

# Steam Explosion of Straw in Batch and Continuous Systems

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## Abstract

The effects of the steam-explosion treatment on aqueous fractionation and bioconversion of wheat straw have been investigated. The treatments have been carried out in batch and continuous reactors with capacity of 0.5 Kg/cycle and 150 Kg/h, respectively. The exploded materials have been sequentially extracted with water at 65°C and sodium hydroxide 1.5%. Analytical determinations of liquid fractions and solid residues have led to the fractionation pattern of the carbohydrates as monomers, oligomers, and polymers. Evaluations of total acidity, ash content, and lignin recovery have improved understanding of the process. This part of the work has allowed us to derive: the empiric relationship between the batch and the continuous reactors and the yield and availability of pentoses and hexoses in various phases. Selected samples have been tested in enzymatic-hydrolysis experiments, pointing out the effect of treatment severity and reactor used on the saccharification yield.

**Index Entries:** Enzymatic hydrolysis; steam explosion; straw.

## Introduction

A key step in biomass processing is the feedstock pretreatment that makes it suitable for fractionation and bioreaction. Generally, polysaccharides and lignin are modified and degraded in every pretreatment. The extent of chemical and structural modifications depend strongly on the "treatment severity," i.e., the time and the temperature at which materials are processed. Acids and bases also play an important role as catalyst in the

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hydrolytic cleavage of ether and glucosidic bonds. Acid substances are produced by degradation of the substrate itself, leading to autocatalytic-like reaction pattern (1). The kinetics of hydrothermic degradation of lignocellulosics is a subject widely studied but not yet completely understood because of the complex network of pyrolysis and hydrolysis reactions, the subsequent reactions between substrate and products, and heat and mass transport inside the matrix (2). A first level of approach is to study separately the fate of the three main biomass components—cellulose, hemicellulose, and lignin—under the process conditions. General results have been achieved for cellulose and hemicellulose, but some difficulties in modeling the changes in the case of real matrices have been reported (3).

A significant effort has been made to model the kinetics of hemicellulose solubilization from steam-treated biomass according to the thermodynamic analysis by Abatzoglou et al. (4). The severity parameter,  $R_0$ , was reported to be a good reaction indicator for the whole disruptive process and it is currently used for comparative purposes. In the biochemical processes, such as enzymatic hydrolysis and fermentation, the accessibility of polysaccharides and monomers by proteins and micro-organisms is also important. The morphology of the materials should be assessed on the basis of surface area and porosity in addition to the chemical characterization (5,6).

The steam-explosion (SE) treatment was recognized to be effective in the disruption of raw materials and in the recovery of pentoses, hexoses, and lignin after aqueous extractions and hydrolysis (7,8). The rate and the yield of enzymatic hydrolysis and fermentation to ethanol of lignocellulosics are greatly enhanced after the treatment (9). These findings have encouraged further research using widely different raw materials, particularly low-cost biomass like straw and organic waste because the raw-material cost hampers the economic viability of the production of ethanol from lignocellulosics to the extent of about 40% (10,11). The experiments tested different conditions of treatment time and temperature as well as addition of chemicals (12).

The simplest way to carry out SE is the batch procedure, but continuous reactors are also commercialized. In addition, in this latter system, the mechanical compression is a source of stress in addition to hydrothermic and explosion effects. Although the products obtained at the same treatment severity in batch and continuous reactors are macroscopically different at first sight, there is still a lack of understanding to explain these differences. Most of the data available in the literature have been obtained with small-size batch reactors, whereas the continuous ones are of major interest for industrial applications. Developing theoretical and phenomenological relationships between the two systems useful in making the data transfer straightforward. To achieve this goal, two approaches have been investigated. First, the chemical modifications occurred in materials SE in batch reactor have been determined and fitted to the corresponding data from the continuous reactor.

Table 1  
Percentage Composition of Straw<sup>a</sup>

Extractives	Ash	Lignin	Arabinose	Xylose	Galactose	Glucose	ND
6.7	7.6	21.6	2.6	23.1	0.6	34.3	3.5

<sup>a</sup>The data are referred to the solid dried at 105°C and to the polysaccharide forms.

The second approach consisted of a comparison between the results of enzymatic hydrolysis carried out on lignocellulosics material SE in batch and continuous reactor at the same treatment conditions. Because this reaction depends strongly on substrate composition and morphology, the results have been interpreted accordingly.

