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Influence of Pressure in Ethanol/Water Pulping of Sugarcane Bagasse

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Abstract

The influence of the pressure in the ethanol/water pulping of sugarcane bagasse was studied using argon pressure varying from 0.5 to 1.5 MPa. The reaction volume and activation volume were studied. For the reaction volume, temperature and time were constant and pressure was varied, and for the activation volume, temperature was constant and pressure and time were varied. The degradation of cellulose was not promoted by the pressure with positive reaction volume (4100 cm^3/mol). On the other hand, degradation of xylan (polyoses) and lignin was strongly favored by the pressure and reaction volume ranged from –1000 to –3000 cm^3/mol.

Index Entries: Ethanol/water pulping; sugarcane bagasse; pressure; reaction volume; activation volume.

Introduction

Organosolv is a pulping process that uses organic solvents, and it has been proposed as an alternative for chemical pulp production *(1)*. An ethanol/water mixture is one of the most promising organosolv delignification process options because it combines high delignification rates with favorable conditions for organic solvent recovery, low cost, and abundance of ethanol in countries where sugarcane is economically important *(2)*.

We studied the influence of pressure of an inert gas (argon) in the pulping of sugarcane bagasse. The effect of pressure can be evaluated by the reaction volume (ΔV) and activation volume ($\Delta V^{\ddagger}$).

In any reaction

$$\text{reactants (R)} \rightarrow \text{transition state } (\ddagger) \rightarrow \text{products (P)}$$

Reaction volume, ΔV, is given by $\Delta V = V_P - V_R$ and activation volume, $\Delta V^{\ddagger}$, is defined by $\Delta V^{\ddagger} = V^{\ddagger} - V_R$.

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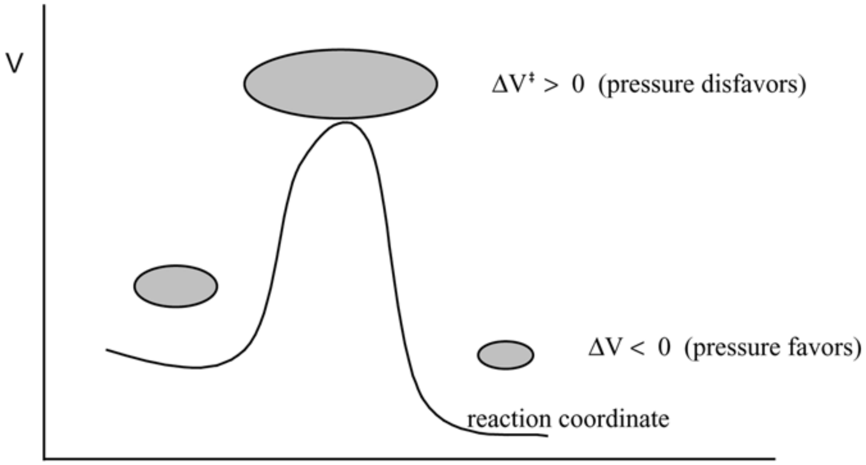

Fig. 1. Example of reaction volume and activation volume.

Figure 1 illustrates a hypothetical reaction process in which the volume of the transition state (shown by the upper shaded ellipse) is higher than that of the reactants ($V^{\ddagger} > 0$) and the volume of the reactants is higher than that of the products ($V < 0$) *(3)*.

The parameters V and $V^{\ddagger}$ are useful in the determination of the better conditions of reactions performed in a closed system, such as the production of cellulosic pulps.

The volume changes just defined can be determined by making use of the fundamental thermodynamic equation $\delta G/\delta p = V$, in which G is the Gibbs' free energy and p is the pressure. Since $G = -RT \ln K$, by combining these two equations the following relationship is obtained *(4,5)*:

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V}{RT} \tag{1}$$

Analogously using $G^{\ddagger}$ Eq. 2 is obtained:

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} \tag{2}$$

in whick K is the equilibrium constant; k is the rate constant; V is the reaction volume; $V^{\ddagger}$ is the activation volume; p is the pressure (Mpa); T is the temperature (K); and R is the gas constant (8.314 J/[mol·K]).

