



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Process Integration of Bioethanol from Sugar Cane and Hydrogen Production

L. Hernández and V. Kafarov

Simulation and Control of Process Research Centre, Industrial University of Santander,
Cra 27 Cl 9, Bucaramanga, Colombia

Abstract: In this study several alternatives for process integration of bioethanol from sugar cane and hydrogen production were evaluated. Bioethanol was produced above all in the fermentation of sweetened juice from sugar cane, stillage was removed. Stillage and bagasse are the process byproducts. The bioethanol steam reforming is an endothermic catalytic process when vaporized ethanol and steam are fed using a 1:6 molar ratio to reformer with a Ni-catalyst at atmospheric pressure and 350°C. Taking into account the processes properties mentioned above, it is possible to integrate the bioethanol production from sugar cane and its reforming by using byproducts like bagasse and stillage and to produce energy for steam reforming and bioethanol solution concentration by direct firing (for bagasse) or anaerobic digestion to get methane (for stillage).

Key words: Bioethanol, hydrogen, sugar cane, steam reforming, stillage, bagasse

INTRODUCTION

The fossil fuels have been for decades, the first source to get energy (the world energy consumption for 2001 was: oil 37%, coal 25% and natural gas 24%) (Jean, 2004). However, nowadays a combination of technological, environmental (climatic change), wealthy and politic aspects as well as some socio economic changes have been addressing the use of new energetic sources as biofuels and are promoting the development of modern systems for energy cogeneration (Garcia, 2001).

Bioethanol at all, is produced for microbiologic conversion of sugars which, can be obtained from sugar, starch and lignocelulosic biomass. Production of bioethanol from sugarcane (sugarcane requires a tropical climate to grow productively) returns about 8 units of energy for each unit expended and when compared to corn which only returns about 1.34 units of fuel energy for each unit of energy expended. This fact makes more energetically efficient production of bioethanol from sugarcane with existing technology.

At the present time, bioethanol is used mainly as fuel additive and industrial chemical product. The most of bioethanol fuel is used as gasoline additive because it improves the octane number by direct blending to gasoline. A bioethanol blend in volume of 10% (E10) named gasohol, can improve the octane number in two or three points, giving an added value to medium or low octane number gasolines. The bioethanol fuel can be used as E85 too, a blend of bioethanol 85% and gasoline 15% which is used on flexible fuel vehicles (FFV) (DOE and NREL, 2000).

Hydrogen is the lightest chemical element and has the best energy-to-weight ratio of any fuel. Because of this, hydrogen can be economically competitive with gasoline or diesel as a transportation fuel. It has high energetic density by mass unit (hydrogen: 120 MJ kg⁻¹, natural gas: 50 MJ kg⁻¹ and naphthalene: 44.5 MJ kg⁻¹). Moreover, the hydrogen is considered a clean fuel because its combustion yields pure water vapour (with minimal NO_x) as exhaust when oxidised in air (Crabtree *et al.*, 2005). Although, the hydrogen is a secondary fuel because it is not founded alone on the nature, always it is jointed to other atoms as carbon and oxygen. For this reason, is necessary to spend energy to get it and the hydrogen becomes a clean energy source (Laborde, 2004).

Although the most used technology to produce hydrogen is the natural gas steam reforming, the hydrogen production from biomass is a new and promising technology for the future, because of the used raw material is renewable. But, if oil or gases are used to provide this energy, fossil fuels are consumed, forming pollution and nullifying the value of using a fuel cell, in a posterior stage.

A technology in developing stage to produce hydrogen from biomass is the biofuels reforming, among them bioethanol (Fatsikosta *et al.*, 2002). Several researchers have demonstrated the technical feasibility to produce hydrogen by breaking down of bioethanol (Auprêtre *et al.*, 2002; Batista *et al.*, 2004; Benito *et al.*, 2007; Zhang *et al.*, 2006). That process can be carried out to atmospheric pressure and temperatures over 300°C (Sun *et al.*, 2004). Additionally, the bioethanol as

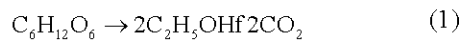
hydrogen source has some advantages, as easy transport and storage, is not toxic and is a clean source because it is produced from biomass which takes the CO₂ produced on the reforming process for its growth (Benito *et al.*, 2005).

In this study, two strategies are presented for process integration of bioethanol and hydrogen production by steam reforming with the aim to develop a clean processes to get clean fuels.

