Wood Modification

Chemical, Thermal and Other Processes

CALLUM A.S. HILL

School of Agricultural and Forest Sciences, University of Wales, Bangor

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Wood Modification

Chemical, Thermal and Other Processes

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This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

I should like to dedicate this book to my wife Joanne and our children for their support and understanding; and to my late father Alan Bernard Hill and my good friend Cameron Settle, who both made beautiful things from wood.

Contents

Foreword

In this book of the series, a ‘more traditional’ area of research in the field of renewable resources is discussed. It is indeed a long-standing topic to utilize wood for a vast number of applications; however, it is a very active and changing field of research. The modification of wood needs to be compatible with the increasing demands at the environmental level, the social role of forests and woods’ and the technical characteristics needed to create certain materials. This book certainly paves the way to give the professional reader a taste of this area and offers an up-to-date overview of the different kinds of modification and the impact on the durability of the materials.

The success of a book strongly depends on the author, on his approach and his expertise. I was particular happy that Callum Hill took on this project in view of his extensive knowledge in the field. He has succeeded in presenting an overview of the modification of wood in sufficient detail and with great attention to the literature. Thanks’ Callum.

This book will be very helpful to scientists in the field of modification of wood, but hopefully also to a variety of people in other disciplines either in the academic world, in industry or in the area of policy.

Christian V. Stevens
Faculty of Bioscience Engineering
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Series Editor, ‘*Renewable Resources*’
June 2005

Series Preface

Renewable resources, their use and modification are involved in a multitude of important processes with a major influence on our everyday lives. Applications can be found in the energy sector, chemistry, pharmacy, the textile industry, paints and coatings, to name but a few.

The area interconnects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry, etc.), which makes it very difficult to have an expert view on the complicated interaction. Therefore, the idea of creating a series of scientific books, focusing on specific topics concerning renewable resources, has been very opportune and can help to clarify some of the underlying connections in this area.

In a very fast changing world, trends are not only characteristic for fashion and political standpoints; also, science is not free from hypes and buzzwords. The use of renewable resources is again more important nowadays; however, it is not part of a hype or a fashion. As the lively discussions among scientists continue about for how many years we will still be able to use fossil fuels, opinions ranging from 50 to 500 years, they do agree that the reserve is limited and that it is essential not only to search for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives for fossil-based raw materials and energy. In the field of energy supply, biomass and renewable-based resources will be part of the solution, alongside other alternatives such as solar energy, wind energy, hydraulic power, hydrogen technology and nuclear energy.

In the field of material sciences, the impact of renewable resources will probably be even bigger. Integral utilization of crops and the use of waste streams in certain industries will grow in importance, leading to a more sustainable way of producing materials.

Although our society was much more (almost exclusively) based on renewable resources centuries ago, this disappeared in the Western world in the 19th century. Now it is time to focus again on this field of research. However, this should not mean a ‘retour à la nature’, but it should be a multidisciplinary effort on a highly technological level to perform research towards new opportunities, to develop new crops and products from renewable resources. This will be essential to guarantee a level of comfort for a growing number of people living on our planet. It is ‘the’ challenge for the coming generations of scientists to develop more sustainable ways to create prosperity and to fight poverty and hunger in the world. A global approach is certainly favoured.

This challenge can only be dealt with if scientists are attracted to this area and are recognized for their efforts in this interdisciplinary field. It is therefore also essential that consumers recognize the fate of renewable resources in a number of products.

Furthermore, scientists do need to communicate and discuss the relevance of their work. The use and modification of renewable resources may not follow the path of the genetic engineering concept in view of consumer acceptance in Europe. Related to this aspect, the series will certainly help to increase the visibility of the importance of renewable resources.

Being convinced of the value of the renewables approach for the industrial world, as well as for developing countries, I was myself delighted to collaborate on this series of books focusing on different aspects of renewable resources. I hope that readers become aware of the complexity, the interaction and interconnections, and the challenges of this field and that they will help to communicate on the importance of renewable resources.

I certainly want to thank the people at Wiley from the Chichester office, especially David Hughes, Jenny Cossham and Lyn Roberts, in seeing the need for such a series of books on renewable resources, for initiating and supporting it, and for helping to carry the project through to the end.

Last but not least, I want to thank my family, especially my wife Hilde and my children Paulien and Pieter-Jan, for their patience and for giving me the time to work on the series when other activities seemed to be more inviting.