## Experimental

### *Materials and Sample Analysis*

The substrate used in this study has been freshly harvested Italian wheat straw. The chemical analysis of is reported in Table 1. The ash content in raw and exploded materials was determined by sample combustion at 600°C. The exploded materials were extracted by rinsing two times for 10 min, with water at 65°C, at solid-liquid ratio equal to 10% w/w. The extracted fraction was analyzed directly by high-performance liquid chromatography (HPLC) to determine the carbohydrate-monomers. The oligomer content was determined by the difference of total sugar after hydrolysis with 4% H<sub>2</sub>SO<sub>4</sub> at 120°C for 1 h and the initial monomer content. Sugar degradation was accounted for by introducing experimental coefficients. The solid residue was delignified twice in 1.5% w/v NaOH at 90°C for 15 min at a solid-liquid ratio of 8% w/w. Lignin was recovered from the alkaline phase by precipitation at pH 2 with H<sub>2</sub>SO<sub>4</sub>. Acid-soluble lignin was determined spectrophotometrically by ultraviolet (UV) spectrophotometry at 205 nm, assuming the extinction coefficient of 110 dm<sup>3</sup>/g·cm. The residue was hydrolyzed following the Klason methodology, determining the residual lignin in the fibers and the carbohydrate content.

### *Steam Explosion Treatments*

The SE treatments were carried out in batch (0.5 kg/cycle) and in continuous reactors (150 kg/h). Water content of the materials has been adjusted to 50% before the treatment. Straw was treated at 13 different conditions in the batch reactor at temperatures ranging from 193–230°C and times ranging from 2–10 min. The choice of the experimental conditions was made on a statistical basis to obtain the recoveries as function of time and temperature at mild and extreme conditions.

Straw was processed in the continuous reactor at temperatures ranging from 193–225°C and times ranging from 2–6 min for a total of 23 different conditions. All steam-exploded samples were stored at 5°C.

### Enzymatic Hydrolysis of Steam-Exploded Straw

Four samples of wheat straw-treated in batch and continuous reactors at 193°C for 2 min (logRo 3.04) and 210°C for 4 min (logRo 3.84) were tested for enzymatic hydrolysis. The experiments were carried out at enzyme loading of 1 g/L, in duplicate at 45°C in 250-mL flasks shaken at 150 rpm. The enzyme used was the *Safizym C80L*, from SAF-ISIS (France). The FPase activity resulted 61.7 IU/mL, the protein content 279 g/L. The reaction volume was adjusted to 100 mL with distilled water, leading to a biomass concentration of 25 g/L.

At 24, 48, and 72 h, 2 mL samples were collected from supernatant liquor. The samples were introduced in glass tubes and heated at 80°C for 5 min to ensure the enzymatic deactivation. The glucose content was determined by a HPLC apparatus, equipped with a CARBOPAC PA1 column (DIONEX, Sunnyvale, CA), using water as mobile phase, at 1 mL/min of flow rate and a temperature of 27°C.

## Results and Discussion

### Steam-Explosion Effects on Wheat Straw

In the SE process, low-weight molecules such as acetic acid and furfural are produced at a high rate. These substances volatilize at the flash stage and should be condensed efficiently. In addition, CO<sub>2</sub> and H<sub>2</sub>O are also present as degradation products, and consequently it is difficult to recover all of these products (13). In this work, the mass loss was evaluated from ash-content measurements. The ash content in straw samples, steam-exploded in batch and continuous reactor, are reported in Fig. 1 as contour plots (generated by MATHCAD 4.0).

At the highest treatment severity, 10 min at 230°C, mass loss as high as 53.0% occurs in the batch reactor. This result indicates a 37.5% loss of organic matter. When treated in the continuous reactor at the highest severity, 6 min at 225°C, the mass loss of straw reaches a value as high as 59.5%. This result corresponds to an organic matter loss of 40.8%. Direct comparison of organic losses shows that experimental data obtained from batch reactor can be referred to those from the continuous one according to the following relationship:

$$T_{batch} = 1.4219 \cdot T_{continuous} - 77.43 \quad (1)$$

where  $T_{continuous}$  is considered as the true temperature of the process and  $T_{batch}$  the temperature that is affected by spurious effects (transient period, steam condensation, segregation). Rearranging the data as function of the severity parameter (4):

$$Ro = t \cdot \exp(T - 100/14.75) \quad (t \text{ in min, } T \text{ in } ^\circ\text{C}) \quad (2)$$

the diagram of Fig. 2 is obtained. The Ro parameter satisfactorily correlates the data rather well with a linear law in the case of the continuous reactor.

