# FURFURAL PRODUCTION THROUGH TWO BIOCONVERSION ROUTES: EXPERIMENTAL OPTIMIZATION AND PROCESS SIMULATION

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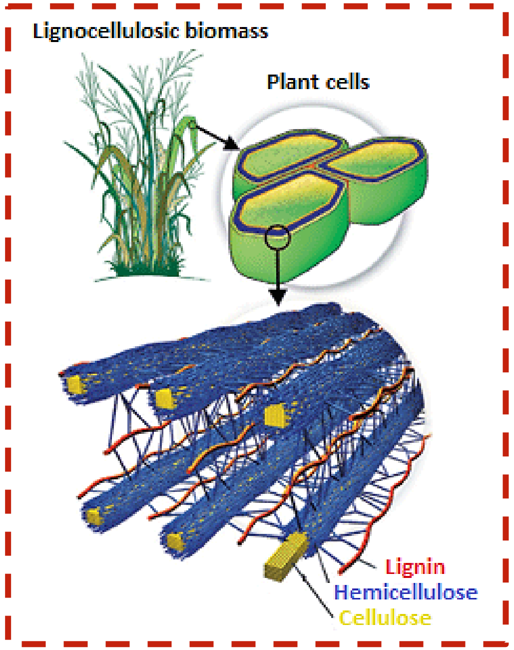
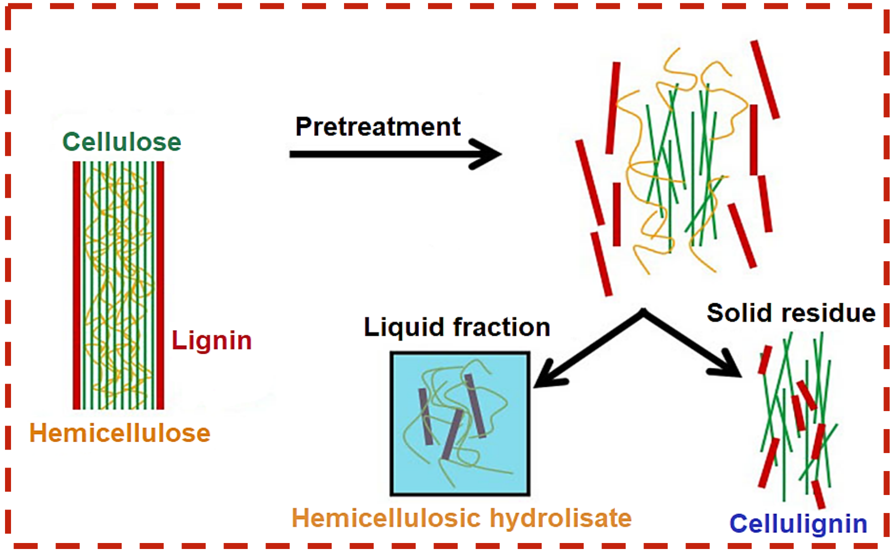
The <u>main objectives</u> of this study were **optimizing** experimentally the **production of furfural** from **sugarcane biomass** (50% **bagasse** and 50% **straw**), the furfural production **from hemicellulosic hydrolysate** and **simulate** the **optimal condition** in Aspen Plus® and Aspen Economic Analyzer under <u>two conditions</u>: in the first, **pre-treatment** and **reaction** occur **separately** (**case 1 - two steps**); in the second, **both occurring** in the **same equipment** (**case 2 - one step**) for comparative purpose. The novelty consists of **incorporating** the **high added-value product furfural** into a **Brazilian mill** using **sugarcane bagasse/straw mixture increasing** the portfolio of this **sector**.




