Wet oxidation pretreatment of lignocellulosic residues of sugarcane, rice, cassava and peanuts for ethanol production

Introduction

- Worldwide interests in fuel ethanol increased

- Lignocellulosic residues are available on a renewable basis

- WO(wet oxidation) has been effective for different biomass resources

Materials and methods

- Raw materials

  Sugarcane bagasse was from sugar mill (Matanzas, Cuba)

- Pretreatment

  WO in a 2-L loop reactor with continuous circulation and stirring constructed at the Riso National Laboratory

Materials and methods

● Analysis of the pretreated materials

The dry matter content was analysed using a halogen moisture analyser (HR73).

The contens of glucan, xylan, arabinan and lignin were determined by a two-step acid hydrolysis procedure using in the first step 720g/kg sulphuric acid, which was diluted to 25g/kg in the second step.

The sugars obtained after the hydrolysis were analysed using HPLC .

Materials and methods

○ Analysis of the pretreated materials

Glucose, xylose and arabinose were separated on an Aminex HPX-87H column.

Overall recovery

$$Glucan(g/kg) = \frac{Glucan_{SF} + Glucan_{LF}/1.11}{Glucan_{RM}} \times 1000$$

$$Xylan(g/Kg) = \frac{Xylan_{SF} + Xylose_{LF}/1.14}{Xylan_{RM}} \times 1000$$
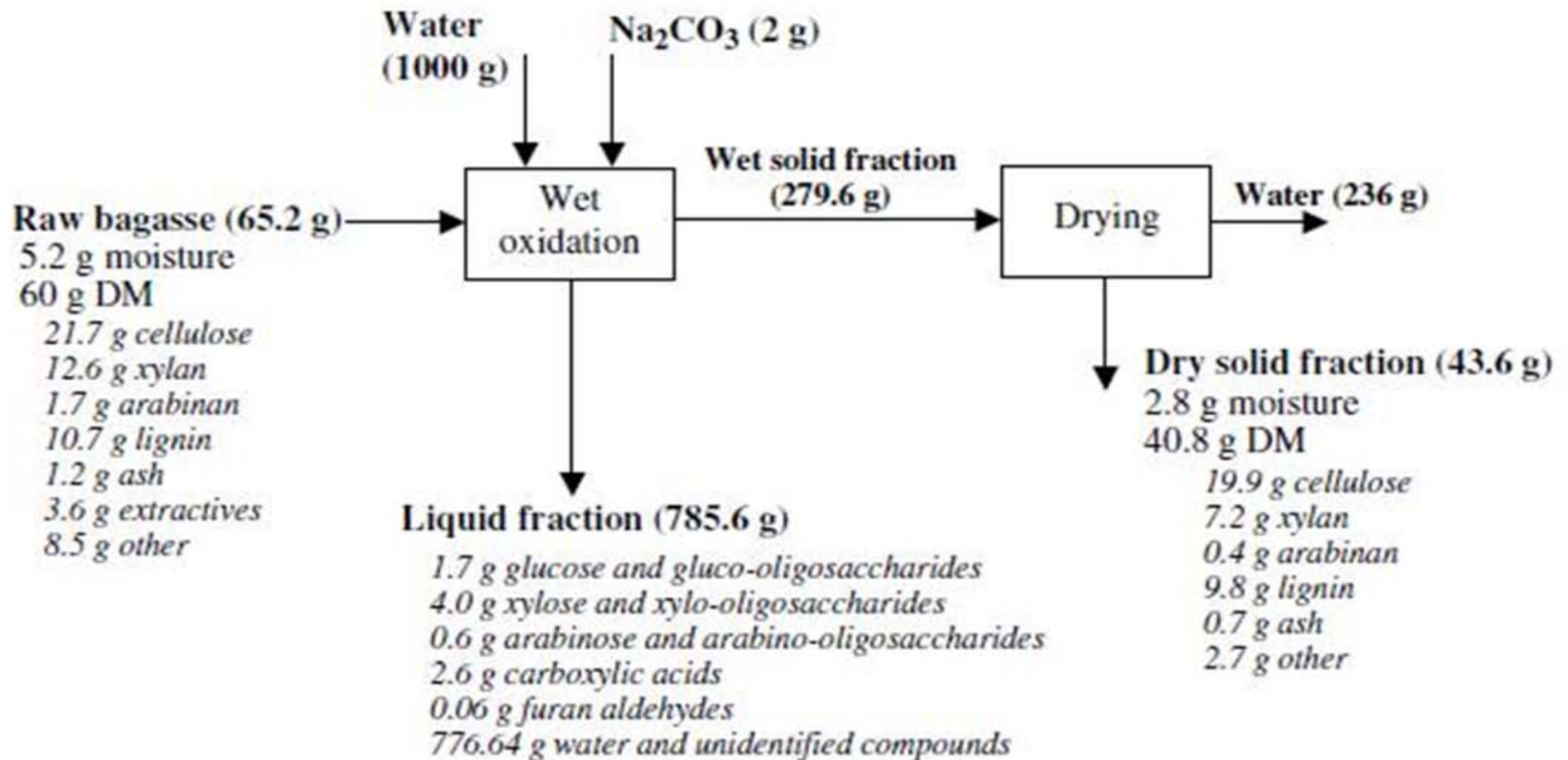
Materials and methods

