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Shurong Wang, Zhongyang Luo

PYROLYSIS OF BIOMASS

生物质热解

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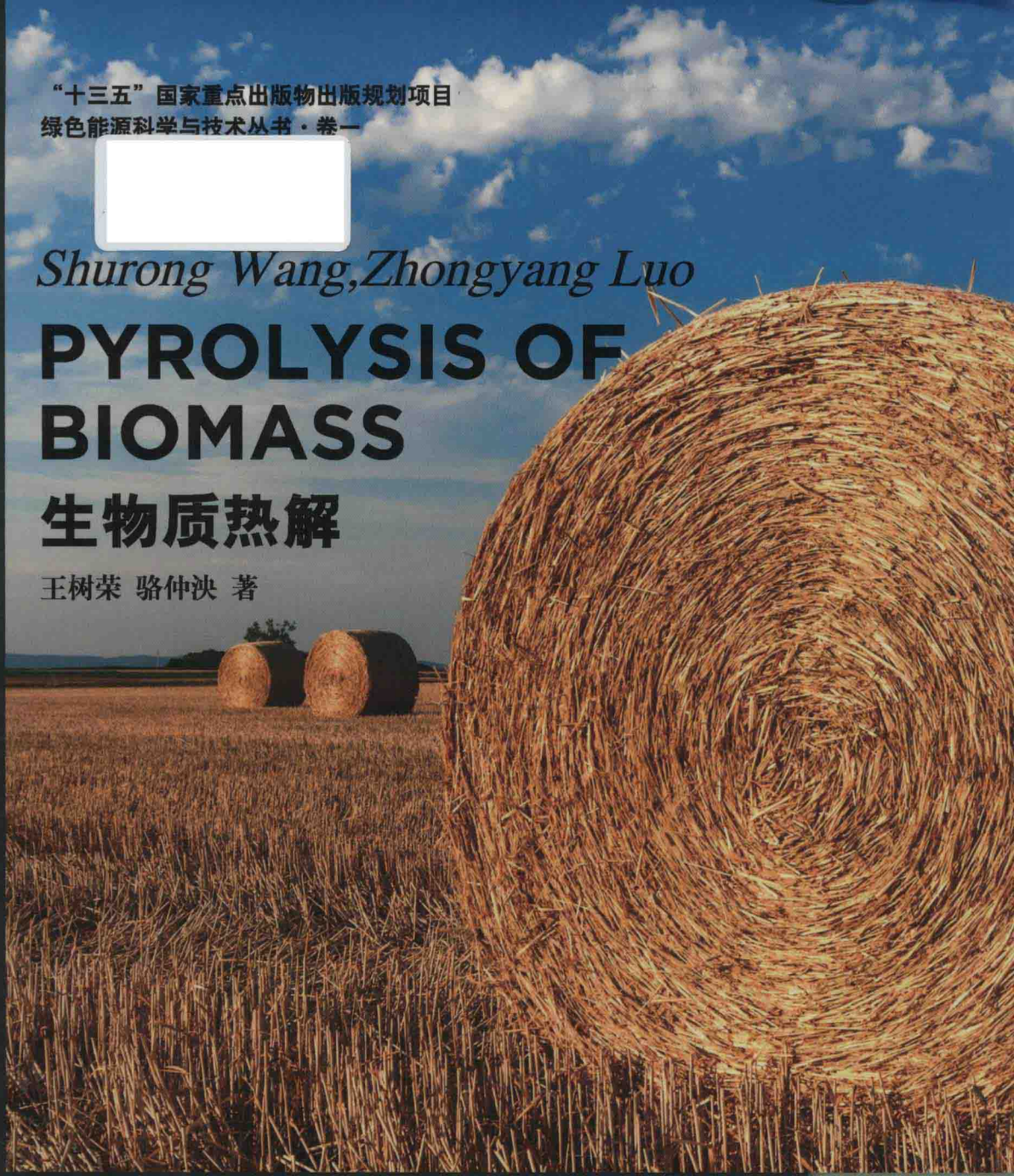

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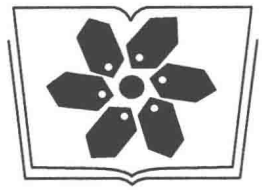

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Preface

Energy is a fundamental resource for the survival of human society. Significant progress in human civilization is bound to be accompanied by the improvement and adjustment of energy structures. Nowadays, energy is one of the core issues in the world, and the demand for energy intensifies every day with the expansion of the global economy. However, problems due to the lack of primary energy, such as coal, oil and natural gas, and further potential risks still exist, which may add to the hazards of energy safety. Moreover, environmental pollution resulting from the utilization of fossil fuels cannot be ignored. The harm caused by increasing greenhouse gas emissions, acid rain and PM2.5 is raising more and more concern.