Source: adapted from Hsu et al. (1980)

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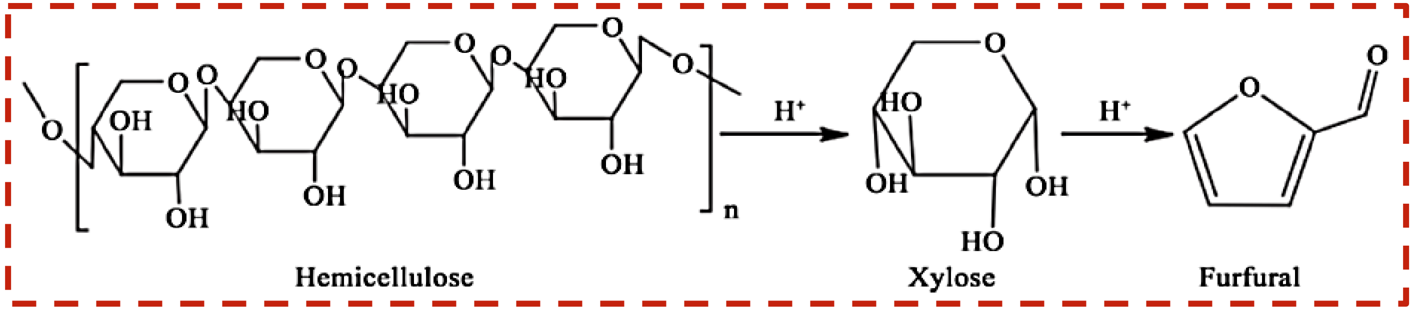


# MATERIAL AND METHODS


6WW9+HJ Américo Brasiliense, São Paulo

## Sugarcane Biomass
**(Straw 50% + Bagasse 50%)**

- 38.50% Cellulose
- 29.06% Hemicelulose
- 21.73% Lignin
- 5.31% Acetyl groups
- 13.30% Extractives
- 3.28% Ashes

## *Furfural Production from Hemicellulosic Hydrolysate (Case 1 - two steps)*

**ACID HYDROLYSIS**

- **Sugarcane biomass** (straw 50% + bagasse 50%)
- **$H_2SO_4$** 1.25% v/v ; S/L ratio 1:5
- 130 ºC ; 45 min

**Filtration**

- Separations of solid mass (cellulignin) and **hemicellulosic hydrolysate**

**CATALYTIC EXPERIMENTS**

- **Hemicelulosic hydrolysate**
- **$H_2SO_4$**
- CCRD*

* $2^3$ Central Composite Rotational Design with 4 repetitions at the central point (total 18 experiments), operational parameters:

- temperature (76 - 194 ºC)
- reaction time (40 - 134 min)
- $H_2SO_4$ concentration (1.24 - 24.76% v/v)

## *Furfural Production from Sugarcane Biomass (Case 2 - one step)*

sugarcane biomass

- straw 50%
- bagasse 50%

→

dry block reactor (2L)

