmental impacts. Nevertheless, results obtained for the economic return of the n-butanol biorefinery compared to autonomous ethanol plants were very similar, which can be unattractive for investors dealing with the high risks involved in a novel biorefinery process.
In this work, the possibility of enhancing the financial and environmental impacts of n-butanol and other high value chemicals production integrated to a second generation sugarcane biorefinery is explored. Computer simulation is used to quantify the influence of technical parameters, including down-stream operations required to separate coproducts, adding value to the mix of products and commercial flexibility. Risk analysis is used to evaluate uncertain parameters such as the investments in n-butanol and second generation ethanol plants and the market prices assumed for the new products. Results obtained show that production of n-butanol and other high valued chemicals integrated to a first and second generation sugarcane biorefinery could be an economically and environmentally attractive alternative. However, the financial risk involved is high and hugely dependent on the selling prices of the new products of the portfolio investigated in this work, mainly n-butanol.

1. Introduction

Second generation has been envisioned as an alternative for increasing ethanol production in sugarcane biorefineries using the same cultivated area. The concept is defined by the utilization of fermentable sugars obtained from the lignocellulosic portion of the plant, such as bagasse and straw. Dias et al. (2012) have pointed out several potential advantages of integrating second generation units with conventional first

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generation biorefineries such as sharing important operations (juice concentration, fermentation, distillation and cogeneration) as well as feedstock availability in the production area (bagasse and straw).

Benefiting from the existing structure and the use of first and second generation ethanol as feedstock, production of high valued chemicals by the alcoholchemistry route would add flexibility to the portfolio and, possibly, increase the revenues of sugarcane biorefineries.

In recent quest for catalysts with convenient selectivity and fair yields able to convert ethanol into desired higher alcohols, Downson et al. (2013) have reported the discovery of a new ruthenium-bis(diphenylphosphanyl)methane catalyst for the upgrading of ethanol to n-butanol with 94 % selectivity at over 20 % conversion. Other studies in the literature have already detailed the development of catalysts for the conversion of ethanol to various desired products, such as n-butanol in Carvalho et al. (2012) using Mg and Al mixed oxides and Riittonen et al. (2012) using Al oxides; hydrocarbons in Chistyakov et al. (2013) using Pd-Zn catalysts; and acetaldehydes in Sannino et al. (2013) using RuO_x-VO_x/TiO_2 catalysts. Due to catalyst selectivity, the same process can generate a series of chemicals, which can be separated and purified to be sold as feedstock for the industry.

Previous studies have pointed out that the use of ethanol as feedstock to produce n-butanol and higher alcohols integrated to first generation (Dias et al., 2013a) and first and second generation sugarcane refineries (Pereira et al., 2013) presents good economic and environmental impacts. Nevertheless, results obtained for the economic return of the n-butanol biorefinery compared to autonomous ethanol plants were very similar, which can be unattractive for investors dealing with high risks involved in a novel biorefinery process.

In this work, the possibility of enhancing the financial and environmental impacts associated with the production of n-butanol and other high valued chemicals integrated to a second generation sugarcane biorefinery is explored. Computer simulation is used to quantify the influence of technical parameters, including the down-stream operations required to separate co-products, adding value to products. Monte Carlo simulation is applied to evaluate uncertainties associated with parameters such as investments on second generation and ethanol catalysis plants and market prices assumed for products.

2. Process description and scenarios definition

In this work an integrated first and second generation ethanol production plant from sugarcane is considered. An optimized first generation autonomous distillery with reduced steam consumption and efficient cogeneration system using bagasse and straw (50 % recovery of the amount produced in the field) is assumed; surplus bagasse and straw is used as feedstock for second generation ethanol production, which is comprised by steam explosion pretreatment (150 °C, 10 min, 0.5 wt % H_2SO_4) with conversion of hemicellulose to pentoses and furfural of 65 % and 10 %, and of cellulose to glucose and hydroxymethylfurfural (HMF) of 5 % and 1.5 %, respectively; enzymatic hydrolysis (15 wt % solids, 50 °C, 48 h, 10 FPU/g cellulose) with conversion of cellulose to glucose of 70 % and hemicellulose to pentoses of 35 %, and separate fermentation of C5 and C6 sugars (hexoses are fermented in a mixture with sugarcane juice), assuming 90 % and 80 % yields for C6 and C5 fermentation, respectively. Both first and second generation ethanol are used as feedstock for butanol production using a Ruthenium based catalyst ([RuCl(η^6-p-cymene)(3)]Cl) (22.1 % conversion) in a single step batch reaction carried out for 4 hours under 150 ºC. In the reactor, ethanol is converted to n-butanol (93.6 % selectivity and 20.1 % yield), 2-ethylbutanol (3.2 % selectivity and 1.1 % yield) and n-hexanol (5.1 % selectivity and 1.7 % yield). The used catalyst presents a remarkable selectivity and the highest ethanol conversion in 4 hours residence time among the catalysts investigated by Downson et al. (2013).

