

José J. G. Moura
Isabel Moura
Luisa B. Maia *Editors*

Enzymes for Solving Humankind's Problems

Natural and Artificial Systems in Health,
Agriculture, Environment and Energy

 Springer

Enzymes for Solving Humankind's Problems

José J. G. Moura, Isabel Moura and Luisa B. Maia Editors

Table of Contents

Preface

1. Carbon economy and carbon footprint

Júlia Seixas and Francisco Ferreira

1. Introduction
2. Carbon emissions at the core of climate changes
 - 2.1. Climate changes
 - 2.2. Global carbon emissions
3. Tackling climate change: from Science to political decisions
4. Carbon emissions reduction
 - 4.1. Carbon pricing and climate mitigation policies
 - 4.2. Carbon footprint assessment
 - 4.2.1. Concept
 - 4.2.2. Individual carbon footprint
 - 4.2.3. Urban scale
 - 4.2.4. Country scale
 - 4.2.5. Carbon footprint for organizations and products
 - 4.2.6. Carbon Footprint ISO standards and calculators
5. Final prospects

References

2. Carbon dioxide utilisation - the formate route

Luisa B. Maia, Isabel Moura and José J. G. Moura

1. The relentless rise of carbon dioxide
2. Formic acid - the stepping stone towards carbon dioxide utilisation
3. How to convert carbon dioxide to formic acid/formate? - The chemical way
4. How to convert carbon dioxide to formic acid/formate? - Exploiting the power of formate dehydrogenases
(Enzymes for solving humankind's problems)
 - 4.1. The biochemical way
 - 4.2. Formate dehydrogenases - Enzymatic machineries
 - 4.2.1. The metal-independent formate dehydrogenases
 - 4.2.2. The metal-dependent formate dehydrogenases
 - 4.3. Formate dehydrogenases - Mechanism of action
 - 4.3.1. The metal-independent formate dehydrogenases
 - 4.3.2. The metal-dependent formate dehydrogenases
 - a) Presently, several key points are well established
 - b) Two interrelated points are not yet consensual
 - c) Currently accepted mechanistic hypotheses

4.4. Formate dehydrogenases in the context of carbon dioxide utilisation

4.5. Formate dehydrogenases in action

5. Outlook

Acknowledgments

References

3. Carbon dioxide utilisation - bioelectrochemical approaches

Cristina Cordas, José J. G. Moura, Adrián Escapa and Raúl Mateos

1. Introduction

1.1 Electrochemical/bioelectrochemical advantages

2. Enzymatic systems and CO₂

2.1 Enzymes catalysing CO₂ reactions

2.2 Redox properties of CO₂-related enzymes

2.3 Bioelectrochemical enzymatic approaches for CO₂ utilisation

3. Microbial electrosynthesis: bioelectrochemical systems for CO₂ valorisation

3.1 Principles, mechanisms and metabolic pathways

3.2 Possible products

3.3 Challenges and future perspectives. Towards practical application

4. Conclusion and future perspectives

Acknowledgements

References

4. Acetogenic bacteria for biotechnological applications

Dennis Litty and Volker Müller

1. Introduction

2. Biochemistry of the Wood-Ljungdahl pathway

3. Acetogens as biocatalysts

3.1. *Acetobacterium woodii*

3.2. *Thermoanaerobacter kivui*

3.3. *Clostridium autoethanogenum*

3.4. *Clostridium carboxidivorans*

4. Metabolic engineering in acetogens

5. Conclusion

References

5. Nitrogen footprints and the role of soil enzymes

Claudia M. dS. Cordovil, Joana Marinheiro, João Serra, Soraia Cruz, Eve Palmer,

Kevin Hicks and Jan-Willem Erisman

1. Introduction

2. Soil quality, nutrients and crop production

3. Relevance of enzymes in soils

4. How enzymes influence nitrogen availability in soils

5. Soil characteristics influencing enzymatic activity

6. Effect of agricultural management practices (e.g. Tillage, organic fertilization)

7. Relation of enzymes with N and C cycles

8. The importance of nitrogen fertilization

9. Climate change impact and mitigation, and related effects on nitrogen footprint

10. Conclusion

References

6. Assembly and function of nitrogenase

Chi-Chung Lee, Martin Tillmann Stiebritz, Yilin Hu and Markus Walter Ribbe

1. Introduction
 2. Structure and properties of nitrogenase
 - 2.1. Structure and properties of Mo-nitrogenase
 - 2.2. Structures and properties of P- and M-cluster of Mo-nitrogenase
 3. Assembly of nitrogenase
 - 3.1. Overview: general scheme & major players
 - 3.2. Assembly of P-cluster
 - 3.3. Assembly of M-cluster
 - 3.3.1. Formation of the [Fe₈S₉C] L-cluster on NifB
 - 3.3.2. Maturation of the L-cluster on NifEN
 - 3.3.3. Insertion of M-cluster into the NifDK scaffold
 4. Mechanism of nitrogenase
 - 4.1. Overview: reactive properties and the Thornley-Lowe Cycle
 - 4.2. Spectroscopic insights into the mechanism of N₂ reduction
 - 4.3. Structural insights into the mechanism of N₂ reduction
 5. Conclusion and future prospects
- Acknowledgement
- References

