Steam explosion for biomass pre-treatment

Resultat Kontrakt (RK) Report

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1 INTRODUCTION

Steam explosion of biomass is a pre-treatment process that opens up the fibers, and makes the biomass polymers more accessible for subsequent processes, i.e. fermentation, hydrolysis or densification processes.

Biomass materials such as wood are composite materials with high mechanical strength. The major components are cellulose, embedded in a matrix of lignin and hemicelluloses (Fengel, 1983). Together they form tightly packed cellular structures (fibers) that form fiber bundles, and are the base for biomass tissues such as wood. Their natural function is to bear high mechanical loads, and to resist chemical and enzymatic degradation through microorganisms. This common feature of plant fibers is often termed as biomass recalcitrance, and is a major technical obstacle for most bio-refinery processes.

Steam explosion has been shown to be a valuable and important technology to open up the biomass fibers, to improve the recovery of sugars and other useful compounds from biomass. It is also discussed as pre-treatment process for the production of solid biofuel pellets to increase the calorific value, and to improve the pelletizing properties of the biomass. Numerous studies have been made investigating the effect of steam explosion on biomass composition and its effect on bio-refinery processes and densification (see reference list).

The present report reviews steam explosion processes in general, and summarizes the most important technologies, process parameters and product properties.

2 STEAM EXPLOSION

Steam explosion was introduced and patented as a biomass pre-treatment process in 1926 by Mason et al. (1926). The patent describes a steam explosion process for the pre-treatment of wood. In this process, wood chips are fed from a bin through a screw loading valve in a masonite gun. The chips are then steam heated at a temperature of about 285°C and a pressure of 3.5 MPa for about 2 min. The pressure is increased rapidly to about 7 MPa (70 bar) for about 5 s, and the chips are then discharged through restricted orifices (slotted port) and explode at atmospheric pressure into a pulp.

In general steam explosion is a process in which biomass is treated with hot steam (180 to 240 °C) under pressure (1 to 3.5 MPa) followed by an explosive decompression of the biomass that results in a rupture of the biomass fibers rigid structure. The sudden pressure release defibrillates the cellulose bundles, and this result in a better accessibility of the cellulose for enzymatic hydrolysis and fermentation. Depending on residence time and temperature, steam explosion can result in anything from small cracks in the wood structure, to total defibrillation of the wood fibers (Tanahashi, 1990). Acetic acid is released from the wood, and this result in partial hydrolysis of the cell wall components (Glasser and Wright, 1998). It has been shown that the use of diluted acids (i.e. sulfuric or nitric acid) can accelerate the process i.e. result in higher hydrolysis rates of the hemicelluloses (Boussaid et al., 2000; Shevchenlo et al., 2001; Bura et al., 2002).

General advantages of steam explosion processes compared to other pre-treatment technologies for chemical utilization of lignocellulose are according to Garrote et al. (1999):

- No chemical are used except water
- Good yield of hemicelluloses with low degraded byproducts
- Equipment corrosion is minimum due to a mild pH of reaction media when compared to acid hydrolysis processes
- Stages of acid handling and acid recycling are avoided
- Disruption of the solid residues from bundles to individual fibers occur due to explosion effect

Steam explosion of biomass can be used as an environmental friendly pulping process (Kokta and Ahmed, 1998), as pre-treatment for microbial bioethanol or biogas production (Cara et al., 2006; Dererie et al., 2011). It is also used for the pre-treatment of wood prior pelletization to increase heating value, bonding properties and hydrophobicity of the wood (Adapa et al. 2010; Adapa et al. 2010a, Lam et al. 2011).

Steam explosion treatment has been suggested to be used as pre-treatment process in the wood pellets industry as a method to get dimensionally stable and durable pellets (Obernberger and Thek, 2010). During steam explosion, lignin is softened, released from the cell wall and distributed evenly onto the raw material. The steam exploded material gets usually directly into the pellet mill where it is again exerted to high pressure and temperature. Pellets from steam explosion processes are dark brown in color, and stiffer than conventional wood pellets. They are less abrasive and more stable towards moisture as common wood pellets. The bulk density of steam exploded pellets is relatively high in comparison to conventional wood pellets and different values where found in literature ranging between 630 to 750 kg/m$^3$.

The release of lignin during steam explosion and it’s softening and flow during the pre-treatment and pelletizing process, result in a deposition of lignin onto the wood particles surface, and this is expected to be the reason for a higher stiffness and water resistance (Oberberger and Thek, 2010).