Reaction products are cooled and sent to the purification system, comprised by absorption and distillation columns and adsorption for products purification. Distillation columns recover unreacted ethanol, which is dehydrated using molecular sieves, and butanol (99.8 wt %); 2-ethylbutanol is separated from n-hexanol using selective adsorption, producing streams with > 98 wt % purity.

In order to evaluate the integration of the alcoholchemistry route into the first and second generation ethanol biorefinery, three different scenarios were investigated.

Scenario 1G represents an optimized autonomous sugarcane distillery with maximization of surplus electricity (all the bagasse and straw are used as fuel for electricity production). In scenario 1G2G, integrated first and second generation ethanol production takes place. Scenario 1G2G-B represents an integrated first and second generation ethanol production process, with n-butanol and coproducts production using all anhydrous ethanol as feedstock, using the catalyst described.

3. Methodology

3.1. Process simulation

Simulations were carried out using Aspen Plus. The sugarcane biorefinery processes 500 tonnes of sugarcane per hour, approximately 2 Mt/y. Simulation of the sugarcane biorefinery has considered conservative values for the main industrial parameters.

3.2. Financial analysis

Financial sustainability is measured based on the internal rate of return and on the revenues calculated for each scenario investigated.
The internal rate of return is calculated considering the current Brazilian economic scenario. Project lifetime was assumed to be 25 y, requiring 2 y for construction and start-up of the plant. Linear 10 years depreciation was assumed as well. Income taxes and social contributions account for 34 % of the taxable income. Cost of the cellulase enzyme was estimated as 0.05 US$/L of second generation ethanol produced (Bonomi et al., 2012).
Investment data for the annexed sugarcane distillery were obtained from Sousa and Macedo (2010); values for 2009 were updated to June 2013 (reference year for this study) considering the inflation rates in Brazil. For the second generation ethanol production process, investment data was obtained in the literature (CGEE, 2009). Details on the investment for the first and second generation ethanol production plant are provided in previous studies from Dias et al. (2012, 2013). Investment for the ethanol catalytic conversion plant was estimated based on data for equipment investment (e.g. packed bed reactor, distillation columns) provided in NREL reports (Humbird et al., 2011), using information from mass and energy balances obtained in the simulation.
The prices adopted in this study for the main inputs and products generated are shown in Table 1.

Table 1: Prices adopted (exchange rate Jan-Jun/2013: US$ 1.00 = R$ 2.03)

Product	Price/Cost	Unit	Reference
Anhydrous ethanol	0.61	US$/L	CEPEA (2013)
Electricity	59.82	US$/MWh	EPE (2013)
Sugarcane	24.18	US$/t	UDOP (2013)
Sugarcane straw (dry basis)	22.44	US$/t	Cardoso et al. (2013)
n-butanol	1.89	US$/kg	MDIC (2013)
n-hexanol	3.29	US$/kg	ICIS (2012)
2-ethylbutanol	8.00	US$/kg	Wuxi Hexia Chemical Company (2013)

3.3. Environmental analysis

The evaluation of environmental impacts was carried out through the life cycle assessment methodology. The method evaluates the environmental burden associated with a product, process or activity, by the identification and quantification of energy and materials used and waste and emissions released, in addition to evaluating the impact on the environment on a scientific and quantitative basis.
The life cycle of biofuels takes into account stages of production, cropping and harvesting of biomass until the final use, including industrial process and transportation stages when required. Guidelines for the LCA method are described in ISO documents (ISO 14044, 2006).
In this study, the software package SimaPro 7.3.3 and the CML 2 Baseline 2000 v2.05 method (described by Guinée et al. (2002)) were used as tools for the environmental impact assessment.

3.4. Risk analysis

Risk analysis was performed to measure the influence of uncertainties related to prices of products and investment for second generation and ethanol catalysis plants on the economic return of the assessed scenarios. In this work, the effect of uncertainties on the technical parameters has not been assessed. The software @Risk 6.2 and Monte Carlo simulation analysis (5,000 iterations) were used to obtain the density of probabilities associated with the internal rate of return for each scenario.
Normal distribution (10 % SD) was assumed for investment values, whereas uniform distribution was considered for the prices of products generated by the conversion of ethanol: n-butanol (0.95 (price as fuel) – 1.89 (price as chemical) US$/kg); n-hexanol (1.65 – 4.94 US$/kg (±50 % variation for adopted price) and 2-ethylbutanol (4.00 – 12.00 US$/kg (±50 % variation for adopted price)).

