WOLFGANG KUNZE

TECHNOLOGY

Brewing and Malting

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The chapters at a glance

Beer – the oldest drink		21
1	Raw Materials	35
2	Malt Production	109
3	Wort Production	199
4	Beer Production (Fermentation, Maturation, Filtration)	367
5	Filling the Beer	537
6	Cleaning and Disinfection	691
7	Finished Beer	707
8	Small Scale Brewing	763
9	Waste Disposal and the Environment	783
10	Energy Management in the Brewery and Malting	797
11	Automation and Plant Planning	849

Contents

Beer – The Oldest Fermented Drink for the Common People 25

1 Raw Materials 39
1.1 Barley 39
1.1.1 Barley Cultivation and Varieties 39
- Barley Cultivation 39
- Barley Varieties 40

1.1.2 Barley Cultivation 41
1.1.3 Structure of the Barley Grain 42
- External Structure 42
- Internal Structure 42

1.1.4 Composition and Properties of the Components 44
- Carbohydrates 44
- Proteins 48
- Fats (Lipids) 50
- Minerals 51
- Other Substances 52
- Barley Enzymes 53

1.1.5 Barley Evaluation 55
- Hand Evaluation 55
- Physical and Chemical Examinations 57
- Physiological Examinations 58

1.2 Hops 59
- Growing Regions 59

1.2.2 Harvesting, Drying, Stabilizing Hops .. 62
- Harvest 62
- Drying 62
- Stabilizing the Hops 62

1.2.3 Hop Cone Structure 63
1.2.4 Composition and Properties of the Hops Components 63
- Bitter Substances or Hop Resins 63
- Hop Oil 64
- Tannins or Polyphenols 66
- Proteins 67

1.2.5 Hop Evaluation 67
- Hand evaluation of the Whole Cone Hops 68
- Bitter Substance Content 68

1.2.6 Hop Varieties 69
1.2.7 Hop Products 70
- Hop Pellets 71
- Hop Extracts 73

1.3 Water 77
1.3.1 Water Cycle 78
1.3.2 Fresh Water use in the Brewery 78
1.3.3 Obtaining Water 79
- Extracting Groundwater 79
- Extraction of Spring Water 80
- Extraction of Surface Water 80
- Importance Private Water Supply ... 80
1.3.4 Water Requirements 81
- Drinking Water Requirements 81
- Brewing Water Requirements 82
- Significance of Individual Ions 84
1.3.5 Water Improvement Procedures 85
- Procedure to Remove Suspended Matter 85
- Removal of Dissolved Materials 86
- Improving the Residual Alkalinity of Water 87
- Water Sterilization 90
- Degassing of Water 91
1.3.6 Possibilities for Saving Water 93
1.4 Yeast 94
1.4.1 Structure and Composition of the Yeast Cell 94
1.4.2 Metabolism of the Yeast Cell 97
1.4.3 Yeast Multiplication and Growth 98
1.4.4 Characteristics of Brewing Yeasts .. 100
- Morphological Characteristics 100
- Physiological Differences 100
- Fermentation Technology Differences 100
- Systematic Classification 101
1.5 Adjuncts 102
1.5.1 Corn 102
1.5.2 Rice 103
1.5.3 Barley 104
1.5.4 Millet and Sorghum 104
1.5.5 Wheat 104
1.5.6 Sugar 105
1.5.7 Glucose Syrup 106
1.5.8 Coloring Sugar (also Couleur) 106

2 Malt Production 109
2.1 Receiving, Cleaning, Grading, and Transfer of Barley 109
2.1.1 Receiving the Barley 110
- Receiving from Trucks or Rail Cars 110
- Receiving from Ships 111
2.1.2 Cleaning and Grading the Barley ... 111
- Barley Pre-cleaning 112
- Magnetic Devices 113
- Dry Destoner 114
- Deawner 114
- Grain Cleaner 115
- Barley Grading 116
2.1.3 Transfer of Barley and Malt 120
- Mechanical Conveyors 120
- Pneumatic Conveyors 123
2.1.4 Dust Removal Equipment 125
- Cyclones 125
- Dust Filters 126
2.2 Drying and Storage of Barley 128
2.2.1. Respiration of the Barley 128
2.2.2 Drying the Barley 130
2.2.3 Cooling the Barley 130
2.2.4 Storing the Barley 131
- Storage in Silos 131
- Storage in Granaries 132
- Pest Infestations 133
2.3 Steeping the Barley 134
2.3.1 Processes During Steeping 134
- Water Uptake 134
- Oxygen Supply 137
- Cleaning 137
2.3.2 Steeping Vessels 137
2.3.3 The Steeping Process 142
2.4 Germination of the Barley 144
2.4.1 Processes Occurring During Germination 144
- Growth Processes 144
- Enzyme Formation 145
- Substance Conversion During Germination 147
- Conclusions for Performing Germination 154
2.4.2 Germination Methods 154
- Floor Maltings 154
- Pneumatically Operated Malting Systems 155
- Carrying Out Germination 165
- Control of Germination 166
2.5 Kilning the Malt 167
2.5.1 Changes During Kilning 167
- Lowering the Water Content 167

- Termination of Germination and Modification 167
- Formation of Color and Flavor Substances (Maillard Reaction) 167
- Formation of DMS Precursors and Free DMS During Kilning 169
- Influence of the Kilning Temperature and Duration 169
- Formation of Nitrosamines 170
- Enzyme Inactivation 171
2.5.2 Structure of the Kiln 171
- Heating and Ventilation of Kiln 171
- Older Type Two-floor Kilns 174
- Kilns with Dumping Floors 174
- Horizontal Kilns with a Loader and Unloader 175
- Vertical Kiln 176
2.5.3 Management of Kilning 177
- Production of Pilsner Malt 178
- Production of Munich Malt 179
- Unloading the Kiln 179
- Control of Kilning 179
2.6 Treatment of malt after kilning ... 179
2.6.1 Cooling of the Cured Malt 179
2.6.2 Malt Cleaning 180
2.6.3 Malt Storage 180
2.6.4 Malt Polishing 181
2.7 Yield During Malting 181
2.8 Malt Evaluation 181
2.8.1 Hand Evaluation 181
2.8.2 Mechanical Examinations 182
- Grading 182
- Thousand Kernel Weight 182
- Hectoliter Mass 182
- Sinker Test (Floaters) 182
- Glassiness 182
- Friability 182
- Acrospire Development 182
- Germination Capacity 183
- Density 183
- Carlsberg Calcofluor Method 183
2.8.3 Chemical-technological Examinations 183
- Water Content 183
- Congress Mashing Method 183
2.8.4 Malt Supply Contract 186
2.9 Special Malts and Malts from Other Cereals 187
2.9.1 Pilsner Malt (Pale Malt) 187
2.9.2 Dark Malt (Munich type) 187
2.9.3 Vienna Malt 188
2.9.4 Brumalt/Melanoidin Malt 188
2.9.5 Caramel Malt 188
2.9.6 Acid Malt 189
2.9.7 Short-Grown and Chit Malt 190
2.9.8 Smoked Malt 190
2.9.9 Diastase Malt 190
2.9.10 Roasted Malt 190
2.9.11 Roasted Malt Beer 190
2.9.12 Wheat Malt 191
2.9.13 Malt Extract 192
2.9.14 Malt from Other Bread Cereals 192
2.9.15 Sorghum Malt 193
2.9.16 Usage of different types of malt for various types of beer 194
2.10 Safety Precautions in Maltings 196