Figure 1. Mass balance concerning pretreatment of sugarcane bagasse under condition A.

Materials and methods

○ Enzymatic convertibility

Glucose and xylose in the hydrolysate obtained were analysed by HPLC

Calculation of the converted cellulose and xylan(g/kg)

$$Converted\ cellulose = \frac{Glu\cos e_{hydrolysate}}{SDM} \times 1000 \times 0.9$$

The enzymatic convertibility of cellulose(g/kg) was calculated

$$EC_{cellulose} = \frac{Converted\ cellulose}{Cellulose_{SDM}} \times 1000$$
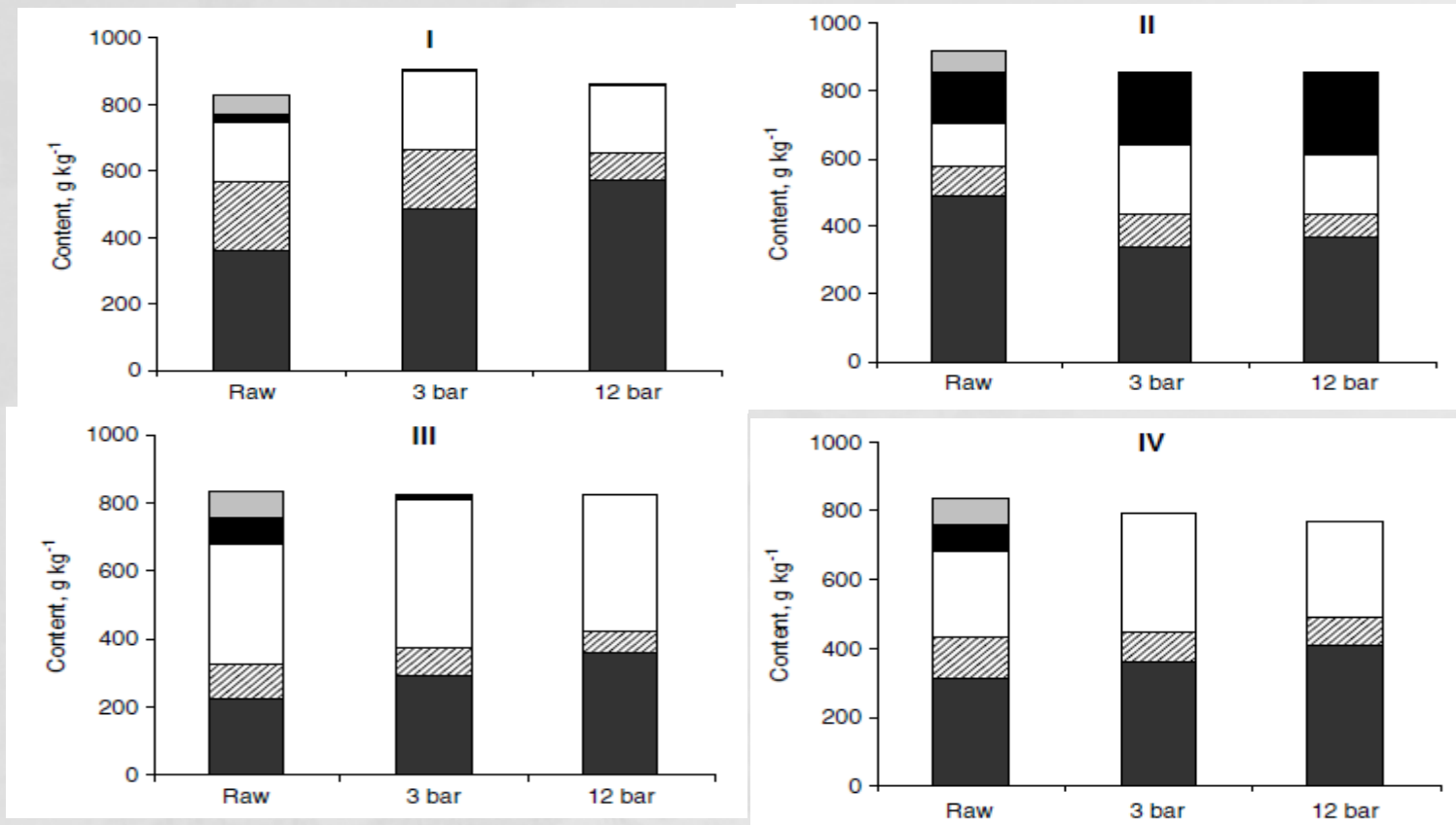
Results and discussion

