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Potential Effects of Mechanical Pre-treatments on Methane Yield from Solid Waste Anaerobically Digested

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Abstract The increasing demand of energy supply requires the development of systems of energy production based on the exploitation of renewable energy sources as an alternative to fossil fuels in common use. Through the process of anaerobic digestion it is possible to convert into biogas agricultural biomass, zootechnical waste, sewage sludge and organic fraction of municipal solid waste. After that it is possible to generate energy from biogas through the process of cogeneration. More recent concerns about global warming have stimulated further anaerobic digestion application and the improvement the processes in order to maximize biogas production, which is a renewable and versatile energy source that can be used for heat and electricity production, and as transportation fuel. It is in the interest of operators of anaerobic digestion plants to maximize methane production whilst concomitantly reducing the chemical oxygen demand of the digested material. The pre-treatment of solid waste is regarded as a prerequisite of the anaerobic digestion process to reduce volume and increase methane yield. The aim of the mechanical treatment is the reduction of the size of the biomass and its degree of crystallization, in order to increase the surface area available to enzymatic hydrolysis. This generates an increase on biogas production and a decrease in the time required for the digestion. In this work the link between mechanical pretreatment and the increase of methane yield of some samples of a dedicated crop (triticale) was discussed.

Keywords: *anaerobic digestion, mechanical pre-treatment, specific surface, methane yield*

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1. Introduction

Anaerobic digestion (AD) is the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment. The AD of particulate material and macromolecules is considered to follow a sequence of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. This process consists in the degradation of organic matter into simple compounds and subsequently in the conversion of such substances in biogas. The digestion process begins with bacterial hydrolysis of the input materials. Insoluble organici polymers are broken down to soluble derivatives that become available for other bacteria. Acidogenic bacteria then convert sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. These bacteria convert these last compounds into acetic acid. Finally, methanogens convert these products into methane and carbon dioxide. Each step of the process is affected by many physical and chemical parameters (temperature, pH, etc ...) and complex microbiological equilibrium. Depending on the type and complexity of the organic molecules that constitute the input of the biomass in the digester, the process can be faster or slower.

AD is used as part of the process to treat biodegradable waste, reducing the emission of landfill gas into the atmosphere. In case of dedicated biomass digestion (crop) the target is oriented to renewable energy generation.

The generated biogas can be used directly as fuel, in combined heat and power gas engines, or upgraded to natural gas-quality biomethane. The nutrient-rich digestate produced can be used as fertilizer, generally after post-treatments.

Considerable efforts to improve biogas production via AD have focused on understanding the associated microbial process in order to optimise environmental condictions, reactor designs and substrate selection [1,2]. Substrate manipulation poses improvement opportunities as well as challenges for AD since the substrates available for AD have different properties, representing different types and levels of limitations to achieve optimal AD performance [3].

In this work some aspects about the link between mechanical pre-treatment and the increase of methane yield of some samples of a dedicated crop (triticale) was discussed after a short state of the art. The discussion is oriented to understand which design criteria could be preferred:

- develop enhanced pre-treatment steps in order to decrease the volume needs for AD
- simplify pre-treatment steps accepting a larger AD volume.

Consequences of these criteria are significant: AD requires a preliminary heating of the input and digesters must keep steady their temperature; thus different volumes affect not only the management costs for energy consumption but also the capital cost of the approach.

2. Pre-treatments Overview

It is recognized that hydrolysis is one of the rate limiting steps in AD especially for the presence of organic complex substrates and particulate materials [4]. The rate of degradation is one of the most important parameters in the dimensioning of the volume of the digester and/or choice of installation techniques. It changes from 20-25 days for pig manure, 35-40 days for cattle manure, until 50-70 days in the case of biomass derived from dedicated crops.

Results of many studies [4,5] and others indicate that an acceleration of hydrolysis step could greatly improve the anaerobic digestion process.

The anaerobic process is widely used for treating wet residues in order to produce methane or bio-hydrogen [6,7]. Recently the interest for this process has increased thanks to the availability of incentives applied to electricity generated from biomass.