A recent study by Lam et al. (2011) suggests that steam explosion of wood results in a material with favorable fuel properties (high heating value, low moisture absorption) and good pelletizing properties. Their manufactured pellets do not show any defects (Fig. 1) and pellet density increased, compared to untreated wood. Similar results have been obtained by Biswas et al. (2011) who studied the pelletizing properties of steam exploded salix. It was found that steam explosion treatment reduced the amount of alkali metals in the biomass, and the pressed pellets showed an increased density, impact and abrasion resistance. Nevertheless, small decreases in ash fusion characteristics and char reactivity was reported for elevated temperatures and residence times.

![Fig. 1. Physical appearance of wood pellets treated at different steam explosion conditions. From left to right: untreated, 200°C for 5 min, 200°C for 10 min, 220°C for 5 min, and 220°C for 10 min (Lam et al. 2011).](image-url)
2.1 Mode of operation

Steam explosion processes can be run in continuous or batch mode. A batch reactor is usually used for lab scale pre-treatment while continuous systems are commonly used for large scale, industrial processes.

2.1.1 Batch systems

Batch systems are usually used in experimental laboratory scale set-ups. Lab scale batch reactors are usually designed as shown in Figure 2. The biomass is put into a small vessel, pressurized, and heated with steam which is quickly released afterwards.

![Figure 2. Lab-scale steam explosion reactor. The lid has an inlet for steam and a large vent for pressure release (Figure from Jedvert et al., 2012).](image)

The working principle of a more advanced batch reactor is shown in Figure 3. The biomass is placed into a 10 liter reactor with heat jacket and automatic control for steam pressure and sampler retention time. About 1 kg material is loaded, the valve is closed and steam is entered into the chamber up to a pre-set pressure. After a given reaction time, the steam saturated biomass is released into a big, 160 liter discharge tank “blow down chamber”. The shown system allows also the collection of gas emitted from the biomass during the reaction.
2.1.2 Continuous steam explosion systems

Continuous systems are more sophisticated and used in industrial production processes. Figure 4 shows an example of a continuous reactor. The material is fed from a storage bin using a coaxial feeder. The feeder moves and forms a dense plug. The plug is pushed into the digester, and high pressure is exerted onto the choke cone. The back pressure of the choke cone against the biomass plug can be adjusted manually. The material is conveyed through the digester towards the end using an auger and steam is added through nozzles. The exposure time can be regulated by varying the speed of the auger and at the end of the digester the biomass is discharged through a valve with a large diameter. The opening of the valve can be regulated using a timer or by detecting the torque onto the last transfer auger. Every time the valve is opened the high pressure inside the digester is released creating a small explosion. The sudden pressure drop over the valve enlarges the volume of the biomass rapidly leading to a rupture of the fibers (Heitz et al., 1990, Lam 2011).

Figure 4. Continuous steam explosion system STAKE II Pilot Plant Facility Having a Maximum Capacity of 4 t/h Located in Sherbooke, Quebec, Canada (Heitz et al., 1990). Figure was reproduced from Lam, 2011.
2.1.3 Alternative steam explosion techniques

There are different alternatives to steam explosion treatment that have been used for pre-treatment of biomass for fermentation processes.

Steam refining

In conventional steam explosion processes the defibration is achieved by an explosion at the end of the treatment. The explosion can be replaced with a refining step. The difference to conventional steam explosion treatment is that the biomass is not released from the steaming reactor in form of an explosion like pressure drop but by passing the steamed material in a refiner.

Fang et al. (2011) have demonstrated the use of a pressurized mechanical refining system for continuous steam treatment of wheat straw using a commercially available system from Andritz and consist of a pre-steaming bin, an extruder like digester, refiner and a cyclone as shown in Figure 5. They used the continuous system to produce sugars for bioconversion to be used for bioethanol production.

![Figure 5. Continuous steam explosion using a high pressure mechanical refining system (Fang et al., 2011)](image)

The steam explosion process starts with a pre-steaming process in the pre-steaming hopper from which the biomass is discharged and fed into a plug feeder below the bin. A plug screw feeder is used to squeeze out moisture and condensate and prior to feeding into the reactor. The steam treatment takes place in the reactor in the so called “cooking screw” which is an extruder like set up with a disk refiner at its end. The pressure in the reactor can be up to 1.6 MPa (16 bar) and temperatures up to about 200 °C (Feng et al., 2011).

