Conservation of unusual substrates

Ulrich Küntzel

Institute of Grassland- and Forage Research

Federal Research Center of Agriculture (FAL)

Braunschweig-Völkenrode, Bundesallee 50, Federal Republic of Germany

Introduction

Unusual substrates are, in this lecture, defined as byproducts and wastes generated by agricultural production, processing industry and different refuses from municipality and industial manufacture.

More effective byproduct and waste utilization is inevitable because of ecological and economic pressure especially in developing countries. Byproducts are to be regarded as valuable raw materials which otherwise contaminate the environment.

Fig. 1: Natural cycle of materials (according to R. BRAUN, 1978)
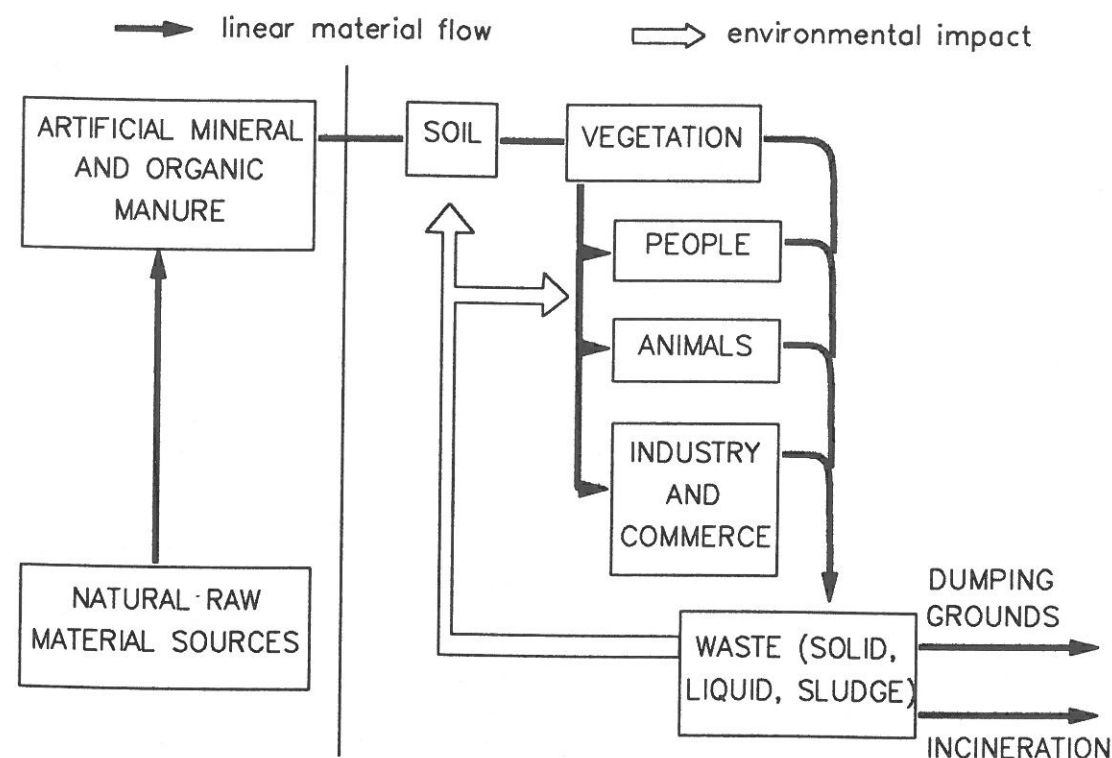
Biogenic byproducts often can be used in form of food for animals, which sometimes have to be treated before being suitable (fig.1).

Byproducts are most perishable because they have digestible nutrients and sufficient moisture for growth of fungi and yeasts. Therefore the safeguarding of feeding rations over a longer period require the conservation of byproducts.

In the last years we have investigated the feeding value and the possibilities for conservation of different byproducts.

Composition of byproducts

At the production of ethanol, starch, sugar and beer big amounts of stillages, pulps, scraps and brewers grain fall on. These byproducts have a low dry matter (DM)-content, mostly less than 10%.