Biomass is a clean renewable energy resource, and it is much more environmentally friendly than fossil fuels like coal, because neutral emission of CO_2 is achieved when utilizing biomass. Furthermore, biomass is the only renewable carbon-containing energy resource that can be used for large-scale production of liquid fuels. If the abundant biomass resources in the world can be converted to liquid fuels, the tense and unbalanced status of the oil supply will be greatly alleviated. Biomass fast pyrolysis liquefaction is a mainstream technology that can efficiently convert biomass into high-energy-density bio-oil, which is a type of liquid fuel that is easy to store and transport. Bio-oil can be directly used as fuel in a boiler or be further modified for high-grade liquid motor fuel applications. However, raw bio-oil has some disadvantages such as high water content, high oxygen content, low heating value, low pH value, complicated composition and instability, which have greatly limited its application. There are two key points for solving these problems: the first is to fundamentally analyze the mechanisms involved in biomass pyrolysis so as to understand the laws of pyrolysis, which can be helpful for improving the quality of bio-oil during the preparation process; the second point is to promote research on bio-oil upgrading. For example, some bio-oil upgrading technologies, such as catalytic hydrogenation, catalytic cracking and catalytic esterification, can combine distributed biomass pyrolysis liquefaction with centralized bio-oil upgrading, so that high-grade vehicle fuels and even aviation fuels can be obtained. I have devoted myself to research on the biomass pyrolysis mechanisms and the production of high-grade liquid fuels through biomass fast pyrolysis liquefaction since 1998. And it is my great pleasure to have cooperated with Prof. Zhongyang Luo in writing this book with the aim of introducing the pyrolysis of biomass.

The book is divided into seven chapters. It follows the thread of the three major components of biomass and systematically illustrates the theories involved in biomass pyrolysis liquefaction. This book begins with the structure of lignocellulosic biomass. The basic structure, physical and chemical properties of the three major components of biomass, namely cellulose, hemicellulose and lignin, are introduced in detail, and common model compounds of the three major components as well as their proper-

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ties and corresponding extraction methods are also expounded in the first chapter. Then from Chapter 2 to Chapter 4 we give an in-depth illustration of the pyrolysis mechanism of the three major components of biomass. Beginning with the basic process of pyrolysis, the influence of different factors on biomass component pyrolysis is elaborated, and the biomass component pyrolysis mechanism is discussed based on kinetics research, product formation processes and theoretical simulation at molecular level. Chapters 5 and 6 introduce the influence of the interaction of components, catalysts and inorganic salts on the pyrolysis behavior of biomass. Finally, pyrolysis behavior and pyrolysis liquefaction characteristics of different biomass species are illustrated, and research about bio-oil graded upgrading based on the separation of bio-oil is presented in Chapter 7.

I have been engaged in researching pyrolysis mechanisms and biomass pyrolysis liquefaction for almost 20 years. None of the achievements could have been obtained without support from the State Key Laboratory of Clean Energy Utilization at Zhejiang University and my colleagues, especially the long-term guidance from Academician Kefa Cen, Prof. Mingjiang Ni and Prof. Zhongyang Luo. I am also deeply grateful for the project funding for the biomass energy research field from the National Natural Science Foundation of China, Ministry of Science and Technology of China, Ministry of Education of China, and Science and Technology Department of Zhejiang Province, and some of the research results are also reflected in corresponding chapters. I sincerely offer my special thanks to all of my postgraduate students. Their theses greatly enrich this book. It is because of their hard work that the group's biomass pyrolysis liquefaction research has become much more systematic and thorough over time. Special thanks also to Bin Ru, Xiujuan Guo, Qinjie Cai, Lingjun Zhu, Qi Wang, Yurong Wang, Xinbao Li, Qianqian Yin and Wenwen Guo who have already graduated, and Haizhou Lin, Gongxin Dai, Fan Zhang, Yuan Zhao, Junhao Chen, Xiaoliu Wang and Shi Yin who are still studying, for their great help in collecting literature, arranging illustrations and text proofreading. In addition, I would like to express my sincere thanks to the publisher De Gruyter for their excellent work at every stage of this project.

Finally, many thanks to my wife Ruoqun Luo and my son Ziyang Wang for their full support and sincere understanding during the years of writing this book.

Although the authors have made every effort to accurately reflect related work on biomass pyrolysis and its results, some improper renderings or omissions may unavoidably exist. Every comment from readers and relevant experts in this field is deeply appreciated, and will be used to further improve future versions.

Shurong Wang
August 2016

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1 Biomass components and characteristics

1.1 Biomass components

Generally, biomass is organic matter derived from living organisms. Its formation is closely connected with photosynthesis, directly or indirectly, and it includes all animals, plants and microbes, as well as organic matter derived, excreted or metabolized from or by these living organisms. Biomass can be used as a source of energy and it most often refers to plants or plant-based materials which are not used for food or feed, specifically called lignocellulosic biomass, especially focusing on agricultural and forestry wastes, such as woodchip and rice straw.

