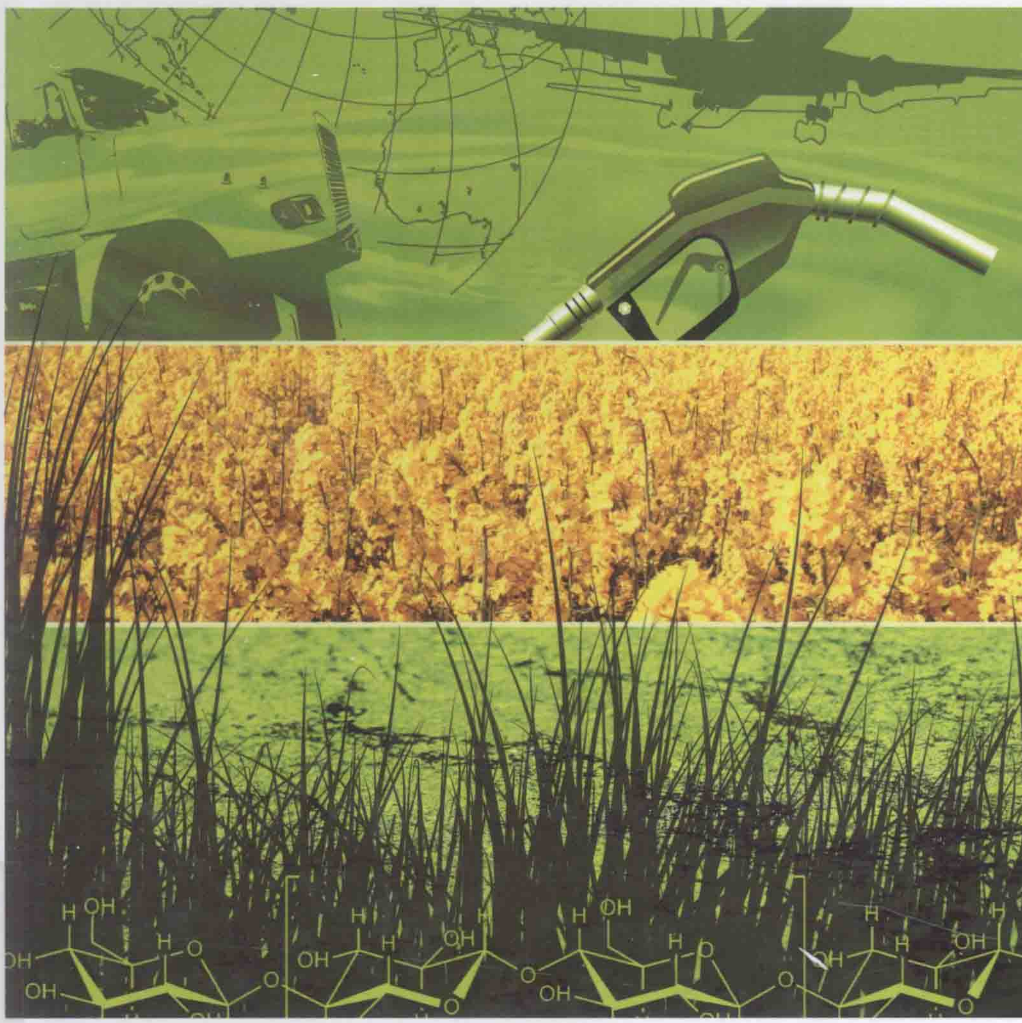
RSC Energy and Environment Series

Edited by Mark Crocker

Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals



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RSC Energy and Environment Series No. 1

ISBN: 978-1-84973-035-8
ISSN: 2044-0774

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

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1: Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals

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Foreword

The thrust for alternative, renewable sources of liquid transportation fuels is driven by two different, but related occurrences. One of these factors is the global warming issue, where a wealth of scientific data points to greenhouse-gas (GHG) emissions as being a major contributor to this burgeoning problem. Of these GHGs, the biggest in terms of volume and concentration is carbon dioxide, which is released when fossil-based fuels are burnt for energy generation. The second factor concerns the long-term availability of the fossil-based crude oil that has powered the world's economic growth over the last century or so. "Peak Oil" or "Hubbert's Peak", devised by the late Shell scientist M. King Hubbert, predicted in 1956 that US oil production would peak in about 1970 (history proved this prediction to be correct) and global production would peak some 40 years later (today). The ramifications of this latter point will be enormous as production rates start to decline and demand worldwide continues to increase.

The combined pressures of rising fuel prices, diminishing global supplies of crude oil and legislation to control climate change by reducing greenhouse-gas emissions has resulted in both aggressive renewable fuel policies and a rapid growth in the emerging biofuels industry. Surplus agricultural feedstocks in the US and Europe are quickly being exhausted, contributing to commodity price increases, including corn, soybean and rapeseed and other biofuel feedstocks. It is widely argued that the continued commercialization and development of first-generation fuels such as corn ethanol and soy biodiesel will put additional pressure on food supplies during a time of rapid growth in demand from developing countries.

As a result of the foregoing there has been a growing acknowledgement of, and emphasis on, next-generation (some refer to these as second-generation, some as third-generation) biofuels such as cellulosic ethanol, algae-derived biodiesel and pyrolysis oil (bio-oil) from woody biomass. More recently, attention has turned to more advanced biofuels made from renewable sources. These advanced biofuels are often referred to as "drop-in fuels" since these final fuels (renewable diesel, gasoline and jet fuel) are literally drop-in replacements for today's diesel, gasoline and jet fuel: like fossil-derived fuels they are hydrocarbons (devoid of oxygen), with the same high energy content and are very similar in terms of molecular structures. The fact that these advanced biofuels are drop-in replacements is a critical factor in their anticipated commercial success because they can be readily used in the existing infrastructure (from pipelines to refineries, from automobiles to military aircraft, *etc.*). The importance of this latter point cannot be overstated – in the United States alone this infrastructure represents an investment of more than 12 trillion dollars.

