Pectin – An Alternative to Isinglass for Fining of Beer

Frank-Jürgen Methner | EBC Brewing Science Group | Vienna 2014

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. 4: Dried apple pomace

Fig. 5: Sugar beet pulp

Fig. 2: Citrus fruits

Fig. 3: Sunflower seed head

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)

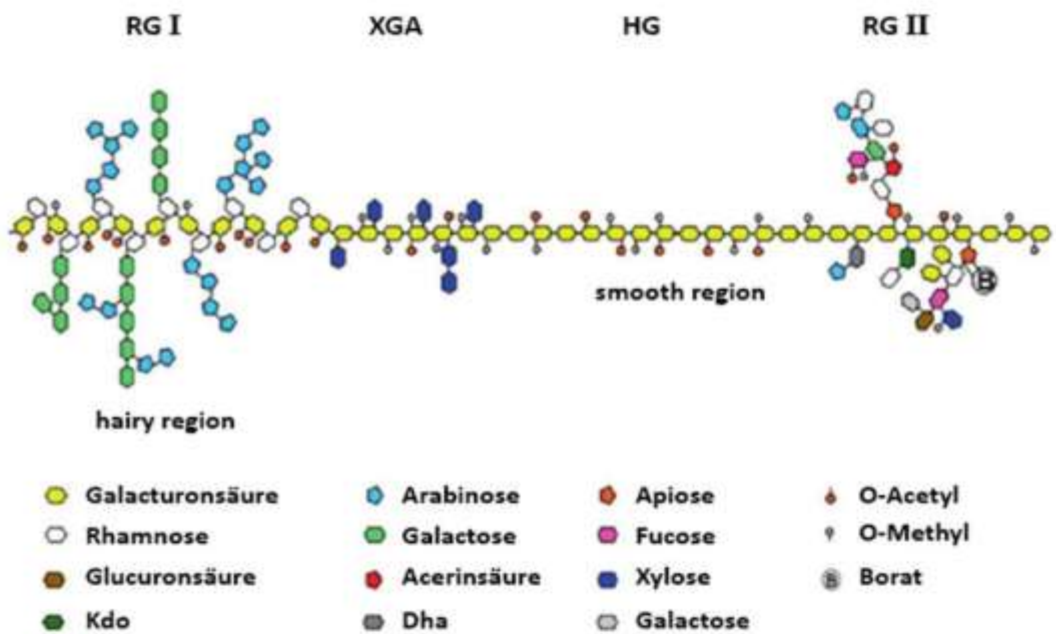

Fig. 6: Schematic structure of pectin. (RG I & II: Rhamnogalacturonan I & II,
XGA: Xylogalacturonan
HG: Homogalacturonan
Kdo: 3-Deoxy-D-manno-oct-2-ulosonic acid,
Dha: 3-Deoxy-D-lyxo-heptulosaric acid

1.2 Structure

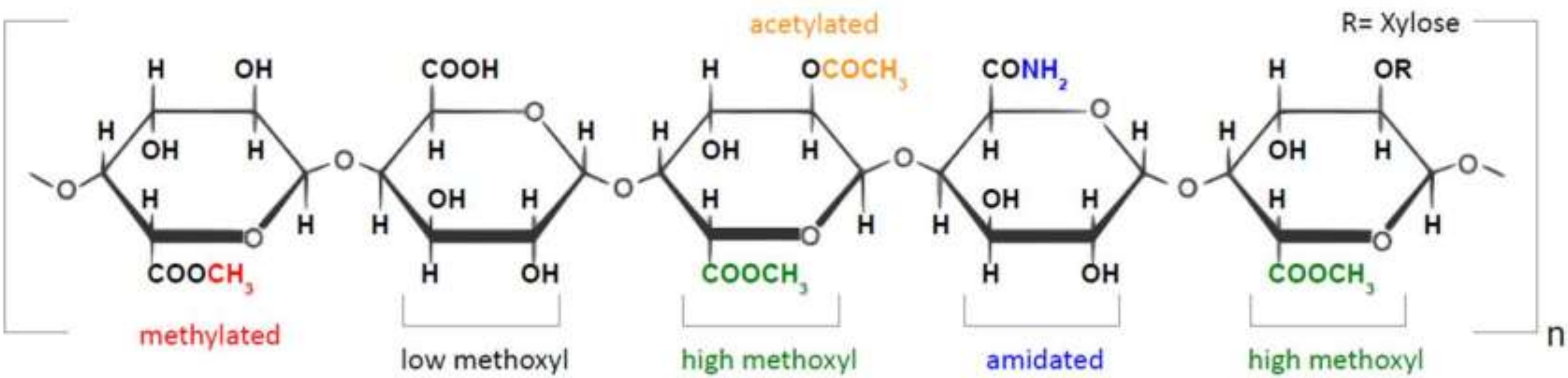

Fig. 7: Basic structures of pectin.