3 Wort Production 199
3.1 Milling the Malt 199
3.1.1 Pretreatment of the Malt 200
- Removal of Dust and Stones 200
- Weighing the Grist 201
3.1.2 Basic Aspects of Milling 203
3.1.3 Dry Milling 204
- Six-Roller Mills 204
- Five-Roller Mills 206
- Four-Roller Mills 206
- Two-Roller Mills 206
- Grist Mill Rollers 206
- Conditioned Dry Milling 208
- Grist Case 209
- Hammer Mills 209
- Other Milling Systems 212
3.1.4 Wet Milling 212
3.1.5 Steep Conditioning 214
3.1.6 Fine Comminution with Water 216
3.1.7 Evaluation of the Grist 217
3.2 Mashing 219
3.2.1 Transformations During Mashing ... 219
- Purpose of Mashing 219
- Properties of the Enzymes 219
- Starch Degradation 220
- Breakdown of the β-glucan 226
- Breakdown of Proteins 230
- Conversion of Fatty Acids (Lipids) 231

- Other Degradation and Breakdown Processes 233
- Biological Acidification 233
- Composition of the Extract 237
- Conclusions for Mashing Process .. 239
3.2.2 Vessels for Mashing 239
- Mash Vessels 239
3.2.3 Mashing-In 243
- Mashing Process 243
- Mashing-In Temperature 244
- Mixing the Water and Malt Grist . 245
3.2.4 Mashing Process 246
- Parameters to Consider when Mashing 247
- Infusion Process 250
- Decotion Process 252
3.2.5 Mashing Duration..... 264
3.2.6 Control of Mashing 265
3.2.7 Mashing Intensity 265
3.3 Lautering 265
3.3.1 Mashing-In Liquor & Sparge Liquor . 265
3.3.2 Last Runnings 267
3.3.3 Lautering with the Lauter Tun 268
- Structure of the Lauter Tun 268
- Design of Newer Lauter Tuns 268
- Operating Sequence when Lautering with a Conventional Lauter Tun ... 272
3.3.4 Lautering with the Mash Filter 275
- Conventional Mash Filters 275
- Mash Filters Next Generation 277
3.3.5 Spent Grains 285
- Transfer of Spent Grains 286
- Spent Grain Analysis 286
3.4 Wort Boiling 289
3.4.1 Processes During Wort Boiling 289
- Dissolution and Transformation of Hop Components 289
- Precipitation of Protein 290
- Evaporation of Water 290
- Wort Sterilization 291
- Destruction of all Enzymes 291
- Thermal Exposure of the Wort 292
- Lowering the pH of the Wort 292
- Formation of Reducing Substances (Reductones) 292
- Stripping of Volatile Flavor Substances 293
- Zinc Content of the Wort 295
- Copper Wort 295
3.4.2 Design and Heating of Wort Kettle . 295
- Brew Kettle with Direct Heating ... 296
- Brew Kettle with Steam Heating .. 296
- Wort Kettles with 299
- High-Temperature Wort Boiling ... 307
- Energy-Saving Wort Boiling Systems 307
- Modern Wort Boiling Systems 310
- Dynamic Low-Pressure Boiling 311
- Energy Consumption during Wort Boiling 320
- Vapor Condensate Cooler 324
- Pre-Run Vessel 324
3.4.3 Wort Boiling Process 324
- Boiling the Wort 324
- Addition of Hops 325
3.4.4 Monitoring the Casting Wort 329
3.5 Brewhouse Yield 330
3.5.1 Calculating the Brewhouse Yield ... 330
- Determining the Percent by Mass 330
- Determining the Mass of Extract per 1 hl Wort 332
- Converting the Hot Casting Wort Volume to Cold Wort Volume 335
- Calculating the Amount of Extract Obtained in the Brewhouse 336
- Determining the Brewhouse Yield (A_s) 336
3.5.2 Factors Affecting the Brewhouse 337
Yield 337
3.5.3 Evaluating the Brewhouse Yield 338
3.6 Brewhouse Equipment 338
3.6.1 Number and Arrangement 338
of the Vessels 338
3.6.2 Vessel Size 339
3.6.3 Vessel Material 339
3.6.4 Production Capacity of the Brewhouse 339
3.6.5 Special Brewhouse Types 340
- Brewhouses of Pub Breweries 340
- Integral Brewhouse 341
- Research and Training Brewhouses 341
3.7 Casting 342
3.8 Removal of the Hot Break 342
3.8.1 Coolship 342

3.8.2 Settling Tank 343
3.8.3 Whirlpool 343
- Operating Principle of Whirlpool .. 343
- Whirlpool Design 344
- Wort Clarification in Whirlpool 345
- Clarification with the Clarisaver ... 346
3.8.4 Separators 348
- Principle of Centrifugation 348
- Types of Centrifugal Separators (Centrifuges) 348
- Design and Operation of Self-Cleaning Separators..... 349
- Hot Wort Separation 351
- Removing the Hot Break With a Decanter..... 351
3.8.5 Recovery of the Cloudy Wort 351
3.9 Cooling and Clarifying the Wort . 352
3.9.1 Processes During Cooling 352
- Wort Cooling 352
- Formation and Optimal Removal of Cold Break 352
- Changes in Wort Concentration .. 353
3.9.2 Wort Cooling Equipment 353
- Structure of Plate Heat Exchanger 353
- Operating Principle of Plate Heat Exchanger 354
- Advantages of the Plate Heat Exchanger 356
3.9.3 Basic Principles and Performance of Wort Aeration 357
- Wort Aeration Methods 357
- Timing of Yeast Aeration 359
3.9.4 Equipment for Cold Break Removal 359
3.9.5 Wort Cooling Lines 359
3.10 Continuous Wort Production 360
3.11 Process control in brewhouse 362
3.12 Accident prevention in the brewhouse 363
3.12.1 Accident Prevention in the Mill 363
3.12.2 Accident Prevention when Working in Vessels 363
3.12.3 Accident Prevention when Working with Separators 364

