Simulation of Ethanol Production Via Fermentation of the Synthesis Gas Using Aspen Plus[TM]

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With the aim of studying the fermentation of syngas, this work presents an integrated gasification with syngas fermentation process using the Aspen Plus[TM]. A reaction mechanism for the decomposition of sugarcane bagasse was used to represent the pyrolysis. The influence of operating conditions as gasifier temperature, oxidizing agents and gas composition in the fermentation were investigated for the production of ethanol by syngas fermentation. The simulation showed good results according to the validation with experimental data.

1. Introduction

Bioethanol is usually produced by direct fermentation of fermentable sugars (such as sugar cane and corn starch) or by *c*hemical and enzymatic hydrolysis of starch, cellulose and hemicellulose to sugars which are then fermented by microorganisms to produce ethanol. One of the major disadvantages with the use of bagasse, straw, wood or other lignocellulosic biomass is the presence of non-degradable components such as lignin. Unlike the hydrolysis, gasification technologies, can convert the biomass including the lignin, into synthesis gas. The gasification of lignocellulosic biomass can be a suitable route to overcome this obstacle in the use of biomass, since it is a relatively robust process in terms biomass source. The gasification by partial oxidation at elevated temperatures produces synthesis gas (syngas) where, the CO and H_2 are the essential components for subsequent ethanol production. The routes for the conversion of syngas to ethanol involve the gasification of biomass into synthesis gas (a mixture of CO and H_2, mainly), and, then, converts the syngas for fuel using chemical catalysts known as Fischer-Tropsch (FT) or also, using microbial catalysts, known as syngas fermentation. The fermentation of syngas offers several advantages, such as greater specificity of biocatalysts, lower energy costs and no requirement of a fixed ratio of $CO:H_2$. This work presents a simulation of the gasification of the sugarcane bagasse by a mechanism of thermal decomposition based on their major components (celullose, hemicelullose and lignin) to produce syngas, followed by fermentation of the syngas to produce ethanol using Aspen Plus[TM] simulator. The model presented here is simple and it is performed to predict the steady state performance of the gasifier as well as of the fermenter but allows to define compositions and flows in the input and output streams, which are important information for further analysis.

2. Methodology

The development of the process simulation in Aspen Plus[TM] involves the steps described below.

2.1 Assumptions

The process simulation development is based on the following assumptions: (1) the process is isothermal and steady state, (2) drying and devolatilization are instantaneous and are held at the bottom of gasifier, (3) in devolatilization or pyrolysis char and volatiles are formed; the volatiles include non-condensable such as H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, and condensable volatiles (tar) and water, (4) char only contains carbon and ash. The syngas fermentation process involves the mass transfer of gases (substrate) in the

liquid media. In the reactor modeling, the following considerations were taken into consideration: (1) the process occurs at steady state, (2) the bioreactor is perfectly mixed, (3) the process is isothermal and adiabatic, (4) biochemical reactions are considered without take into account explicitly, the microorganisms and (5) resistance to mass transfer is negligible. This analysis was conducted to study the maximum amount of ethanol that can be produced.

2.2 Insertion of components in the simulator Aspen Plus[TM]

The components present in the tar were used according to tests of pyrolysis of each pseudo-component : hemicellulose, cellulose and lignin. To hemicellulose, the studies presented by Peng and Wu (2011) for the pyrolysis of hemicellulose from sugarcane bagasse were used. These authors reported as major components in the tar, xylose, acetic acid and furfural followed by methanol. Components present on the tar after pyrolysis of lignin samples of sugarcane bagasse were applied according to the study published by Gaojin et al. (2010). The relevant components were phenol, 2,3-dihydro-benzofuran and propanedial. The tar of the pyrolysis of celulose are based on the work reported by Lu et al. (2011). Typical components during fast pyrolysis are mainly hydroxymethylfurfural, levoglucosan, hydroxyacetaldehyde, acetic acid and acetone. Table 1 shows the components used for the simulation.