- 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)

Technische Universität Berlin

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

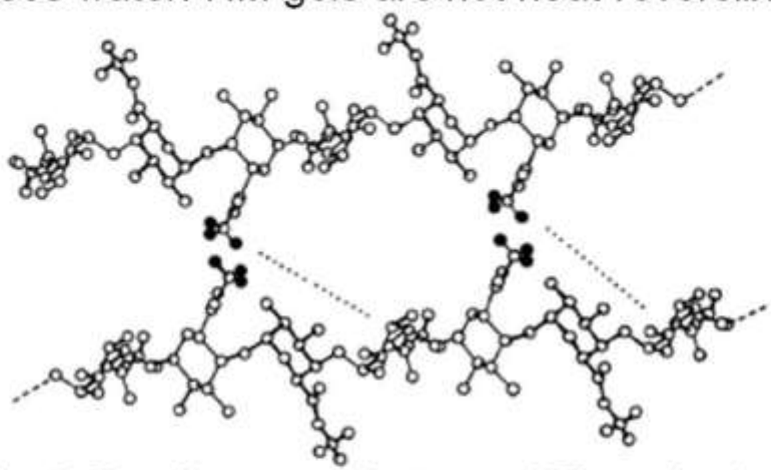

Fig. 8: Bonding zones between HM pectin chains

1.3 Properties

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

- Gel formation in presence of Ca^{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 %

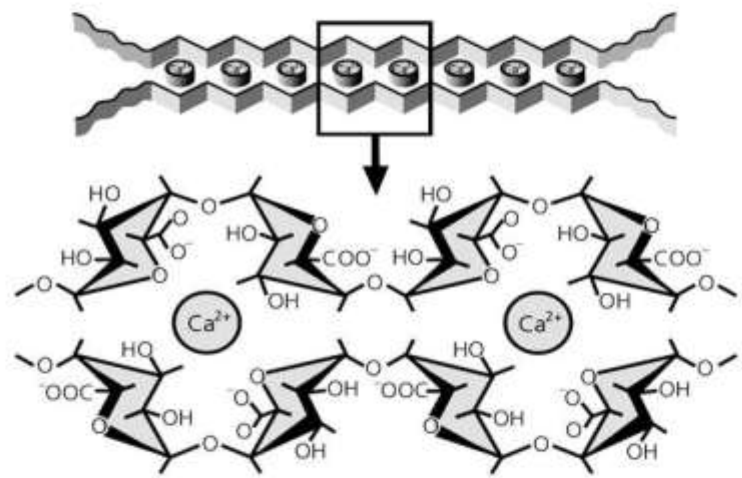

Fig. 9: „Egg-Box-structure“ of LM pectin gels

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

Tab. 1: Used pectins with different DE and DA (provided by Herbstreith & Fox KG).

Pectin	Degree of Esterification (DE) [%]	Degree of Amidation (DA) [%]
1	45	0
2	41	11
3	38	0
4	35	0
5	33	0
6	32	18
7	30	19
8	29	20
9	4.4	-

2.2 Preparation of the Pectin Solution

- Preparation of pectin solution according to Duan, W., Giandinoto, C., Goldsmith, M., Hosking, P., Lentini, A., Oliver, T., Rogers, P., Smith, P., Bacic, A., und Liao, M.L. Methods and compositions for fining beverages. Patent. Pub. No. WO/2006/032088 A2, 2006:

- 2.5 g pectin was dissolved in 100 mL distilled H_2O (70°C) together with:
  - 0.5 % citric acid,
  - 1.5 % sodium citrate and
  - 1 % $K_2O_5S_2$

- or solely 2.5 g pectin was dissolved in 100 mL distilled H_2O (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

