0 Introduction

- Stabilization and removal of haze from beer
  - Clear beer
  - Consumers demands
  - Improvement of filtration properties

- Fining agents
  - Isinglass or gelatine
  - Origin from animal sources
  - Isinglass is discussed

- Alternative
  - Pectin which is originating from plants
  - Certified kosher and halal
  - FAO/WHO and in the EU, no numerical acceptable daily intake (ADI)
  - United States, pectin is GRAS
1.1 Source and Application

- Pectin is a highly viscous, colloidal, plant derived polymer, which is extracted from pressing residues in the fruit processing (e.g. apple or citrus juicing)
- Used in the food and pharma industry as well as for cosmetics as gelling agent, thickener and stabilizer
- Application in food industry
  - Marmelade and jam (Fig. 1)
  - Jellybabies (Fig. 1)
  - Sweets
  - Joghurt
  - Pastries
  - Fining
  - …..
- Fiber and the most important gelling agent in the production of fruit products

Fig. 1: Products produced with pectin
1.1 Source and Application

- Pectin sources
  - Skin of citrus fruits (20-35 %) (Fig. 2)
  - Sunflower seed head (15-25 %) (Fig. 3)
  - Apple pomace (10-15 %) (Fig. 4)
  - Sugar beet pulp (10-20 %) (Fig. 5)

Fig. 2: Citrus fruits  
Fig. 3: Sunflower seed head  
Fig. 4: Dried apple pomace  
Fig. 5: Sugar beet pulp
1.2 Structure

- **Primary structure:** homogalacturonan
- **α-D-galacturonic acid monomers** form the linear backbone (α-1,4 glycosidic bond)
- **Main galacturonic acid chain** is linked by α-1,2 linked glycosidically bound L-rhamnose molecules
- **Smooth regions:** linear parts of the galacturonic acid chain (HG)
- **Hairy regions:** branched sugar side chains (RG I & II, XGA)

Fig. 6: Schematic structure of pectin. (RG I & II: Rhamnogalacturonan I & II, XGA: Xylogalacturonan, HG: Homogalacturonan, Kdo: 3-Deoxy-D-manno-oct-2-ulosonic acid, Dha: 3-Deoxy-D-lyxo-heptulosaric acid)
1.2 Structure

Fig. 7: Basic structures of pectin.

- The carboxyl groups of the galacturonic acid molecules can be esterified with methanol and the hydroxyl groups can be acetylated.
- Pectins are classified according to their degree of esterification (DE).
  - DE > 50 %: high methyl ester or high methoxyl pectins (HM).
  - DE < 50 %: low methyl ester or low methoxyl pectins (LM).
- Amidated low methyl ester pectins with a degree of amidation (DA).
1.3 Properties

High Methoxyl (HM) Pectins (DE> 50%)

- Gel formation in presence of sugar (> 55 %) and low pH values (2.8 - 3.4)
- Bonding zones through hydrophobic interactions of the methyl ester groups and H-bridges between the non-esterified carboxyl groups and the hydroxyl groups
- 3D-network encloses water: HM gels are not heat-reversible

Fig. 8: Bonding zones between HM pectin chains
1.3 Properties

Low Methoxyl (LM) Pectins (DE< 50%)

- Gel formation in presence of Ca\textsuperscript{2+}-ions or other bivalent cations
- Characteristic bonding zones: “egg-box-structure” (Fig. 9)
- DE and DA effect the calcium reactivity of the pectins
- Gels are heat-reversible
- Too high calcium concentration leads to “pre-gelling” and pectin precipitates as calcium pectinate
- Gelling properties depend on pH-value, amount of soluble solids and buffer ions
- Pectic acid: DE < 10 %

Fig. 9: „Egg-Box-structure“ of LM pectin gels
1.3 Properties

Low Methoxyl Amidated (LMA) Pectins (DE< 50%, DA = 15-25 %)

- Amide groups additionally form bonding zones through H-bridges
- The higher the DA, the more bonding zones can be formed and the gels are more firm
- LMA pectins can form all types of bonding zones simultaneously (egg-boxes, H-bridges, hydrophobic interactions)
- Gelling properties depend on pH-value, amount of soluble solids, buffer ions and calcium reactivity
2.1 Used Pectins

<table>
<thead>
<tr>
<th>Pectin</th>
<th>Degree of Esterification (DE) [%]</th>
<th>Degree of Amidation (DA) [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>41</td>
<td>11</td>
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<td>8</td>
<td>29</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>4.4</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 Preparation of the Pectin Solution


  - 2.5 g pectin was dissolved in 100 mL distilled H$_2$O (70°C) together with:
    - 0.5 % citric acid,
    - 1.5 % sodium citrate and
    - 1 % K$_2$O$_5$S$_2$

  - or solely 2.5 g pectin was dissolved in 100 mL distilled H$_2$O (70°C)

- Measuring colloidal stability and the associated formation of turbidity in beer
- Storage experiments by alternating cold and warm cycles (24 h, 0-2 °C/ 24 h, 60 °C)
2.3 Effect of the Ingredients

Fig. 10: Haze formation of pilsner beer during storage experiment; treated with 69 ppm SO₂, 180 ppm sodium citrate, 300 ppm pectin 6 before filtration.
2.4 Comparison with Commercial Stabilizers

Chill Haze

Permanent Haze

Fig. 11: Haze formation of pilsner beer during storage experiment; treated with 50 g/hL SG, 50 g/hL PVPP, pectin 6. Contact time of the substances prior to filtration: 30 min.