Christian V. Stevens
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Ghent University, Belgium
Series Editor, '*Renewable Resources*'
June 2005

Preface

The idea for writing this book came about through discussions with Chris Stevens at the University of Ghent in Belgium. It was considered that this was a good time to write such a book, in view of the rapid developments in the subject over the past decade and, in particular, because of the progress made in commercialization of technologies in this area. The task of writing this book has been immense, but very enjoyable. Although the subject matter of this book is concerned with wood modification, many of the processes described are generic and could be applied to other lignocellulosic materials. In writing this book, I have tried to do justice to the area and cover all the topics in depth. However, as with any textbook, it is necessary to work within editorial constraints. Hence, although the bulk of this subject is covered, it is inevitable that some areas are covered in greater detail than others. In deciding which areas to concentrate upon, I have taken account of other textbooks that have dealt with some of these topics in depth, and made reference to these where appropriate.

This area is undergoing huge developments at the present time, driven in part by environmental concerns regarding the use of wood treated with certain preservatives. There has been considerable commercial interest shown in wood modification over the past decade, with products based upon thermal modification and furfurylation now being actively marketed. The next few years will see the commercialization of acetylation and impregnation modification. This is a new industry, but one that has enormous potential.

The technologies that have been developed for wood modification have required the combined efforts of many hundreds of researchers worldwide. However, it would be impossible to study the literature in this area without encountering the pioneering work of Alfred J. Stamm of the Forest Products Laboratory in Madison, Wisconsin, USA. Nearly every area of wood modification can trace its origins back to the seminal work of Stamm. All those who work in wood modification owe him a great debt.

I hope that this book proves useful to all those with an interest in wood modification. Finally, I should like to say that although I have made every effort to ensure that this book is error-free, any mistakes that may have crept through the very thorough review procedure are entirely my responsibility.

Callum A.S. Hill

List of Abbreviations

ASE	Anti-shrink efficiency
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflection infrared specroscopy
AWPA	American Wood Preservers Association
BC	Bulking coefficient
BET	Brunauer–Emmett–Teller
BPD	Biocidal Products Directive
BPO	Benzoyl peroxide
CCA	Copper chrome arsenic
CP-MAS	Cross-polarized magic angle spinning
CTMP	Chemithermomechanical pulp
DHBP	Dihydroxy benzophenone
DIPCI	Diisopropylcarbodiimide
DMDHEU	Dimethylol dihydroxy ethylene urea
DMF	Dimethyl formamide
DTA	Differential thermal analysis
DP	Degree of polymerization
E'	Dynamic Young's modulus
EDXA	Electron diffuse X-ray analysis
EELS	Electron energy loss spectroscopy
EETMS	β-(3,4, Epoxycyclohexyl)trimethoxysilane
EMC	Equilibrium moisture content
EMC_R	Reduced equilibrium moisture content
ESR	Electron spin resonance
EU	European Union
EW	Earlywood
FA	Furfuryl alcohol
FAO	Food and Agriculture Organisation of the United Nations
FTIR	Fourier transform infrared
FSP	Fibre saturation point
GAI	Gross annual increment
GC-MS	Gas chromatography mass spectrometry
GMA	Glycidyl methacrylate

GPa	Giga pascal
Gt	Giga tonne
ha	Hectare
HDI	1,6-Diisocyanatohexane
HEBP	2-Hydroxy-4-(2, 3-epoxypropoxy)benzophenone
HEMA	2-Hydroxymethylmethacrylate
H–H	Hailwood–Horrobin
HMDA	Hexamethylene diamine
HMDSO	Hexamethyldisiloxane
HPLC	High-pressure liquid chromatography
IBS	Internal bond strength
IR	Infrared
IPCC	Intergovernmental Panel on Climate Change
IPTES	3-Isocyanatopropyltriethoxysilane
IS	Isocyanate
ISS	Interfacial shear strength
JWPA	Japanese Wood Preserving Association
LCA	Life cycle analysis (assessment)
LMWDA	Low molecular weight diffusible agent
LOI	Limiting oxygen index
LVL	Laminated veneer lumber
LW	Latewood
MA	Maleic anhydride
MAPP	Maleic anhydride polypropylene
MC	Moisture content
MDF	Medium density fibreboard
MDI	Diphenylmethane diisocyanate
MEE	Moisture exclusion efficiency
MF	Melamine formaldehyde
MG	Maleic acid glycerol
ML	Middle lamella
MMA	Methylmethacrylate
MMF	Methylolated melamine formaldehyde
MOE	Modulus of elasticity
MOR	Modulus of rupture
MPa	Mega pascal
MTES	Methyltriethoxysilane
MTMS	Methyltrimethoxysilane
MUF	Melamine urea formaldehyde
MPF	Melamine phenol formaldehyde
MW	Molecular weight
NAI	Net annual increment
NMA	*N*-methylolacrylamide
NMR	Nuclear magnetic resonance
OD	Oven dry
OH	Hydroxyl