4. Results and discussion

The main results obtained in the simulation, calculated investment, internal rate of return and revenues are shown in Table 2. Financial results for scenarios 1G and 1G2G were obtained from Pereira et al. (2013) and updated for the reference of June 2013. Although anhydrous ethanol is used as feedstock in 1G2G-B, a fairly high amount of ethanol is still produced in addition to high valued chemicals. Revenues and IRR show that, considering adopted prices and estimated investment, it is economically viable and attractive to produce chemicals from the catalysis of ethanol using the Ruthenium catalyst as described by Downson et al. (2013).

Table 2: Summary of technical and financial results

Parameter	1G	1G2G	1G2G-B
Anhydrous ethanol (L t cane^{-1})	84.3	111.9	77.6
Electricity (kWh t cane^{-1})	193.3	75.4	101.5
n-butanol (kg t cane^{-1})	-	-	12.2
n-hexanol (kg t cane^{-1})	-	-	1.0
2-ethylbutanol (kg t cane^{-1})	-	-	0.6
Second generation ethanol plant (MM US$)	-	75	48
Ethanol catalysis plant (MM US$)	-	-	45
Total investment (MM US$)	240	305	339
Internal rate of return (%)	14.9	15.3	17.6
Revenues (US$ t cane^{-1})	65.2	75.3	86.7

Figure 1 shows the comparative environmental impact scores per US$ of revenue for the investigated scenarios. It is possible to observe that, for most of the environmental impact categories evaluated, scenario 1G2G-B presented the best results. The only exception is the photochemical oxidation category which is hugely influenced by the emissions of ethanol during the industrial stage. In the case of scenario 1G2G-B, besides the ethanol emissions from the distillation process that also takes place in scenarios 1G and 1G2G, there are additional gaseous emissions mainly composed by ethanol, water and nitrogen in the gas washing stage at the ethanol catalysis plant, which affects the photochemical oxidation category leading to a higher impact. It is important to emphasize that there is no available information on the formation of light compounds, such as hydrogen, during the ethanol catalytic conversion, which could also negatively affect the impacts for certain categories.

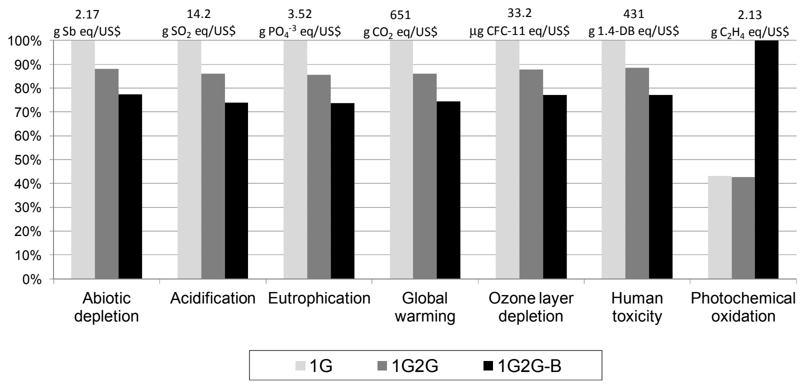

Figure 1: Comparative environmental impact scores per US$ of revenue for autonomous first generation (1G), integrated first and second generation (1G2G) and first and second generation with ethanol catalytic conversion (1G2G-B)

In general, it may be said that the production of n-butanol and other high valued chemicals using ethanol as feedstock is worthy from an environmental standpoint, since less impact is produced by monetary revenue generated, despite the fact that more equipment, materials and resources are needed in the process in comparison to the other scenarios investigated in this work.

Figure 2 depicts the distribution of probabilities for investigated scenarios according to the assumptions considered for the risk analysis. The IRR for scenario 1G is fixed at 14.9 %. IRR distribution for 1G2G shows that there is a high probability (88.6 %) that its IRR is higher than for 1G. On the other hand, the probability that scenario 1G2G-B has an IRR higher than 1G is 74.4 % and 48.5 % than 1G2G. This means that the risk involved in investing in scenario 1G2G-B is much higher, although the deterministic analysis presented in Table 2 has pointed out that the IRR for 1G2G-B (17.6 %) would be the most attractive in comparison to the other investigated scenarios. The probability for scenario 1G2G-B to have an IRR equal or higher than 17.6 % is only 5.7 %.