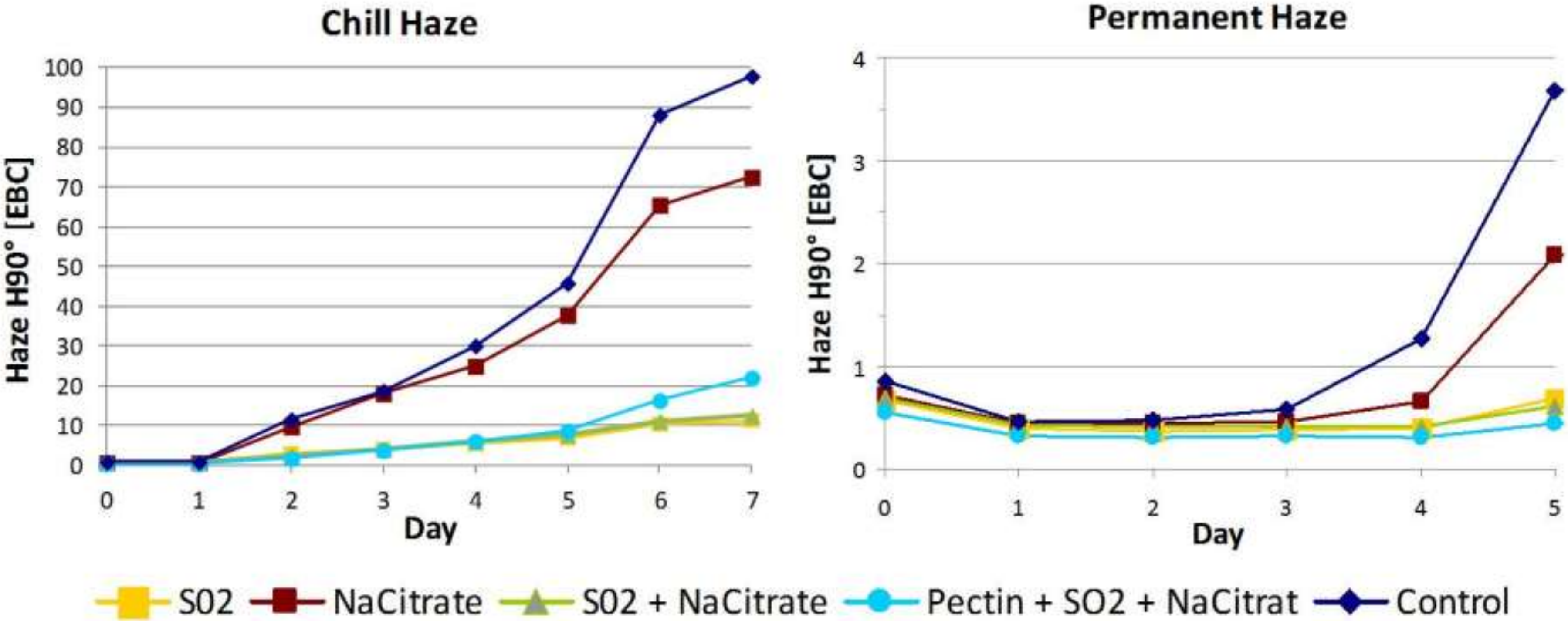

Fig. 10: Haze formation of pilsner beer during storage experiment; treated with 69 ppm SO_2, 180 ppm sodium citrate, 300 ppm pectin 6 before filtration.