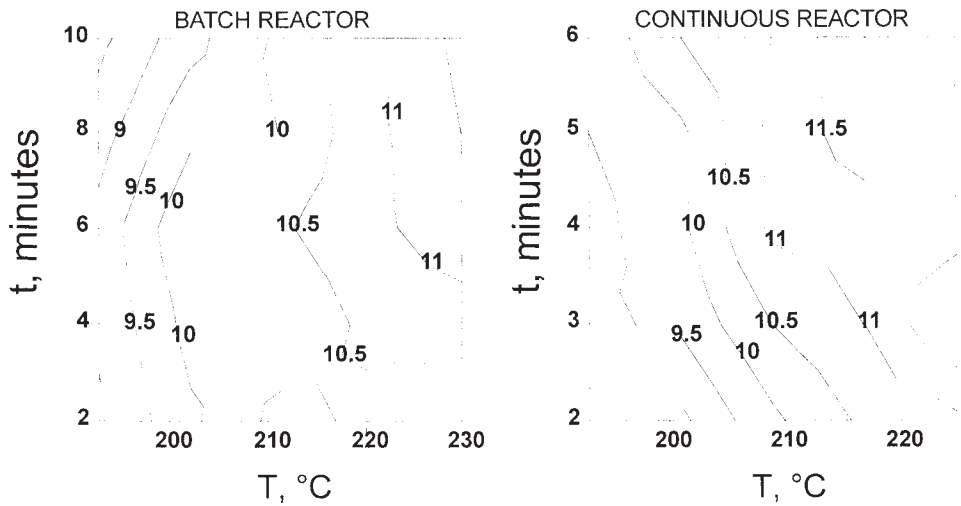


Fig. 1. Percentage of ash in samples of SE straw in batch and continuous reactor. The ash content in straw was 7.6%.

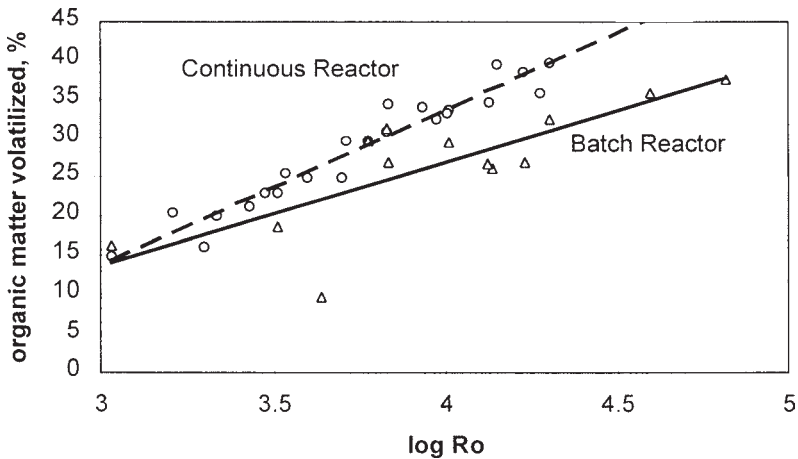


Fig. 2. Loss of organic matter in straw after the SE carried out in batch (△) and continuous reactor (○). The data are referred to the volatile products at  $T > 105^{\circ}\text{C}$ .

A wider scatter is obtained for the data from batch reactor. Significantly, the two systems differ less at low severity than at the highest severities. These differences were attributed to the persistence of transient conditions in the batch system. Because of the batch reactor's lower stability, it would be advisable to collect more samples in order to get significant data. By comparison of the fitting lines it is obtained:

$$\log Ro_{\text{Batch}} = 1.50 \cdot (\log Ro_{\text{Continuous}} - 1) \quad (3)$$

In the investigated range of  $\log Ro$  3–5, the deviation of Eq. (3) from Eq. (1) is between –3% to +6%, indicating their substantial equivalence. Linear