Equations 1 and 2 show that pressure influences the thermodynamics and kinetics of the reaction, and the variation in equilibrium and rate constants as a function of the pressure are proportional to the reaction *(4,5)* and activation volumes *(4)*, respectively. The reaction volume, V, is related to the product formation from the reagents (thermodynamics), while the activation volume, $V^{\ddagger}$, is related to the formation of transition state from the reactants (kinetics).

Pressure favors product formation when the product volume is smaller than that of the reactant (there is an increase in the product density in comparison with reactant density). On the other hand, pressure disfavors product formation when the product volume is higher than that of the reactant (there is a decrease in the product density) *(4,5)*

A recent example of this approach to lignocellulosics is the determination of $V = -817\ \text{cm}^3/\text{mol}$ for the oxidation of organosolv lignins in acetic acid *(6)*. This value confirms the high influence of the pressure in the oxidation of lignin. In another study, delignification of sugarcane bagasse with acetone had a $V = -1533\ \text{cm}^3/\text{mol}$ *(7)*.

Materials and Methods

Pulping

Ethanol/water organosolv pulping of sugarcane bagasse was performed in a 200-mL closed vessel, using a 1:1 ethanol/water mixture (v/v), a 1:10 bagasse to solvent ratio (m/v), and cooking time varying from 1 to 3 h. Before heating, the vessel was closed and pressurized with argon (inert gas) at pressures varying from 0.5 to 1.5 MPa. For the reaction volume study, temperature and time were constant and pressure was varied; for the activation volume study, temperature was constant and pressure and time were varied.

Once the reaction time was complete, the vessel was opened, and the product was removed, filtered, and washed with 2500 mL of a 1:1 ethanol/water mixture (v/v). The obtained pulp was air-dried for yield determination. The total yield was defined as the percentage relationship between pulp weight (Wp) and the initial bagasse weight (Wb): $\text{Yield}(\%) = (Wp/Wb) \times 100\%$.

Pulp samples were analyzed for kappa number (measure of the residual lignin content in pulps) and viscosity by standard methods *(8,9)*. The pulp composition was determined by acid hydrolysis as described next *(10)*.

Hydrolysis of Pulp

One gram of dry pulp was treated with 10 mL of 72% H_2SO_4 with stirring at 45°C for 7 min for the hydrolysis and solubilization of carbohydrates. The reaction was interrupted by adding 50 mL of distilled water, and the mixture was then transferred to a 500-mL Erlenmeyer flask and the volume completed to 275 mL with distilled water. The flask was autoclaved for 30 min at 1.05 bar for the complete hydrolysis of carbohydrate oligomers. The mixture was filtered and the hydrolysate completed to 500 mL with distilled water. A 40-mL sample of the hydrolysate was diluted to 50 mL, and the pH was adjusted to 2.0 with 2 mol/L of NaOH. After filtration in a Sep-Pak C_{18} cartridge to remove aromatic compounds (coming from lignin derivatives), the hydrolysate was analyzed in an Aminex HPX-87H column (300 × 7.8 mm) (Bio-Rad, Hercules, CA) at 45°C by using a Shimadzu chromatograph and refraction index detector.

The mobile phase was 0.005 mol/L of H_2SO_4 at 0.6 mL/min. Sugar concentrations reported as xylan and glucan with respect to the amount of pulp were determined using calibration curves of pure compounds *(10)*. The dark solid obtained in the filtration after hydrolysis was oven-dried and weighed. The obtained mass corresponded to the residual lignin in the pulp and was reported as a percentage with respect to the pulp weight on a dry basis. Mass balance is defined as the sum of the percentage of xylan, glucan, and lignin present in the pulp, with respect to the pulp weight on a dry basis. These values were also normalized to 100% and expressed in centesimal form for calculations using Eqs. 3–5.