Technische Universität Berlin

2.4 Comparison with Commercial Stabilizers

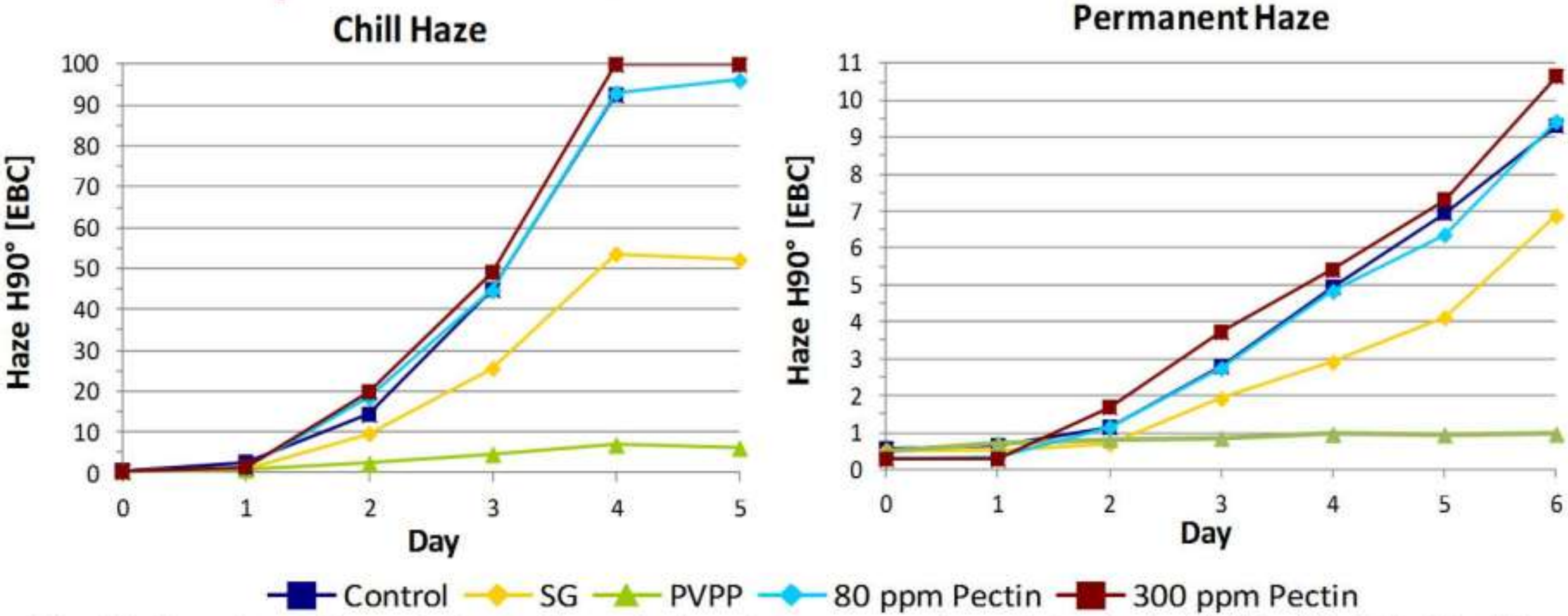

Fig. 11: Haze formation of pilsner beer during storage experiment; treated with 50 g/hL SG, 50 g/hL PVPP, pectin 6. Contact time of the substances prior to filtration: 30 min.

→ 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

Pectin	Beer I EBC	Beer II EBC	Beer III EBC
Pectin A	1.97	3.33	-
Pectin B	1.95	4.52	93.35
Pectin C	-	6.64	9.06
Pectin D	1.95	4.68	5.16
Pectin E	**1.75**	**1.52**	**4.75**
Pectin F	-	1.85	6.7
Pectic acid	-	6.12	99.99
w/o Pectin	30	99.99	99.99