This timely book covers many different routes for utilizing a wide variety of biomass sources *via* a plethora of conversion technologies to afford several families of biofuels. Given the virtually unlimited thirst for energy (the world's largest industry by far) it is likely that many of these approaches will lead to commercial implementation, with the most efficient, scaleable and cost-effective ones having global impact and with others having impact in certain regions by virtue of geographical and/or political considerations. Among the former there is growing consensus that the most promising global-scale biomass solution is represented by microalgae since they are Mother Nature's most efficient practitioners of photosynthesis (the fixation of carbon dioxide), resulting in the highest yields of biomass and oils among all aquatic species, which are in turn an order of magnitude more efficient than terrestrial plants.

Topics included in this book range from biodiesel, made by transesterification of triglycerides (vegetable oils) using different catalysts and processes and utilization of the coproduced glycerol, to the hydrotreating of vegetable oils to afford renewable diesel and renewable jet fuel (more correctly HRJ or hydrotreated renewable jet).

Considerable attention is given to pyrolysis oil that is typically generated by rapid pyrolysis (residence times of a couple of seconds) at high temperature ($>450\,^{\circ}C$) in the absence of oxygen. Many feedstocks have been explored, from woody biomass, to microalgae to vegetable oils. The products of pyrolysis are pyrolysis oil (also known as bio-oil) and char (in addition to some lights). The char can be used as a form of "green coal", while pyrolysis oil can be used in boilers, furnaces and power plants. The oil can also be upgraded (typically using hydrotreating technology) to renewable diesel and possibly renewable jet fuel, although further development is envisaged before commercialization can be commenced.

The use of lignocellulosic feedstocks to generate fuels directly, or *via* the intermediate formation of sugars, is also presented.

Another area receiving significant attention in this work is the development of Fischer–Tropsch (FT) syngas (synthesis gas – a mixture of carbon monoxide and hydrogen) conversion processes. FT technology has long been promoted by the prospect of "stranded" natural gas, predominantly methane, being available at remote global locations at near-zero cost. More recently, increasing attention to low-cost, potentially abundant biomass sources, such as algae, switchgrass, corn stover and the like have added a new stimulus to FT technology development. It is well known that the economic viability of gas-conversion processes is largely determined by the capital cost and the market value of the final hydrocarbon products. It is also a widely accepted fact that the manufacture of syngas is by far the most capital-intensive part of the process, and so a competitive technology must combine low-cost feedstocks (stranded gas or cheap, abundant biomass), and cost-effective syngas generation (*via* gasification of the biomass) with efficient syngas conversion. Clearly, selectivity and efficiency are paramount in the design of a viable FT process, as is catalyst activity, which determines the reactor size, and catalyst lifetime, which directly influences the choice of reactor.

Finally, an emerging trend in the biomass to liquid transportation fuels (and chemicals) arena is the concept of an integrated biorefinery in which both the biology and the chemical engineering are brought together in one locale to complete the process – all the way from agriculture to fuel and chemical feedstocks, and in some cases to final consumer products. This trend is also reviewed in this timely work.

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Preface

Given the increasing world-wide demand for energy, coupled with concerns surrounding global warming and the instability of current petroleum supplies, there is a pressing need for low-cost, high-volume processes for the conversion of biomass to fuels and chemicals. Against this backdrop, this book aims to provide an up to date overview of the thermochemical methods available for biomass conversion to liquid (transport) fuels and chemicals. In so doing, this book is intended to provide researchers and students with a comprehensive introduction to this emerging field, while also functioning as a reference for those already active in the area.

In order to provide the reader with sufficient background information, the first three chapters deal with general aspects of the production of biofuels and chemicals from biomass, focusing on the rationale for biofuels, considerations governing the selection and cultivation of energy crops, and the concept of biorefineries. After this, pathways for the thermochemical valorization of biomass are considered in detail, starting with biomass gasification and subsequent conversion of the obtained syngas to fuels and chemicals via Fischer-Tropsch and alcohol synthesis routes. Biomass pyrolysis, representing an important technology for the direct conversion of biomass to liquid fuels, is then discussed, with emphasis on fast pyrolysis and hydrothermal processing; a discussion of lignin utilization is also included, representing a biomass constituent that to date has received relatively little attention in the context of bio-derived fuels and chemicals. Given that the crude bio-oils resulting from pyrolysis processes require upgrading before they can be refined to transport fuels, bio-oil upgrading via *in situ* (catalytic biomass pyrolysis) and *ex situ* (hydrotreating) approaches is also considered in detail. The conversion of cellulose to sugars and utilization of carbohydrates for the production of fuels and chemicals is next discussed, including a review of recent work employing ionic liquids for the utilization of lignocellulosics. The last five chapters concern

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the upgrading of vegetable oils and fats for the production of liquid fuels, covering both existing and emerging processes.

As editor of this book, I am indebted to the participating authors who responded in such a positive fashion to my requests for contributions and who (mainly) adhered to their deadlines. Thanks are also due to the staff at the RSC, and in particular to Gwen Jones for her unflagging support of this project and to Sue Humphreys for her production expertise. At the Center for Applied Energy Research, Leslie Hughes provided invaluable assistance and somehow remained good natured even when reformatting references by the hundreds. Finally, as ever, my thanks go to Terri and Saskia.

Mark Crocker

Contents

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