The increase in biogas production and AD process is possible through the application of pre-treatment upstream of the anaerobic digestion process. The pre-treatments currently applicable are classified according to different categories [4,8]:

• physical (grinding, heat treatment, ultrasound, etc.)
• chemical (through use of alcohols, acids, ozone, etc..)
• biological (by specific microorganisms)
• enzymatic (by specific enzymes)

Thanks to this pre-tratment, an increase on biogas production and a decrease in the time required for the digestion can be obtained [9].

The pre-treatments depend on the quality of the biomass in input to the digester and are needed to [10]:

• maximize the production of biogas
• reduce maintenance operations on the digesters
• homogenize the mixture
• adjust the moisture content
• adjust temperature of the mixture

The main effects that pre-treatments have on different substrates can be identified as particle-size reduction, solubilisation, biodegradability enhancement, and loss of organic material. Particle-size reduction has been the most commonly used factor to describe the increase in substrate surface area resulting from a pre-treatment of biomass [11,12,13].

Many researchers [11,14,15] reviewed pre-treatment methods applied to lignocellulosic biomass for improved AD performance and bioethanol production. For AD applications, the most frequently studied pre-treatments have been chemical, often in combination with elevated temperature. The surface area can also be increased by particle size reduction, which has only been reported as an effect of mechanical pre-treatment [11,16].

Biodegradability enhancement may result from both the increase in available surface area and the formation of biodegradable compounds from lignin [11].

The pretreatments can be applied to increase the biodegradability of hardly degradable matrices, encouraging digestion. The lignocellulosic materials, for example, represent an abundant component of the waste of the agro-food and agriculture, as well as municipal solid waste (organic waste and cuttings pruning of urban green). The biodegradability and the potential biogas production of lignocellulosic materials mainly depend on their content of cellulose, hemicellulose and lignin. Generally, microorganisms easily degrade cellulose and hemicellulose. However, in lignocellulose materials, they are associated with lignin, which acts as a barrier preventing the biodegradation.

The pre-treatment, by specific microorganisms, acts to remove the content of lignin and hemicellulose, reducing the crystalline structure of cellulose and increasing the porosity of the materials and the surface area available to the attack of microorganisms [16] (Figure 1).

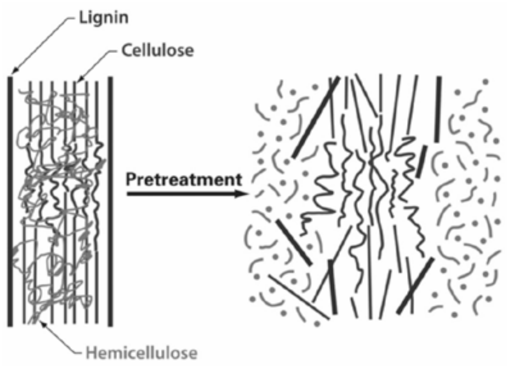

Figure 1. Lignocellulosic materials [17]

Particle size can affect the rate of anaerobic digestion as it affects the availability of a substrate (i.e. the surface area) to hydrolyzing enzymes, and this is particularly true with plant fibres: fibre degradation and methane yield improve with decreasing particle size from 100 mm to 2 mm [18].

Pre-treatment methods to improve AD have been the focus of a large number of scientific studies over the last 30 years [11,19,20,21] and AD improvement in terms of increased methane yield and solids reduction are well established advantages of such pre-treatments. Commonly, the performance in AD is expressed as the methane yield, i.e. the volumetric methane production under standard conditions per unit of material fed, which can be expressed as total solids (TS), volatile solids (VS), chemical oxygen demand (COD) or wet weight. Alternatively, TS or VS reduction (% of incoming TS or VS reduced), and methane productivity ($m^3_{CH4} \cdot m^{-3}_{reactor} \cdot d^{-1}$) are used. In this sense, improved AD performance relies on increasing operational methane yield in order to arrive as close as possible to the actual potential methane yield of the substrate at the highest feasible digestion rate.

The aim of the mechanical treatment is the reduction of the size of the biomass and its degree of crystallization, in order to increase the surface area available to enzymatic hydrolysis. These treatments are based on the reduction of the size and molecular complexity of the biomass. This also generates an increase on biogas production and a decrease in the time required for the digestion [22].

