CHEMICAL ENGINEERING TRANSACTIONS
VOL. 27, 2012
Guest Editors: Enrico Bardone, Alberto Brucato, Tajalli Keshavarz

ISBN 978-88-95608-18-1; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1227018

Generation of Biogas from Textile Waste Waters

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Conventional desizing of cotton is employed since several decades by the use of α-amylases, which hydrolize water-insoluble starch to water-soluble oligosaccharides. This enzymatic desizing process leads to waste waters with an extremely high chemical oxygen demand (COD) due to its high sugar content. Nowadays, these liquors are still disposed without use resulting in an ecological questionable pollution and high emission charges for cotton finishing manufacturers. Here, an innovative technology for the production of energy from textile waste waters from cotton desizing was developed. Such desizing liquors were fermented by methane-producing microbes to biogas. For this purpose a semi-industrial plant with a total volume of more than 500 L was developed and employed over a period of several weeks. The robust and trouble-free system produces high amounts of biogas accompanied with a significant reduction of the COD of more than 85 %. With regard to growing standards and costs for waste water treatment and disposal the new process can be an attractive alternative for textile finishing enterprises in waste water management combining economic and ecological benefits.

1. Introduction

In cotton manufacturing more than one million tons of starch per year are used as sizing agent in order to protect warp threads against mechanical stress in weaving processes. After weaving, the sizing agent has to be removed from the raw cotton fabric to avoid impairments in succeeding finishing steps.
Conventional desizing of cotton is employed since several decades by the use of α-amylases, which hydrolyze water-insoluble starch to water-soluble oligosaccharides, which can be easily removed from the cotton by washing processes (Cavaco-Paulo, 1998). This enzymatic approach has several advantages compared to oxidative procedures, because it can be done at low temperature in the absence of aggressive chemicals. But in present these high carbohydrate-concentrated liquors are still disposed without use and no economic strategy for the recycling of these ecological critical waste waters exists. This results in high emission charges for cotton finishing manufacturers due to the extremely high chemical oxygen demand (COD) of these liquors.

In our previous work we have developed a new strategy for the biological transformation of such sugar-containing waste waters to biogas (Opwis et al., 2010). In principle, carbohydrates are energy sources, which can be used alternatively to other sources such as fossil fuels or nuclear power. Especially in the days of climate change renewable energy sources are playing an important role for the global energy supply in future. Besides hydroelectric power production and the installation of wind plants the generation of energy from organic materials is the most important regenerative source (Deublein and Steinhauser, 2008).

Please cite this article as: Opwis K. and Gutmann J., 2012, Generation of biogas from textile waste waters, Chemical Engineering Transactions, 27, 103-108 DOI: 10.3303/CET1227018

The production of biodiesel, bioalcohol and biogases is employed basically by the use of resources from herbal origin (in the majority of cases carbohydrates). Especially biogas can be stated as an ´all-rounder´ for prospective worldwide energy supply. In contrast to wind and solar energy, the fermentation of biomaterial to biogas can be carried out continuously and, therefore, the biogas production is appropriate to produce base load electricity. Moreover, biogas plants produce electricity without the consumption of irrecoverable fossil resources, the danger of nuclear pollution or additional wastage.

Biogas, which is composed typically of ca. 60 % methane (CH_4), 35 % carbon dioxide (CO_2) and 5 % trace gases (H_2, H_2S, NH_3, etc.), results from the anaerobic fermentation of organic compounds by methane-producing bacteria (e.g. *Methanococcus* or *Methanobacterium*). In nature, this process occurs e.g. in maritim slurries, in oxygen poor soils, in lakes and marshes or in landfill sites. Therefore, depending on the origin one distinguish between marsh gas, sewer gas, landfill gas etc. In agriculture these gases are named biogas. The anaerobic fermentation of organic compounds to bio gas occurs in four biological sub-steps:
- Hydrolysis,
- Acidogenesis,
- Acetogenesis,
- Methanogenic phase.

Based on our previous work, here, new results on our strategy for the biological transformation of sugar-containing waste waters from textile desizing process to biogas are presented.