4 Beer Production..... 369
4.1 Changes During Fermentation and Maturation 369
4.1.1 Yeast as the Brewer's Most Important Partner 369
4.1.2 Metabolism of the Yeast..... 371
- Fermentation of Sugar 371
- Protein Metabolism 376
- Carbohydrate Metabolism 378
- Mineral Metabolism 378
4.1.3 Formation and Breakdown of Fermentation By-products 380
- Diacetyl (Vicinal Diketones) 381
- Aldehydes (Carbonyles) 384
- Higher Alcohols 384
- Esters 384
- Sulfur Compounds 386
- Organic Acids 387
- Evaluation Criteria for Flavor Substances in Beer 387
4.1.4 Additional Processes & Conversions 388
- Changes in the Composition of the Proteins 388
- Lowering of the pH Value 389
- Changes in the Redox Properties of Beer 389
- Changes in the Beer Color 390
- Precipitation of Bitter Substances and Tannins 390
- CO_2 content of the Beer..... 390
- Clarification and Colloidal Stabilization of the Beer 390
4.1.5 Effects of Various Factors on Yeast 390
4.1.6 Flocculation of the Yeast (Break Formation) 392
4.1.7 Degeneration of the Yeast 393
4.1.8 Physiological Condition of Yeast 393
4.2 Yeast Cultivated in Pure Form 395
4.2.1 Basics of Yeast Propagation 395
4.2.2 Extraction of Suitable Yeast Cells ... 396
4.2.3 Propagation in the Laboratory 396
4.2.4 Yeast Propagation in the Brewery .. 398
- Pure Yeast Culture Plants 398
- Optimized Yeast Management According to Back 402
- Single-Vessel Pure Culture Procedure 403
- Open Yeast Propagation 404
4.3 Conventional Fermentation and Maturation 406

4.3.1 Fermenting Tubs – Open Fermentation Cellar Equipment 406
- Fermenting Tubs 406
- Layout of the Open Fermentation Cellar 406
4.3.2 Fermentation Cellar Yield 409
4.3.3 Open Primary Fermentation Process . 409
- Pitching 410
- Fermentation Management in the Fermenting Tub 412
- Attenuation 413
- Transfer Pumping from the Tun ... 416
4.3.4 Yeast Collection in the Tun 418
4.3.5 Processes During Beer Maturation in Conventional Tanks 419
- Saturation of the Beer with Carbon Dioxide under Positive Pressure 419
- Clarification of the Beer 420
4.3.6 Equipment in Conventional Storage Cellars 420
- Storage Cellar Equipment 420
- Storage Tanks 420
4.3.7 Storage in Conventional Tanks 422
- Transfer Pumping 422
- Pressure Regulation Bunging 423
4.3.8 Storage Vessel Tapping 424
- Establishing the Connection 424
- Pressure During Tapping and Emptying 424
4.3.9 Drawing Off from Conventional Tanks 425
- Blending Unit 425
- Pressure Regulator 425
- Recovery of Yeast Beer 425
- Deep Cooling of the Beer 425
- Fore- and Post-Run 426
4.4 Fermentation/Maturation in Cylindroconical Tanks (CCTs) 426
4.4.1 Construction and Installation of Cylindroconical Tanks 426
- Construction, Shape and Material of the CCT 426
- Size of CCT 427
- Installation and Arrangement of the CCTs 429
4.4.2 Cylindroconical Tank Fittings 430
- Control and Operating Elements and Safety Fittings 430
- Cooling of the CCT 438
- Possible Methods for Controlling and Automating Cooling 444
4.4.3 Fermentation and Maturation in a Cylindroconical Tank 447
- Special Points to Consider Fermentation and Maturation in CCTs 448
- Cold Fermentation – Cold Maturation 451
- Cold Fermentation with Specific Maturation in a CCT 452
- Warm Fermentation Without Pressure – Cold Maturation 452
- Pressure Fermentation 453
- Cold Fermentation – Warm Maturation 453
- Cold Primary Fermentation with Programmed Maturation 453
- Warm Primary Fermentation with Normal or Forced Maturation 454
4.4.4 Yeast Collection from the CCT 454
- Yeast Collection Time 454
- Yeast Collection Methods 456
- Treatment and Storage of the Yeast Crop 456
- Inspection of the Yeast Crop 458
4.4.5 Beer Quality Before Filtration 459
4.4.6 Beer Recovery from Surplus Yeast (Tank-Bottom Beer, Yeast Beer) 459
- Separation by means of Sedimentation or Filter Pressing 459
- Yeast Separation 459
- Beer Recovery Using a Decanter ... 460
- Membrane Filtration of the Yeast 461
- Treatment of the Beer from Surplus Yeast (Yeast Beer) 462
4.4.7 CO_2 Recovery 463
4.4.8 Immobilized Yeast 465
4.5 Beer Filtration 466
4.5.1 Filtration Methods 467
- Separation Mechanisms 467
- Filter Medium Carriers 468
- Filter Aids 468
4.5.2 Filter Designs 472
- Mass Filters 472
- Precoat Filters 472

- Layer Filters (Frame Filter) 486
- Membrane Filter 487
- Multi Micro System 488
- Filtration Applications 488
- Kieselguhr-Free Beer Filtration 488
4.6 Beer Stabilization 496
4.6.1 Biological Stabilization of Beer 496
- Pasteurization 497
- Flash Pasteurization (HTST) 497
- Hot Filling of Beer 499
- Pasteurization in Tunnel Pasteurizer 499
- Cold-Aseptic Treatment of the Beer 500
4.6.2 Colloidal Stabilization of Beer 501
- Nature of Colloidal Hazes 501
- Improving the Colloidal Stability of Beer 502
- Technological Measures for Improving Colloidal Stability 502
- Addition of Stabilizing Agents 503
- Dosing with Downstream Hop Products 510
4.6.3 Filtration Plant 511
4.6.4 Flavor Stability 513
- Aging Process 513
- Factors to Promote Flavor Stability 515
- Measures to Avoid Oxygenation During Filtration and Filling 516
- Measures to Prevent Negative Influences on the Flavor Stability After Filling 517
4.7 Carbonation of the Beer 519
4.8 Special Beer Production Methods 520
4.8.1 High-Gravity Brewing 520
4.8.2 Ice Beer Production 523
4.8.3 Processes for Removing Alcohol 525
- Membrane Separation Process 525
- Thermal Process/Distillation 529
- Suppression of Alcohol Formation 532
4.9 Accident Prevention During Fermentation, Maturation, and Filtration ... 534
4.9.1 Risk of Accidents due to Fermentation Carbon Dioxide 534
4.9.2 Work in Pressure Vessels 535
4.9.3 Working with Kieselguhr 536
4.9.4 General Accident Prevention Information 536