Table 1: Components defined in Aspen Plus 7.3[TM] to represent the gasification and fermentation

Name		Name	MF	Name	MF
Methanol	CH_4O	Carbon-monoxide	CO	LIGA	$C_{10}H_{11.6}O_{3.9}$
Water	H_2O	Carbon dioxide	CO_2	Xylose	$C_5H_{10}O_5$
Nitrogen	N_2	Ethanol (Etha)	C_2H_6O	Acetone	C_3H_6O
Ammonia	NH_3	hydroxymethyl-furfural(HMF)[a]	$C_5H_4O_2$	Actcellt	$C_6H_{10}O_5$
Oxygen	O_2	Carbon-graphite	C	formaldehyde	CH_2O
Ash	S_iO_2	Furfural (F-F)	$C_5H_4O_2$	Ethane	C_2H_6
Celulose	$C_6H_{10}O_5$	Levoglucosan (LVG)	$C_6H_{10}O_5$	Methane	CH_4
Hemicel	$C_5H_8O_4$	Acetic-acid (Acte)	$C_2H_4O_2$	Hema2	$C_5H_8O_4$
Lignin	$C_{10}H_{11.6}O_{3.9}$	Hydroxyacetaldehyde (HAA)	$C_2H_4O_2$	Ethylene	C_2H_4
Hydrogen	H_2	Acetaldehyde	C_2H_4O	Propanedial	$C_3H_4O_2$
Phenol	C_6H_6O	1,3-dihydroisobenzofuran	C_8H_8O	Hema1	$C_5H_8O_4$

[a] Because HMF is not on the Aspen Plus[TM], it was selected an aldehyde of similar molecular weight to represent the compound, in this case was used the furfural. MF: molecular formula

The database for biomass components developed by the NREL (Wooley and Putsche, 1996) was used as the basis for insertion of lignocellulosic components (cellulose, hemicellulose and lignin) in the Aspen Plus[TM] simulator. The characterization of these three pseudo-components was based on the work presented by Guo et al. (2011): 44.1 wt. % cellulose, 25.7 wt. % hemicellulose, 21.3 wt. % lignin, 1 wt. % ash and 7.9 wt. % moisture.

2.3 Aspen Plus[TM] simulation

The different stages considered in Aspen Plus[TM] simulation in order to show the overall gasification process are: biomass drying, biomass pyrolysis, char gasification, and gas cleaning, and finally syngas fermentation. Figure 1 shows the flowsheet of the gasification and fermentation of sugarcane bagasse using Aspen Plus[TM].

2.3.1 Biomass drying and pyrolysis

The decomposition of the biomass was considered parallel to its three main components: hemicellulose, cellulose and lignin. To represent the primary pyrolysis, the reactions defined in the mechanism developed by Ranzi et al. (2008) were used, for hemicellulose and cellulose, Miller and Bellan (1997), for lignin and studies of the decomposition of sugarcane bagasse developed by Mothe and Miranda (2013). To represent the secondary pyrolysis, it was used the cracking reactions proposed by Blondeau and Jeanmart (2012). Tables 2 and 3 depict the reactions used in the pyrolysis. At the temperature of 105 °C, it was considered complete dehydration of biomass. DRY1 and DRY2 blocks represents the biomass drying. At the temperature of 230 °C, it was considered complete conversion of hemicellulose to its respective active hemicellulose 1 and 2 (Hema1 and Hema2). The maximum conversion of the hemicelluloses was found in the temperature of 290 °C. The decomposition of cellulose was considered at the starting temperature of 290 °C with the apparition of coal, water and active cellulose (Actcellt). At the temperature of 340 °C, it was considered the largest mass loss celulose conversion, generating mainly the levoglucosan, and a lesser proportion of gases and tar (hydroxymethylfurfural, acetic acid and hydroxyacetaldehyde). The lignin decomposition starts at a temperature of 290 °C with the formation of gases, mainly tar and coal. At the temperature of 340 °C there is the greatest loss of mass of lignin, due to the formation of tar and gases,

which ends at temperature of 380 $^{\circ}$C. The tar from the three pseudo-componets starts the secondary pyrolysis at temperatures above 400 $^{\circ}$C. P1A, P1B, P1C and P1D reactor blocks (Rstoic) represent the primary pyrolysis of the biomass at temperatures of 230, 290, 340 and 380 $^{\circ}$C, respectively. P2 reactor block (Rcstr) represents the secondary pyrolysis.