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

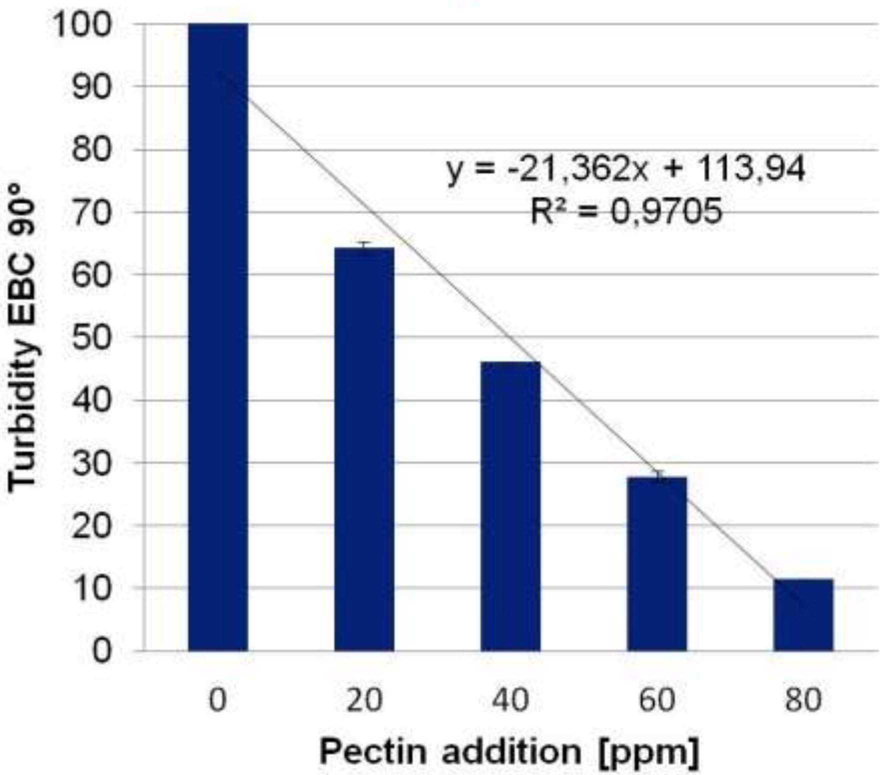

Fig.13: Turbidity of unfiltered young pilsner beer after centrifugation

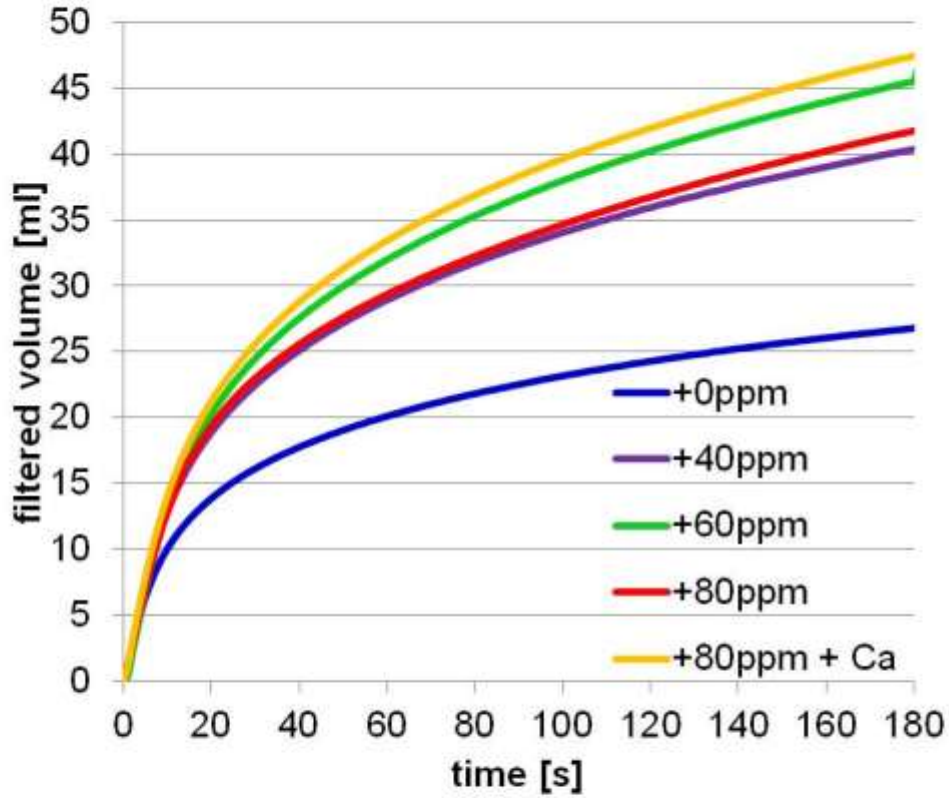

Fig.14: Filtered volume of the centrifuged young pilsner beer in lab scale

3.3 Filterability and Filtration Performance

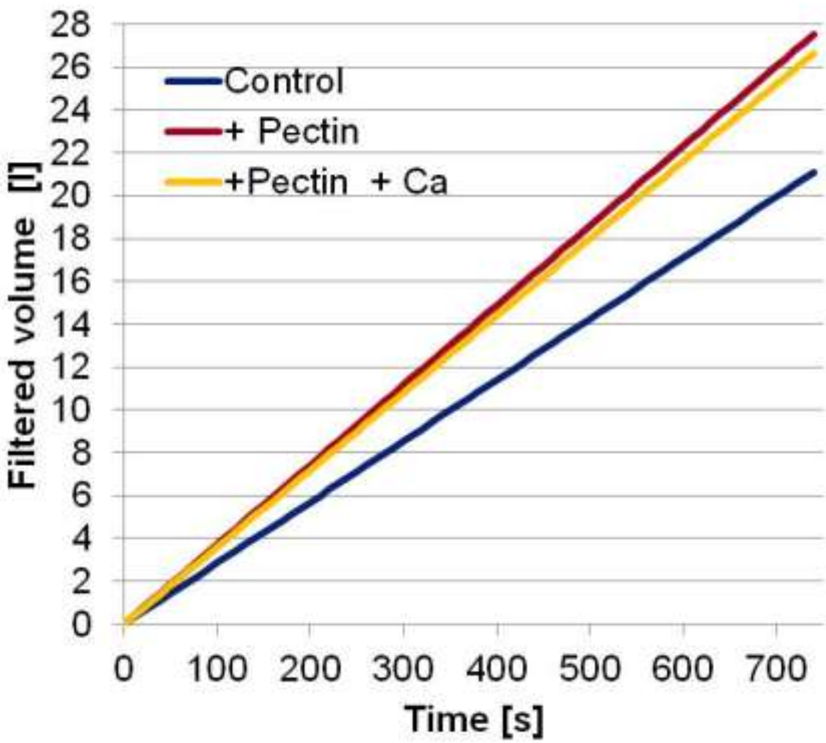

Fig.15: Filtration performance of pilsner beer after centrifugation and filtration.