Table 1: Composition of different byproducts

manufacture / byproduct / natural product / substances	ethanol								starch	sugar	beer
	wet solid stillages					pressed pulps				pressed scraps	pressed brewers grain
	potato	CCM-silage	wheat	rye	Jerusal. Artichoke	sugar beets	fodder beets	potato	sugar beet		barley
% DM % i DM	16	32	27	23	16	20	18	16	20		33
crude ash "	5	2	2	2	6	5	4	2	6		4
crude fiber "	18	23	16	15	20	16	17	16	20		17
crude protein "	37	17	28	32	31	8	6	5	12		23
Nfe[1]+ crude fat "	40	58	54	52	43	71	72	77	62		55
sugar "	3	0,2	0	2	0,7	20	10	0,8	7		0,9
NH_3-N mg/100g DM	55	21	14	15	45	23	24	19	—		7
pH —	3,8	4,1	3,8	3,3	4,0	5,0	4,1	5,1	5,5		5,0
in vitro DOM % i OM	82	67	68	63	78	92	89	93	87		55
NEL MJ/kg DM	8	6	6	6	7	9	8	9	7		5

[1] Nfe = N-free extract

As a recent development the byproducts are partly dehydrated thus reducing the transport volume and increasing the nutrient concentration.

The separated fluids have less than 2 % DM and can conduct to filter plants and can conduct sometimes after repeatedly separation.

The remaining byproducts are named (table 1)
- wet solid stillages: the separated hot stillages
- pressed pulps: residues from cold extracted fresh plant
    material
- pressed scraps and pressed brewers grain: the pressed
    hot original byproducts

The DM-contents varied from 16 to 33 %, the crude ash contents were always low; the crude fiber content was in average 18 % and varied little, the standard deviation was only 3 % absolute (table 1). Ordinarily, the crude protein content was low in pulps and scraps and high in stillages and brewers grain. Nitrogen-free extracts and digestibility were always high and the net energy lactation

(NEL) was relatively high, too. Usually stillages had a lower pH than the other byproducts. Residues from sugar and fodder beets had ever more sugar than byproducts of other plants (table 1).

Deterioration of unprotected aerobe stored byproducts

Fig. 2:

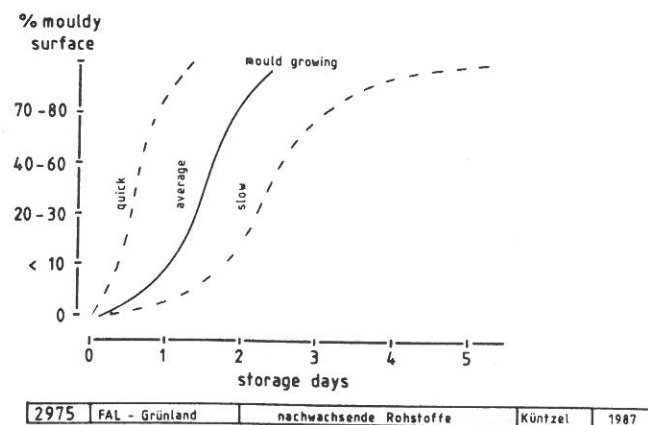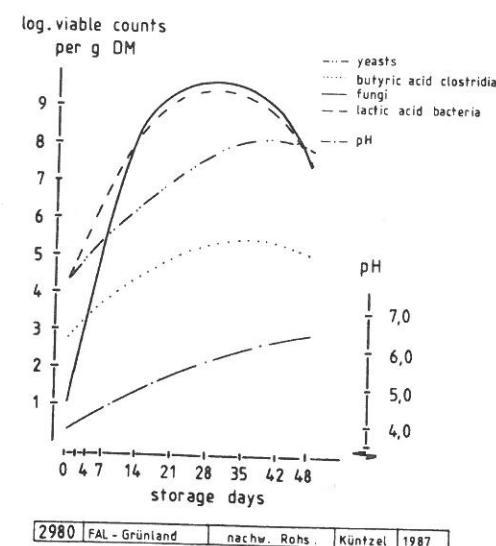Visible mouldiness in open stored solid-potato-stillage

Fig. 3:

Microbial development and increasing pH during the time in open stored solid-potato-stillage

On the surface of unprotected byproducts visible mould growth within 1 to 5 days (fig. 2). Bigger stacks of solid wet potato stillage with heights up to 1,5 m were completely moulded after 10 to 14 days down to the bottom.

