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STUDIES CONCERNING THE REACTION MECHANISMS FOR THE MAIN REDOX AGENTS FROM COW'S MILK

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Abstract

The redox agents from cow's milk are more important for milk processing and preserving. The studies for the mechanisms for main redox agents are important for establish the efficiency for processing and for keeping the organoleptic characteristics.

Keywords*: redox agents, cow's milk, and mechanisms*

Introduction

Generally, for a true image of redox processes, must be make more series of electrochemical analyses (to determinate the redox potential in different cases, verify the electrochemical kinetic –for know the E_H at different times, for proved the optimal "Key" moment necessary for total control the processes, for promoted the synergism or stopped the antagonism in to sequential processes, for partial conclusions), more series of biochemical analyses (for determine the oxidoreductases activity, the generator, activator or inhibitor chains) , more series of microbiological analyses (specify for micro-organisms that generate the oxidoreductase enzymes).

Experimental

In the case of biochemical analyses, the more attention can occur the substances that have in content the thiol groups (-SH) and can be reactive with oxidant reagents (like as Iodine), all depend by electrical load for the molecule with this group. This property can be use for cysteine dosage, for reduced glutathione dosage (Ciobanu, 2002).

The redox potential Eh for milk has a great importance, special for produce and keep the dairy products. For measure the Eh – redox potential, a Multitester C535 with glass electrode and platinum ring tip SP60X was used.

Results and Discussions

For raw milk, the Eh is positively, in the values from +0.20V to +0.30V. The redox potential could be establish from the polydispers system compounded by the aqueous phase (87.5%), the fat phase (lipids, fat acids), the colloidal phase (Casein fractions), the gas phase (CO_2). If the composition is changed (during a lactation cycle), the electrochemical and optical properties are changed. After 2 hours, the Eh redox potential for cow's milk can be decreased from +0.284V to 0.1307V (figure 1).

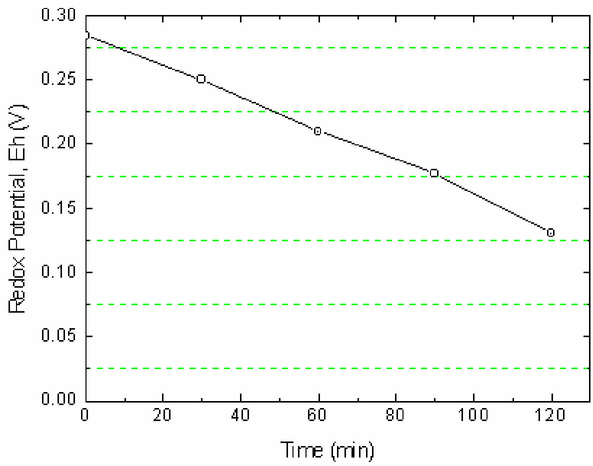

Fig. 1. Correlation for redox potential (V) and time (minutes) for fresh milk

From this figure clearly results that the milk has the oxidant properties. These changes follow exit the solved oxygen; in the forced deoxygenate case – with N_2 infusion, the Eh value can decrease to +0.05V.

Generally, the milk contains a natural reductant system formed by Xhantine oxidase (Mr =275,000) that reacts with many electron donors and acceptors. However, this enzyme is most active with substrates such as xhantine or hypoxhantine as donors and molecular oxygen as the electron acceptor.

During the oxidation of xhantine to uric acid, two electron steps to H_2O_2 by on electron transfer system reduce oxygen (figure 2 and 3).

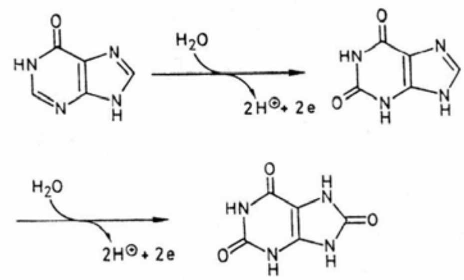

Fig. 2.The oxidation of xhantine to uric acid (Belitz,1999}

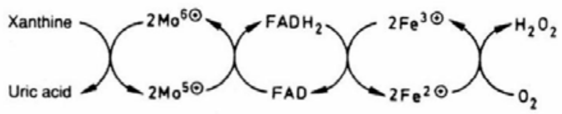

Fig. 3. The electronic transfer system (Belitz, 1999)

The reduced system generated by xhantine oxidase cannot be in natural airless media but can be evident through measure of Eh in inert atmosphere or in the case of contact with hydrogen acceptor (e.g. formaldehyde). This reaction can be evident by reduced metylen blue to colourless form.

During the keep time, the fresh raw milk can be registered (special in the first 3 hours), a descending curve-as result of saprophyte microorganisms action (figure 4). These microorganisms can participate in oxidative reaction or oxidative fermentation and the Eh for cow's milk are changed.

Follow add an electron donor (like as a formic aldehyde) this aldehyde can react with Xhantine oxidase from milk, the milk can be oxidises after 45 minutes, the redox potential fast decrease (after the decrease he can be establish in airless media).