7. Mitigation of laughing gas emissions by nitrous oxide respiring microorganisms

Jörg Simon

1. Introduction
 2. The organismic level: physiology of nitrous oxide respiring bacteria
 3. The genomic level: diversity of nos gene clusters
 4. The enzymatic level, part I: members of the nitrous oxide reductase (NosZ) family and their biogenesis
 5. The enzymatic level, part II: electron transport routes, bioenergetics and function of auxiliary Nos proteins
 6. Mitigation of N₂O emissions by bioaugmentation
 7. Engineering and isolation strategies for efficient and robust N₂O-respiring bacteria
 8. Concluding remarks and perspectives
- Acknowledgements
- References

8. Bacterial power: an alternative energy source

Bruno M. Fonseca, Ricardo M. Soares, Catarina M. Paquete and Ricardo O. Louro

1. Introduction
2. Extracellular electron transfer mechanisms
 - 2.1. Direct EET
 - 2.2. Mediated EET
3. Electroactive microorganisms
 - 3.1. *Shewanella*: a model organism
4. Extracellular electron transfer (EET) pathway
 - 4.1. Cytoplasmic membrane
 - 4.1.1. CymA
 - 4.2. Periplasmic space
 - 4.2.1. FccA
 - 4.2.2. STC
 - 4.3. Outer-membrane

- 4.3.1. MtrB
- 4.3.2. MtrA
- 4.3.3. Decaheme cytochromes MtrC and OmcA

5. EET enhancement in *Shewanella*

6. Conclusion

References

9. Biological production of hydrogen

Mónica Martins, Inês A. C. Pereira, Marcos Pita and Antonio L. De Lacey

1. Introduction

2. Enzymatic production of H₂

2.1. Enzymatic production of H₂ driven by reduced compounds

2.2. Electroenzymatic production of H₂

2.3. Enzymatic production of H₂ assisted by photocatalysts

2.3.1. Homogeneous photobiocatalytic production of H₂

2.3.2. Heterogeneous photobiocatalytic production of H₂

3. Microbial production of H₂

3.1. Biohydrogen production from organic wastes

3.2. Biohydrogen production from one-carbon substrates

3.2.1. Whole-cell biocatalysts for formate-driven H₂ production

3.2.2. Whole-cell biocatalysts for CO-driven H₂ production

References

10. Organometallic Chemistry control of hydrogenases

Marcetta Y. Darensbourg, Erica Lyon Oduaran, Shengda Ding, Allen M. Lunsford,

K.D. Kariyawasam Pathirana, Pokhraj Ghosh, and Xuemei Yang

Prologue

1. Introduction

2. Active site structures and mechanism

3. The mono-iron hydrogenase: from the historical conundrum of "metal-free" hydrogenase

3.1. A Bit of history

3.2. Determination of active site / cofactor structure

3.3. Active site binding and spectral responses

3.4. From active site structure to activity

4. The "hydrogenase" that comes from nitrogenase

5. Features of active sites of [FeFe]- and [NiFe]-H₂ases built into synthetic analogues for hydrogen production or activation

6. Concluding remarks

Acknowledgement

References

11. Selective enzymes at the core of advanced electroanalytical tools: the bloom of biosensors

Tiago Monteiro, Rosaceleste Zumpano, Célia M. Silveira and M. Gabriela Almeida

1. Introduction

2. Oxidases

2.1. Flavoenzymes

2.2. Multicopper oxidases

3. Dehydrogenases

3.1. NAD(P)H dependent dehydrogenases

- 3.2. Other dehydrogenases
- 4. Reductases
 - 4.1. The O₂ scavenging challenge
 - 4.2. Nitrogen oxide reductases
 - 4.3. Other reductase enzymes
- 5. Hydrolases
- 6. Summary and outlook
- Acknowledgments
- References

12. Current applications of artificial metalloenzymes and future developments

Jean-Pierre Mahy, Frédéric Avenier, Wadih Ghattas, Rémy Ricoux and Michèle Salmain