5 Filling the Beer 539
5.1 Filling Returnable Glass Bottles 539
5.1.1 Returnable Glass Bottles 539
- Advantages and Disadvantages of Glass Bottles 539
- Glass Bottle Production 539
- Bottle Shapes 539
- Bottle Color 541
- Surface Treatment 541
- Scuffing 542
- Bottle Aftercoating 542
- Light Glass Returnable Bottles 542
- Process Steps in the Filling of Returnable Glass Bottles 542
5.1.2 Cleaning Returnable Glass Bottles .. 542
- Sorting Empties 543
- Factors Influence Bottle Cleaning ... 543
- Bottle Washing Machines 544
- Cleaning Solution 558
- Cleaning and Maintenance Work on the Bottle Cleaning Machine .. 563
- Offloading New Glass Bottles and Cans 563
5.1.3 Inspection of the Cleaned Returnable Glass Bottles 564
5.1.4 Bottle Filling 570
- Principles of Filling 570
- Principles of Bottle Filling Machine Design 572
- Key Assemblies of Bottle Filling Machines 573
- Construction and Mode of Operation of the Filling Valves 576
- High-pressure Injection 588
5.1.5 Closing the Bottles 588
- Closing with Crown Corks 589
- Closing with a Swing Stopper 593
5.1.6 Cleaning the Filler and Closer 594
5.1.7 Inspection of the Filled and Closed Bottles 598
- Filling Height Verification 598
- Oxygen in the Bottle Neck 600
5.1.8 Pasteurization in Bottles 602
- Basics of Pasteurization in Bottles 602
- Essential Components of the Tunnel Pasteurizer 603
- Safety Measures During

Pasteurizing 604
5.1.9 Labeling and Foiling the Bottles 605
- Labels and Foils 605
- Label Adhesive 606
- Basic Principle of Labeling 608
- Labeling Machine Designs 609
- Head Folding with Foils 610
- Dating the Labels 610
5.2 Particularities when Filling Non-returnable Glass Bottles 612
5.2.1 Offloading New Glass Bottles 612
5.2.2 Rinsing (Flushing) 612
5.3 Filling PET Bottles 613
5.3.1 PET Bottles 613
- Structural Properties of PET 613
- Barrier Properties of PET 614
- Barrier Technologies 614
- Importance of the Scavenger 616
5.3.2 Production of PET Bottles 617
- Manufacturing the Preforms 617
- Streching and Blow-molding PET Bottles 617
- Inspection of the Produced PET Bottles 618
- Rinsing New Bottles 618
5.3.3 Transporting PET Bottles 618
5.3.4 Filling PET Bottles 620
5.3.5 Closing PET Bottles 620
- Plastic Screw Closures 620
- Aluminum Roll-on Caps 622
5.3.6 Labeling PET Bottles 624
5.4 Filling Plastic Bottles as Returnable Bottles 625
5.4.1 PEN/PLA 625
5.4.2 Cleaning of Returnable Plastic Bottles 626
5.4.3 Foreign Substance Inspection 626
5.5 Filling in Cans 631
5.5.1 Cans and Can Closures 631
5.5.2 Storing, Depalletizing, and Offloading the Empty Cans 634
5.5.3 Inspection of the Empty Cans 635
5.5.4 Rinsing the Cans 635
5.5.5 Filling of the Cans 636
- Mechanical Can Fillers 637
- Can Filler with Volumetric Filling 639
5.5.6 Closing the Cans 646
5.5.7 Cleaning the Can Filler and Closer 648
5.5.8 Widgets 648
5.5.9 Inspection of the Filled Cans 649
5.5.10 Pasteurization of Cans 650
5.5.11 Wraparound Labeling of Cans 650
5.5.12 Dating the Cans 651
5.6 Filling into Casks, Kegs, Party Casks, and Large Cans 652
5.6.1 Wooden Barrels and Barrel Filling 652
5.6.2 Kegs and Fittings 655
- Material, Shape, and Size of Keg 655
- Keg Fittings 656
- Plastic Kegs 656
5.6.3 Keg Cleaning and Filling 657
- Keg Cleaning 658
- Keg Filling 658
5.6.4 Keg Plants 660
5.6.5 Filling Small and Party Kegs 660
5.6.6 Filling Large Cans 661
5.7 Transportation and Packaging 662
5.7.1 Transport Containers 662
5.7.2 Treatment of Plastic Crates 664
- Rejecting Third-party and Damaged Crates and Bottles 664
- Washing the Crates 665
- Crate Magazine 665
5.7.3 Transport Technology 666
- Bottle and Can Transport 666
- Container Transport 670
5.7.4 Packing Technology 671
- Packing Head and Packing Tulips 671
- Packer Types 672
5.7.5 Palletizing and Depalletizing Equipment 677
- Robot Technology 677
- Design and Function of the Palletitzers and Depalletizers 677
- Stacking Full Package Pallets 680
- Pallet Transport Systems 680
- Pallet Set Positions 680
- Infeed and Discharge Equipment 680
- Pallet Magazines 681
- Pallet Inspection 681
- Securing Pallets 681
- Palletizing in Keg Filling 682
5.8 Complete Filling Plants 683
5.9 Beer Loss 687

5.9.1 Calculating the Amount of Sales Beer Produced ... 687
5.9.2 Stock Taking and Conversion to Sales Beer ... 687
5.9.3 Calculation of the Volume Loss ... 689
5.9.4 Calculation of Malt Usage in kg Malt/hl Sales Beer ... 690
5.9.5 Importance of the Loss and Ways to Reduce It ... 690

6 Cleaning and Disinfection ... 693
6.1 Materials and their Behavior Towards Cleaning Agents ... 693
6.1.1 Aluminum Vessels ... 693
6.1.2 Chrome-Nickel Steel Vessels, Pipes, and Fittings ... 694
6.1.3 Hoses and Seals ... 696
6.2 Cleaning Agents ... 697
6.3 Disinfectants ... 698
6.4 Cleaning and Disinfection using a CIP System ... 700
6.5 Cleaning Procedure ... 705
6.6 Mechanical Cleaning ... 706
6.7 Monitoring of Cleaning and Disinfection ... 707
6.8 Occupational Health and Safety for Cleaning and Disinfection ... 707