Steam treatment and refining have been used for pre-treatment of biomass for enzymatic hydrolysis and for the production of chemicals (Klupsch et al., 2001 and Puls et al. 1985). Schütt et al., (2012) have compared the steam refining process with a conventional steam explosion process of poplar. Subsequent enzymatic hydrolysis of the steam treated wood showed no significant difference between those two processes.

Briquetting

Biomass briquettes are usually made from wood and agricultural residues i.e. straw, husks, dried pulp and used as fuel in combustion processes or as raw material from biotechnological processes. During briquetting biomass is compacted to a fraction of its volume and this reduces the storage
and transportation costs of biomass significantly. The briquetting process itself takes place in a piston press in which the biomass is pressed through a conical die at high pressure and temperature. It has been reported earlier by Stevens et al. (2004) that the compression release cycles in a piston press are similar to steam explosion conditions. This can result in the disintegration of the briquettes when the pressure is released but it might also result in a release of lignin and sugars from the plant cell walls. Briquetting has been identified as potential pre-treatment for biogas and bioethanol production since briquetting releases sugars from the biomass and thus improve biological and enzymatic fermentation processes (C.F.Nielsen, 2013). A full demonstration plant has been installed at the University of Aarhus’s site in Foulum autumn 2012. The plant consists of a briquetting plant with pretreatment of straw in combination with a local biogas plant (C.F.Nielsen, 2013).

**Extrusion**

In extrusion biomass is exposed to high shear force, pressure and heat by conveying the biomass with help of mechanical screws along an axis and finally pushed through a die of a desired cross-section. The screws of an extruder are usually built of individual elements with different functions such as mixing, fibrillation, cutting, degassing, compression etc. They can be designed to build up and release pressure along the axis resulting in great pressure drops similar to steam explosion processes. A typical screw design is shown in Figure 6 showing different screw elements and kneading blocks with forward and reverse orientation.

![Figure 6. Screw temperature and barrel temperature profiles for laboratory-scale extruder used in the experiments (Lamsal et al., 2010)](image)

Dale et al. (1999) have used extrusion to develop a continuous ammonia fiber explosion (AFEX) process, previously run only in a batch reactor. It was adapted to run on a twin-screw extruder and the sugar yield of AFEX material after enzymatic hydrolysis has been increased up to 3.5 times over that of completely untreated material. Also Lamsal et al. (2010) and Karunanithy and Muthukumarappan (2011a, 2011b) have used extrusion as pre-treatment of fibrous biomass for enzymatic hydrolysis. The extrusion process is neither charring the biomass feedstock and has been used for a range of biomass feedstock. The set-up of an extruder and extruded biomass products
from different feedstock can be seen in Figure 7. The process is not charring the product and results in general in a release of sugars and improved fermentation properties of the biomass.

![Figure 7. Laboratory single screw extruder and screw used for pretreatment of different feedstocks (Karunanithy and Muthukumarappan, 2011a)](image)

### 2.2 Key process parameters

Major parameters of steam explosion processes are the particle size, temperature and the residence time. It has been shown that it is possible to trade these factors and achieve equivalent products (Overend and Chornet, 1987).

Overend and Chornet (1987) have developed a severity index \( R_0 \) that is widely used for optimizing steam explosion processes of biomass. \( R_0 \) is a function of the reaction time (\( t \)) and temperature (\( T \)) and can be described as shown in Equation 1.

\[
R_0 = \int_0^t \exp \left( \frac{(T - 100)}{14.75} \right) \, dt
\]

(Equation 1)

Limitations of this model are the lacking feedstock moisture content and particle size that have a strong influence on the kinetics of steam explosion processes i.e. chemical and physical changes of the biomass. Especially high moisture contents of feedstock have been shown to slow down the kinetics since the voids in the biomass are filled with condensate before the steam temperature is reached (Lam, 2011).

The thermal conductivity of biomass material varies with species and particle size, and this has a strong impact on the product quality of steam exploded biomass. Cullis (2004) has shown that particle size and initial moisture content of biomass feedstock for steam explosion have a strong impact on the recovery of lignin, cellulose and hemicellulose sugars in subsequent processes.
The process parameters and severity index are chosen according to the purpose of the steam explosion pre-treatment. Biomass destruction starts at about 2 and at high severity $R_0 > 4$ dehydration and condensation reaction occur and sugars will be degraded. For biochemical conversion of biomass $R_0$ is chosen to be between 2 and 4 while it can be higher when the aim is to increase heating value and hydrophobicity i.e. pellet production (Lam 2011).