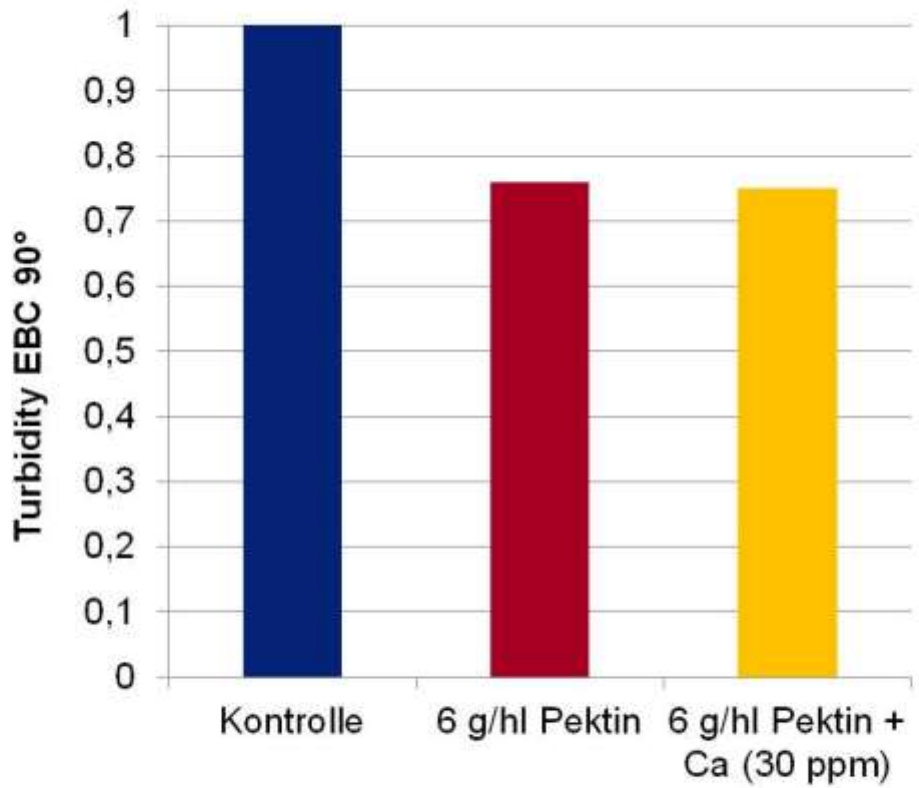

Fig.16: Turbidity of pilsner beer after centrifugation and filtration.