7 The Finished Beer ... 709
7.1 Beer Ingredients ... 709
7.1.1 Components of Beer ... 709
7.1.2 Beer and Health ... 712
7.2 Taste and Foam ... 713
7.2.1 Beer Taste ... 713
- Beer Aroma ... 713
- Palatefulness ... 716
- Carbonation ... 716
- Bitterness of the Beer ... 717
7.2.2 Beer Foam ... 717
7.3 Types of Beer and their Particularities ... 721
7.3.1 Top Fermented Beers ... 721
- Special Features of Top Fermentation ... 721
- Wheat Beer ... 724
- Berliner Weisse ... 728
- Altbier ... 728
- Kölsch ... 729
- Ale ... 729
- Stout ... 730
- Porter ... 730
- Belgian Beer Types ... 730
7.3.2 Bottom Fermented Beer Types ... 731
- Pilsner Type Beers ... 732
- Lager Beer/Full Beer ... 732
- Export ... 733
- Black Beer ... 733
- Festbier ... 734
- Ice Beer ... 734
- Märzen ... 734
- Bock Beer ... 734
- Double Bock Beer ... 735
- Alcohol-Free Beer ... 735
- Low-Carb Beer (Diet Beer) ... 736
- Light Beer ... 737
- Malt Drink ... 737
- Other Special Beer Types ... 738
- Mixed Beer Beverages ... 738
7.3.3 Trends Regarding the Development of Beer Types not Corresponding to the Purity Law ... 741
7.4 Quality Testing ... 744
7.4.1 Tasting the Beer ... 744
7.4.2 Microbiological Testing ... 745
7.4.3 Beer Analysis ... 749
- Analysis of the Original Gravity ... 749
- Measurement of Beer Color ... 753
- Measurement of the pH Value ... 753
- Measurement of the Oxygen Content in Beer ... 754
- Measurement of the Diacetyl Content in Beer ... 755
- Measurement of Head Retention . 755
- Measurement of the Carbon Dioxide Content ... 756
- Measurement of Bitterness Units . 757
- Measurement of the Haze Tendency ... 757
- Filterability of the Beer ... 758
- Other Tests ... 758
7.5 Process Measurement and Analysis Technology ... 759
7.5.1 Temperature Measuring Devices ... 759
7.5.2 Flow Meters ... 759

7.5.3 Filling Level Meters 760
7.5.4 Density Meters 760
7.5.5 Optical Online Measuring Technology 761
7.5.6 Oxygen Meters 763
7.5.7 pH Value Meters 763
7.5.8 Conductivity Meters 764
7.5.9 Threshold Value Probes 764
7.5.10 Pressure Meters 764

8 Small Scale Brewers 767
8.1 Pub Brewery (brew pub) 768
8.1.2 Considerations for Planning a Pub Brewery 770
8.2 Microbrewery 774
8.3 Contract Brewer 776
8.4 Home Brewer 776
8.4.1 The Legal Side of Hobby Brewing ... 776
8.4.2 Procuring the Raw Materials 776
8.4.3 Malt Production on a Small Scale 777
8.4.4 Beer Production for the Home Brewer 778
- Specifications 779
- Calculating the Bulk 779
- Calculation of the Mashing-In Liquor 782
- Calculating the Total Mash 782
- Lautering 783
- Calculation of the Sparge Liquor .. 783
- Wort Boiling 784

9 Waste Disposal and the Environment 787
9.1 Environmental Law 788
9.2 Wastewater 788
9.2.1 Wastewater Costs 788
9.2.2 Definition of Wastewater Terms 790
9.2.3 Wastewater Treatment 791
- Aerobic Wastewater Treatment Plants 791
- Anaerobic Wastewater Treatment Plants 792
- Amount and Composition of Brewery Wastewater 793
- Wastewater Treatment with Mixing and Equalizing Tanks 793
9.3 Residues and Waste 795
9.3.1 Spent Grain and Spent Hops 795
9.3.2 Trub 796
9.3.3 Surplus Yeast 797
9.3.4 Kieselguhr Sludge 797
9.3.5 Used Labels 797
9.3.6 Broken Glass 798
9.3.7 Beer Cans 798
9.3.8 Minor Sources of Waste 798
9.4 Emissions 798
9.4.1 Dust and Dust Emissions 798
9.4.2 Brewhouse Emissions 798
9.4.3 Exhaust Gas Emissions 798
9.4.4 Sound Emissions 798
9.5 Recycling PET Bottles 799
9.5.1 Inspecting the PET Recyclate 800

10 Energy Management in the Brewery and Malting 801
10.1 Energy Requirements in Malt and Beer Production 801
10.2 Steam Boiler Systems 802
- Fuels 802
- Steam 803
- Steam Boilers 805
- Steam Engines 809
- Combined Heat and Power Plants (CHP) 810
10.3 Refrigeration Plants 812
10.3.1 Refrigerants and Cooling Agents ... 812
- Refrigerants 812
- Cooling Agents 813
- Operating Principle Refrigeration .. 813
10.3.2 Compression Refrigeration Plants .. 817
- Operating Principle 817
- Evaporator 819
- Compressors 819
- Condensers (Liquefiers) 821
- Control Valve 822
- Ice Water Storage System 823
10.3.3 Absorption Cooling Machine 824
10.3.4 Space and Liquid Cooling 824
- Cooling of Conventional Fermentation and Storage Cellars 825
- Modern Refrigeration Plants 826
- Liquid Cooling 826
10.3.5 Advice for the Economical Operation of Refrigeration Plants 829

10.4 Electrical Systems 830
10.4.1 Supply of Electrical Energy 830
10.4.2 Power Factor cos j 831
10.4.3 Transforming the Electric Current .. 833
10.4.4 Safety Measures 833
10.4.5 Information Concerning the Economical Use of Electrical Energy 834
10.4.6 Other Energy Sources 834
10.5 Pumps, Fans, and Compressors .. 835
10.5.1 Pumps 835
- Rotary Pumps 835
- Positive Displacement Pumps 838
- Dimensioning of Pumps 842
- Speed Control of Pumps 842
- Lubricative Ring Seal 843
10.5.2 Fans and Compressors..... 844
- Fans and Blowers 844
10.5.3 Compressed Air Systems 844
- Air Compressors..... 845
- Air Dryers 848
- Pressure Tanks 849
- Compressed Air Network 849
- Air Filters..... 850