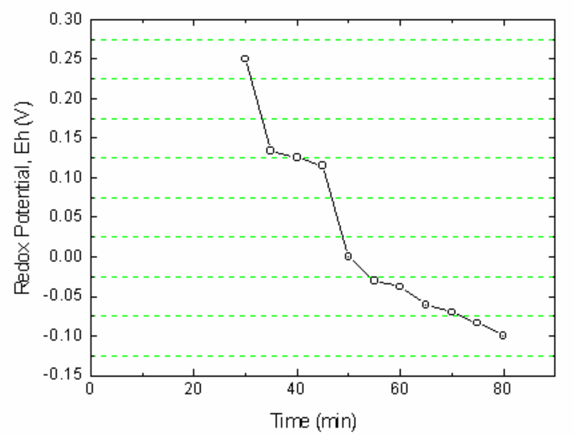

Fig. 4. Correlation for redox potential (V) and time (minutes) for milk attacked by formaldehyde

The redox system from milk can be destroyed during thermal treatments (over 80^{o} C) and in this case the value of redox potential for boiling milk are constant (table 1).

Table 1. Correlation for redox potential (V) and time (min.) for boiled milk

Eh (V)	+ 0.284	+ 0.284	+ 0.284	+ 0.284	+ 0.284
Time (min)	0	30	60	90	120

Xhantine oxidase is implicated in taste and stability of milk. The absence of xhantine oxidase and peroxidase prove the boiling milk. At sterilisation level (high temperature), appears another more different redox system and the difference are produced by lactoserum potential. The lactoserum proteins can free the thiol group in media, follow the cleavage the disulfide bonds. And cleavage of cystine disulphide bond can occur by nucleophilic attack on sulphur and through thiol and sulfinate intermediates way, yielding a dehydroalanine residue (figure 5).

Cleavage of cysteine residues with cyanides (nitrites in the case of strong pollution) is of inters since the thiocyanate formed in the reaction is cycled into a 3-acyl-2-iminothiazolidine under cleavage of the N-acyl bond.

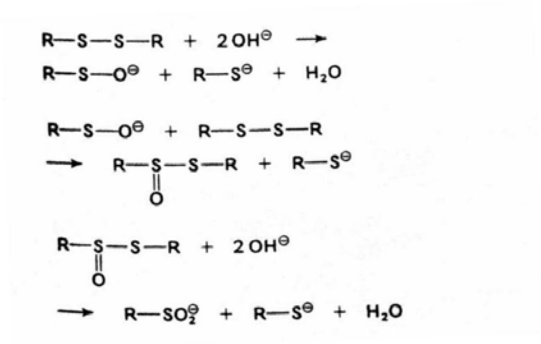

Fig. 6. Cleavage of cystine disulfide bond-mechanism (Belitz,1999)

In maxim 120 minutes the Eh value decreases from +0.284V to –0.163 V for strong pollution milk (figure 7).

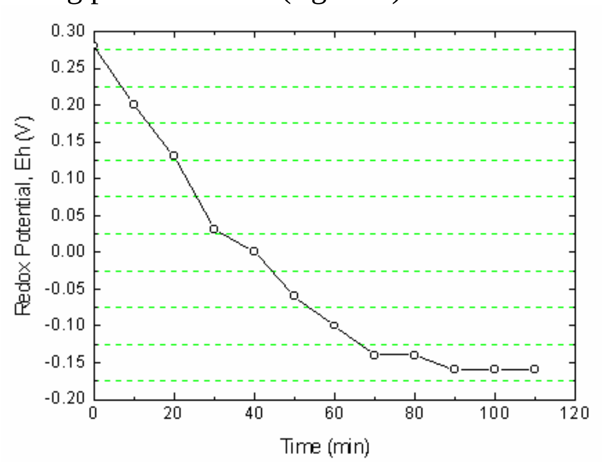

Fig. 7. Correlation for redox potential (V) and time (min) for strong pollution milk

Lactate peroxydase contain ferri-protophirin IX (hemin) as their prosthetic group and as the chromophore responsible for the brown colour of the enzyme. In catalytic reactions there is a change in the electron excitation spectra which is caused by a valence change of the iron ion; intermediary compounds I (green colour) and II (red colour) are formed during this change by reaction with H_2O_2 and reducing agent AH. Another single electron transfer completes the reaction cycle (figure 8).

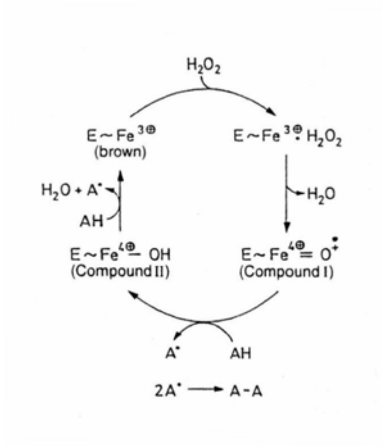

Fig. 8. Peroxidase reaction with H_2O_2 and a hydrogen donor (AH)-mechanism of catalysis (Belitz, 1999)

Conclusions

The study and the knowledge of mechanisms for redox agents from cow's milk are very important because:

- Gives the oxidative status and chemical stability
- Could be changed during and / or after milk processing
- Are most influenced by microorganisms, enzymes and influence the chemical composition and physical and chemical properties.

References

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