The counts of microorganisms increased over 4 to 5 weeks. Later on they decreased due to lack of available nutrients. Parallel to this the pH increased and the DM-losses grew up to 30 % (fig. 3).

DM losses were correlated with growth of fungi. However, visible moulding and measurable losses occured when mould counts exceeded one million per g DM (fig. 4).

Fig. 4:

Relations between counts of moulds and dry matter losses as also visible mouldi-ness (estimation 0-5 = no-total mouldy) (average from 132 investigations on potato-, CCM-silage-solid wet stillage and sugar beet pulp, air stored)
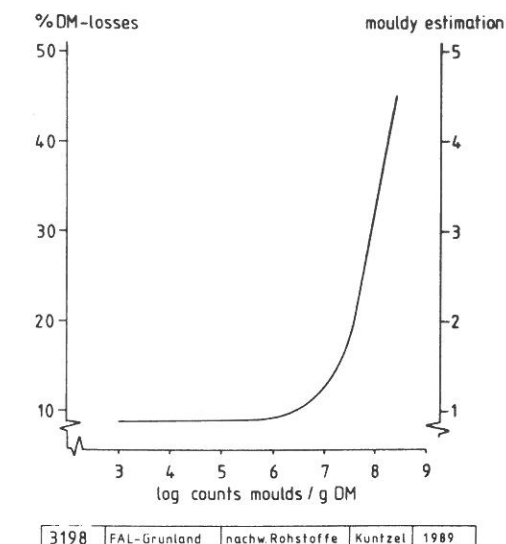
Therefore, in conclusion:
-1.: Byproducts must be preserved,
    even for a limited storage time
-2.: presering action has to start immediately
    as soon as the byproduct comes up.

Preservation
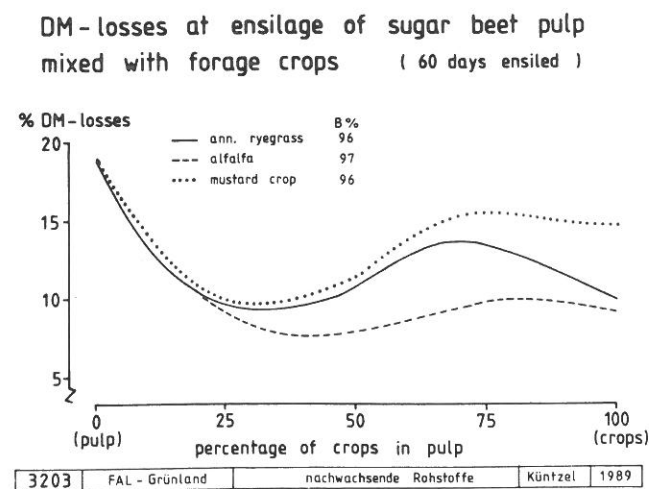
Three preserving processes for byproducts are applicable:
- drying
- ensiling and
- conservation with preservatives.

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Drying with hot air is the most care and safe preserving technique but it is also the most expensive. Therefore artificial drying for byproducts is only used as in exception.

Ensiling needs for fermentation enough sugar, lactic acid bacteria, anaerob conditions and no pollutants.
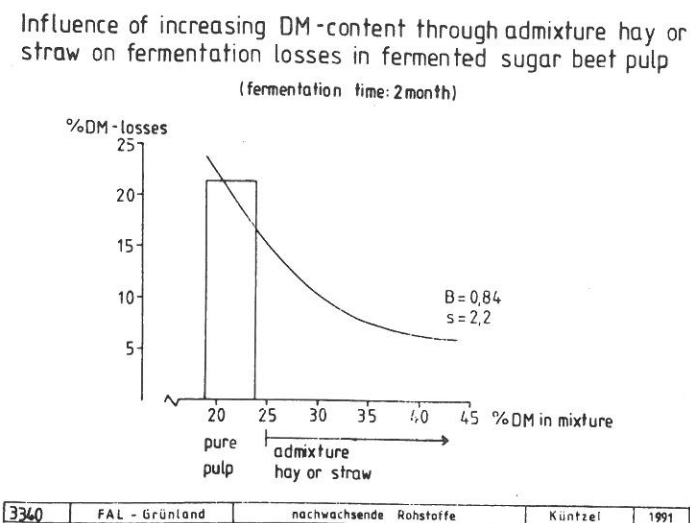
Byproducts with more than 1,2 % sugar in fresh weight like pulps and scraps from sugar and fodder beets could be fermented and gave good silage quality always. But the DM-losses were very high, quite often more than 20 %. Admixture of forage crops reduced these losses by half at unaltered good silage quality (fig. 5).

