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# Short communication

# The shrinking core model applied on anaerobic digestion

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#### a r t i c l e i n f o

## A B S T R A C T

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Keywords: Shrinking core model Mass transport Anaerobic digestion Lignocellulosic fibers Hydrothermal treatment In this study, the gas formation of anaerobic digestion was analyzed by the shrinking core model. This model is based on the mass transport equations. The experiments were carried out with hydrothermal treated wheat straw. Additionally a control group of untreated wheat straw was examined.

With untreated straw the beginning of microbiological growth was limited by convection through the surrounding fluid film. With further incubation time the bacteria formed a biofilm. Diffusion through this layer limited the degradation.

A short hydrothermal treatment decreased the convection-limited phase.

The gas yield of the straw was 0.54 dm<sup>3</sup> (0  $\degree$ C, 1 atm) per gram volatile solid. The pretreated straw yielded in 0.51 dm<sup>3</sup> ( $0^\circ$ C, 1 atm) per gram volatile solids with the same mean content of methane (49 vol%) and carbon dioxide (51 vol%).

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## **1. Introduction**

The shortage of resources is a challenge for the energy production. It will be necessary to use renewable energy sources. The energetic utilization of organic residues is an interesting possibility, because they are left over in high amounts in agriculture. The residues mostly consist of lignocellulosic fibers. These are a composite of carbohydrates (cellulose, hemicelluloses) and lignin, a phenolic macromolecule. The lignocelluloses provide the plant's framework. It also protects the plant against physical and biological influence from the environment. These properties deteriorate the utilization of residues for energy production, [\[1\].](#page--1-0)

Compared to energy crops the methane yield and the degradation kinetic of lignocelluloses are lower. The fibers also impede the pump and stirring properties of the ferment, Chen et al. [\[2\],](#page--1-0) Karla and Panwar [\[3,4\].](#page--1-0) Pretreatments similar to the ethanol production from lignocellulosic matter could solve these problems, [\[5–7\].](#page--1-0)

Batstone et al. [\[8\]](#page--1-0) published the Anaerobic Digestion Model No. 1 (ADM1) and gave a good standard for modeling the biogas process. In case of straw and other crops rich of fiber the rate limiting step is the disintegration and hydrolysis of the carbohydrates. They assumed in a first approximation a first order kinetic for both processes and suggested a more accurate surface related model if necessary. This surface related model was developed by Vavilin et al. [\[9\].](#page--1-0) They assumed shrinking spherical particles for the hydrolysis of cellulose and sewage sludge. They divided the kinetic in two phases. The First one is the colonization of the particle surface by hydrolytic bacteria. In a second phase the bacteria grow on the surface and the particle shrinks.

In the case of lignocellulosic fibers the shape of the particles is not spherical but rather cylindrical, as suggested by [\[10\].](#page--1-0) He also mentioned that the macroscopic shape of the particles was not as important for the hydrolysis kinetics, because in the scale of the organisms the particle's shape appears nearly planar. However, the microstructure of the plant material consists mostly of lignin, celluloses and hemicelluloses and these are organized in a structure of cylindrical bundles.

Furthermore the particles do not shrink because the framework of the lignin is not biodegradable. Therefore, in this paper the shrinking core model was used to describe the hydrolysis of lignocellulosic framework.

## **2. Materials and methods**

#### 2.1. Materials

Wheat straw was used to study the biological degradation of lignocellulosic fibers. To get fibers with nearly same size, the straw was comminuted in a knife mill and it was sieved through 1 mm and 0.25 mm mesh. For investigations the sieve residual of the 0.25 mm mesh was used. The water content of the straw amounted to 8.7 wt%. It was dried at 105 ℃ for 17.5 h. The dry matter was combusted at 600 °C for 8 h and yielded an ash content of 3.0 wt% of the dry matter.



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S substrate, solid

The inoculum arose from an agricultural anaerobic digester (Dummerstorf, Germany), mainly fed with corn silage and cow manure. Water and ash contents were determined. They amounted to 91.9 wt% of water and 20.8 wt% ash referring to the dry matter. After taking from the digester, the inoculum was stored two weeks at 20 ◦C to decrease own gas formation. The light microscopic studies were carried out with a Carl Zeiss Laboval 4 at a magnification of  $\times$ 400.

#### 2.2. Anaerobic digestion

The gas formation was observed according to the 'Hohenheimer Yield Test', [\[11\].](#page--1-0) Therefore 100 ml glass syringes were used as digesters. They are sorted in a carousel for mixing the ferment. The whole apparatus was placed in an incubator (Memmert INE-600) at 38 ◦C. The syringes had a scale of 1 ml steps to measure the produced gas. They were sealed with highly viscous paraffin. The digester was filled with 30 g of inoculum and 1 g of wet wheat straw. Three syringes were just filled with inoculum to subtract its own gas formation from the inoculum.



**Fig. 1.** Wheat straw before (a) and after (b) 40 days of incubation, magnified 400 times with a light microscope. The microstructure of the straw is preserved after the incubation.

The carbon dioxide and methane contents were measured with a Brüel & Kjær gas monitor type 1302. This device was tightly connected to a 500 ml Erlenmeyer flask by the gas inlet and outlet. For determination of the gas, 2 ml of the formatted biogas were injected into the flask and well mixed by the internal pump of the gas monitor. When the maximum capacity of the gas monitor (4000 ppm) was reached, the flask was flushed with silica gel dried air. With this assembly the ratio of carbon dioxide and methane could be determined with a precision of  $\pm 2\%$ . The mass of the produced gas was calculated under assumption of ideal gas behavior.

### 2.3. Hydrothermal treatment

The hydrothermal treatment was done in a 100 ml autoclave (Parr reactor No. 4593, temperature controller 4842). The reactor was equipped with a magnetically coupled blade stirrer, which was running at 1000 rpm. It was filled with 6g straw (wet) and 54g deionized water. The heat up time to reach 200 ℃ amounted to 40 min. By reaching the predefined temperature the reaction was stopped by cooling the reactor in an ice-water bath. The time for cooling to 40 $\degree$ C required less than 5 min. The pressure could be observed by a gauge (0–50 bar).

### 2.4. Characterization

The gas yield of the untreated straw amounted to 0.70 g of gas per gram dry matter or  $0.54 \text{ dm}^3$  (0 °C, 1 atm) per gram volatile solids. The mean chemical composition of the gas was 51 vol%  $CO<sub>2</sub>$ and 49 vol%  $CH<sub>4</sub>$ .

The straw, which was treated at  $200^{\circ}$ C for a short time, has nearly the same biogas yield, 0.67 g of gas per gram dry matter or 0.51 dm<sup>3</sup> (0  $\degree$ C, 1 atm) per gram volatile solids. The mean carbon dioxide content was 49 vol% and the mean methane content amounted to 51 vol%.

The degradation of straw fibers was examined under a light microscope. Fig. 1a and b shows the straw fibers before and after 40 days of incubation. The micro structure of the fibers is unscathed over the time.

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