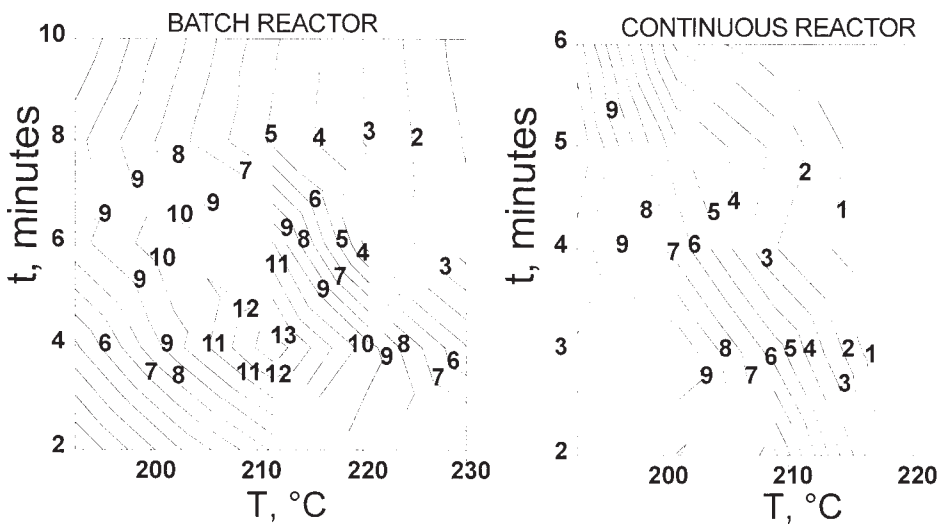


Fig. 3. Total xylose (monomer+oligomers) recovered by aqueous extraction from SE straw in batch and continuous reactor (g/100 g exploded material).

relationships of the type in Eq. (3) have also been obtained by comparing the acid content; xylose, arabinose, and glucose solubilized in the aqueous phase; lignin solubilized in alkali; cellulose content in the residue. The deviations between those expressions and Eq. (3) are comprised in  $-5\%$  and  $+20\%$  range. It is argued that the relationship in Eq. (3) should be more precise and of greater general validity in comparison with the others because it relies on the measurement of a global, primary effect, such as pyrolysis. In addition, such as solubilization, sugar degradation, recovery, acidity content, experimental errors may cumulate in the course of extractions and chemical analyses.

Hemicellulose is the most degradable component under the SE conditions. The percentage of xylose in aqueous extract is vanishing at the highest severities in samples from both batch and continuous reactors (Fig. 3). A maximum value of 13% (calculated on the exploded mass basis) is achieved in samples treated at  $210^{\circ}\text{C}$  for 4 min in the batch reactor. Referred to the processed straw, it correspond to a recovery yield of 44%, a residual 12% is found in the fiber after the alkaline extraction. The xylose in samples from continuous reactor never reaches the levels measured in the samples from batch reactor, in spite of the milder treatment severity.

The lignin recovered in alkaline phase increases rather regularly with severity (Fig. 4). In both systems, and the recovery yields reach values of 90% at the highest treatment conditions. Also, the disruption of the lignocellulosic matrix, greatly enhancing lignin solubility in alkali, is greater in continuous reactor.

The glucose determined content in residues after aqueous and the alkaline extractions is reported in Fig. 5. The materials from continuous batch reactor have higher cellulose content at any treatment condition as a

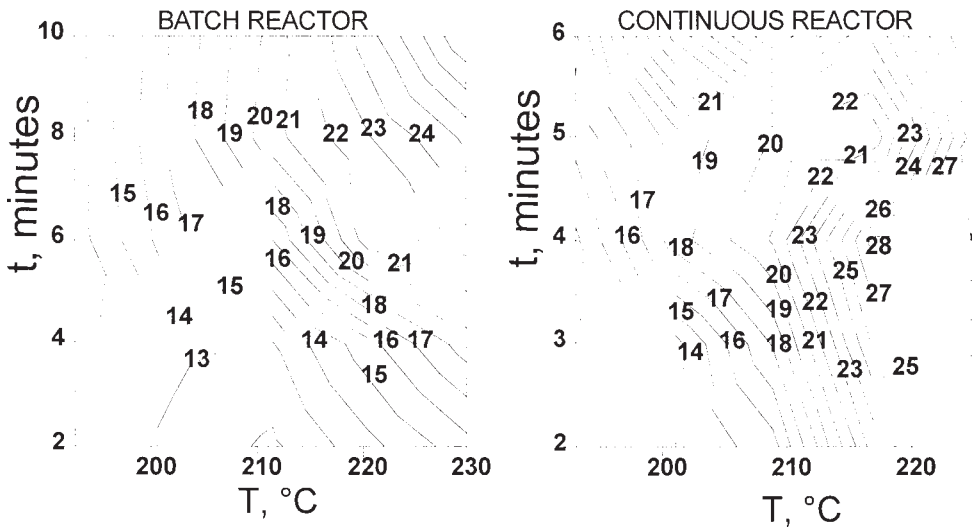


Fig. 4. Lignin recovered by alkali extraction from SE straw in batch and continuous reactor (g/100 g exploded material).