Table 2: Reactions used to represent the primary pyrolysis

No	Stoichiometry	x_c^b	C-B	T($^{\circ}$C)
1	Hemicel-->0.4 Hema1+ 0.6 Hema2	1.0	Hemicel	230
3	Celulose--> 6C+ 5H$_2$O	0.08	Celulose	
4	Celulose--> actcellt	0.92	Celulose	
5[a]	Hema1--> 0.6 xylose + 0.1667 C$_2$H$_4$O$_2$ + 0.33332 F-F	0.48	Hema1	
6	Lignin --> LIGA	1	Lignin[a]	290
7	Hema1 --> 0.2 H$_2$ + CO$_2$ + CO+ 0.5CH$_2$O + 0.25 CH$_4$O + 0.125 C$_2$H$_6$O + 0.125H$_2$O + 0.7CH$_4$ + 0.3 C$_2$H$_6$ + 0.7C	0.52	Hema1	
8	Hema2--> CO$_2$ + 0.8 CO + 0.25 CH$_4$O+0.125 C$_2$H$_6$O + 0.125 H$_2$O + C + 0.8 H$_2$ + 0.7 CH$_2$O + 0.5 CH4 + 0.25 C2H4	1.0	Hema2	
9	Actcellt--> 0.2CO$_2$ + 0.15CO + 1.2 H2O + 0.25 C$_2$H$_4$O$_2$ +0.2 HMF + 0.075 CH$_4$ + 0.2 C$_3$H$_6$O + 1.325C+ 0.95 HAA +0.25 CH$_2$O	0.1	Actcellt	350
10	Actcellt--> LVG	0.90	Actcellt	
11[a]	LIGA--> 0.5 C$_8$H$_8$O + 1.6 C$_3$H$_4$O$_2$ + 0.2 Phenol	0.25	LGA	380
12	LIGA-->0.8 H2 +3.4H$_2$O+0.1CO$_2$+0.3CH$_4$+0.2C$_2$H$_4$+0.3CO+8.5C+ 0.2C$_2$H$_6$	0.75	LGA	

[a] Indicates modified reaction in this work. [b] Conversion values proposed in this work, initially by using the kinetics the Ranzi et al. (2008) and Miller and Bellan (1997). C-B: Based component, x_c: fraction conversion.

Table 3: Secondary reactions, corresponding to cracking of tar. Blondeau and Jeanmart (2012)

E_a (kJ/mole): 108 k_0 (s^{-1}) 4,28x10^6 6

No	Stoichiometry	No	Stoichiometry
13	LVG --> CO$_2$ + 2 H$_2$ + 0.5 C$_2$H$_4$ + 3CO + CH$_4$	18[a]	C$_8$H$_8$O --> CO + CH$_4$ + C+ C$_2$H$_4$
14	C$_3$H$_6$O --> 0.5 CO2 + 0.5H$_2$ + 1.25 C$_2$H$_4$	19	HAA --> 2 CO + 2 H$_2$
15	xylose --> 1.35 CO$_2$ + 3 H$_2$ + CH$_4$ + 0.35 C+ 2.3 CO	20	C$_2$H$_4$O$_2$ --> 2 CO + 2 H$_2$
16	F-F --> CH$_4$ + 2 CO + 2 C	21	HMF --> CH$_4$ + 2CO + 2 C
17	C$_3$H$_4$O$_2$ --> CO2 + C$_2$H$_4$	22	Phenol --> 0.5 CO$_2$+ 1.5 C$_2$H$_4$+ 2.5 C

[a] Indicates proposed reaction in this work.
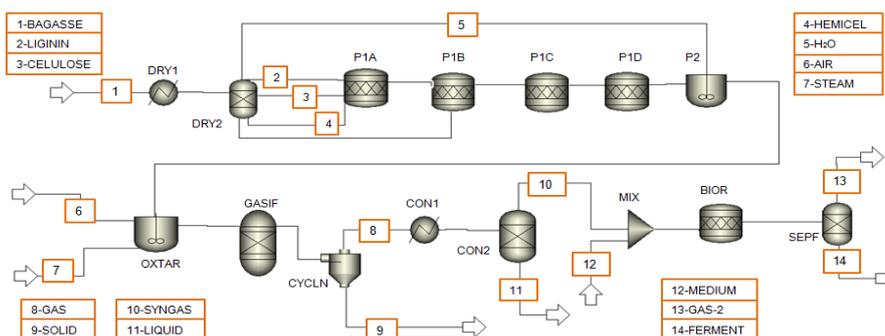
Figure 1: Flowsheet of the gasification and fermentation of sugarcane bagasse using the method of minimization of Gibbs free energy

2.3.2 Char Gasification

The process of biomass gasification may be represented by the reactions (23-34) shown in Table 4. The streams STEAM, AIR and PIRO2 are the gasifier input represented by OXTAR (Rcstr) and GASIF (Rgibbs). The function block OXTAR simulates the oxidation and gasification reactions using chemical kinetics (23-27) and the GASIF block simulates water-gas shift reaction (28), char combustion and

gasification reactions (29-33) and formation of NH_3 (34) using the minimization of the Gibbs free energy with restricted equilibrium.