11 Automation and Plant Planning ... 853
1.1 Notes about the Use of Measurement and Control Technology 853
11.1.1 General Information 853
11.1.2 Requirements Concerning the Measurement Uncertainty of the Measuring Technology Used 853
11.1.3 Requirements for Installation Location and Cleaning/Disinfection 854
11.1.4 Operational Reliability and Plant Safety Requirements 856
11.1.5 Maintenance and Upkeep Requirements 856
11.1.6 Requirements for Automatic Controls 857
11.2 Plant Planning 859
11.2.1 Introduction 859
- General Planning Considerations 859
- General Information About the Planning Process 860
11.2.2 Basic Aspects of Plant Planning 862
11.2.3 Different Procedures for Plant Planning and Realization 864
11.2.4 Important Documents and Documentation in Plant Planning ... 865
- General Information 865
- The Procedure Scheme 866
- The Basic Mimic Diagram 868
- The Procedural Mimic Diagram 868
- The Piping and Instrumentation Mimic Diagram 868
- Piping and Assembly Plans 871
- The Process Description 871
- The Design of Implementation Documents 872
11.2.5 Notes on Contract Design 873
11.2.6 Commissioning and Performance Run 874
11.2.7 Project Conclusion 874
11.2.8 Project Documentation 875
11.3 Plant Design and Requirements . 876
11.3.1 General Information 876
11.3.2 Requirements for the Automation of Modern Plants 876
11.3.3 Hygienic Design of Pipework and Equipment 876
11.3.4 Operational Safety Requirements for Plants 877
- Media Separation 877
- Protecting the Plant Against Prohibited Pressures 879
11.3.5 Notes on the Design of Pipework ... 880
- General Information 880
- Pipe Connections 880
- Installing Pipework and Designing Pipe Holders 882
- Flow Velocity in Pipework/Pressure Losses 884
- Measures Against Water Hammer and Vibrations 887
- Venting Pipework, Oxygen Removal 887
- Design of Heat Insulation for Pipework 888
- Design of Pipe Outlets..... 888
- Protecting Pipework Against Frost and Plugging 888
- Dead Spaces in Pipework 889
- Steam Pipes 889
11.3.6 Notes on Pipe Connection, Use of Fittings, and Sample Collection 889

- General Information 889
- Manual Connecting Technique 890
- Fixed Piping 890
- Fittings for Pipes and Plant Components 891
- Sampling Fittings 893
- Fitting Designs 894

11.3.7 Notes on the Design and Operation of CIP Stations – Requirements for Automatic Cleaning and Disinfection 896

11.3.8 Notes Regarding the Storage of Chemicals 898

11.3.9 Notes Regarding the Surface Quality of Machines and Apparatuses 898

Appendix

Conversion of legally defined and commonly used measurement units 901

List of advertisers 904

Reference to diagrams and documents used in this book 905

Literature references 909

Index 920

3.2 Mashing

Mashing is the most important process in wort production. During mashing the grist and water are mixed (mashed), the contents of the malt are thereby brought into solution, and the extract is obtained with the help of enzymes.
The changes that take place during mashing are of great significance.

3.2.1 Transformations During Mashing

3.2.1.1 Purpose of Mashing

The large and small starch granules are still present in their original form contained in the barley, even after milling. Thus the purpose of mashing is to convert this starch fully into as much fermentable sugar as possible, as well as non-fermentable but soluble dextrins. All of the substances that go into solution are referred to as extract.
Examples of soluble substances are sugars, dextrins, minerals, and certain proteins. Insoluble substances include starch, cellulose, part of the high-molecular proteins, and other compounds that remain as spent grains at the end of the lautering process.
One attempts to convert as much insoluble material as possible into soluble compounds, in other words to get as much extract as possible, for economic reasons. This is indicated by the brewhouse yield (section 3.5) and the spent grains extract (section 3.3.5.2).
Not only the amount but also the quality of the extract is important however, because some compounds are unwanted whereas others (such as certain sugars or protein degradation products) are particularly desirable.
During mashing, most of the extract is produced by the activity of enzymes, which are allowed to act at their optimum temperatures.

3.2.1.2 Properties of the Enzymes

The most important property of enzymes is their activity in breaking chemical bonds in the substrates (Fig. 1.23). This activity depends on various factors.

Dependence of Enzyme Activity on Temperature and Exposure Time

The activity of enzymes depends above all on the temperature. It increases as the temperature rises and reaches its maximum at an optimum temperature specific to each enzyme (Fig. 3.23). Rapidly increasing inactivation occurs at higher temperatures due to unfolding of the three-dimensional structure of the enzyme (denaturation).

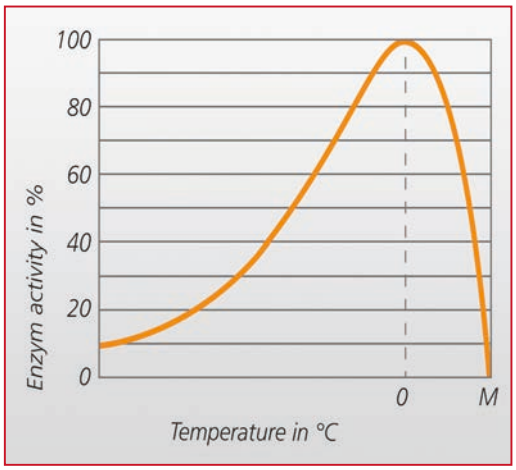

Fig. 3.23
Dependence of enzyme activity on temperature
O = optimum temperature M = maximum temperature

The inactivation and destruction of enzyme activity is greater the more the optimum temperature is exceeded. Enzyme activity drops considerably when the temperature is below the optimum.
The typical enzyme activity for a particular temperature is not constant. The activity decreases rapidly with time at higher temperatures, whereas at low temperatures it remains constant almost indefinitely (Fig. 3.24).

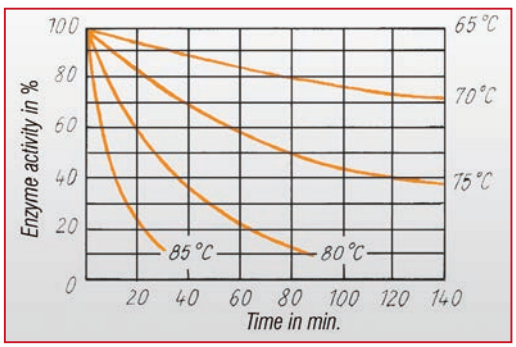

Fig. 3.24
Dependence of enzyme activity on exposure time

Dependence of Enzyme Activity on pH

Because the three-dimensional structures of enzymes also changes depending on the pH value, this influences the enzyme activity as well. It reaches its optimum at a specific value for each enzyme. The activity drops considerably at a higher and lower pH value (Fig. 3.25). The effect of pH on enzyme activity is generally not as large as the effect of temperature.

Dependence of Enzyme Activity on the Mashing Process

The activity of the enzymes and especially the β-amylases is dependent on the mashing process. Enzyme activity lasts longer in thicker mashes than in thinner mashes (Fig. 3.26). The part by weight of the grist load in the chart is in relation to the part by weight of the liquor (water).