Fig.5:

DM-losses at ensilage of sugar beet pulp
mixed with forage crops   (60 days ensiled)

	B %
ann. ryegrass	96
alfalfa	97
mustard crop	96

% DM-losses

percentage of crops in pulp

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Rise of DM-content by admixture of hay or straw reduced also the fermentation losses (fig. 6).

Fig. 6:

Influence of increasing DM-content through admixture hay or straw on fermentation losses in fermented sugar beet pulp
(fermentation time: 2 month)

%DM-losses

B = 0,84
s = 2,2

% DM in mixture

pure pulp   admixture hay or straw

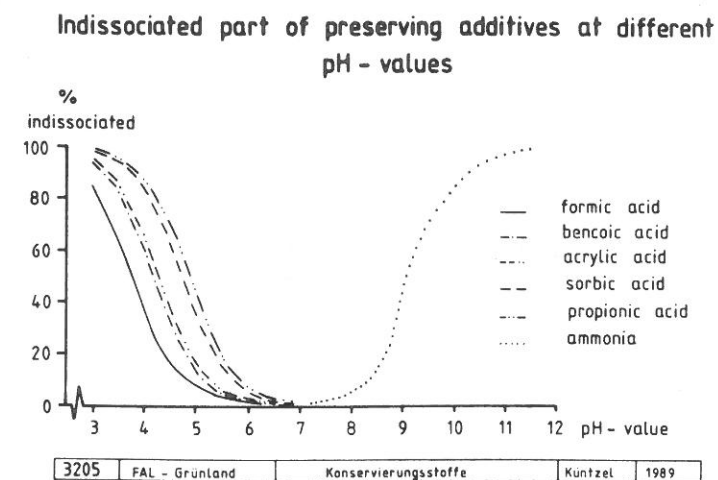| 3340 | FAL - Grünland | nachwachsende Rohstoffe | Küntzel | 1991 |

In practice the homogenous mixing of plant material into pulps and scraps is very difficult. There are no mixing machines on the market at all.

In stillages, scraps and brewers grain the deficiency of fermentable carbohydrates and the low pH were limiting the fermentation process. No acids were formed and the pH-value was not reduced. Lack of fermentation resulted in low storage losses. After opening the silos these ensiled byproducts spoilt as quickly as before. Even if mixed with forage crops or inoculated with lactic bacteria or add enzymes for starch cracking byproducts with too less sugar and pH lower than 4,5 could not be fermented.

Stabilizing by preserving additives

These byproducts can be conserved by use of organic acids as preservatives among aerobe storage. Especially the undissociated part of an additive is effective against moulds. Therefore the conservation efficiency increases with the dissociation constant (pK_a) of an organic acid and with a lower initial pH of the byproduct (fig. 7).

Fig. 7:

Indissociated part of preserving additives at different pH - values

%
indissociated

formic acid		
bencoic acid		
acrylic acid		
sorbic acid		
propionic acid		
ammonia		

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Increasing undissociated amounts of an additive raise the buffering capacity (fig. 8).

This can indicate the conservation effect to be expected. The common evaluation of 119 preserving experiments of different solid wet stillages and pulps with variable doses of different organic acids as preservatives resulted increasing buffering capacity was related with increasing hindrance of mould growth (fig.8).

Fig. 8:

