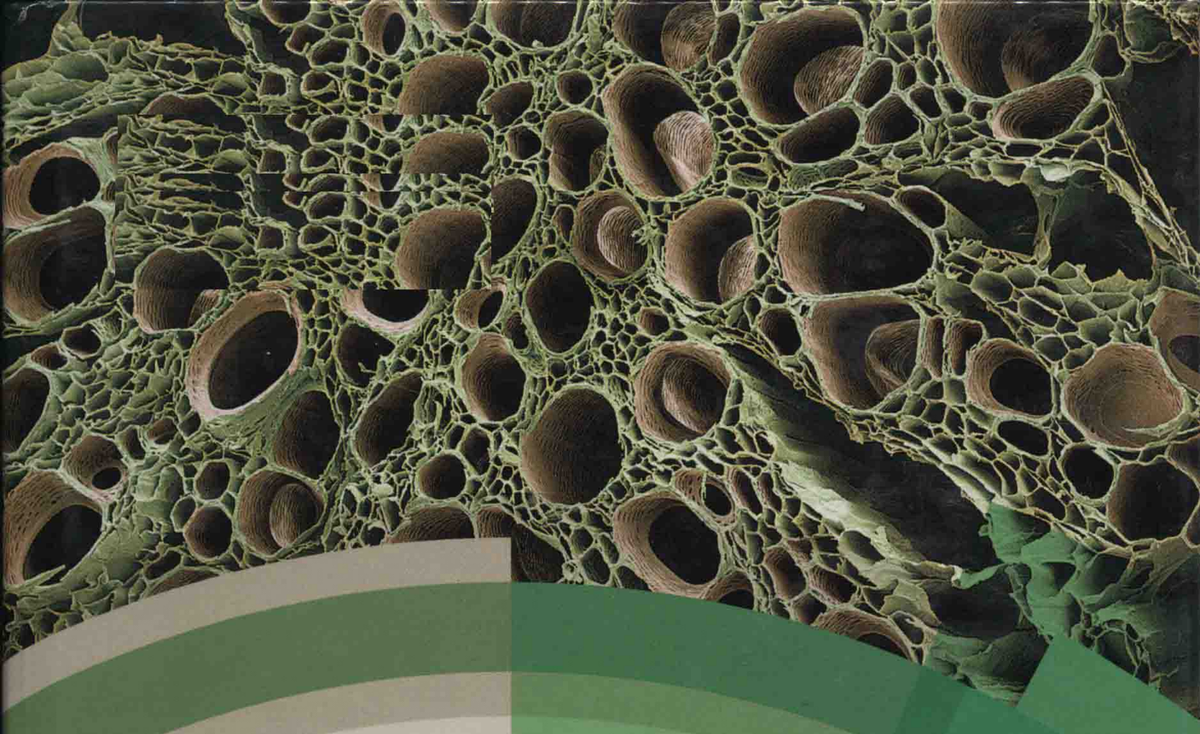

RSC Energy & Environmental Series

Catalytic Hydrogenation for Biomass Valorization

Edited by Roberto Rinaldi

ROYAL SOCIETY OF CHEMISTRY

Catalytic Hydrogenation for Biomass Valorization

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Preface

Catalytic hydrogenation and hydrogenolysis are key reaction classes in the upgrading of biomass molecules into platform chemicals and synthetic fuels. Over the last two decades, the catalytic community has devoted a considerable amount of experimental and computational work to develop new methodologies and processes, and to understand the intricacies of hydrogenation and hydrogenolysis performed on bioderived molecules. The main objective of this book is to bring together and synthesize the scattered information from around the world through the perspective of leading researchers in the field. This book is intended to serve as an excellent source of information in addition to providing a platform for critical discussion connecting the multitude of fields related to catalytic hydrogenation. To facilitate a well-balanced discussion pertaining to the several subfields, the overlap among the chapters was kept to a minimum. To guide the reader through the array of opinions commonly found in this field, related topics are clearly linked throughout this book. Finally, I present this book with my sincere gratitude to the authors for their contributions. Without their valuable insight, the creation of this book would not have been possible. Furthermore, I am indebted to Katrina Hong and Marco Kennema for discussions and a careful review of this work. These students provided me with valuable comments and constructive criticism, helping me to edit a book worthy of being accessible key literature to even young undergraduate students in the field.