2. Materials and Methods

Industrial liquors from enzymatic desizing processes were delivered by Textilverdlung an der Wiese (Lörrach, Germany). The desizing liquors were pressed out from the wetted cotton material with a high pressure squeezer. Sample drawing was done in the first washing compartment with the highest carbohydrate concentration. The COD amounts to 40.0 g/L. The industrial desizing liquors were taken as substrate for the anaerobic biogas generation without any additives.

On lab-scale the anaerobic fermentation of the desizing liquors was carried out in a double-stage biogas reactor with biomass recirculation (total volume 4.8 L). The sugar-containing media was supplied in an upstream mixing chamber, where pH value was adjusted to 7.2. For the biological transformation an anaerobic mixed culture was taken from an agriculture biogas plant (Wassenberg, Germany) and settled on a carrier material inside the main reactor.

By up-scaling the reactor to a total volume of 550 L (main fermenter 430 L) the continuous semi-industrial fermentation was conducted in a system schematically shown in Figure 1. The system is able to measure several parameters such as temperature, pressure, pH value, tank filling height, volume flow, generated gas amount and chemical gas composition online and simultaneously.
All further mentioned analyses were carried out by approved methods in microbiology and chemistry.

3. Results

3.1 Characterization of the desizing liquors

The typical industrial desizing liquors were taken out of the first washing compartment of an industrial washing machine. These liquors show a high concentration of various oligosaccharides from the enzymatic hydrolysis of starch with α-amylases. The chemical oxygen demand (COD) was found to be

40.0 g/L, which allows an economic use in the bio reactor without further accumulation and without any additives. Due to the optimum of the enzymatic desizing process the pH-value was 6.0.

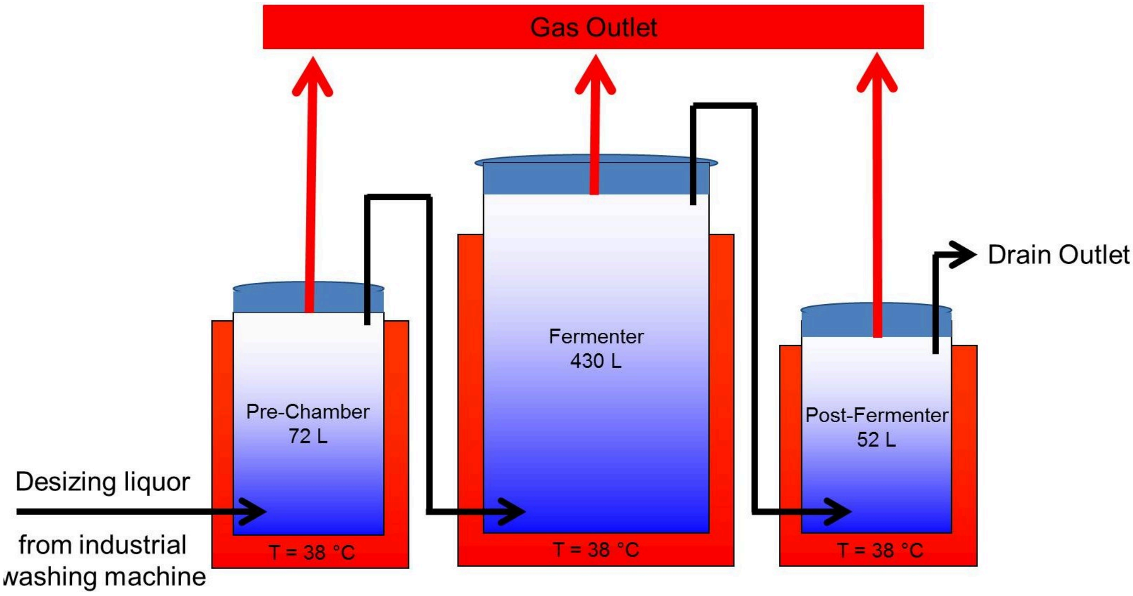

Figure 1: Semi-industrial biogas plant (schematic)