OSB	Oriented strand board
PA	Phthalic anhydride
PDMSO	Poly(dimethylsiloxane)
PEG	Poly(ethyleneglycol)
PF	Phenol formaldehyde
PGMA	Poly(glycerol methacrylate)
PhNCO	Phenyl isocyanate
PMPPIC	Poly(methylene) poly(phenylene) isocyanate
PP	Poly(propylene)
PRF	Phenol resorcinol formaldehyde
psi	Pounds per square inch
PTES	Propyltriethoxysilane
PTMS	*n*-Propyltrimethoxysilane
PTSC	*p*-Toluene sulphonyl chloride
PVAc	Poly(vinylacetate)
PVC	Poly(vinylchloride)
RH	Relative humidity
S %	Percentage swelling coefficient
SA	Succinic anhydride
SEM	Scanning electron microscopy
SEM-EDXA	Scanning electron microscopy electron diffuse X-ray analysis
SN_2	Bimolecular nucleophilic substitution
TBTO	Tributyl tin oxide
TDI	Toluene diisocyanate
TEA	Triethylamine
TEM	Transmission electron microscopy
TES	Tetraethoxysilane
TFA	Trifluoro acetic acid
TGA	Thermogravimetric analysis
TMS	Tetramethoxysilane
TMP	Thermomechanical pulp
TMPS	γ–Methacryloxypropyltrimethoxysilane
TPS	Tetrapropoxysilane
USGS	United States Geological Survey
UV	Ultraviolet
VC	Volume change
VOC	Volatile organic compound
VTMS	Vinyltrimethoxysilane
WPG	Weight percentage gain
WS	Water soak
XPS	X-ray photoelectron spectroscopy

1

The Use of Timber in the Twenty-first Century

1.1 Introduction

There is an increasing need to develop technologies in which renewable materials are used as direct replacements for nonrenewables. Our current rates of consumption of nonrenewables are high and in most cases increasing, but the reserves from which they are obtained are finite and exhaustible. Our present patterns of consumption are not sustainable in the long term. Although this problem appears to be unique to the 21st century, these concerns are not new. The idea that resource scarcity could act as a constraint upon economic development can be traced back to the writings of Thomas Malthus, who showed that expanding populations will outstrip their food supplies. The concepts that he discussed apply equally to all finite resources. In the event, advances in technology have tended to compensate for resource scarcity, but this process cannot continue indefinitely.

It is only comparatively recently that we have become acutely aware of the need to utilize resources in a sustainable manner. The concept of sustainability began to receive attention during the 1970s and was first formalized internationally in the World Conservation Strategy of 1980. The initial concepts were taken from the idea of *sustainable yield*, as applied in forestry and agriculture. This is defined as the amount of crop that can be harvested without compromising the capacity of future harvests to produce an equal crop. The level of consumption of a resource to support an activity should meet the needs of the present, whilst ensuring that sufficient resources are available to meet the needs of the future. The concepts of sustainability include social, economic and environmental factors. All three must be taken into account if the absolute sustainability of a process is to be determined.

As the study of the interactions between the environment and economic processes has developed, there has been increasing emphasis placed upon analyses of materials/energy

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flows within economies. This has led to the development of the subject of biophysical economics, which views the economy in terms of flows of energy and materials within ecosystem processes. As a consequence, thermodynamic principles have become closely involved in the construction of biophysical economic models. The incorporation of environmental considerations into economics will be an important factor in improving the competitiveness of renewable materials.

1.2 Nonrenewables: a Finite and Exhaustible Resource

The consumption of nonrenewable materials tends to exhibit a classic relationship, which was first demonstrated by M. King Hubbert in an analysis of oil production from the 48 contiguous states of the USA. The shape of this ‘Hubbert curve’ is similar to, although not identical with, a normal distribution (Figure 1.1). With some variation, this pattern of production/consumption is exhibited for all nonrenewables. The finite life span of nonrenewable reserves has been commented upon by many workers in the area.

It is important to distinguish between the commonly used terms, resource, reserve base and reserve:

- A resource is the amount of material that is known to exist plus the quantity that is thought to exist.
- A reserve base is the amount of material in the resource that meets certain physical criteria for extraction.
- A reserve is the amount of material in a reserve base that can be economically extracted at the present time.