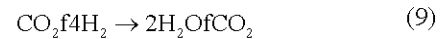
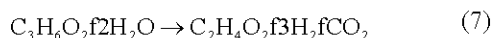
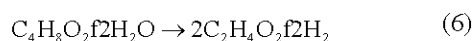
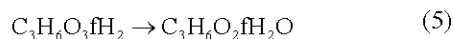
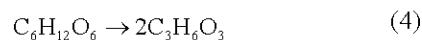
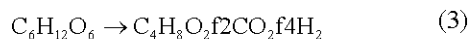
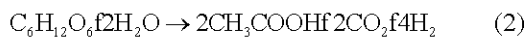
MATERIALS AND METHODS

For this process integration a process simulation of bioethanol production using sugar cane as raw material and a simulation of hydrogen production by steam reforming of bioethanol, were made.

At first, for simulation of bioethanol production a typical composition of sweetened juice from sugar cane clarified and filtrated was used. The process to get bioethanol studied was the anaerobic fermentation of glucose (reaction 1) (Bu'Lock, 1987) the conversion was reported as near to 0.9.

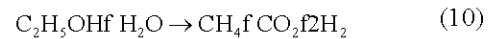


Moreover, stillage is produced during the bioethanol concentration. A typical characterization for stillage from sugar cane juices fermentation was used with a COD of 25 kg m⁻³. The treatment system for stillage studied was the anaerobic digestion (Wilke *et al.*, 2000) which, involve the reactions 2 to 9 (Swarbrick and Lethlean, 2001) has a conversion of glucose to methane near to 0.7 with a reaction temperature of 55°C (Barajas, 1989).



From sweetened juice production of sugar cane, bagasse is obtained which has a mass superior heating value among 7069 and 8623 kJ kg⁻¹ according to its moisture content (Carvajal *et al.*, 2004).

On the other hand, bioethanol steam reforming uses a vaporized blend 1:6 molar of bioethanol and water with a Ni-catalyst, carries out at atmospheric pressure and 500°C for a bioethanol conversion of 100% with a selectivity of 91% (Comas *et al.*, 2004). Bioethanol steam reforming takes place by the 10-12 reactions (Mariño *et al.*, 2004).



For simulation and process integration HYSYS® together with software developed by authors were used.

RESULTS AND DISCUSSION

Taking into account the previous operation conditions for bioethanol and hydrogen production by steam reforming, this process was simulated and two choices were founded for its integration which, are shown in Fig. 1 and 2. The first one for mainly bioethanol and second one for hydrogen production.

On Fig. 1, the process integration was studied using the biogas produced of stillage anaerobic digestion to get energy for bioethanol steam reforming. For this an alternative method was founded. The biogas volume produced from stillage was be able to give energy to reform the 4% of bioethanol formed on fermentation producing 18 m³ h⁻¹ of biosyngas (44% hydrogen, 36.8% water, 18.5% CO and 0.7% bioethanol) from 100 kg h⁻¹ of sweetened juice. Other 96% was conducted to produce industrial bioethanol with 96% purity.

On this proposed flow sheet the bioethanol is concentrated near to 50% volume in the first stage, with the aim of reducing the equipment and utilities for subsequent stages to produce industrial bioethanol. But, for bioethanol steam reforming, a molar ratio of 1:6 is needed. For this reason, a mass integration, taking some water from slurry produced on anaerobic digestion was made. The operation conditions for this process are shown on Table 1.