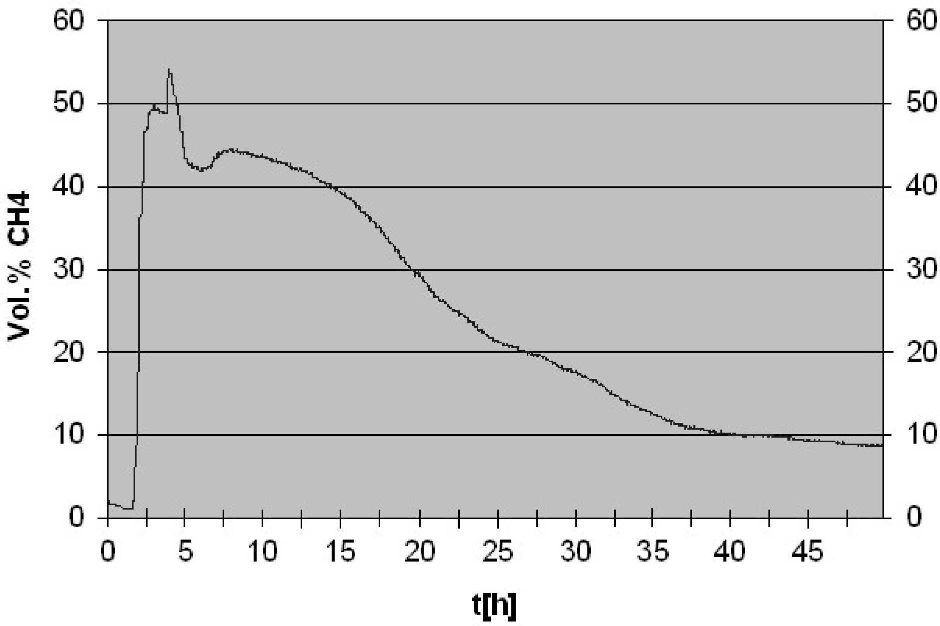

Figure 2: Time-dependant production of methane from industrial desizing liquors

Toxicological studies show no negative influence on the growth of *E. coli* (as model organism) and the quantitative measurement of trace elements (via ICP) results in the presence of various essential elements (e.g. selen), whose influence on the long-term stability of the biological systems indeed has to be investigated more in detail.

3.2 Biogas generation/COD reduction

To implement a stable bio gas reactor the methane-producing bacteria were fed with a glucose medium until first gas production was detected. After reaching balanced conditions the medium supply was switched to a batch feed of the industrial desizing liquors. Figure 2 shows the time-dependant production of methane. A maximum was reached after four hours. Afterwards the total gas production and the content of methane decreased slowly indicating a starvation of the microbes. After 27 h the VOA/TIC (volatile organic acids/total inorganic carbon) of the system fell below 0.3, which means a concrete hunger situation. At this time the COD of the desizing liquor was fallen to 14.0 g/L.