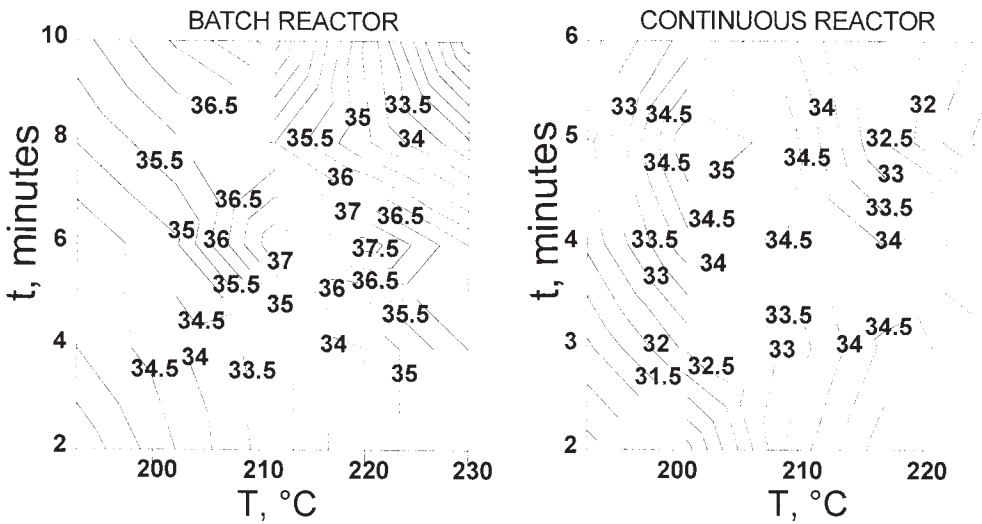


Fig. 5. Glucose content in the straw residue after the alkaline extraction (g/100 g exploded material).

consequence of lower decomposition. The recovery yields of glucose in residue, calculated on the basis of glucose in processed straw, range from 55–84% for the batch reactor and from 55–75% for the continuous one. The glucose recovered as monomer or oligomer by aqueous extraction ranges from 1.8–3.9% for the batch reactor, and from 5.7% (lowest severity) to 0.7% (highest severity) for the continuous one. Therefore, the importance of carrying out SE treatments at optimized conditions is assessed.



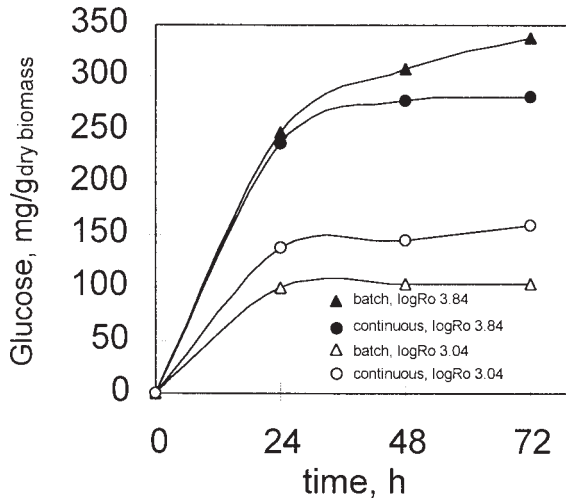


Fig. 6. Saccharification yields of wheat straw steam exploded in batch and continuous reactor.

### Wheat-Straw Hydrolysis

Samples of wheat straw treated at logRo 3.04 and logRo 3.84 were tested for enzymatic hydrolysis to point out if the treatment system used affects the bioconversion processes. The experiments were carried out at 45°C using 1 g/L of “Safizym C80L” and 25 g/L of biomass. Results are shown in Fig. 6; data reported show that saccharification yield in samples from continuous process was higher than in samples obtained from batch process if the treatment severity are low. The opposite result was shown at high-treatment severity. The hypothesis was made that the observed behavior is determined by two competitive effects. In the continuous reactor, the disruption and hydrolysis of cellulose fibers is more effective, but mechanical compression causes reduction of fiber accessibility to the enzyme. Further on, at the operational conditions of SE, the lignin tends to fill up the pores generated during the process. Wheat straw exploded in the continuous reactor is more dense and allows the hydrolysis to be carried out with 200 g/L of substrate.

### Conclusions

The SE treatment of lignocellulosics is more effective and reproducible when carried out in continuous reactor in comparison with the batch procedure. The effects on the materials treated in the two systems and evaluated as pyrolytic loss, solubility, and recoveries in aqueous phases of carbohydrates and lignin are satisfactory correlated by the relationship:  $\log Ro_{Batch} = 1.50 \cdot (\log Ro_{Continuous} - 1)$ .

The lignocellulosic materials steam-exploded at high-severity parameter are efficiently converted into glucose at temperatures of 45–50°C and



enzyme concentration of 1.5 g/L. In addition to the treatment severity, the yield of enzymatic saccharification depends on the type of reactor, whether batch or continuous.

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