- **$H_2SO_4$: catalyst***

→

Filtration

- liquid fraction ⇒ characterization ⇒ concentration of sugar and furfural

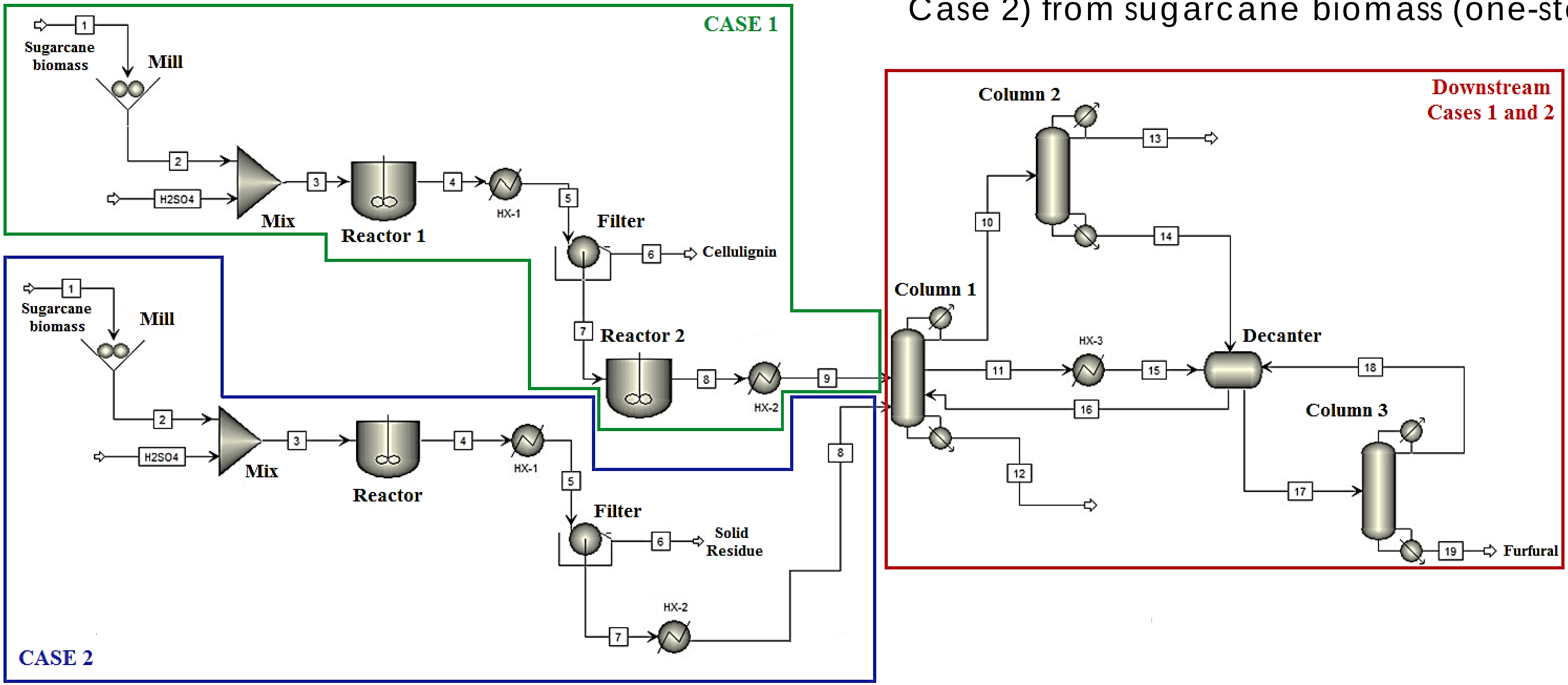
*$2^4$ Central Composite Rotational Design (CCRD) with 4 repetitions at the central point (total 28 experiments), operational parameters:

- temperature (80 - 240 ºC)
- reaction time (15 - 235 min)
- solid-liquid ratio (1:2 - 1:6)
- $H_2SO_4$ concentration (0 - 4% v/v)

# *Simulation Procedure*

## Scenarios for furfural production:

Case 1) from sugarcane biomass hemicellulosic hydrolysate (two-steps)
Case 2) from sugarcane biomass (one-step)




- Aspen Plus® simulator version 11.0

# *Economic Analysis*

**Table 1.** Parameters used for economic evaluation of two cases.

| Parameters | Value |
|---|---|
| Project lifetime (years) | 25 |
| Construction time (years) | 2 |
| Linear depreciation (years) | 10 |
| Minimal return on investment (ROI) | 10% |
| Taxes (%) | 30 |
| Lang factor | 3.63 |
| CE Plant Cost Index (2020) | 596.2 |
| Furfural (U$/ton) | 2100 |
| Electricity (U$/kWh) | 0.056 |
| Sugarcane Bagasse (U$/ton) | 10.64 |
| Sugarcane Straw (U$/ton | 10.88 |
| Water (U$/m$^3$) | 2.76 |
| Sulfuric Acid (U$/ton) | 172.4 |
| Vapor Steam (U$/ton) | 9.91 |

all values used were indexed for the period from November 2020 to April 2021.

average exchange rate of R$ 5.566.

it was also considered autonomous distilleries in which the demands of heat, electricity and mechanical energy are assembled by the cogeneration plant that consumes 1/3 of residual biomass generated in the sugar and ethanol production process.

Aspen Economic Analyzer.

# RESULTS

## Furfural Production from Sugarcane Biomass (one step)

## Table 2.

$2^4$ Central Composite Rotational Design to study the influence of variables: acid concentration