Results and Discussion

Reaction Volume and Activation Volume

Results for ethanol/water pulping of sugarcane bagasse as a function of different argon pressures and reaction times are presented in Table 1. A decrease was observed in the yield when the reaction time increased from 1 to 3 h and the pressure increased from 0.5 to 1.5 MPa. This was also observed in the results of the viscosity, decreasing 20% when the reaction time increased from 1 to 3 h and decreasing about 30% when the pressure increased. Values of kappa number in 1 h decreased with an increase in the pressure; for the 2-h reaction-time data, kappa number increased with an increase in pressure, and at 3 h (excluding kappa number at 1.0 MPa), kappa number also increased with an increase in pressure. Residual lignin (RsL) follows kappa number, with an average relationship of RsL = 0.2 × kappa. Viscosity to kappa ratio is a measure of the compromise between carbohydrate preservation (high viscosity) and delignification (low kappa number). Increasing pressure favored delignification but carbohydrates were degraded to some extent.

The chemical composition of the organosolv pulps expressed as glucan, xylan, and residual lignin is also given in Table 1. Xylan degradation occurred with an increase in the pressure and reaction time. This degradation was also assessed by the xylan/glucan content ratio.

The values of glucan, xylan, residual lignin, and total yield were used for the determination of constants used in calculating the reaction volume and activation volume.

Calculation of Reaction Volume

Initially, the following equilibrium situation was considered for each individual component:

$$\text{component in the pulp} \leftrightarrows \text{component in solution}$$

The total volume of the system was constant (closed vessel) and mass values were used to determine equilibrium constants:

$$(K = \text{concentration}_{\text{component in solution}}/\text{concentration}_{\text{component in pulp}}).$$

Calculations of the reaction volume were made using concentrations of glucan, xylan, residual lignin, as well as pulp yield.

Table 1
Ethanol/Water Pulping of Sugarcane Bagasse
as Function of Argon Pressure and Reaction Time and Composition of Pulps
(% in Dry Basis with Respect to Pulp Weight)[a]

Time (h)	Pressure (MPa)	Total yield (%)[b]	Kappa number	Viscosity (cP)	Viscosity/ kappa ratio	Residual lignin (%)	Glucan (%)	Xylan (%)	Xylan/ glucan ratio	Mass Balance (%)
1	0.5	51.5	52.7	9.3	0.18	12.0	71.2	9.0	0.13	92.1
2	0.5	49.0	38.7	7.5	0.19	9.3	75.1	7.3	0.10	91.7
3	0.5	48.5	43.0	7.6	0.18	8.5	46.3	4.7	0.10	59.5
1	1.0	48.2	50.4	5.4	0.11	9.8	64.7	4.4	0.07	78.9
2	1.0	44.7	45.7	5.3	0.12	10.0	64.1	4.1	0.06	78.2
3	1.0	43.4	37.4	4.7	0.12	8.8	78.1	4.3	0.06	91.1
1	1.5	47.0	43.5	6.5	0.15	9.0	76.1	6.0	0.08	90.9
2	1.5	46.0	48.9	5.4	0.11	10.3	77.0	4.9	0.06	92.2
3	1.5	44.0	50.1	4.8	0.10	9.4	78.1	4.3	0.06	91.8

[a] Composition of original sugarcane bagasse: 43.7% glucan, 24.4% xylan, 28.0% lignin.

[b] Total yield = (pulp weight/bagasse weight) × 100%.