Figure 2. Chemical composition of the raw and pretreated materials. I, sugarcane bagasse; II, rice hulls; III, peanut shells;IV, cassava stalks.

Results and discussion

Table 1. Recovery of the main components in the solid fraction after wet oxidation of the materials, g kg^{-1}. Standard deviation of two replicates is shown in parentheses. A, pretreatment conditions: 195 °C, 10 min, 2 g Na$_2$CO$_3$, 3 bar O$_2$; B, pretreatment conditions: 195 °C, 10 min, 2 g Na$_2$CO$_3$, 12 bar O$_2$

	Bagasse		Rice hulls		Peanut shells		Cassava stalks	
	A	B	A	B	A	B	A	B
Dry matter yield[1]	681 (6.4)	530 (9.2)	364 (17.5)	359 (19.1)	711 (9.9)	585 (14.8)	661 (9.2)	563 (14.1)
Glucan[2]	917 (2.7)	843 (3.9)	256 (8.5)	268 (9.9)	941 (5.6)	945 (8.7)	765 (7.8)	739 (9.2)
Xylan[2]	582 (5.5)	206 (7.6)	434 (4.5)	301 (6.2)	542 (11.5)	355 (9.8)	472 (8.4)	366 (10.2)
Lignin[2]	904 (7.5)	609 (23.4)	566 (6.8)	481 (10.2)	881 (10.1)	662 (19.5)	927 (5.3)	637 (11.1)

[1] Yield based on dry raw materials.
[2] Recovery expressed as g of the component in the pretreated materials per kg of the component in the raw materials.

• Around 900g of glucan was recovered in pretreated bagasse and peanut shell

• The low glucan recovery observed for rice hulls and cassava stalks

• For all materials, xylan recovery in the solid fraction decreased when the pressure was increased from 3 to 12 bar

• Lignin recovery decreased with increasing oxygen pressure

Results and discussion

Table 2. Characterisation of the liquid fraction. A and B, pretreatment conditions as indicated in Table 1. Mean of two replicates

	Bagasse		Rice hulls		Peanut shells		Cassava stalks	
	A	B	A	B	A	B	A	B
pH before Na_2CO_3 addition	5.4	5.4	6.0	6.0	6.0	6.0	7.4	7.4
Initial (pH before WO)	10.4	10.4	10.4	10.4	10.2	10.2	10.3	10.3
Final pH (after WO)	4.8	3.7	5.1	4.4	5.2	4.2	5.1	4.4
Glucose[1], $g\,kg^{-1}$	29.8	27.0	233.4	213.9	8.1	8.2	36.8	35.7
Xylose[1], $g\,kg^{-1}$	70.2	109.3	35.1	45.0	31.2	45.6	46.4	54.7
Arabinose[1], $g\,kg^{-1}$	11.1	13.4	8.1	7.9	5.6	5.6	3.7	4.1
Acetic acid, $g\,kg^{-1}$	34.0	36.1	11.7	16.2	21.1	27.7	15.5	29.0
Formic acid, $g\,kg^{-1}$	5.5	23.2	10.7	12.3	11.7	14.3	6.1	18.9
Glycolic acid, $g\,kg^{-1}$	4.6	11.2	6.2	7.8	6.7	8.8	5.7	8.8
Succinic acid, $g\,kg^{-1}$	ND	2.2	1.8	2.8	2.3	3.8	2.8	3.8
Total acids, $g\,kg^{-1}$	44.1	72.7	30.4	39.1	41.8	54.6	30.1	60.5
Furfural, $g\,kg^{-1}$	0.7	1.8	0.4	0.9	0.6	1.4	0.4	0.9
HMF, $g\,kg^{-1}$	0.1	0.2	0.2	0.3	0.1	0.2	0.1	0.3

[1] Measured after weak acid hydrolysis of the prehydrolysates.
ND, not detected.