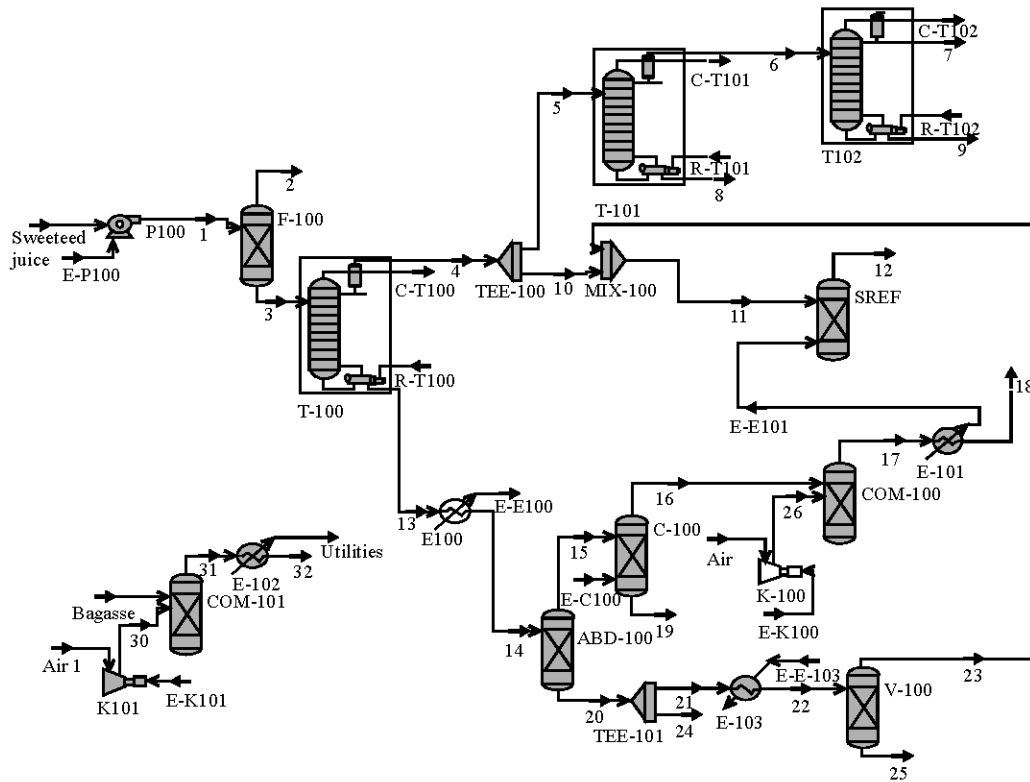


Fig. 1: Flow sheet for process integration case 1. ABD-100 Anaerobic digester; C-100 Condenser; COM-100 Biogas furnace; COM-101 Bagasse furnace; E-100-E-102 Heaters; E-103 Cooler; F-100 Fermenter; K-100, K-101 Air compressors; P-100 Sweetened juice pump; SREF Steam reformer; T-100-T-102 Distillation towers and V-100 Vaporizer

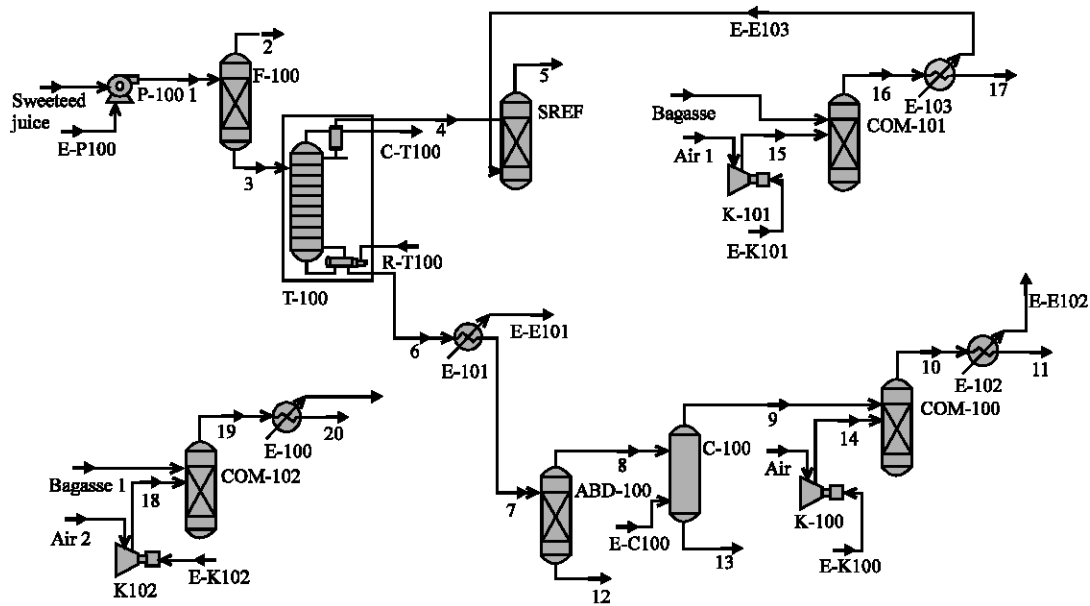


Fig. 2: Flowsheet for process integration case 2. ABD-100 Anaerobic digester; COM-100 Biogas furnace; COM-101, COM-102 Bagasse furnaces; E-100-E-103 Heaters; F-100 Fomenter; K-100-K-102 Air compressors; P-100 Sweetened juice pump; T-100 Distillation tower and SREF Steam reformer