3.4 Determination for Optimal Pectin Type

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

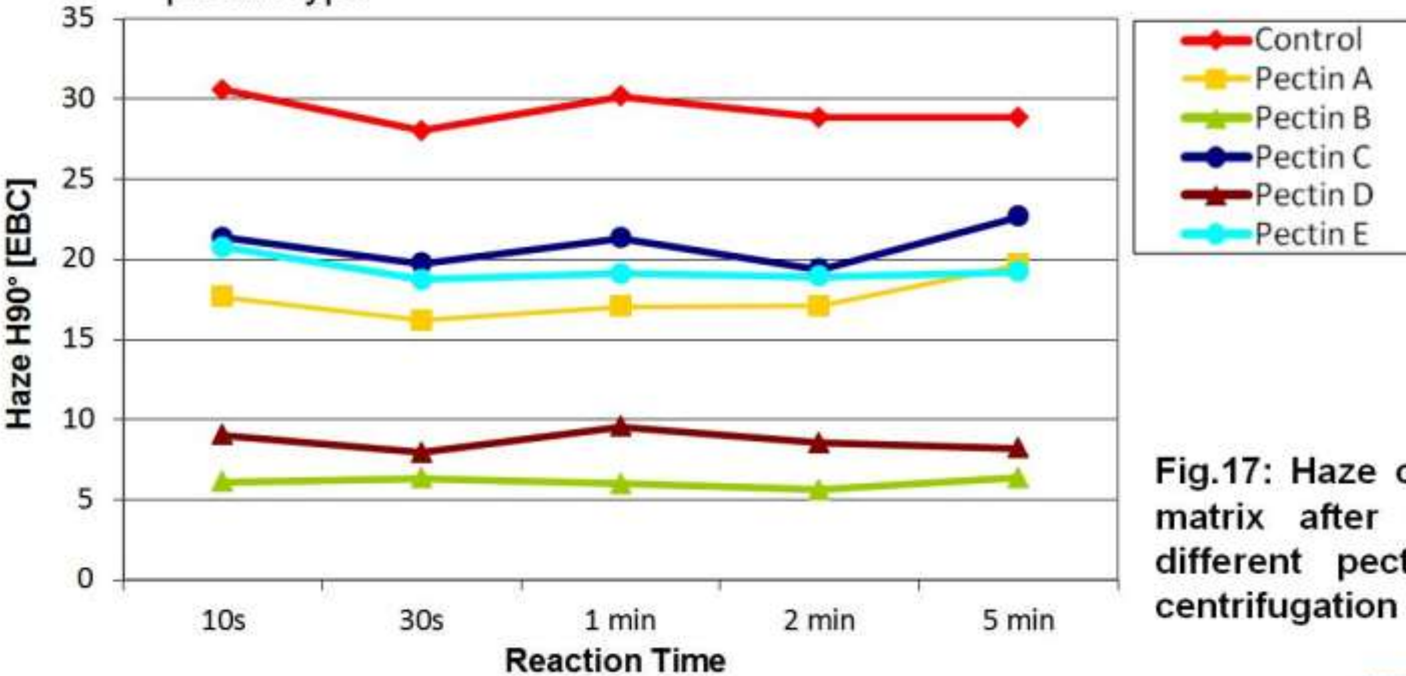

Fig.17: Haze of a given beer matrix after application of different pectin types and centrifugation (RCF= 12000),

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)

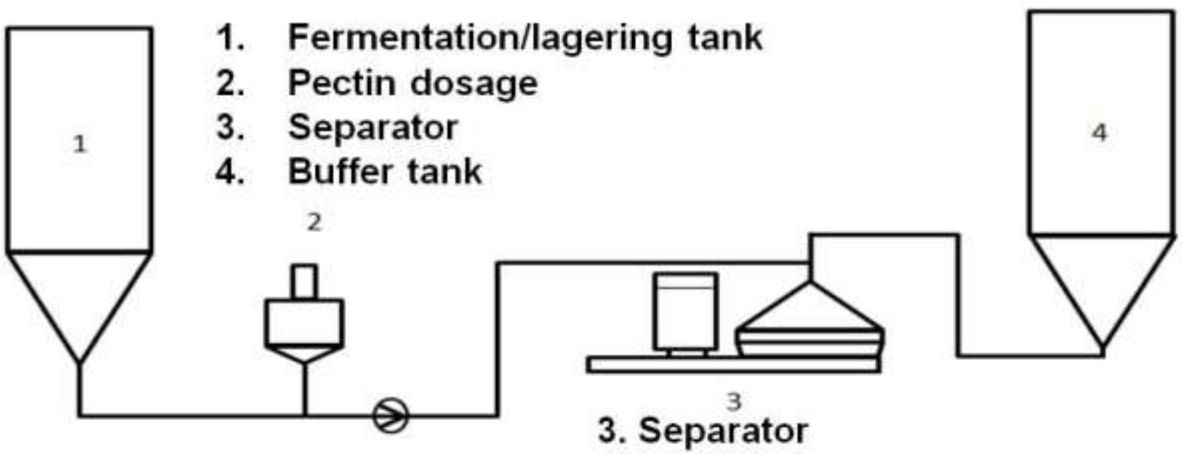

Fig. 19: Possible filtration concept of the application of pectin as a fining agent in the brewing process.