- The high glucose yields achieved for rice hulls

- Formic and glycolic acids were detected

- Furfural and HMF was low, but it slight increased at high oxygen pressure
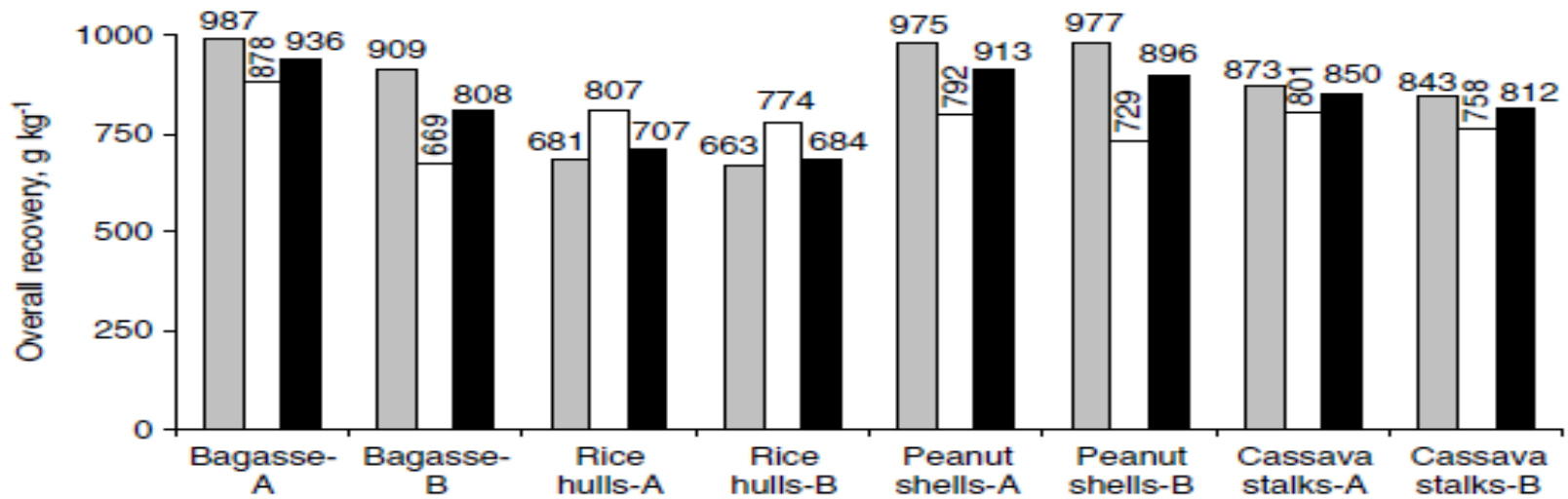
Results and Discussion

Figure 3. Overall recovery of polysaccharides for each pretreatment condition (g kg^{-1}). Gray bars, glucan; white bars, xylan; black bars, Total polysaccharides; A and B, pretreatment conditions as indicated in Table 1.

- The overall recovery is useful for estimating the losses of polysaccharides occurred during WO

- The overall recovery decreased with increasing oxygen pressure

Results and Discussion

Table 3. Enzymatic convertibility (EC) of the pretreated materials. A and B, pretreatment conditions as indicated in Table 1. Calculations were based on mean glucose and xylose concentrations from two replicate determinations

Material	Condition	EC_{Glucan} (g kg^{-1})	EC_{Xylan} (g kg^{-1})
Sugarcane bagasse	No pretreatment	152.4	53.9
	A	465.0	494.4
	B	670.2	444.4
Rice hulls	No pretreatment	73.3	36.1
	A	217.3	152.5
	B	391.5	261.9
Peanut shells	No pretreatment	104.1	84.1
	A	111.5	62.7
	B	171.1	92.3
Cassava stalks	No pretreatment	103.2	40.6
	A	214.5	272.7
	B	432.4	412.5

- Enzymatic convertibility of glucan was higher than that of raw materials

- The enzymatic convertibility achieved for bagasse was 670.2g/kg

- Peanut shells displayed the lowest conversion efficiency

- The conversion of xylan was lower than that of cellulose

Conclusions

◉ Good fractionation yielding high cellulose recovery in the solid fraction was achieved for sugarcane bagasse and peanut shells.

◉ WO efficiently enhances the enzymatic convertibility of bagasse cellulose, but was not efficient in the case of the other materials.