Table 2
Equilibrium Constants (K) for Glucan, Xylan, Residual Lignin, and Total Yield (Yt total) and Corrected Values

		Equilibrium constants				Corrected equilibrium constants		
Time (h)	Pressure (MPa)	K (glucan)	K (xylan)	K (residual lignin)	K (Yt total)	K (glucan)	K (xylan)	K (residual lignin)
1	0.5	0.2912	4.0957	3.6983	0.9418	0.1892	3.6932	3.3272
1	1.0	0.5182	10.137	5.1470	1.0747	0.1979	7.7868	3.8499
1	1.5	0.3237	7.3754	5.8642	1.1277	0.2033	6.6132	5.2396
2	0.5	0.2866	5.6029	5.3717	1.0408	0.1798	5.0549	4.8428
2	1.0	0.6524	11.887	5.4957	1.2371	0.2922	9.0779	4.0796
2	1.5	0.3367	9.4785	5.1283	1.1739	0.2324	8.6612	4.6503
3	0.5	1.1084	9.3613	6.0432	1.0619	0.2545	5.165	3.1907
3	1.0	0.3968	11.656	6.6026	1.3042	0.2725	10.53	5.9259
3	1.5	0.3778	11.483	3.0202	1.2727	0.2648	10.46	5.4446

Table 3
Slopes of Straight Line $\ln K = (-\ V/RT) \times p$ and Linear Correlations (r^2) and Corrected Values at Different Reaction Times[a]

	Linear correlations					Corrected linear correlations			
	Glucan	Xylan	Residual lignin	Glucan + xylan	Yt total	Glucan	Xylan	Residual lignin	Glucan + xylan
1 h, slope	0.1059	0.5888	**0.461**	0.1556	**0.1802**	**0.0717**	0.5826	**0.4541**	**0.1427**
1 h, r^2	0.0298	0.4092	**0.9409**	0.1138	**0.9325**	**0.9798**	0.5519	**0.9592**	**0.6778**
2 h, slope	0.1611	0.5257	-0.046	0.1539	0.1203	0.2567	**0.5385**	–0.041	0.1860
2 h, r^2	0.341	0.464	0.4324	0.0705	0.4613	0.2793	**0.685**	0.0512	0.3921
3 h, slope	**–1.076**	**0.2043**	–0.004	**–0.6690**	**0.1811**	0.0396	**0.7056**	**0.5344**	**0.1195**
3 h, r^2	**0.7842**	**0.6955**	0.0013	**0.7812**	**0.6506**	0.3334	**0.7429**	**0.6336**	**0.6654**

[a] Bold numbers (significant correlations) were used to calculate the results of the reaction volume and corrected reaction volume.

Table 4
Calculated and Corrected Reaction Volumes

	Reaction volume (cm^3/mol)				Corrected reaction volume (cm^3/mol)		
Time (h)	Glucan	Xylan	Residual lignin	*Yt* total	Glucan	Xylan	Residual lignin
1	—	—	–1757	–687	–273	—	–1730
2					—	–2052	—
3	4102	–779	—	–690	—	–2689	–2036

Equation 3 was used to calculate the equilibrium constants for individual components, and Eq. 4 was used to calculate total equilibrium constant:

$$K_i = \frac{r_i - (p_i \times Yt)}{(p_i \times Yt)} \tag{3}$$

$$K = \frac{1 - Yt}{Yt} \tag{4}$$

in which K_i = equilibrium constant of component *i*; r_i is the content of component *i* in the original sugarcane bagasse (%), p_i is the content of component *i* in the pulp (%), *Yt* is the pulp total yield (centesimal form), and *K* is the total equilibrium constant.

In Table 1, the mass balance after chemical analysis was <100%, owing mainly to the incomplete hydrolysis of the carbohydrates and material losses in the gravimetric quantifications. The values obtained by Eq. 3 were corrected by the mass balance ($p_i \times Yt$ divided by balance in the centesimal form).

Table 2 presents the values of the equilibrium constants and corrected equilibrium constants (*K*) of glucan, xylan, residual lignin, and pulp yield. At constant reaction times, the pressure was varied from 0.5 to 1.5 MPa, and nine equilibrium constants were obtained and used for the calculation of the reaction volume, according to Eq. 1.

Table 3 shows the best results of the slope and linear correlation obtained, both before and after correction by the normalized mass balance. The results of the reaction volume and corrected reaction volume were calculated using the results in Table 3 shown in bold (significant correlations).