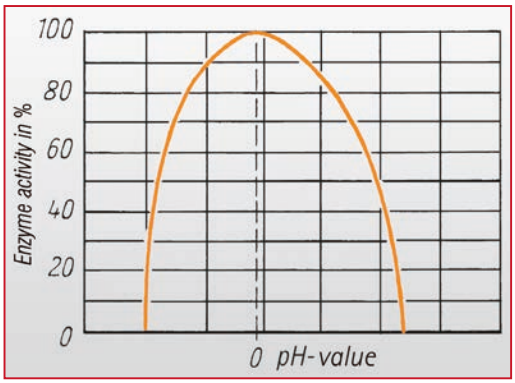

Fig. 3.25
Dependence of enzyme activity on pH value
O = optimum value

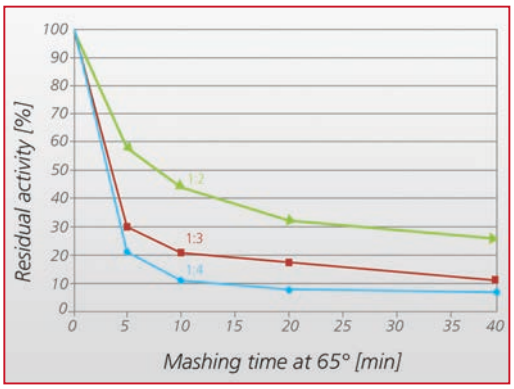

Fig. 3.26
Residual activity of the β-amylase at 65 °C depending on the liquor ratio (according to Narziß)

The degradation processes of importance for the brewer are

- the breakdown of starch,
- the breakdown of undissolved β-glucans,
- the breakdown of proteins,
- the conversion of fatty acids, and
- a number of other degradation processes.

3.2.1.3 Starch Degradation

The most important component of beer is the alcohol formed during fermentation from sugars. Therefore it is necessary to degrade the starch, primarily to maltose. Intermediate products, the dextrins, that are soluble but not fermented and remain in the beer are however always produced as well.

Starch must be degraded to sugars and limit dextrins that are not stained by iodine. Complete degradation to this state is necessary to obtain clear beer. Incomplete starch degradation leads to a higher content of dextrins and therefore to haze in the beer due to β-glucans.
Starch degradation occurs in three stages, the sequence of which is unchangeable but that merge into one another:

- Gelatinization
- Liquefaction
- Saccharification

Gelatinization

Large numbers of water molecules abruptly settle on the starch molecules at a certain temperature in a hot aqueous solution. This results in an increase in volume that causes the closely packed starch granules to swell and finally burst. The starch molecules lose their crystalline state and become amorphous (non-crystalline, unshaped) in this process. An increasingly viscous (sticky) solution is formed. The degree of the viscosity increase depends on the extent of water uptake and differs between cereal varieties. This process is called gelatinization (Fig. 3.27).
The gelatinization temperature of most cereals is between 65 – 80°C. However, the gelatinization temperature drops noticeably in the presence of starch-degrading enzymes. Malt starch normally

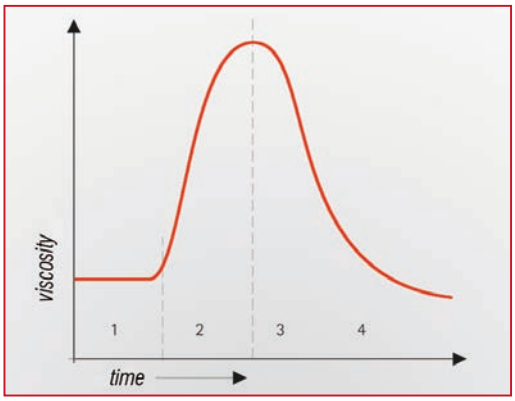

Fig. 3.27
Viscosity curve during starch degradation
(1) Mash before gelatinization
(2) gelatinization
(3) liquefaction
(4) saccharification

begins to gelatinize at 59 – 61°C. Small starch granules gelatinize at 1 – 3 K more than large granules. Complete gelatinization is the precondition for the complete breakdown of starch. If this is not the case, the results can include a lower extract yield, lower final attenuation, filtration difficulties, and starch haze. Gelatinization is not usually controlled.

Some types of starch, for example, rice starch, gelatinize at considerably higher temperatures (75 – 85°C) and swell up far more than malt starch. The gelatinized starch may scorch if this is not taken into account and can only be removed with great difficulty.

Rather than an enzymic reaction, gelatinization is a physical process and no catabolism occurs. Gelatinization is an important component of everyday food production (for example, when preparing pudding, making soups, or thickening sauces).

Gelatinized starch can be attacked more easily by the enzymes contained in the liquid (mash) because it is no longer packed in the solid starch granules. On the other hand, the degradation of ungelatinized starch, for example, during germination in the malting, takes several hours or even days.

Liquefaction

The long chains of unbranched and branched starch molecule chains composed of glucose residues (amylose and amylopectin) are very rapidly broken down by the α-amylase to form smaller chains (Fig. 3.28). This causes very rapid reduction of the viscosity of the gelatinized mash. The β-amylase on the other hand can only slowly degrade the long chains from the non-reducing end, and so degradation by this enzyme alone would take days. Also it would not be possible to break down the chains between the 1,6-bonds.
Liquefaction means the rapid reduction of viscosity of the gelatinized starch by α-amylase.

Saccharification

The α-amylase breaks down the chains of amylose and amylopectin to form shorter chains. Each split results in two chain ends that are immediately attacked by the β-amylase by splitting off dyads of glucose residues (= maltose) (Fig. 3.28, c). Other sugars such as glucose and maltotriose are produced in this process, in addition to maltose.

In all cases the breakdown stops two or three glucose residues away from the 1,6-bonds of the amylopectin because neither α-amylase nor β-amylase can break these 1,6-bonds. Malt does contain an enzyme, limit dextrinase, that can break the 1,6-bond as well as the 1,4-bond. It has no effect during mashing however, since it has an optimum temperature of 50 °C and is therefore inactive after gelatinization.
Accordingly the following summarizes the effects of malt amylases in starch degradation:
The α-amylase breaks down the long starch chains to smaller dextrins. It acts optimally at 70 – 74°C and is rapidly destroyed at 80°C. The optimum pH value is 5.6 – 5.8.

The β-amylase splits maltose off from the non-reducing ends of chains, but it also produces glucose and maltotriose (Fig. 3.29). It acts optimally at 62 °C (59 – 63°C) and is very sensitive to higher temperatures. At just 65°C it is inactivated relatively quickly. Thicker mash (1:2) is gentler on the β-amylase (Fig. 3.26). This is important in high-