This effect can be obtained through cutting, milling or grinding of the material or through a combination of these. The size of the obtained particles generally depends on the type of treatment used (10-30 mm with the cutting, 0.2-2 mm with milling or grinding). Another way to reduce the size of substrate is the ultrasound treatment and the cavitation.

The *ultrasound treatment* causes the formation of cavitation bubbles in the liquid phase, leading to the collapse of these bubbles up and explosion when they reach the critical size [9]. The mechanical impact caused by the collapse of cavitation gets a major benefit in the opening of the solid surface of the substrate and therefore the action of enzymes. It is possible to achieve the effect of cavitation even at temperatures of 50°C, which represent the optimum for many hydrolytic enzymes.

During this practice, the energy used for the treatment is converted into an alternating formation and implosion of micro bubbles, which in turn generates a sequence of shock waves. This alternation is responsible for a mechanical and thermal activity on the organic matter present in water solution that determines a partial deconstruction physical, a lysis of the cell walls and the consequent release of intracellular content. This action results in increased availability of cellular juices, in an acceleration of the processes of hydrolysis and, consequently, in an acceleration of the AD process. Several studies already conducted have shown that the rate of bacterial degradation can accelerate up to 4 times compared to conventional treatment. Cavitation involves the use of a frequency range between 20 and 10,000 kHz for chopping the biomass input to the digester. To generate a physical change of the material you normally work within a narrower range (between 20-100kHz) [9]. The main benefits expected are related to the reduction of the size of the organic material, the reduction of the viscosity and the resulting easeness in mixing inside the digester, as well as increase the homogeneity of the digestate and improved pumpability.

3. Materials and Methods

Thanks to the collaboration among expertises present in the Euregio area (referring to specific Italian and Austrian regions) in the frame of a project called "BIOGAS IN AREE ALPINE: pre-trattamento delle matrici organiche" (Biogas In Alpine Areas: pre-treatment of organic matrices) it was planned to analyze three different samples of triticale. The project was promoted by the Autonomous Province of Bozen with the provincial law 14/2008.

The triticale is a typical solid biomass used as supply in the reactor to AD. Triticale is a hybrid of wheat (Triticum) and rye (Secale) first bred in laboratories during the late 19th century. As a rule, triticale combines the yield potential and grain quality of wheat with the disease and environmental tolerance (including soil conditions) of rye. It was analysed three different samples of triticale, each with a different degree of particle size (Figure 2). The samples are:

1. triticale as is (taken from the trench storage)
2. triticale after treatment with mounted silage harvester (a machine that enables the loading, mixing, and distribution of corn silage. The machine has a silage cutter to load silage) (Figure 3a).
3. Triticale chopped with half-moon knife in laboratory (Figure 3b).

Figure 2. a) triticale as is; b) triticale after mounted silage harvester; c) triticale chopped

Figure 3. a) mounted silage harvester model Dobermann SW 300 GP; b) half-moon knife

It was decided to determine the particle size for these samples and then determine the granulometric distribution curve; this is because there is a potential link between the particle size of the biomass entering the AD and yield terms of biogas. To determinate the granulometric curve, it was used five sieves in agreement with the standard ISO 3310/1.

The five sieves had the following granulometry (Figure 4):

- sieve with a mesh size of 5 mm
- sieve with a mesh size of 3.15 mm
- sieve with a mesh size of 2 mm
- sieve with a mesh size of 1 mm
- sieve with a mesh size of 0.5 mm

Figure 4. Series of sieves used for particle size analysis

Three granulometric tests were performed for each sample of triticale for better emphasizing the obtained results, due to the heterogeneity of the materials.

The production of biogas from each sample was determined using the Automatic Methane Potential Test System (AMPTS) from the comapany Bioprocess Control AB, Sweden. All methane production measurements were run in triplicates. Digestate from the biogas plant in Ferrara, italy was used as inoculation substrate (IS). Microcrystalline cellulose (MCC) was used as a positive control. Incubation time of the experiment was 47 days. In Table 1 an overview of the AMPTS AD experiment is shown.