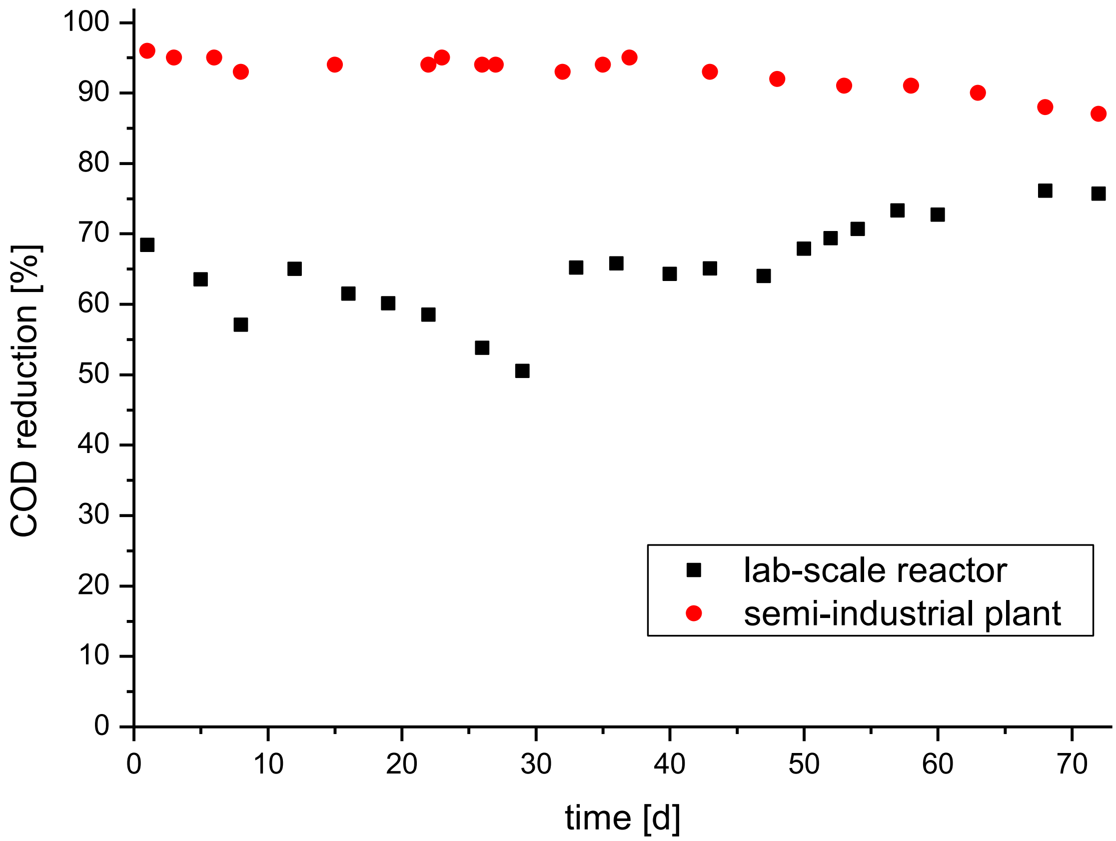

Figure 3: Time-depending COD reduction of industrial desizing liquors from cotton pre-treatment in a lab-scale and a semi-industrial biogas reactor.

3.3 Up-scale

Based on these results the feed supply within the lab-scale reactor was adjusted to 0.22 mL of the desizing liquor per minute, which is corresponding to an absolute residence time of approximately 15 - 16 days (reactor volume = 4.8 L). Under these continuous fermentation conditions an effective biogas production was observed with a COD reduction in the range of 50-75% over a period of 72 days (see Figure 3, lab scale reactor).

The hydraulic design of the semi-industrial plant was aligned with the results from the lab-scale reactor. The measured residence time (15 - 16 days) was supplemented by a conservative overhead of 50 %, coming to a maximal expected residence time in the new reactor of 24 days. The main fermenter has an absolute volume of 430 L and, therefore, a needed input of 18 L desizing liquor per day coming to a calculated biogas production of 486 L/day.
After implementing the continuous fermentation process a constant biogas production was observed. The continuous determination of the chemical composition of the biogas leads to an average methane content of almost 60 vol.%.
Moreover, a high reduction of the COD within the drain outlet was detected. Figure 3 shows the relative decrease of COD over the regarded period of 72 days. Compared to the lab-scale reactor, the semi-industrial plant exhibits a further improvement of the degradation performance to average levels of more than 85 % due to the higher residence time of 24 days (instead of 15 days within the lab scale reactor).

4. Discussion

Nowadays, sugar-containing desizing liquors from enzymatic cotton desizing are undesired waste waters. In Western Europe the disposal of such high carbohydrate-concentrated waters results in high emission charges and these polluted waters are ecological critical due to their high COD. In principle, these waste waters are suitable for the generation of methane-containing biogas, whereas the pre-hydrolyzed oligosaccharides seem to be an ideal substrate for methane-producing microbes.
The investigations have shown that the microbial fermentation of textile desizing liquors into biogas is possible. Without further treatment of the sugar-containing medium biogas with a high methane content up to 60 vol.-% can be produced in a simple biogas reactor with biomass recirculation and pH control. Therefore, in textile industry these ecological and economic undesired waste waters can be used for the generation of energy (e.g. in a block heating station). Moreover, this new process reduces the COD of the waste water by more than 85 %.

Thus, the suggested technology combines ecological and economic benefit by the production of energy from a renewable source. With respect to the global dimension of cotton pre-treatment (global annual output 25 million tons) the investigations can be a substantial contribution to the minimization of greenhouse gases and, therefore, global warming in distant future.

Acknowledgement

The authors would like to thank the Deutsche Bundesstiftung Umwelt e.V. for the financial support of the project DBU Az 26589 “Entwicklung einer Verfahrenstechnik zur Generierung von Methan aus Stärkeschlichte in der textilen Vorbehandlung von Baumwolle”.

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