| Assays | $H_2SO_4$ (%v/v) | Temperature (°C) | S/L ratio | Time (min) | Furfural (g $L^{-1}$) | Yield (%) | Efficiency (%) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 120 | 3 | 70 | 3.16 | 3.3 | 5.1 |
| 2 | 1 | 120 | 3 | 180 | 4.59 | 4.7 | 7.4 |
| 3 | 1 | 120 | 5 | 70 | 2.60 | 4.5 | 7.0 |
| 4 | 1 | 120 | 5 | 180 | 4.73 | 8.1 | 12.7 |
| 5 | 1 | 200 | 3 | 70 | 15.06 | 15.6 | 24.3 |
| 6 | 1 | 200 | 3 | 180 | 16.02 | 10.3 | 16.2 |
| 7 | 1 | 200 | 5 | 70 | 6.04 | 8.7 | 13.6 |
| 8 | 1 | 200 | 5 | 180 | 1.25 | 4.2 | 6.6 |
| 9 | 3 | 120 | 3 | 70 | 2.86 | 2.9 | 4.6 |
| 10 | 3 | 120 | 3 | 180 | 5.96 | 6.2 | 9.6 |
| 11 | 3 | 120 | 5 | 70 | 2.54 | 9.5 | 14.9 |
| 12 | 3 | 120 | 5 | 180 | 8.38 | 14.4 | 22.5 |
| 13 | 3 | 200 | 3 | 70 | 8.95 | 9.2 | 14.4 |
| 14 | 3 | 200 | 3 | 180 | 2.11 | 4.2 | 6.6 |
| 15 | 3 | 200 | 5 | 70 | 0.70 | 4.6 | 7.2 |
| 16 | 3 | 200 | 5 | 180 | 0.14 | 2.5 | 3.9 |
| 17* | 0 | 160 | 4 | 125 | 4.10 | 5.6 | 8.8 |
| 18* | 4 | 160 | 4 | 125 | 13.11 | 11.2 | 17.4 |
| 19* | 2 | 80 | 4 | 125 | 0.06 | 2.2 | 3.4 |
| 20* | 2 | 240 | 4 | 125 | 0.01 | 1.5 | 2.3 |
| 21* | 2 | 160 | 2 | 125 | 12.32 | 8.5 | 13.2 |
| 22* | 2 | 160 | 6 | 125 | 8.54 | 11.4 | 17.9 |
| 23* | 2 | 160 | 4 | 15 | 9.05 | 12.5 | 19.5 |
| 24* | 2 | 160 | 4 | 235 | 8.65 | 11.9 | 18.6 |
| 25 (CP) | 2 | 160 | 4 | 125 | 10.38 | 14.3 | 22.3 |
| 26 (CP) | 2 | 160 | 4 | 125 | 9.91 | 13.6 | 21.3 |
| 27 (CP) | 2 | 160 | 4 | 125 | 12.64 | 14.6 | 22.9 |

*axial points; CP: central points; **Efficiency = Yield theorical/Yield experimental

## After analysis in the STATITISCA software:

- The analysis of variance (ANOVA) allowed to verify that the yield response showed a correlation coefficient ($R^2$) of 0.94.
- It is observed that, the proposed model was significant, with no lack of adjustment to the significance level of 0.05 (95% confidence).
- The furfural yield presented the maximum value in the temperature range of 140 to 200 ºC, from time residence of 70 to 235 min, S/L ratio of 3 to 5 and acid concentration in 1 to 3 %v/v.
- This model was optimized using the desirability function (FD) $\Rightarrow$ an optimal value of yield 15.6% was found under conditions of 3.3% (v/v) acid concentration, 133 ºC, 1:6 S/L ratio and 235 min reaction time.
- This condition was validated experimentally obtained 15.4% ± 0.01 yield and 2.68 g furfural.

- Furfural efficiency: 24 %
- Furfural yield: 15.4%

$$\boldsymbol{Yield\ (\%) = \frac{Furfural\ (g/L) \times Reation\ Volume}{Initial\ mass\ of\ pentoses\ (g)} \times 100}$$