Table 1. overview of AMPTS AD experiment

Sample		Inoculation sludge [g]	Substrate FM [g]	VS % (w/w)
Triticale as is	1	300	10.00	34
	2	300	10.00	34
	3	300	10.19	34
Triticale Silage Harverest	4	300	10.16	32
	5	300	10.70	32
	6	300	10.25	32
Triticale Chopped	7	300	10.05	34
	8	300	10.00	34
	9	300	10.18	34
Negative	10	300	-	-
	11	300	-	-
	12	300	-	-
Positive (MCC)	13	300	1	100
	14	300	1	100
	15	300	1	100

4. Results and Discussion

Results are presented in the following figures. The graphs refer to the average of three tests and the percentage of various size classes as ordinates and the size classes in the horizontal axis are shown.

From the granulometric distribution of first triticale, sample shows (Figure 5) that 86.3% of the particles have a size greater than 3.15 mm and only 13.7% of the particles that make up the sample have a particle size under 3.15 mm.

Same results stand if you look at the granulometric distribution of triticale after treatment with mounted silage harvester (Figure 6). The 87% of the mass is composed of particle with a diameter greater than 3.15 mm and only 13% of the particles that make up the sample have a particle size under 3.15 mm.

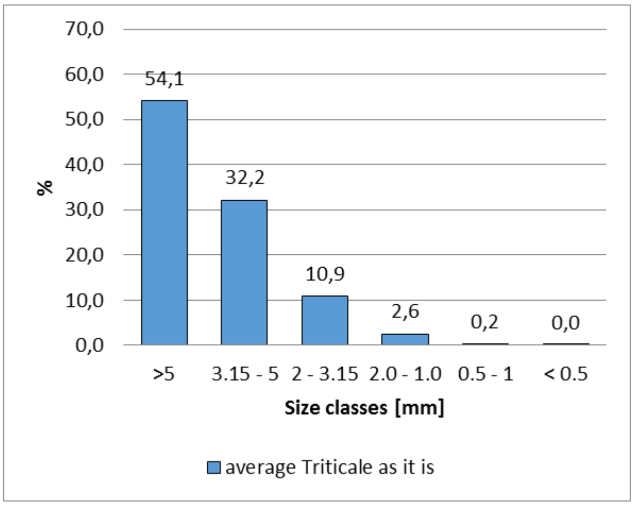

Figure 5. Granulometric distribution of triticale as it is

Comparing the results of the two samples in terms of granulometric percentage, it is seen that the value do not change very much. If you look the percentage inside the two class greater 3.15 mm, you can see that the percentages are slightly different. In the first sample the percentage of mass with size greater 5 mm is 54.1, while in the second sample is 48.6. This is an important information if we take into account that this step, belonging to the pre-treatment approach, can be coupled with a significant consumption of energy.

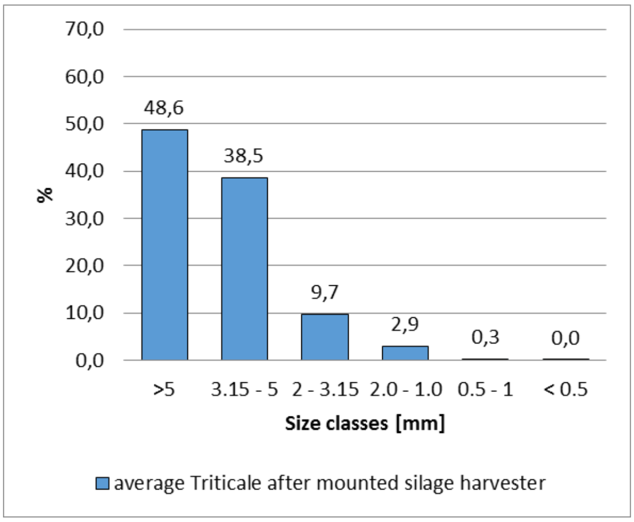

Figure 6. Granulometric distribution of triticale after treatment with mounted silage harvester

The results mean that a part of particle size is reduced, symptom that the pre-treatment process has some effects but this is also an indication of a limited shredding during the treatment with mounted silage harvester: such a process is not efficient enough to reduce significantly the particles size.

Things are different if you look at the average particle size of the sample of triticale treated simply with half-moon knife (Figure 7).