→ Addition of pectin w/o additives does not increase the colloidal stability
→ Furthermore no reduction of haze active polyphenols and proteins could be observed
3.1 Fining Activity of Pectin

Fig. 12: Settling tests with unfiltered Beer II treated with different pectins. Left: control.

Tab. 2: Haze values of different beer matrices after pectin application

<table>
<thead>
<tr>
<th>Pectin</th>
<th>Beer I EBC</th>
<th>Beer II EBC</th>
<th>Beer III EBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin A</td>
<td>1.97</td>
<td>3.33</td>
<td>-</td>
</tr>
<tr>
<td>Pectin B</td>
<td>1.95</td>
<td>4.52</td>
<td>93.35</td>
</tr>
<tr>
<td>Pectin C</td>
<td>-</td>
<td>6.64</td>
<td>9.06</td>
</tr>
<tr>
<td>Pectin D</td>
<td>1.95</td>
<td>4.68</td>
<td>5.16</td>
</tr>
<tr>
<td>Pectin E</td>
<td>1.75</td>
<td>1.52</td>
<td>4.75</td>
</tr>
<tr>
<td>Pectin F</td>
<td>-</td>
<td>1.85</td>
<td>6.7</td>
</tr>
<tr>
<td>Pectic acid w/o Pectin</td>
<td>30</td>
<td>99.99</td>
<td>99.99</td>
</tr>
</tbody>
</table>
3.2 Fining Efficiency and Applicability of Pectin

- The fining efficiency depends on
  - Chemistry of the used pectin (DE & DA)
  - Beer matrix (pH value, free Ca\(^{2+}\), sugar content, etc.)
- The application of pectin at the beginning of maturation showed problems:
  - Loss of a stable network
  - Partial solution of pectin in the beer matrix with filtration problems
- Influence of pectin dosage by pre-trials
  - Pectin addition at the end of fermentation
  - No influence on the fermentation by pectin could be observed
  - Removal of pectin floc by a centrifuge between CCT and lagering tank
3.3 Filterability and Filtration Performance

![Graph showing turbidity of unfiltered young pilsner beer after centrifugation.](image)

\[ y = -21.362x + 113.94 \]
\[ R^2 = 0.9705 \]

**Fig. 13**: Turbidity of unfiltered young pilsner beer after centrifugation

![Graph showing filtered volume of the centrifuged young pilsner beer in lab scale.](image)

**Fig. 14**: Filtered volume of the centrifuged young pilsner beer in lab scale

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3.3 Filterability and Filtration Performance

Fig. 15: Filtration performance of pilsner beer after centrifugation and filtration.

Fig. 16: Turbidity of pilsner beer after centrifugation and filtration.
3.4 Determination for Optimal Pectin Type

- Application of pectin type:
  - Finding optimum pectin type with respect to beer matrix
  - Development of a quick-test with respect to fining properties and reaction time of pectin type

Fig. 17: Haze of a given beer matrix after application of different pectin types and centrifugation (RCF= 12000),
3.5 Application of Pectin in the Brewing Process

- Good dispersion of pectin
- Short pectin reaction time (≤ 10 sec)
- Improved filtration performance of up to 31%
- Useful pectin application: dosage shortly after fermentation tank prior to centrifugation (Fig. 19)

![Diagram of the brewing process](image)

Fig. 19: Possible filtration concept of the application of pectin as a fining agent in the brewing process.
4.1 Pectin as a Substitute for Isinglass

2.5 h after addition

15 ppm Pectin A  39 ppm Isinglass

18.5 h after addition

15 ppm Pectin A  39 ppm Isinglass

Fig. 20: Semi-technical trials
4.1 Pectin as a Substitute for Isinglass

- Best sedimentation could be achieved with 15 ppm
- The fining effect of both pectin types are close to that of isinglass
- Application of pectin A resulted in better sedimentation
- Increased pectin dosage leads to more turbidity
- Surplus pectin can have a negative effect on the filtration
- TU & Herbstreith & Fox common patent pending

Fig. 21: Turbidity values of a sedimentation test in yeast-clouded beer
4.2 Pectin Dosage in Hazy Beer

- Additional centrifuge quick-tests were performed to figure out the right pectin dosage for the given hazy beer:

![Graph showing determination of ideal dosage](image)

**Fig. 22:** Correlation between pectin efficiency and its dosage. Green: Optimal area. Dashed: Ideal concentrations.
5. Conclusion

- Pectin has no stabilizing but very good fining effect
- The fining efficiency depends on the pectin type, amount and beer matrix
- Application of pectin is most effective shortly before separation of the hose beer
- Residual galacturonic acid was not detectable in the final beer
- Semi-scale trials show that the strong flow conditions in the CCT’s can disturb the sedimentation of the fluffy pectin floc
- The use of a centrifuge after pectin application is suggested
- By right selection and handling pectin can be an effective low-cost alternative to conventional fining agents like isinglass in the brewing process
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Thank You for Your Attention!

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