Table 1: Operation conditions for flow sheet of Fig. 1

Parameters	1	2	3	4	5	6	8	7	9	10	11
T (°C)	30.00	31.66	31.66	82.95	82.95	78.87	87.09	66.52	80.28	82.95	100.17
mol fl (kg mole h ⁻¹)	4.55	0.22	4.64	0.37	0.33	0.19	0.14	0.14	0.05	0.04	0.14
Mass fl (kg h ⁻¹)	100.00	9.28	90.72	12.00	10.80	8.00	2.80	6.20	1.80	1.20	3.10
Parameters	12	13	14	15	16	17	18	19	20	21	22
T (°C)	648.18	99.86	55.00	48.68	10.00	1,462.46	700.00	10.00	48.68	48.68	110.00
mol fl (kg mole h ⁻¹)	0.24	4.27	4.27	0.07	0.06	0.41	0.41	0.01	4.24	0.11	0.11
Mass fl (kg h ⁻¹)	3.10	78.72	78.72	1.94	1.81	11.81	11.81	0.13	76.78	1.92	1.92
Parameters	23	24	25	26	30	31	32	Bagasse	Sweeteed juice	Air	Air 1
T (°C)	110.00	48.68	110.00	27.00	25.00	1,371.52	200.00	25.00	30.00	25.87	23.88
mol fl (kgmole h ⁻¹)	0.11	4.13	0.00	0.35	5.24	5.97	5.97	0.26	4.55	0.35	5.24
Mass fl (kg h ⁻¹)	1.90	74.86	0.02	10.00	151.20	175.20	175.20	48.00	100.00	10.00	151.20

Table 2: Operation conditions for flow sheet of Fig. 2

Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13
T (°C)	30.00	31.68	31.68	95.78	562.44	99.88	55.00	46.91	10.00	1,462.35	500.00	46.91	10.00
mol fl (kg mole h ⁻¹)	4.55	0.22	4.63	1.36	2.33	3.27	3.27	0.07	0.06	0.41	0.41	3.24	0.01
Mass fl (kg h ⁻¹)	100.00	9.28	90.72	30.00	30.00	60.72	60.72	1.93	1.81	11.81	11.81	58.79	0.12
Parameters	14	15	16	17	18	19	20	Bagasse	Bagasse 1	Sweetened juice	Air	Air 1	Air 2
T (°C)	27.00	25.00	1,521.48	580.00	25.00	1,371.52	200.00	25.00	25.00	30.00	25.87	23.88	23.88
mol fl (kg mole h ⁻¹)	0.35	2.62	3.05	3.05	3.93	4.48	4.48	0.16	0.20	4.55	0.35	2.62	3.93
Mass fl (kg h ⁻¹)	10.00	75.60	89.60	89.60	113.40	131.40	131.40	28.00	36.00	100.00	10.00	75.60	113.40

The flow sheet proposed on Fig. 1 can be used for low hydrogen production but, if it is necessary to produce more quantities, it must use other additional energy sources as bagasse. That is the case shown in Fig. 2.

Figure 2, shows process integration, using bioethanol steam reforming energy produced from combustion of bagasse. For this case the bagasse combustion gases are used to heat the steam reformer. Then, it is possible to produce near to 160 m³ h⁻¹ of biosyngas (70.4 m³ h⁻¹ of hydrogen), from 100 kg h⁻¹ of sweetened juice. The bagasse needed to get this production is 28 kg h⁻¹ only for reforming process, without utilities.

For last case, first stage concentrates near to 14% volume which is equivalent to molar ratio of 1:6 bioethanol-water for an appropriated process operation. Moreover, in this process the energy generated from combustion of biogas can be used to produce steam as utility fluid. The operation conditions for this process are shown on Table 2.

On the other hand, the utilities for two process integration cases were calculated as mass of bagasse necessary to supply this demand and for second case this quantity was inferior 36 kg bagasse/h vs 48 kg bagasse/h for first case for 100 kg h⁻¹ of sweetened juice processed. That is because of bioethanol concentration by distillation requires most energy consumption. But, to produce hydrogen from bioethanol it is necessary to use more additional energy for steam reforming, this process consumes 28 kg bagasse/h. In summary, to produce

hydrogen, 64 kg bagasse/h for 100 kg sweetened juice processed only required

CONCLUSIONS

Two strategies for process integration of bioethanol from sugar cane and hydrogen production were developed. First case, a lot of bioethanol produced was concentrated to industrial ethanol and other was used to get hydrogen by steam reforming with the utilities consumption of 2.6×10⁵ kJ h⁻¹ for 100 kg h⁻¹ of sweetened juice processed. On second alternative for process integration, all bioethanol produced was used to obtain hydrogen. In this case the utilities required are 2×10⁵ kJ h⁻¹ for 100 kg h⁻¹ of sweetened juice processed but, this process has a disadvantage that for bioethanol steam reforming is necessary and which requires an additional energy 1.14×10⁵ kJ h⁻¹ on the same basis.