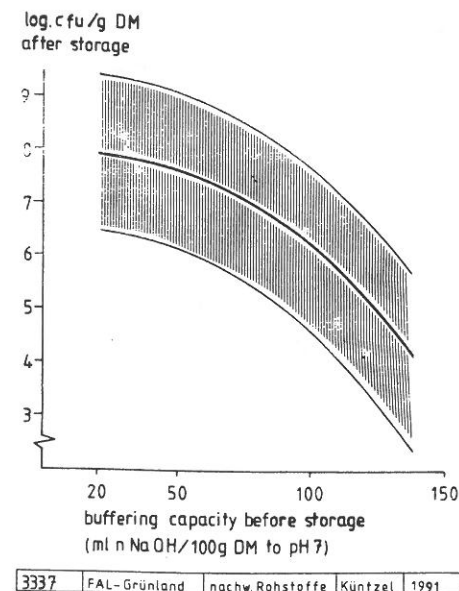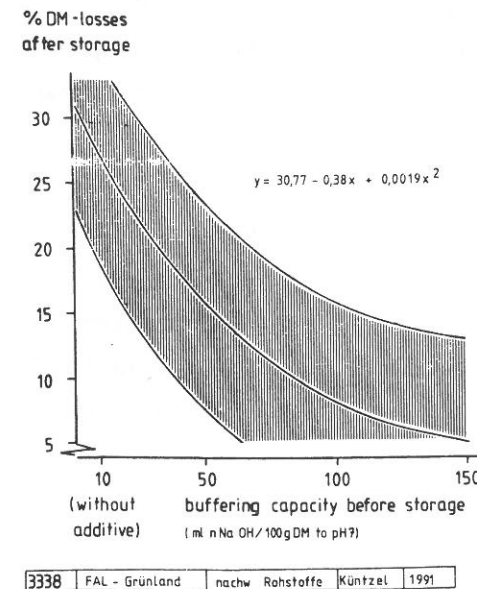Reduction of moulds by rise of buffering capacity through organic acids in aerob stored stillages

log. cfu/g DM after storage

20   50   100   150
buffering capacity before storage
(ml n Na OH/100g DM to pH 7)

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Fig. 9:

Reduction of DM-losses by rise of buffering capacity through organic acids in aerob stored stillages and pulps (n = 119)

% DM-losses after storage

$y = 30,77 - 0,38x + 0,0019x^2$

10   50   100   150
(without additive)   buffering capacity before storage
(ml n Na OH/100g DM to pH7)

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In consequence of decreasing microbial activity the DM-losses became smaller. So we get a negative correlation between buffering capacity and DM losses (fig. 9).

Comparable dose-rate of different preservatives require equal mol amounts of undissociate acid.

Table 2:

dry matter losses (in %) by raising dose at % mol undis-soziated organic acids in solid wet potato stillage after 48 days storage (start-pH adjusted with HCl)

dose / acid	start-pH 3,9				start-pH 3,5			
	1%	2%	3%	4%	1%	2%	3%	4%
without	28,8 v				15,1 v			
oxalic -	15,8 v	16,9 v	16,3 v	14,6 v	13,4 v	14,7 v	18,0 v	13,1 v
malic -	17,0 v	16,2 v	15,9 v	18,5 v	14,6 v	13,7 v	14,9 v	19,4 v
formic -	22,3 v	21,6 v	19,8 v	23,2 v	19,6 v	20,6 v	22,3 v	20,0 v
bencoic -	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
acrylic -	24,3 v	6,1	< 1	< 1	21,0 v	7,9	< 1	< 1
sorbic -	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
propionic-	22,6 v	20,8 v	15,5 v	18,6 v	9,4 v	13,1 v	14,8 v	13,0 v

v = visible mouldy

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Acids with low dissociation constant, less than pH 3,8, like trichloracetic, oxalic, pyruvic, malic and formic acid did not prevent mould growth, even at higher application rate. At adjusted pH with hydrochloric acid in solid wet potato stillage the acids with higher dissociation constant like benzoic, acrylic and sorbic acid were inhibitors at doses from 1 or 2 % mol undissociated acid on. The DM losses were small and no visible mould appeared. Propionic acid in spite of his high dissociation constant of pH4,9 was less effective, probably due to its volatility (table 2).

Table 3:

Reduction of microbial counts by acid additives in 48days stored unmoulded solid wet potato stillage
(dose is conform to 2% mol undissoziated acid)

microbial groups	log viable counts per g dry matter			
	acid additive			
	without	0,37% bencoic	0,13% acrylic	0,13% sorbic
fungi	8,8	5,1	8,1	4,6
yeast	7,4	2,6	2,9	2,3
lactat assimi-lating yeasts	7,1	0	0	2,3
lactic acid bacteria	8,8	4,3	4,6	5,7
butyric acid clostridia	5,6	5,5	5,5	4,7

propionic acid: microbial counts higher than in untreated variety

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Table 3 shows the decrease of microbial counts in aerobe stabilized solid wet potato stillage with different preservatives at one dose of 2 % mol undissociate acid. The viable counts decreased but did not get zero.