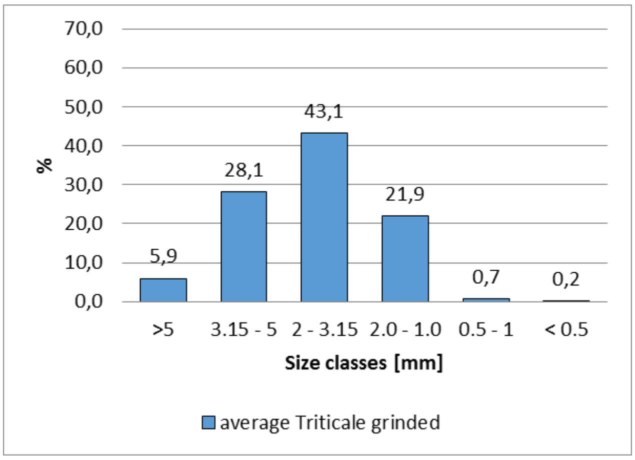

Figure 7. Granulometric distribution of triticale chopped

In this case, 43.1% of the biomass has a diameter between 2 and 3.15 mm and the particles larger than 5 mm are present with a much lower percentage, equal to 5.9%. Even the percentage between 1 and 2 mm increases drastically, going from a 3% to about 22%. A total of the particles of the sample with a diameter less than 3.15 mm are increased up to 64%. This means that we shoud expect a value of methane yield higher than the other samples, because the decrease in particle size causes the increases the specific surface area that can be attacked by micro-organisms responsible for the production of biogas; from another point of view, the specific surface area could be changed not enough to see practical effects on the biogas yield.

As explained later, from the results obtained in terms of granulometric distribution and biogas yield, it emerges that the reduction of particle size is not as efficient as expected. In order to obtain high yields in terms of methane production it is necessary to reach higher percentages for the size classes less than 1 mm. Tho this concern the CRPA *(Research Center Animal Production)* based in Emilia Romagna (Italy), conducted tests to verify the application of the technology cavitation to increase the methane yield in pilot scale [23]. The table (Table 2) and graphic data (Figure 9) on the size distribution of the dry matter of a digestate taken from a plant fed with slurry and dedicated crops and treated with the reactor Spr (hydrodynamic cavitation controlled), in comparison with the same untreated digestate, are reported.

Table 2. Percentage of size of the particles of dry matter [20]

Percentage of the size distribution of the particles of dry matter						
Digestate	size (mm)					
	>5	3.3-5	2-3.3	1-2.0	0.5-1	<0.5
untreated	15.5	13.93	6.81	5.64	4.44	53.62
treated	0.14	0.65	7.02	8.94	7.05	76.19

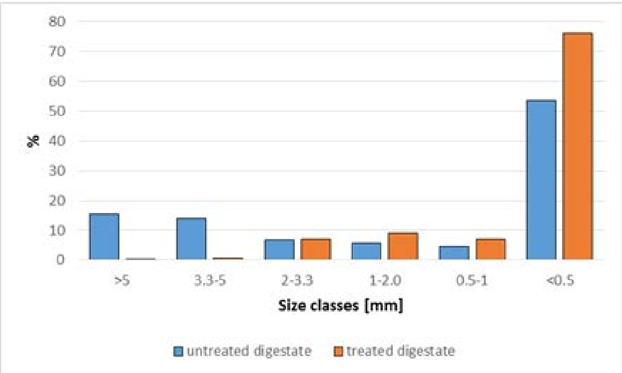

Figure 8. Percentage size distribution of the particles of an untreated digestate and treated digestate sample [20]

The cavitation treatment has a clear impact on the sample. The size greater than 3 mm is practically no longer present in the treated digestate, while the fraction less than 0.5 mm is higher than 42% if compared with the untreated digestate.

To understand better the effect of such treatment the CRPA has conducted tests on potential production on methane. The same analysis were conducted on both the sample treated with the Spr reactor that is not coated. The result is that the potential production on methane of the treated digestate resulted 22% higher compared to the untreated sample with reactor Spr (test duration 25 days).

To this concern, a comparison of the biogas generation data between our samples is reported in Figure 9 and Figure 10.

In Figure 8 kinetics of biogas production over 47 days of incubation at 37°C is shown. Mechanical treatment of triticale in the lab resulted in an increased methane production kinetics over the first 30 days of incubation whereas tretament triticale with the silage harvester had no effect. However, all the triticale samples reached the same final methane yield afer 30 days of incubation.