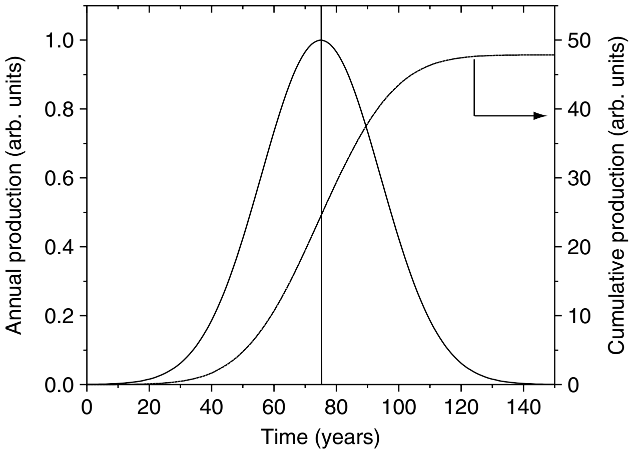

Figure 1.1 An example of a Hubbert curve, representing an idealized history of resource extraction. The amount of material extracted in a year is represented by the bell-shaped curve, whereas the cumulative amount of material extracted is given by the sigmoidal curve.

The extraction of nonrenewable materials follows a common pattern, in that the highest-quality reserves are the first to be extracted, and as these are worked out, progressively lower-quality reserves are then processed. As technology advances and the price of the commodity rises, the reserves increase.

However, although the level of reserves will rise as technology improves and prices increase, eventually there comes a point at which the effort (energy) expended in extracting the material is greater than the advantage gained by using that material. A good example would be the extraction of low-quality oil reserves, where a point is reached at which the energy expended in extracting the oil is greater than the energy obtained from the oil once it is extracted. Another example of this is illustrated by considering the amount of gold existing in seawater, with a total amount of 10 million tonnes being present in the world's oceans. However, this is at such a low concentration (10 parts per trillion) that extraction would be hopelessly uneconomic.

The US Geological Survey (USGS) produces annual mineral commodity summaries, from which it is possible to crudely estimate reserve lifetimes (Figure 1.2).

Calculations of this type are very approximate (obtained by dividing the current reserves by the annual production), but although the figures may be criticized in terms of absolute accuracy, the basic principle that the reserves will eventually be depleted cannot be denied.

The use of nonrenewable resources is characterized by linear mass/energy flows through economic systems. A resource is extracted, processed, utilized and ultimately discarded. Until recently, the final stage of this linear throughput has not been a factor when considering the economics of a process. Physical processes involving chemical transformations are subject to the laws of thermodynamics. An inevitable consequence associated with any chemical transformation is the unavoidable related increase in the entropy of the environment. This results in dissipation, the conversion of high-quality energy and materials into lower-quality forms (a decrease in organization at the atomic/

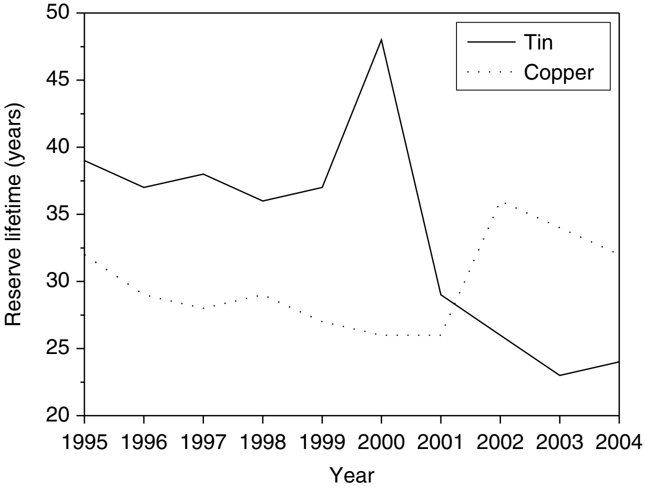

Figure 1.2 *The reserve lifetimes of copper and zinc ores, estimated from the annual data supplied by the US Geological Survey.*

molecular level). A classic example would be the combustion of fossil fuels, where the high-grade heat (that which can do useful work) is emitted into the environment as low-grade heat, and the atoms in the fuel are lost into the environment as high-entropy gases (such as carbon dioxide).

Natural processes are distinguished from the material and energy throughputs of economic processes in two main ways:

- Cyclic materials flows, where the wastes from a metabolic process become the feedstocks for other metabolic processes.
- Assimilative rather than dissipative processes, where atoms are taken from a dissipated state and formed into organized structures.