ACKNOWLEDGMENTS

We thank the international projects CYTED IV.21: Bioethanol fed fuel cells, CYTED 307RT0324: Hydrogen: production and purification, storage and transport, CYTED 306RT0279: Network of new technologies for biofuels production; at the Colombian Institute for Science and Technology Development Francisco José de Caldas-COLCIENCIAS and The Iberoamerican Cooperation on Science and Technology for the Development for the financial support of this research.

REFERENCES

- Auprêtre, F., C. Descorme and D. Duprez, 2002. Bio-ethanol catalytic steam reforming over supported metal catalysis. *Catalysis Commun.*, 3: 263-267.
- Bu'Lock, J.D., 1987. *Basic Biotechnology*. Academic Press. London.
- Batista, M.S., R.K.S. Santos, E.M. Assaf, J.M. Assaf and E.A. Ticianelli, 2004. High efficiency steam reforming of ethanol. Characterization and performance of copper-nickel supported catalysts. *J. Power Sour.*, 134: 27-32.
- Benito, M., R. Padilla, L. Rodríguez, J.L. Sanz and L. Daza, 2007. Zirconia supported catalysts for bioethanol steam reforming: Effect of active phase and zirconia structure. *J. Power Sour.*, 169: 167-176.
- Benito, M., J.L. Sanz, R. Isabel, R. Padilla, R. Arjona and L. Daza, 2005. Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production. *J. Power Sour.*, 151: 11-17.
- Crabtree, G., M. Dresselhaus and M. Buchanan, 2005. The hydrogen economy. *Phys. Today*, 57: 39.
- Carvajal, A., A. Gómez and C. Briceño, 2004. Efecto de las cenizas en el poder calorífico superior del bagazo de la caña de azúcar. *Carta trimestral CENICAÑA*, 4: 10-12.
- Comas, J., F. Mariño, M. Laborde and N. Amadeo, 2004. Bioethanol steam reforming on Ni/Al₂O₃ catalyst. *Chem. Eng. J.*, 98: 61-68.
- DOE and NREL, 2000. Bioethanol fueling sustainable transportation. Report DOE/GO-102000-0907.
- García, P., 2001. *Tecnologías energéticas e impacto ambiental*. Mc Graw Hill, Madrid.
- Fatsikostas, A., D. Kondarides and X. Verykios, 2002. Production of hydrogen for fuel cells by reformation of biomass-derived ethanol. *Catalysis Today*, 75: 145-155.
- Jean, P.C., 2004. *About Sustainable Development. Pollution, Energies and Politics*, 2004, CIURE, Cali, Colombia.
- Laborde, M., 2004. El hidrógeno como combustible. Universidade Estadual de Campinas. 2º Workshop Internacional de Células a Combustível. Brasil, Octubre, (presentación magistral).
- Mariño, F., M. Boveri, G. Baronetti and M. Laborde, 2004. Hydrogen production via catalytic gasification of ethanol. A mechanism proposal over copper-nickel catalysts. *Int. J. Hydrogen Energy*, 29: 67-71.
- Sun, J., X. Qiu, F. Wu, W. Zhu, W. Wang and S. Hao, 2004. Hydrogen from steam reforming of ethanol in low and middle temperature range for fuel cell application. *Int. J. Hydrogen Energy*, 29: 1075-1081.
- Swarbrick, G. and J. Lethlean, 2001. A thermodynamic model for MSW landfill degradation. 8th International Waste Management and Landfill Symposium, Cagliari, Italy, 1-5 October, 1: 99-108.
- Wilkie, A., K. Riedesel and J. Owens, 2000. Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. *Biomass and Bioenergy*, 19: 63-102.
- Zhang, X. Tang, Y. Li, W. Cai, Y. Xu and W. Shen, 2006. Steam reforming of bio-ethanol on alkali-doped Ni/MgO catalysts: Hydrogen production for MC fuel cell. *Catalysis Commun.*, 7: 367-372.