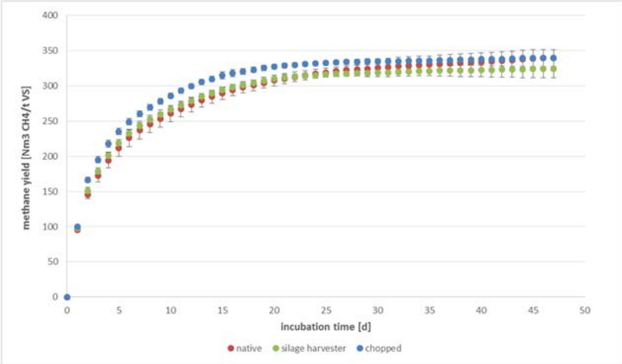

Figure 9. Biogas production over 47 days of incubation at 37°C

In Figure 10 the cumulative methane production after 47 days of incubation is shown. Morover, biogas yield data of triticale found in the literature [24,25] are shown. The data presented here clearly show that the use of the silage harvester will not lead to an increased methane production in the case of the present triticale biomass. Morover, an additional mecchanical treatment as carried out in this study can only increase methane production kinetics in the first 30 days but will not increase total methane production of the triticale biomass too.

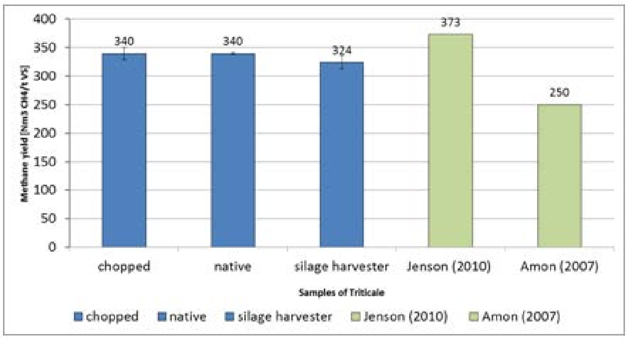

Figure 10. Biogas production over 47 days of incubation at 37°C

For the analysed triticale a retention time of about 40 days could be adequate for a technical development od AD, allowing a cumulated generation of methane of 340 Nm^3 methane per ton volatile solids. These results agree with literture data for tricale ranging between 250 Nm^3 methane/t_{VS} [24] and 370 Nm^3 methane/t_{VS} [25].

Comparing the data obtained from the tests in the laboratory and the data obtained from the CRPA is seen that the benefit of the mechanical treatment by simple trituration (with a half-moon knife) has not increased by much the yield of production of methane (4% more than in triticale as is, after the first 25-day trial). This is due to the size of the still coarse crushed triticale. To obtain a further improvement of the production of methane is therefore necessary to subject the sample to a pre-treatment more stringent, that allows obtaining a higher percentage (60-70%) of material with a particle size under 1mm.

In this frame the availability of a low construction cost digester can be coupled to a simplified management of the pre-treatment, as the retention time can virtually substitute a part of the preliminary activities before the feeding of the biomass. It is a problem of cost-benefits balance. Concerning cavitation, its role should be analysed also in terms of intermediate treatment when two sequential reactors are available and the discharge of the first has a limited residual biodegradability. Of course, the viability of pre-treatment must be analyzed preliminarily as not all the kinds of biomass need a modification of the granulometric distribution [26].

5. Conclusions

From this study it emerges that the mechanical pre-treatment can contribute differently to an increase in the production of methane. Through the processes of mechanical pre-treatment it is possible to get a feedstock consist of fine size material. These technologies can increase the specific surface area of the substrate, which therefore will be more easily digestible. This involves an increase in production of methane. This phenomenon is confirmed by the studies and tests carried out by different authors in the last 20 years. The CRPA has conducted tests on potential production on methane in two different samples, the first one treated with cavitation and the second one untreated. It was found that the production of methane for the first one has increased by 22% compared with the untreated sample. In agreement to that, pre-treatment needs an enhanced technology to be useful. Its efficiency is not guaranteed by simplified approaches, thus, in presence of a strategy that keeps low the construction costs for a AD, pre-treatment could be simplified.

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