### 2.3 Chemical and physical changes of the biomass

Wood fibers are a cellular composite material consisting of lignin, cellulose and hemicelluloses. The wood cell walls are built up out of cellulose micro fibrils with a diameter in the order of a few nanometers and different orientations in different layers (Fengel, 1984). The micro fibrils are embedded into a matrix of hemicelluloses and lignin with hydrophilic hemicelluloses binding to the polar surface of the cellulose fibrils and this forming a gel-like matrix around them. Cellulose micro fibrils are wound around hollow wood cells and are semi-crystalline bundles of cellulose molecules held together by hydrogen bonds (Klemm, 2002; Krassig, 2004). The plant cell wall is organized in different layers as shown in Figure 8. The primary cell wall is composed of loosely aggregated, irregular arranged micro fibrils allowing stretching of the cell during growth. The secondary wall is synthesized during cell growth on the inside of the primary wall and consists out of three layers S1, S2 and S3. The two outer layers S1 and S3 are 0,2-0,3µm respectively 0,1 µm thick. The S2-layer is much stronger and about 1-5 µm thick. The three different layers distinct from each other by the orientation of the micro fibrils as shown in Figure 8.

![Figure 8. Simplified model of the cell wall structure of softwood tracheids and hardwood fibers (Fengel, 1983).](image)

Steam explosion treatment can open up the fiber as shown in Figure 9. On the left side a schematic image of a fiber is shown consisting of cellulose embedded in a matrix of lignin and cross connected with hemicellulose. The cellulose is partly amorphous and partly crystalline. The composite structure of the wood cell wall is destroyed during steam explosion and the individual components are released (Hsu et al., 1980).
Steam explosion treatment releases hemicelluloses from the wood cell walls and makes them accessible to chemical and biochemical degradation. Both steam and acetic acid (released from the biomass during steam explosion) trigger the hydrolysis of hemicelluloses. The polymer chains is cleaved and C₅ sugars, mainly xylose is released and further degraded into furfural (as shown in Figure 10).

The major role of hemicelluloses in wood is to impart viscoelastic properties. The degradation of hemicellulose makes wood more brittle and rigid. The removal of OH groups (dehydration reactions) results in a more hydrophobic surface. The brittleness (better grindability) and higher moisture resistance are important properties that are used as an argument for the use of steam exploded biomass for the production of fuel pellets to substitute coal in heat and power plants.

Cellulose and lignin are also affected by steam explosion conditions. At high pressures cellulose molecules were deconstructed and degraded to furfural (5-hydroxymethylfurfural) (Suzuki et al, 1998). Lignin undergoes cleavage reactions of the acid insoluble (high molecular weight) lignin and low molecular weight lignin are formed due to condensation reactions. Donohoe (2008) suggests that lignin is melting, flowing and condensing in form of beads on the surface of the cellulose microfibrills and as such increases porosity. Miranda et al. (1978) suggested a mechanism of depolymerization and re-polymerization of the lignin. The apparent increase of lignin content during heat treatment was according to their work due to hemicellulose degradation product, furfural and lignin polymerization.
3 **PRODUCT CHARACTERISTICS AND UTILIZATION**

While steam explosion is traditionally used as pre-treatment for chemical and biochemical conversion of biomass i.e. pulping, fermentation and bio-refinery processes it has also been used as pretreatment for the production fuel pellets recently.

Steam explosion treatment increases the calorific value of biomass due to the removal of moisture and volatiles and the thermal degradation of hemicelluloses. The carbon content of the biomass increases, oxygen and hydrogen are removed from the biomass. The hygroscopicity of biomass is high due to the presence of hydroxyl (OH) groups of hemicellulose and cellulose. Those OH groups provide active bonding sites for water molecules. Depending on the severity of the steam explosion process the number of available hydroxyl groups is drastically reduced. The removal of hemicelluloses changes also the mechanical properties of the biomass. Steam explosion turn biomass from a tenacious flexible material into a brittle rigid material. This behavior is interesting since the mechanical properties of biomass are often limiting its utilization in existing coal fired heat and power plants (CHP-plants). The steam exploded biomass has more “coal like” properties as the untreated biomass and more favorable grinding and combustion characteristics.
REFERENCES