So, the conservation effect is not the death of microorganisms but the inhibition of their growth.

The respective salts gave a similar effect as their acids. But the dose rate must be higher because the mol weight of the salts is higher than to the acid's mol weight.

For a given pH in any byproduct and the dissociation constant pK_a of the preservative you can calculate the undissociated part of the preserving acid as $\%\alpha_{pH}$:

$$\%\alpha_{pH} = \frac{(H^+) \cdot 100}{(H^+) \cdot K_a}$$

(H^+) = H-Ionenkonzentration of byproduct-pH
K_a = H-Ionenkonzentration of preservative-pK_a

From $\%\alpha$ the mol weight of the preservative in g and the desired effective dose in % mol undissociate acid (% mua) you can calculate the dose rate D_{pH} in g preservative per kg byproduct respectively as kg preservative per t byproduct :

$$D_{pH} = \frac{mol \cdot \% \; mua}{\% \alpha_{pH}}$$

In all our trials with the mentioned solid wet stillages we found correspondence between the calculated and the experimental measured minimal inhibition concentration (mic). Often an addition of table salt improved the preservation effect (table 4).

Table 4: Minimal inhibition concentration (mic) —dose of conserving means for aerobe stabilization of solid wet stillages with pH lower than 4,5

conservation means	mic (% of material)	judgement of effective strength
sorbic acid	0.34	good
benzoic acid	0.37	sufficient
acrylic acid	0.46	sufficient
propionic acid	1.27	unsafe
combined means:		
hydrochloric acid/sorbic acid	0.09 / 0.13	good
hydrochloric acid/benzoic acid	0.09 / 0.18	good
hydrochloric acid/acrylic acid	0.06 / 0.31	good
table salt/sorbic acid/propionic acid	0.5 / 0.03 / 0.3	sufficient
table salt/sorbic acid/propionic acid	0.5 / 0.02 / 0.5	sufficient
table salt/sorbic acid/propionic acid	1.0 / 0.02 / 0.3	sufficient
table salt/sorbic acid/propionic acid	2.0 / 0.08 / 0.3	good
table salt/K—sorbate	0.5 / 0.195	sufficient
table salt/K—sorbate	1.5 / 0.120	sufficient
table salt/K—sorbate/propionic acid	0.5 / 0.05 / 0.3	sufficient
table salt/K—sorbate/propionic acid	0.5 / 0.03 / 0.5	sufficient
table salt/K—sorbate/propionic acid	1.0 / 0.03 / 0.3	sufficient
table salt/K—sorbate/propionic acid	2.0 / 0.12 / 0.3	good

At this point of knowledge we started last year a preserving experiment in practical scale. We installed a customery plough-share-mixer in an ethanol pilot plant with an output of nearly 0.5 t solid wet potato stillage per hour. As preservative we took potassium sorbate, solved in water. The promotion and dosage of this solution could be managed very simply with a tube pump. The dose rate was 0,45 % potassium sorbate, a third more as the theoretical calculation; because we couldn't assess the mixing effect. Within 2 days we preserved 6 t solid wet potato stillage. This material was transported in open lorries nearly 100 km to the FAL-experimental station and had enough opportunities for microbial contamination.

Then the solid wet potato stillage was covered with plastic sheet, but only loose, not airtight like silage. After 2 weeks storage at the surface of the stack single spots of moulds were visible.

We determined the viable counts of microorganisms weekly. The mould growth was defected only on the surface. The reason is that we had stored the stillageat 35 °C and therefore the water was vaporized and condensed under the sheet. Therefore, in the upper layer the preservative was diluted

below the minimal inhibition concentration. In the feed shed open stored preserved stillage had grown no mould and no change of nutrients was observed over more than 3 months.

In a feeding experiment by FAL-Institute of Animal Nutrition with dairy cows in performance of 3o kg milk per cow and day were investigated the feeding value and the acceptance of this preserved solid wet potato stillage. The feeding ration was 9,3 kg DM as silage of grass and maize plus 7,4 kg concentrate. The cows intake ad libitum 2,8 kg DM of solid wet potato stillage, this are nearly 17 kg fresh matter. This replaced the same amount of concentrate without reducing the milk yield and its contents of protein and fat.

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