Table 4: Main process reactions of gasification and fermentation

No	Stoichiometry	No	Stoichiometry	No	Stoichiometry
23	$C_wH_zO_Y+_{(Z-Y)}O_2->_{(2W-1.5Z-Y)}CO$ $+_{(1.5Z-Y-W)}CO_2+_{(0.5z)}H_2O^a$	28	$CO+ H_2O <-> 2CO_2 + H_2$	34	$0.5N_2 +1.5H_2 --> NH_3$
		29	$0.5O_2+CO --> CO_2$	35	$6CO +3H_2O --> Etha +4CO_2$
24	$C_nH_m +0.5nO_2 --> nCO + 0.5H_2$	30	$C+2H_2 --> CH_4$	36	$2CO_2 +6H_2 --> Etha +3H_2O$
25	$CH_4 +2O_2 --> CO_2 + H_2O$	31	$C+O_2 --> CO_2$	37	$4CO +2H_2O --> Acte +2CO_2$
26	$0.5O_2+H_2 --> H_2O$	32	$C+CO_2--> 2CO$	38	$2CO_2 +4H_2 --> Acte +2H_2O$
27	$C_nH_m +nH_2O -->CO +(0.5m+n)H_2$	33	$C+H_2O --> CO + H_2$		

[a] Kinetics of oxidation of tar published $r=MW_i \cdot 9.2x10^6 \cdot e(9650/T) \cdot T \cdot C_{Tar} \cdot C^{0.5}_{O_2}$, MW= molecular weight, kinetics of oxidation and gasification reported in Gomez and Leckner (2010).

2.3.3 Gas Cleaning

The syngas cleaning corresponds to the separation of solids and tar present. The block CYCLN simulates the cyclone separator that is commonly used for separating dispersed solid particles from gas phase. The streams SOLID corresponds to char (C) and ash. The next blocks, CON1 and CON2 represent the tar condensation. Finally, the stream SYNGAS represents the synthesis gas. This cooling step, favors gas cleaning and subsequent fermentation because it is necessary to operate at low temperatures.

2.3.4 Fermentation of Syngas

The stoichiometry of ethanol and acetate formation from CO and H_2/CO_2 has been established as the reaction 35-38 shown in Table 4.The blocks MIX, BIOR and SP-2 represent the fermentation step. The MEDIUM and SYNGAS are initially mixed in the block MIX. The MEDIUM fed to the fermentation contains a solution of nutrients in water, which are necessary for microbial growth. In the simulated model, the media feed stream is assumed to be pure water since biomass is neglected in the model. The fermentation process was modeled in a stoichiometric reactor (Rstoic).

3. Results

The yields of sugarcane bagasse reported by Xu et al. (2011) were used to validate the proposed pyrolysis stage. Figure 2 compares the experimental results of these authors with the pyrolysis simulation predictions. The gasification model was validated against the experiments of Jaimes-Figueroa et al. (2013) and Akay and Jordan (2011). In gasification by Jaimes-Figueroa et al. (2013) steam and reaction temperature of 900 °C were considered with steam to biomass ratio (SB) of 2 and in the gasification process by Akay and Jordan (2011) with air at reaction temperature of 800 °C and a equivalence ratio (ER) of 0.26. Comparison of experimental data with model predictions is given in Table 5.

Table 5: Experimental results versus simulation predictions for gasification

Gas Composition Volume % dry basis				
Component	Experimental study		Gasification model	
	Jaimes Figueroa et al. (2013) Case a	Akay and Jordan (2011)[a] Case b	Case a	Case b
H_2	60.00	11.82	61.32	23.48
CO	17.00	16.94	18.48	15.66
CO_2	20.00	14.07	20.18	15.75
CH_4	3.00	3.26	0.00	1.67
RMS error[b] (%)			5.00	6.00

[a] With nitrogen and minor amounts of higher hydrocarbons (C2+).

[b] $RMS = \sqrt{\sum_{i=1}^{N} (n_{i,exp} - n_{i,model})^2 \big/ N}$, RMS: root-mean-square, N: number of species, n_i: Composition volume %

The RMS error varies between 0.9-22 % for the stage pyrolysis proposed at different temperatures for the three products (tar, char and gas), as presented in Figure 2. As it can be observed in Table 5 the value of RMS error in the gasification process has a good agreement between experimental and calculated data. These values of RMS indicate that the proposed simulation is representing suitably the process so that it can be applied to the gasification study.
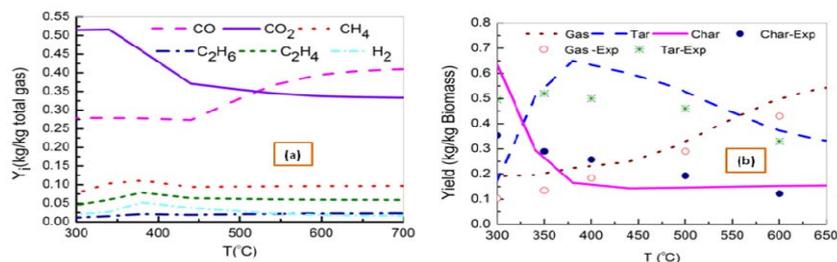
Figure 2: a) Calculated composition (mass fraction) of pyrolysis gas as a function of pyrolysis temperature; b) Comparison of the outputs of the proposed model with the experimental pyrolysis data by Xu et al. (2011)