Of course, natural systems do not operate outside of the laws of thermodynamics. The process of assimilating atoms to form organized structures requires energy, and this energy is derived (with a few exceptions) from the sun, via photosynthetic processes.

The challenge for mankind in the 21st century is to design our industrial processes so that they become integrated with natural metabolic processes. This is why the study of renewable materials is becoming so important.

1.3 Renewable Materials

Mankind has used (and hopefully will continue to use) renewable materials for millennia, but the idea of using renewable materials as industrial feedstocks began to be taken seriously in the 1930s in the USA (Geiser, 2001; Finlay, 2004). George Washington Carver was an early pioneer of this idea, who developed many industrial products derived from peanuts. The idea of using agricultural crops for industrial feedstocks was also promoted by William J. Hale, an organic chemist who published a book called *The Farm Chemurgic* in 1934. This was the start of the chemurgy movement. Hale argued that it was important from a strategic point of view for the USA not to rely upon foreign imports in order to support its domestic chemicals industry. This is an idea that seems just as pertinent now as it did then.

Hale worked with Wheeler McMillen, Thomas Edison, Irenee DuPont and Henry Ford to promote the chemurgy principles. Thomas Edison was interested in using the wild flower goldenrod as a feedstock for rubber production. Henry Ford had a particular interest in producing industrial organic chemicals from soybeans. In 1938, Ford constructed the first of several industrial soy processing plants to make soy oil based enamels for car body paints, using the glycerol by-product in shock absorbers. He supported a great deal of research into crop-based products that could be used for producing car components.

The chemurgy movement grew rapidly during the time of the Great Depression, and the advent of the Second World War resulted in a huge amount of activity to derive as many products as possible from domestic sources, for strategic reasons. However, with the end of the war, the development of many new cheap products by the petrochemicals industry led to the rapid demise of the chemurgy movement.

With renewables, assuming that the biomass resource is obtained in a sustainable manner, there should be a constant supply of materials, although there is a finite limit to the amount of material that can be obtained. Figure 1.3 shows a classic growth curve

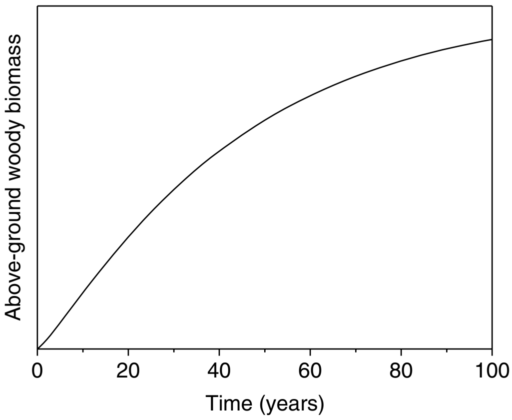

Figure 1.3 A growth curve showing the increase of biomass in forestry plantation over a 100-year period.

representing the amount of biomass stored in a crop, which is then available after harvesting to be utilized in products. It should also be noted that, theoretically, there is no downgrading of material quality for a renewable resource.

The biomass in (for example) a forest can be harvested and the sequestered carbon can either be used for energy production (with rapid return of the carbon to the atmosphere) or it can be stored for longer periods in timber products. The example given in Figure 1.4 shows a forest that is clear-felled after 100 years of growth.

The rate of growth of the trees slows as the forest reaches maturity and canopy closure occurs. In addition, the forest eventually establishes equilibrium with the environment, where the rate of carbon sequestration is exactly balanced by the loss of carbon dioxide to the atmosphere due to decay of dead trees and other biomass.

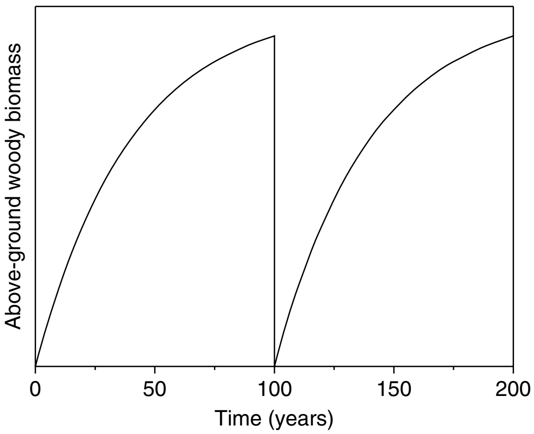

Figure 1.4 A forest plantation that is clear-felled after 100 years of growth, and subsequent regeneration over the following century.