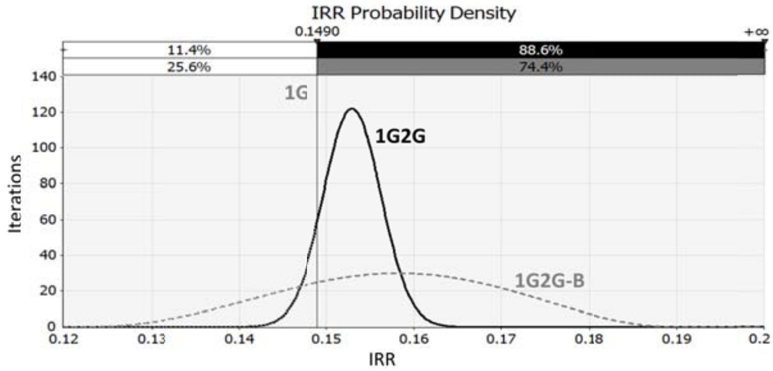

Figure 2: Internal rate of return distribution of probabilities for the investigated scenarios

Figure 3 shows how prices and investments affect the internal rate of return for scenario 1G2G-B. It is possible to observe that n-butanol price plays a fundamental role on the definition of the financial viability, whereas investments on the 2G and ethanol catalytic conversion plants have minor impact.

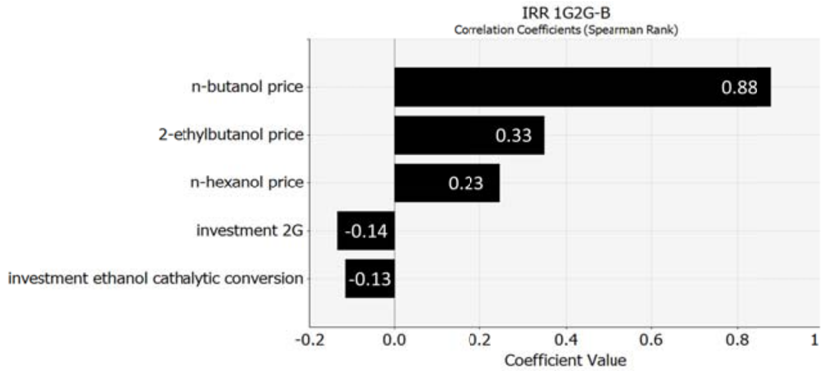

Figure 3: Effects of prices and investment on the IRR for scenario 1G2G-B

5. Conclusions

Production of n-butanol and other high valued chemicals integrated to a first and second generation sugarcane biorefinery has potential to be an economically and environmentally viable technological alternative. However, the financial risk involved is high: assumptions made for the market prices of the new products of the portfolio, mainly n-butanol, play a huge role on the economic viability result. However, in any case, n-butanol may be considered as a drop-in fuel, which adds commercial flexibility to the biorefinery.

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References

Bonomi A., Mariano A.P., Jesus C.D.F., Franco H.C.J., Cunha M.P., Dias M.O.S., Chagas M.F., Cavalett O., Mantelatto P.E., Maciel Filho R., Junqueira T.L, Cardoso T.F., 2012. The Virtual Sugarcane

Biorefinery (VSB): 2011 Report. Campinas, São Paulo: Brazilian Bioethanol Science and Technology Laboratory (CTBE), Technological Assessment Program (PAT), Internal Report. <goo.gl/x1Ach>. Accessed 12.12.2013.

Cardoso T., Cavalett O., Chagas M.F., Morais E.R., Carvalho J.L.N., Franco H.C.J., Galdos M.V., Scarpare F.V., Braunbeck O.A., Cortez L.A.B., Bonomi A., 2013. Technical and economic assessment of trash recovery in the sugarcane bioenergy production system. Scientia agricola, 70, 353-360.

Carvalho D.L., Avillez R.R. de, Rodrigues M.T., Borges L.E.P., Appel L.G., 2012. Mg and Al mixed oxides and the synthesis of n-butanol from ethanol, Appl. Catal. A: Gen., 415-416, 96-100.

CEPEA, 2013. Center for Advanced Studies on Applied Economics. <www.cepea.esalq.usp.br>. Accessed 11.03.2013.

CGEE, 2009. Center for Strategic Studies and Management in Science, Technology and Innovation. Bioethanol fuel: an oportunity for Brazil (in Portuguese). CGEE, Brasília.

Chistyakov A.V., Murzin V.Y., Gubanov M.A., Tsodikov M.V., 2013. Pd-Zn Containing Catalysts for Ethanol Conversion Towards Hydrocarbons. Chemical Engineering Transactions, 32, 619-624. DOI: 10.3303/CET1332104.