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CHAPTER 1

Hydrogen: Economics and its Role in Biorefining

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1.1 Introduction

Hydrogen is perhaps one of the most promising energy carriers of the future. In renewable energy systems with high fractions of intermittent supply (*e.g.* wind power and solar thermal energy), potential surplus electricity could be converted into hydrogen through water electrolysis. This hydrogen can be used in a wide variety of applications. The most often discussed option, the reconversion of hydrogen into electricity, be it by gas turbines or by fuel cells, appears to be rather unattractive, due to the low round-trip efficiencies. Electrolysis – based on the process scale – can be estimated to have an efficiency of about 60% (if higher efficiencies are given, they are typically relative to the cell level). A recent NREL analysis, based on questionnaires given to manufacturers, indicate a mean efficiency value of 53% for the system.[1] Considering that the fuel-cell efficiency on the systems' level and gas turbines (not available for hydrogen yet) is estimated at about 50–60%, the overall round-trip efficiency is thus reduced to slightly above 30%. It will certainly be possible to improve this figure to some extent, but substantial losses in the round trip from electricity to electricity will invariably always be present. Therefore, the use of "renewable" hydrogen – not for the reconversion into electricity, but rather as a feedstock for the chemical industry, in oil refineries, or in biorefineries – appears to be promising. For

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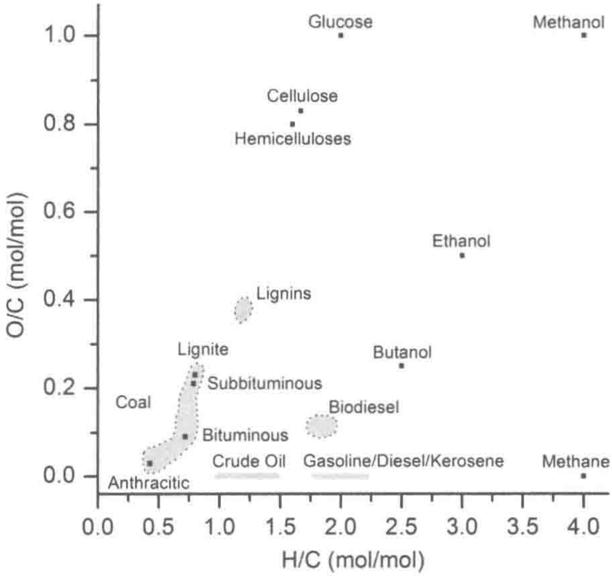

Figure 1.1 O/C and H/C molar ratios of biomass components, fossil energy resources and fuels derived from them. Oil biomass has approximately the same composition as biodiesel (fatty acid methyl esters). Reproduced with permission from Ref. 2.

biomass upgrading, a substantial need for hydrogen undoubtedly exists due to the high oxygen content present in biogenic molecules.

Figure 1.1 plots the chemical composition of different energy carriers in an O/C *vs.* H/C diagram.[2] The typical biomass constituents contain much more oxygen than potential target molecules. In addition, the hydrogen content often needs to be increased. Decarboxylation and decarbonylation pathways are one of the possibilities for the reduction of the O/C ratio, but they alone are insufficient for this purpose. Accordingly, for further oxygen removal, hydrogen is often required as a reducing agent in order to convert biogenic molecules into less-oxygenated target compounds. In order to increase the H/C ratio, hydrogen is needed directly either in the hydrogenation and hydrogenolysis pathways, or indirectly after dehydration, since the dehydration leads to unsaturated compounds that are often undesired intermediates, as they are very reactive, and thus may undergo side reactions, decreasing overall product yields. The various process options that hydrogen is used for in order to convert biomass into chemical intermediates and end products will be briefly discussed at the end of this chapter.

1.2 Conventional Routes for Hydrogen Production and Corresponding Costs

The vast majority of hydrogen is currently produced from fossil fuels (estimated at 49% from natural gas, 29% from liquid hydrocarbons, either

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