For sensitivity analyses the gasification process was simulated for different situations varying the equivalence ratio (ER), steam to biomass ratio (SB) and the reaction temperature. The results are shown in Figures 3 and 4.
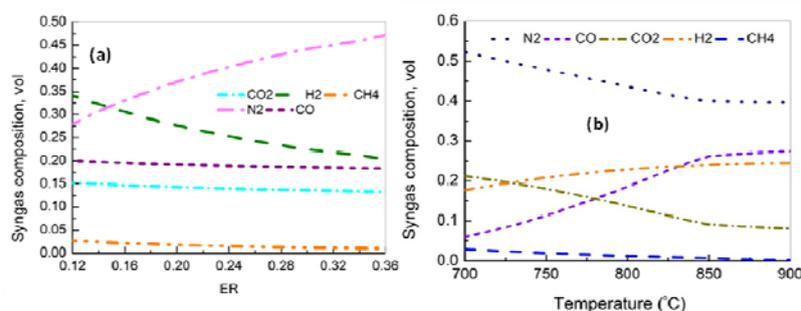
Figure 3: a) Effect of ER in the composition of syngas (T=800 °C) b) Effect of temperature in the composition of syngas (ER=0.25)

As it can observed in Figure 3a, the syngas composition is affected by the value of ER. For a given temperature (800 °C), increasing ER decreases H2 composition in the syngas. In ER=0.25 (Figure 3b), it is clear that increasing the temperature favors the formation of H2 and CO, and decreases methane composition. Figure 4 depicts a gasification with steam and air as oxidizing agents.
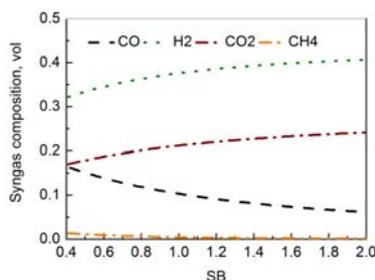
Figure 4: Effect of SB in the composition of syngas (ER=0.25 and T=800 °C)

In Figure 4, with a value of ER=0.25, it is observed that increasing the value of SB favors the formation of H_2. The greater the SB increase more drastically CO decreases.
The fermentation was studied by variation of the ER and hence syngas composition on the fermenter.
The results of sensitivity analyses to study the fermentation can be found in Figures 5 (for a conversion of 100 % CO and 78 % H_2). An increase in ER favors mainly the production of acetic acid. For a value of ER=0.25, it produces 2.5 ethanol g/L and 5.2 acetic acid g/L. Gaddy (2000), using a syngas composition of 14 % H2 and 13% of CO found similar concentrations of ethanol and acetic acid (2.74 g/L and 5.60 g/L, respectively), so it may be concluded that the proposed simulation represents satisfactorily the fermentation process.
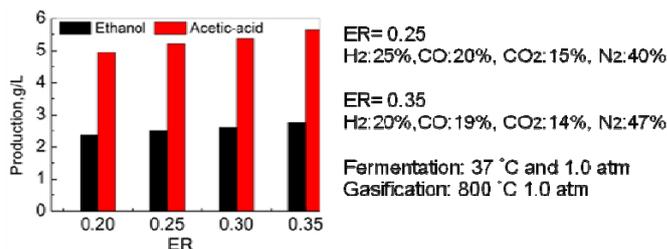
Figure 5: Effect of variation of ER on the production of ethanol and acetic acid

4. Conclusion

Simulation of gasification of the sugarcane bagasse and fermentation of the syngas were developed using Aspen Plus[TM]. Good agreement between simulation prediction and experimental data was found. The effects of varying the ER, SB, temperature on the gasifier, and synthesis gas composition on the fermenter were studied. High values of temperature favor the formation of syngas. ER values of approximately 0.28-0.35 composition favors H_2 and CO production. For a value of ER=0.25, low values of SB maintain a proportional relation of the H_2 and CO in the syngas For syngas fermentation produced in the sugarcane bagasse gasification using air as the oxidizing agent (ER=0.25) can be found concentrations of ethanol and acetic acid of 2.5 g/L and 5.2 g/L, respectively.

Acknowledgment

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