Dias M.O.S., Junqueira T.L., Cavalett O., Cunha M.P., Jesus C.D.F., Rossell C.E.V., Maciel Filho R., Bonomi A., 2012, Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash, Bioresour. Technol., 103, 152-161.

Dias M.O.S., Pereira, L.G., Junqueira T.L., Pavanello L.G., Chagas M.F., Cavalett O., Maciel Filho, R., Bonomi A., 2013. Butanol production in a sugarcane biorefinery using ethanol as feedstock - Part I: integration to a first generation sugarcane distillery. Accepted for publication in the Journal of Chemical Engineering Research and Design – Special Issue: Green Processes.

Dias M.O.S., Junqueira T.L., Cavalett O., Cunha M.P., Jesus C.D.F., Mantelatto P.E., Rossell C.E.V., Maciel Filho R., Bonomi A., 2013b. Cogeneration in integrated first and second generation ethanol from sugarcane. Chem. Eng. Res. Des. DOI: 10.1016/j.cherd.2013.05.009.

Downson G.R.M., Haddow M.F., Lee J., Wingad R.L., Wass D.F., 2013. Catalytic Conversion of Ethanol into an Advanced Biofuel: Unprecedented Selectivity for n-Butanol, Angew. Chem. Int., 52, 9005-9008.

EPE, 2013. Company of Research on Energy. Price of renewable energy from sugarcane. Sao Paulo, Brazil. http://www.epe.gov.br/imprensa/PressReleases/20131213_1.pdf. Accessed 03.06.2014.

Guinée J.B., Gorrée M., Heijungs R., Huppes G., Kleijn R., Koning A. de, Oers L. van, Wegener Sleeswijk A., Suh S., Udo de Haes H.A., Bruijn H. de, Duin R. van, Huijbregts M.A.J., 2002, Handbook on life cycle assessment: operational guide to the ISO standards, Dordrecht, Netherlands, Kluwer Academic Publishers, 692 pp, ISBN 1-4020-0228-9.

Humbird, D., Davis R., Tao L., Kinchin C., Hsu D., Aden A., Schoen P., Lukas J., Olthof B., Worley M., Sexton D., Dudgeon D., 2011. Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol - dilute-acid pretreatment and enzymatic hydrolysis of corn stover. Technical Report NREL/TP-5100-47764, Golden, Colorado, USA, NREL, 136 pp. <www.nrel.gov/biomass/pdfs/47764.pdf>. Accessed 03.06.2014.

ICIS, 2012. Indicative Chemical Prices: 1-Hexanol. <www.icis.com/chemicals/channel-info-chemicals-a-z/>. Accessed 11.28.2013.

ISO 14044, 2006, Environmental management - Life cycle assessment - Requirements and guidelines, The International Organization for Standardization, Geneva, Switzerland, 46 pp.

MDIC, 2013. Brazilian Ministry of Development, Industry and Commerce. Aliceweb: FOB Prices for n-butanol, Brasilia, DF, Brazil. http://aliceweb.mdic.gov.br/. Accessed 03.06.2014.

Pereira L.G., Dias M.O.S., Junqueira T.L., Pavanello L.G., Chagas M.F., Cavalett O., Maciel Filho R., Bonomi A., 2013. Butanol production in a sugarcane biorefinery using ethanol as feedstock - Part II: integration to a second generation sugarcane distillery. Accepted for publication in the Journal of Chemical Engineering Research and Design – Special Issue: Green Processes.

Riittonen T., Toukoniitty E., Madnani D.K., Leino A.-R., Kordas K., Szabo M., Sapi A., Arve K., Wärna J., Mikkola J.-P., 2012, One-Pot Liquid-Phase Catalytic Conversion of Ethanol to 1-butanol over Aluminium Oxide-The Effect of the Active Metal on the Selectivity, J. Catal., 2, 68-84.

Sannino D., Vaiano V., Ciambelli P., 2013. Photocatalytic Synthesis of Acetaldehyde by Selective Oxidation of Ethanol on RuO_x-VO_x/TiO_2. Chemical Engineering Transactions, 32, 625-630. DOI: 10.3303/CET2105

UDOP, 2013. Union of Biofuel Producers. Technical report on Sugarcane prices - 2013, Aracatuba, SP, Brazil. http://www.udop.com.br/. Accessed 03.06.2014.

Wuxi Hexia Chemical Company, 2013. Selected product categories: Butanol. Price of 2-ethyl-1-butanol. <http://www.hexiachem.com/>. Accessed 11.28.2013.