Technische Universität Berlin

4.1 Pectin as a Substitute for Isinglass

2,5 h after addition | **18,5 h after addition**

15 ppm Pectin A | 39 ppm Isinglass | 15 ppm Pectin A | 39 ppm Isinglass

Fig.20: Semi-technical trials

4.1 Pectin as a Substitute for Isinglass

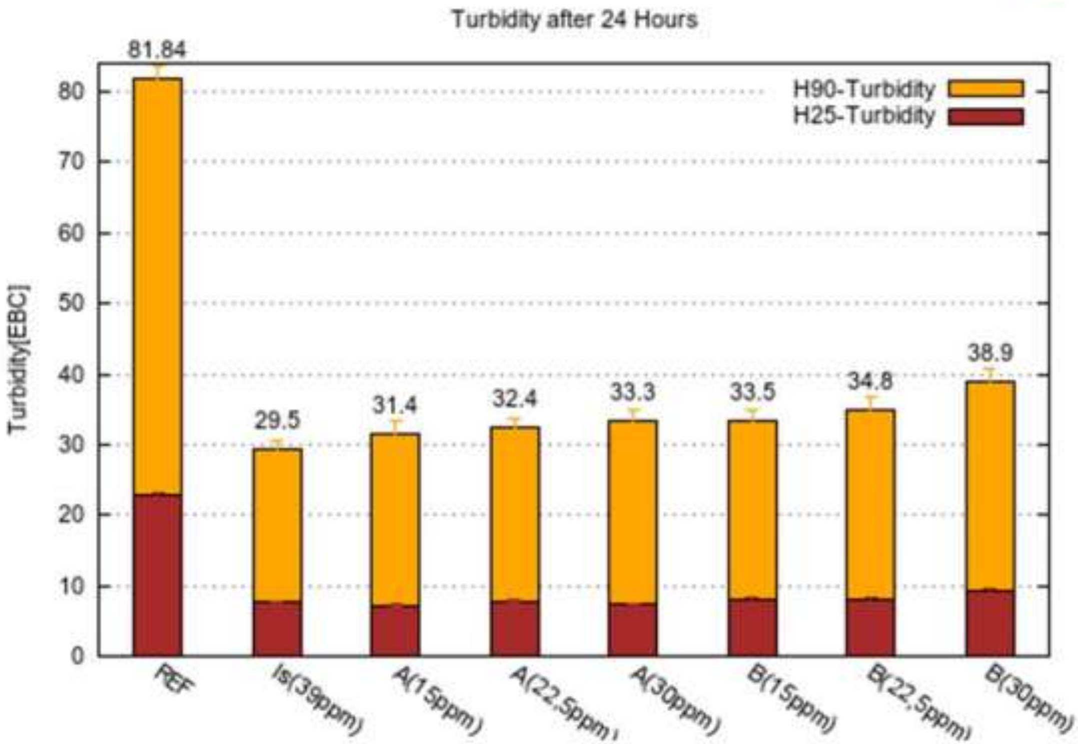

Fig.21: Turbidity values of a sedimentation test in yeast-clouded beer

- 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

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:

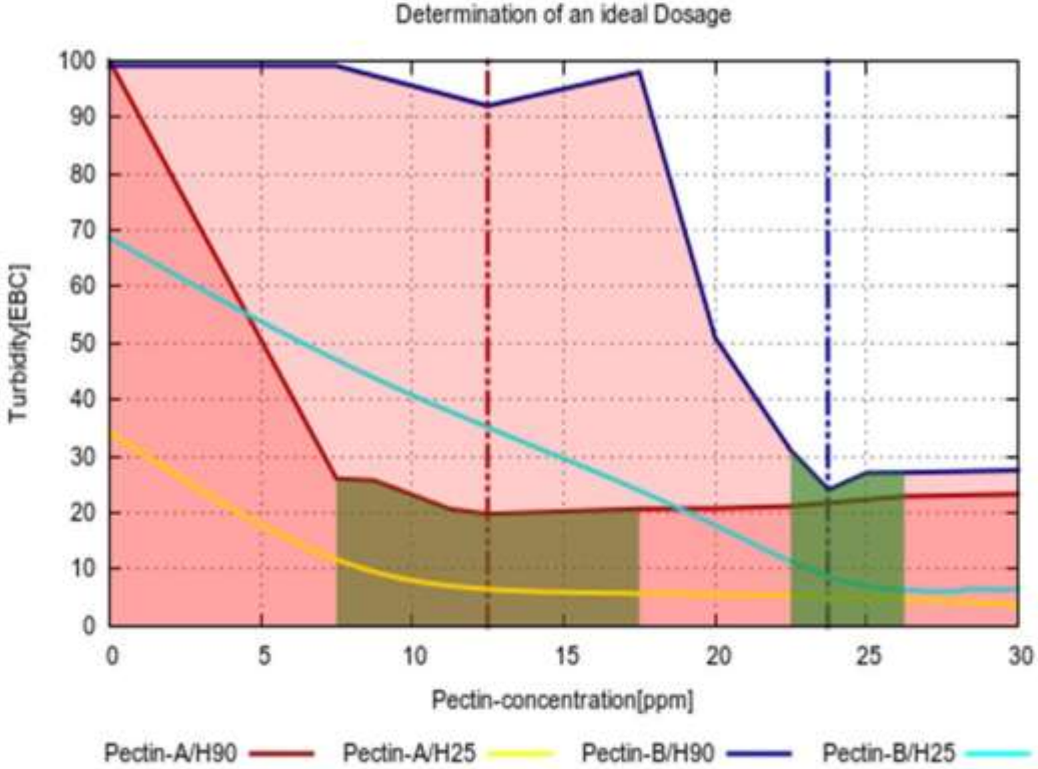

Fig.22: Correlation between pectin efficiency and its dosage.
Green: Optimal area
Dashed: Ideal concentrations.

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**

Acknowledgement

Dipl.-Ing. Thomas Kunz
Dipl.-Ing. Kerstin Rudolph
Hannes Gierth
Gunnar Dingel
Prof. Dr. Hans-Ulrich Endress (Herbstreith & Fox)

Technische
Universität
Berlin

Thank You for Your Attention!

For further Information, please contact:
frank-juergen.methner@tu-berlin.de
thomas.kunz@tu-berlin.de