The reaction volume for the total yield seems to be constant with an increase in reaction time. On the other hand, with negative reaction volume (Table 4) the degradation of the glucan was not favored by an increase of the pressure (Table 4; 3 h).

The degradation of xylans (polyoses) and lignin was favored strongly by the pressure and the reaction volume ranged from –1000 to –3000 cm^3/mol, with the same magnitude of values obtained for the delignification

Table 5
Rate Constants (k) at Different Reaction Pressures for Glucan, Xylan, Residual Lignin, and Total Yield (Yt total) and Corrected Values

	Rate constants				Corrected rate constants		
	k (glucan)	k (xylan)	k (residual lignin)	k (Yt total)	k (glucan)	k (xylan)	k (residual lignin)
0.5 MPa, slope	**0.2452**	**0.3548**	**0.2024**	**0.0300**	0.0267	**0.1364**	–0.0160
0.5 MPa, r^2	**0.7445**	**0.9763**	**0.9217**	**0.8738**	0.6410	**0.7993**	0.0076
1.0 MPa, slope	0.0417	0.0639	**0.1063**	**0.0524**	0.0302	**0.1358**	**0.1782**
1.0 MPa, r^2	0.2459	0.6456	**0.9285**	**0.9401**	0.5689	**1.0000**	**0.8455**
1.5 MPa, slope	**0.0200**	**0.1996**	0.0110	**0.0330**	**0.0249**	**0.2045**	0.0160
1.5 MPa, r^2	**0.9194**	**0.9950**	0.0238	**0.9612**	**0.9995**	**0.9910**	0.0556

[a] Bold numbers (significant correlations) were used to calculate the results of the reaction volume and corrected reaction volume.

Table 6
Calculated Activation Volume

Activation volume	Glucan	Xylan	Residual lignin	Yt total
$V^{\ddagger}$	9549	2193	4912	–360

of sugarcane bagasse with acetone (–1533 cm^3/mol) *(7)*. This fact explains the decrease in kappa number and viscosity shown in Table 1.

Calculation of Activation Volume

For the calculation of activation volume, the same conditions used in the calculation of reaction volume were initially considered. A first-order kinetics was assumed and the rate constant was determined by Eq. 5.

$$\mathrm{Ln}\,(p_i \times Yt) = -k_i \times t \tag{5}$$

in which k_i is the rate constant for component i, p_i is the content of the component i in the pulp (%), Yt is the pulp total yield (centesimal form), and t is the time (h).

As already mentioned, the obtained values after the application of Eq. 5 were corrected by the mass balance ($p_i \times Yt$ divided by the balance in the centesimal form). The values of k obtained with the linear correlations are given in Table 5 (original and corrected).

The values of activation volume were calculated using Eq. 2 and the results of Table 5 (shown in bold, significant correlations).

The value of the activation volume was higher for glucan than for xylan and lignin (Table 6), showing that degradation of the glucan was disfavored by pressure. The use of pressure favored first the degradation of the xylan followed by the lignin; glucan was degraded last.

The final yield was low owing to the delignification and degradation of the xylans that causes the decrease in viscosity.

The easy degradation of the xylans can be explained by their ramified and amorphous structure. The cellulose has a linear structure with crystalline and amorphous parts, being more difficult to intumesce (to increase the volume) during the reaction. In an aqueous reaction, xylans tend to swell more easily than the glucan and xylans tends to degrade, also promoting dissolution of the lignin.

Conclusion

Reaction and activation volume can be calculated for complex systems such as lignocellulose conversion by using appropriate equations, analyses, and considerations. For the ethanol/water pulping of sugarcane bagasse, pressure disfavored the degradation of cellulose and favored lignin dissolution. These facts are positive for the system, with kappa reduction. On the other hand, xylans were easily degraded by the pressure, decreasing the viscosity of the obtained pulps. The use of pressure for the conversion in terms of yield was disfavored, and favored with respect to delignification.

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