1.1.1 Composition analysis of biomass

Biomass is composed primarily of three elements: carbon, hydrogen and oxygen, whose total content generally reaches above 95 %. It also contains small amounts of nitrogen and sulfur, which are generally recognized as deriving from the residual proteins in protoplasm at the early growth stage of a cell [1]. Tab. 1.1 lists the composition analysis of several typical types of biomass, such as Mongolian Scots pine and rosewood in forestry biomass, rice straw and husk in agricultural biomass, bamboo and grassiness in herbaceous biomass, and algae in aquatic biomass. The fixed carbon and volatiles content are similar for different biomass species, while the ash content varies markedly. As typical forestry biomass, Mongolian Scots pine and rosewood have the lowest ash content, while agricultural biomass has relatively higher ash content. Except for carbon, hydrogen, oxygen, nitrogen and sulfur, biomass still contains some inorganic metal elements like potassium, calcium, sodium, magnesium, aluminum, iron and copper etc., in the form of inorganic compounds. Furthermore, potassium and calcium content are significantly higher than those of

Tab. 1.1: Proximate and ultimate analysis of various kinds of biomass.

Biomass	M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	Fc_{ad} (%)	$Q_{b,ad}$ (MJ/kg)	C_{ad} (%)	H_{ad} (%)	N_{ad} (%)	S_{ad} (%)	O_{ad} (%)
Mongolian Scots pine	13.90	0.30	73.74	12.06	18.84	45.92	4.41	0.10	0.03	35.34
Rosewood	13.45	0.35	71.07	15.13	17.07	44.32	4.88	0.16	0	36.84
Rice straw	11.21	16.12	61.36	11.31	13.87	36.89	3.44	1.19	0.20	30.95
Rice husk	12.30	12.26	60.98	14.46	14.57	40.0	3.66	0.53	0.13	31.12
Bamboo	5.40	3.68	75.70	15.22	17.54	45.32	2.51	0.82	0.04	42.23
Grassiness	8.21	2.44	73.09	16.26	16.65	44.45	4.68	0.31	0.16	39.75
Algae	16.30	10.09	60.39	13.22	12.65	34.17	3.84	2.16	1.04	32.40

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other elements. Potassium content is relatively higher in herbaceous biomass like straw, while wood contains more calcium. In addition, biomass may still differ in appearance and reaction characteristics, even with similar chemical compositions.

1.1.2 Distribution of biomass components

Cellulose, hemicellulose and lignin are the three main components of lignocellulosic biomass, constituting the cell wall of plants. As displayed in Fig. 1.1, the main components are distributed unevenly in the cell wall, forming the skeleton, linking material and hard solids. Cellulose molecules regularly gather as pipes forming tough microfibers that function as the skeleton material of a plant's cell wall, and the inner space is filled with amorphous linking material, namely hemicellulose and hard-solid lignin [2]. The connection between cellulose and hemicellulose or lignin molecules is mainly by hydrogen bonds, while that between hemicellulose and lignin contains both hydrogen and covalent bonds, resulting in small amounts of carbohydrates adhered to the lignin extracted from lignocellulosic biomass [3]. Furthermore, biomass also contains free compounds, called extractives, which can be extracted by polar or nonpolar organic solvents. The extractives are nonstructural compounds, mainly including paraffin, fat, resin, tannin, starch and pigment etc. [4]. In addition, there are a few inorganic metal salts, mainly composed of alkali and alkaline earth metal salts. Overall, the physical and chemical behaviors of biomass are closely related to its composition and the relative content of cellulose, hemicellulose and lignin, as well as the extractives and inorganic salts.

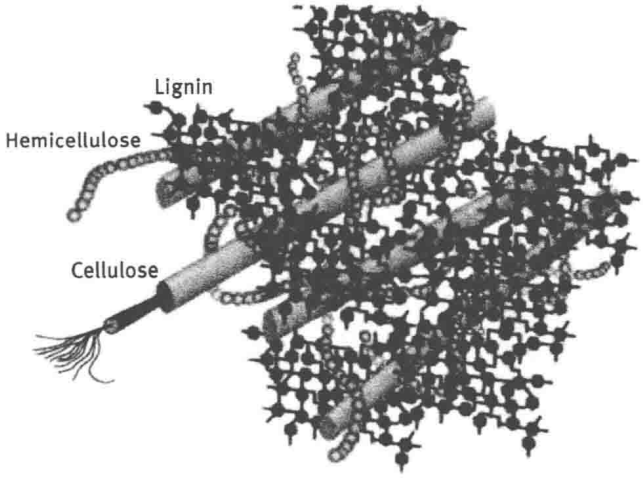

Fig. 1.1: Biomass components.

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