- 1. Introduction
- 2. Biotechnological applications of artificial metalloenzymes
 - 2.1. Oxidations
 - 2.1.1. Alcohol oxidation
 - 2.1.2. Amine oxidation
 - 2.1.3. Sulfide oxidation
 - 2.1.4. Catechol oxidation
 - 2.1.5. C-H oxidation
 - 2.1.6. Epoxidation
 - 2.1.7. Dihydroxylation
 - 2.2. Reductions
 - 2.2.1. HydrogEN PROduction
 - 2.2.2. Carbon dioxide hydrogenation and reduction
 - 2.2.3. Enantioselective cyclic imine reduction
 - 2.3. Artificial metalloenzymes for polymerization catalysis
 - 2.3.1. Polymerization of phenylacetylene
 - 2.3.2. Ring opening metathesis polymerization (ROMP) of olefins
- 3. Advanced developments of artificial metalloenzymes
 - 3.1. Cascade reactions
 - 3.1.1. Cascade reactions employing artificial transfer hydrogenase
 - 3.1.2. Cascade reactions employing other artificial reductases
 - 3.2. *In vivo* catalysis
 - 3.2.1. Olefin metathesis
 - 3.2.2. Polymerization of phenylacetylene
 - 3.2.3. Deallylation
 - 3.2.4. Enantioselective cyclic imine reduction
 - 3.2.5. C-N and C-C bond formation
 - 3.2.6. Diels-Alder reaction
- 4. Conclusions
- References

13. New phototrophic factories for resource recovery

Joana C. Fradinho, Virgínia C.F. Carvalho and Maria A.M. Reis

- 1. Introduction
- 2. Diversity of phototrophic organisms: overview
- 3. Wastewater treatment and resource recovery
 - 3.1. Microalgae-bacterial processes

- 3.2. Purple Phototrophic Bacteria processes
- 4. Nutrient recovery: phosphorous and nitrogen
 - 4.1. Phosphate recovery: the case of Photo-EBPR
- 5. Value-added products recovery: polyhydroxyalkanoates
 - 5.1. Phototrophic mixed culture PHA production: from lab to demo PPBPonds

Acknowledgments

References

14. Recent advances in enzymatic conversion of lignin to value added products

Giang-Son Nguyen, Anna Sofia Lewin, Francesca Di Bartolomeo and Alexander Wentzel

- 1. Lignin – structure and functions, sources and uses
 - 1.1. Occurrence of lignin and its composition and natural roles
 - 1.2. Types and sources of lignin
 - 1.3. Lignin valorization and added value of lignin derived products
- 2. Biocatalytic depolymerization of lignin
 - 2.1. Peroxidases
 - 2.1.1. Lignin peroxidases (LiPs) (EC 1.11.1.14)
 - 2.1.2. Manganese peroxidases (MnPs) (EC 1.11.1.13)
 - 2.1.3. Versatile peroxidases (VPs) (EC 1.11.1.6)
 - 2.1.4. Dye-decolorizing peroxidases (DyPs) (EC 1.11.1.19)
 - 2.2. Laccases (EC 1.10.3.2)
 - 2.3. Etherases
- 3. Discovery of new ligninolytic enzymes
- 4. Challenges of enzymatic lignin depolymerization for value-added products
- 5. Microbial lignin valorization
- 6. Conclusions and outlook

Acknowledgements

References

15. Enzymatic production of bioactive peptides from whey proteins: their active role and potential health benefits

Alexandra F.A. Salvado, Jorge H. Leitão and Luis P. Fonseca

- 1. Bioactive peptides
- 2. Protein source and research of bioactive peptides
- 3. Production of bioactive peptides
 - 3.1. Effect of industrial pre-treatment of proteins
 - 3.2. Protein hydrolysis – the "classical" approach
 - 3.2.1. Digestive enzymes
 - 3.2.2. Microbial proteases
 - 3.2.3. Fermentation processes
 - 3.2.4. Plant proteolytic enzymes
 - 3.3. Protein hydrolysis strategies
 - 3.3.1. Using free enzymes in solution
 - 3.3.2. Using immobilized enzymes
 - 3.4. Synthesis of peptides - the "rational" approach
 - 3.4.1. Chemical synthesis
 - 3.4.2. Recombinant DNA technology
 - 3.4.3. Enzymatic synthesis
 - 3.4.4. Bioinformatic tools on *in silico* design of bioactive peptides

4. Bioactive peptides isolation and purification methods
 - 4.1. Precipitation
 - 4.2. Membrane modules
 - 4.3. Chromatographic techniques
 5. Bioactive peptides derived from whey proteins
 - 5.1. Anticancer peptides
 - 5.2. Antidiabetic peptides
 - 5.2.1. Inhibition of the DPP IV enzyme
 - 5.2.2. Inhibition of α -glucosidase
 - 5.3. Antihypertensive peptides in the cardiovascular system
 - 5.4. Antimicrobial peptides
 - 5.5. Antioxidant peptides
 - 5.6. Immunomodulatory peptides
 - 5.7. Opioid peptides
 6. Conclusions and perspectives
- Acknowledgments
- References