| Assays | $H_2SO_4$ (%v/v) | Temperature (°C) | Time (min) | Furfural (g $L^{-1}$) | Yield (%) | Efficiency (%)** |
|---|---|---|---|---|---|---|
| 1 | 6 | 100 | 40 | 2.74 | 8.81 | 13.77 |
| 2 | 20 | 100 | 40 | 0.46 | 1.74 | 2.72 |
| 3 | 6 | 170 | 40 | 3.74 | 12.04 | 18.81 |
| 4 | 20 | 170 | 40 | 0.01 | 0.04 | 0.07 |
| 5 | 6 | 100 | 110 | 1.86 | 6.00 | 9.38 |
| 6 | 20 | 100 | 110 | 1.12 | 4.24 | 6.62 |
| 7 | 6 | 170 | 110 | 2.70 | 8.71 | 13.61 |
| 8 | 20 | 170 | 110 | 0.03 | 0.11 | 0.17 |
| 9* | 1.24 | 135 | 75 | 6.58 | 20.16 | 31.50 |
| 10* | 24.76 | 135 | 75 | 1.53 | 6.17 | 9.63 |
| 11* | 13 | 76 | 75 | 0.18 | 0.62 | 0.97 |
| 12* | 13 | 194 | 75 | 0.02 | 0.06 | 0.09 |
| 13* | 13 | 135 | 16 | 0.79 | 2.74 | 4.27 |
| 14* | 13 | 135 | 134 | 0.29 | 1.02 | 1.59 |
| 15 (CP) | 13 | 135 | 75 | 0.37 | 1.28 | 1.99 |
| 16 (CP) | 13 | 135 | 75 | 0.55 | 1.90 | 2.96 |
| 17 (CP) | 13 | 135 | 75 | 0.32 | 1.13 | 1.76 |
| 18 (CP) | 13 | 135 | 75 | 0.44 | 1.52 | 2.38 |

*axial points; CP: central points; **Efficiency = Yield theorical/Yield experimental

# Furfural Production from Sugarcane Biomass Hemicellulosic Hydrolysate (two steps)

## Table 3.

$2^3$ Central Composite Rotational Design to study the influence of variables: acid concentration, temperature and time in furfural production from sugarcane biomass hemicellulosic hydrolysate.

## After analysis in the STATITISCA software:

- The analysis of variance (ANOVA) allowed to verify that the yield response showed a correlation coefficient ($R^2$) of 0.99.
- It is observed that, the proposed model was significant, with no lack of adjustment to the significance level of 0.05 (95% confidence).
- The response yield presents maximum value when the temperature, acid concentration and reaction time ranging were 150 to 200 ºC; 0.05 to 2% v/v; and 10 to 100 min, respectively.
- Optimal value of yield 21%, was found under conditions of 1.24% (v/v) acid concentration, 194 ºC and a reaction time 95 min.
- This condition was validated experimentally obtained a yield 21.9% ± 0.65, efficiency 34.15% and 1.426 g furfural.

- Furfural efficiency: 34 %

| Parameters | Case 1 Two-step | Case 2 One-step |
|---|---|---|
| Sugarcane Biomass (ton $h^{-1}$) | 2400 | 2400 |
| Furfural Production (ton $h^{-1}$) | 76.22 | 73.56 |
| Treated Biomass (ton $h^{-1}$) | 1679 | - |
| Solid residue (ton $h^{-1}$) | - | 1013 |
| Revenue (U$, billions) | 3.09 | 2.46 |
| Net present value (NPV, U$, billions) | 4.20 | 1.10 |
| Internal rate of return (IRR, %) | 27.56 | 13.52 |
| PI (Profitability Index) | 1.36 | 1.08 |

**Table 4.**

Results of the economic evaluation of each scenario.

# CONCLUSIONS

- In agreement to the approach for **development** of **efficient biorefinery** this work proposed the **integration** of **furfural production** from **sugarcane biomass** to the **second-generation ethanol production chain**.
- in **case 1** (**two-steps**) **hydrolysis** (1.25% v/v $H_2SO_4$, S/L ratio 1:5, 130 ºC, 45 min) and **furfural production** with 1.24% v/v $H_2SO_4$, 194 °C, 95 min resulted in a **21.9% yield furfural**;
- in **case 2** (**one-step**) a **15.4% yield furfural** was achieved with 3.3% v/v $H_2SO_4$, S/L ratio 1:6, 133 °C and 235 min.
- These results, together with **economic evaluation** of two cases that revealed **revenues** of **US$ 3.1 billion (case 1)** and **US$ 2.46 billion (case 2)**, indicate this **coupling-process could boost the full use of biomass**, with the **generation** of **higher value-added bioproduct** and **bioelectricity**, give **sustainability** to the **productive chain**, being a clear **motivation** to **enlarge sugarcane industry**.

# ACKNOWLEDGEMENTS

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