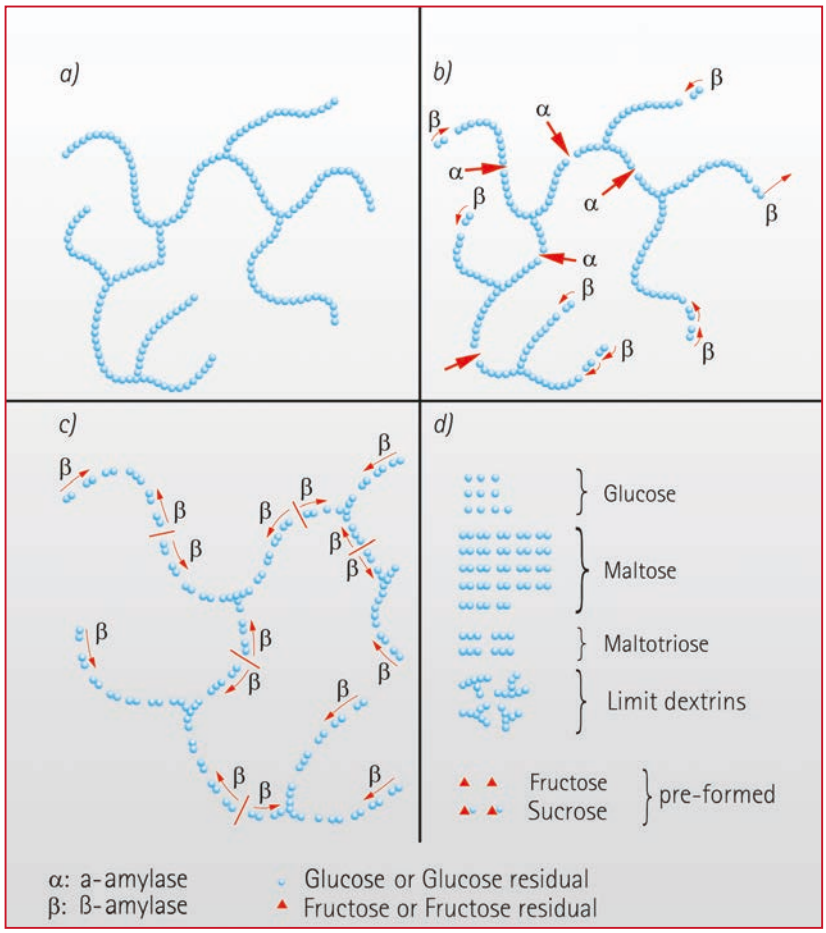

Fig. 3.28
Starch degradation during mashing using amylopectin as an example

gravity brewing. The optimum pH value is 5.4 – 5.5. β-amylase is more thermally stable in the presence of proteins.

Starch must be fully broken down into soluble products (sugar and limit dextrins). The complete breakdown of starch has to be monitored because residues of undegraded starch and larger dextrins cause a β-glucan haze in beer.

With a normal mashing process, about two thirds (65.5 %) of the sugar that goes into solution can be expected to consist of maltose, about 17.5 % maltotriose, and the same amount of saccharose, glucose, and fructose [3-8].
Starch degradation is monitored using 0.02N tincture of iodine (a solution of iodine and potassium iodide in alcohol). This procedure is called the *iodine test* and is always performed on a cooled mash sample. The iodine test is based on the fact that the iodine solution makes a blue to red color at room temperature with gelatinized starch and

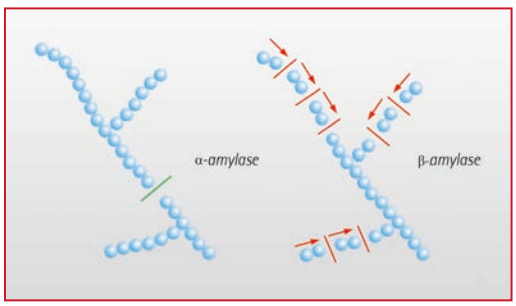

Fig. 3.29
Differences in the effect of α- and β-amylase

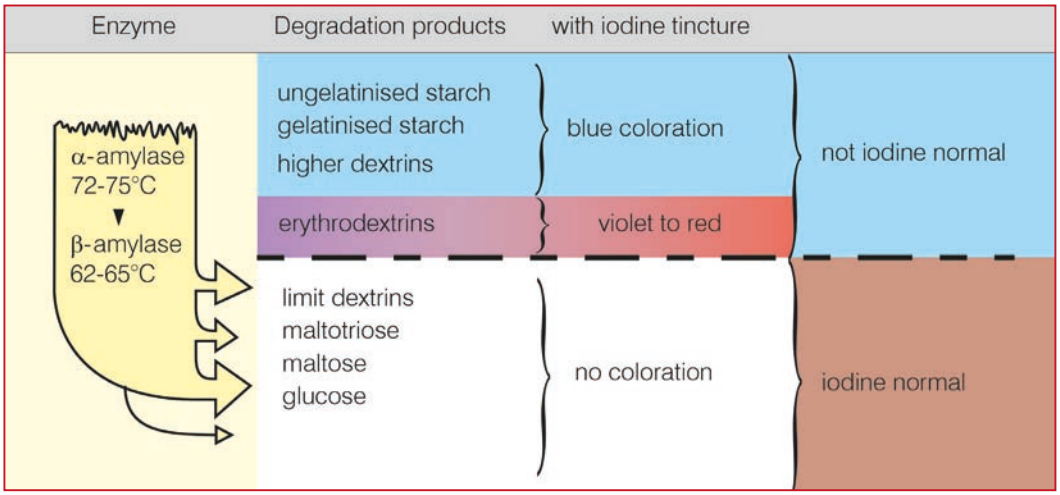

Fig. 3.30
Starch degradation to iodine normality

larger dextrins with more than 10 glucose residues, whereas all sugars and smaller dextrins from four to about ten glucose residues do not cause a discoloration of the yellow-brown tincture of iodine (Fig. 3.30). Higher to medium dextrins with about 11 – 12 glucose residues still produce a red to violet iodine coloration. This coloration is not always easy to see but it indicates a wort that is still not iodine normal.

A stricter iodine test according to W. Windisch monitors the presence of these dextrins by precipitation with ethanol, removal of the ethanol, redissolving, and coloration with iodine (iodine value). This method is used in problem cases.

The brewer must be able to evaluate the iodine test correctly. If discoloration of the iodine tincture no longer occurs when it is mixed with the mash sample, the mash is said to be iodine normal. Degradation of the starch molecules until the iodine normal condition is reached is called saccharification. Saccharification means complete degradation of the liquefied starch to maltose and iodine normal dextrins by the amylases.

The starch degradation products formed during mashing differ substantially with regard to fermentability by brewing yeast:

Dextrins are not fermented. These include all glucose chains up to 10 glucose residues.

Maltotriose is fermented by all top-fermenting yeast strains. However, maltotriose is not fermented by yeast until the maltose has been fermented, so preferably only during storage (late fermentation sugar).

Maltose and other disaccharides are easily and rapidly fermented by yeast (main fermentation sugar).

Glucose is the first sugar used by yeast (initial fermentation sugar).

The percentage of fermentable sugar in the total extract of the wort determines the final attenuation ($V_{s\,end}$). Since the final attenuation establishes the potential alcohol content of the beer, it has a decisive influence on its character.

The proportion of fermentable sugars is determined by the variable activity of the enzymes during mashing (Table 3.4). Thus the final attenuation that is subsequently possible is established while mashing.