

THERMOCHEMICAL WASTE TREATMENT

Combustion, Gasification,
and Other Methodologies

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and Other Methodologies

Edited by

Elena Cristina Rada, PhD

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Acknowledgment and How to Cite

The editor and publisher thank each of the authors who contributed to this book. The chapters in this book were previously published elsewhere. To cite the work contained in this book and to view the individual permissions, please refer to the citation at the beginning of each chapter. Each chapter was carefully selected by the editor; the result is a book that looks at thermochemical waste treatment from a variety of perspectives. The chapters included are broken into four sections, which describe the following topics:

1. Combustion
2. Gasification
3. Pyrolysis
4. Hydrothermal Carbonization

The articles in each of these categories represent recent important research in thermochemical waste.

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Introduction

Our world faces enormous challenges. With a growing world population, diminishing fossil fuel resources combined with increasing waste generation will become a critical problem. We need to begin to think in a different way about the materials we no longer use or need.

There is increasing attention being paid to the conversion or valorization of solid wastes. Even in case of optimal source separation of waste aimed to material valorization, a residual amount remains and can be exploited for energy recovery through a thermochemical process. The research collected here in this volume includes four thermochemical processes: combustion, gasification, pyrolysis, and hydrothermal carbonization.

Combustion incinerates wastes, converting them into ash, flue gas, and heat. The ash—mostly the inorganic parts of the waste—is either solid lumps (slag) or particulates carried by the flue gas. To reduce the negative environmental impact, gaseous and particulate pollutants must be removed from the flue gases before they are emitted into the atmosphere. In some cases, the heat generated by incineration can be used to generate electric power. Even if the waste ultimately goes into a landfill, incineration radically reduces the amount of land required. Depending on the composition of the waste material, incinerators can reduce the solid mass of the original waste by as much as 80 to 85 percent; the volume of the original waste can be reduced up to 95 to 96 percent [1]. Recently it has been demonstrated in real scale that slag can be treated to recover metals and inert material for the building construction sector, thus reducing landfilling near to zero. Combustion may be particularly appropriate for the treatment of certain hazardous wastes, where the high temperature will destroy pathogens and toxins. Waste combustion tends to be popular in countries such as Japan where land is a scarce resource, while Denmark and Sweden have been using the energy generated from incineration for more than a century [2]. Worldwide, combustion is an option for the valorization of waste materials into energy. The modern age of

waste combustion can be set since late in the 90s, when the European Union adopted more stringent limits for the emissions into the atmosphere.

Using high temperatures but without combustion, gasification converts carbonaceous materials into carbon monoxide, hydrogen, and carbon dioxide. The gasification method to produce energy has been in use for nearly two centuries. It was initially developed in the nineteenth century to produce gas for lighting and cooking from peat and coal. Since the 1920s, gasification has been used to produce synthetic chemicals, and during both world wars, the shortage of petroleum created an increased need for gasification-produced fuels [3]. Today, it is another option for valorizing solid waste. Controlled amounts of oxygen and/or steam are used in the process, and the resulting gas mixture is called syngas, which can be used as fuel. Chemical processing of the syngas may produce other synthetic fuels as well.

Using high temperatures and an external source of heat, pyrolysis decomposes organic material with very little oxidation involved. When pyrolysis is applied to organic substances, it produces gas and liquid products, while leaving a solid residue called char that is rich in carbon. The lignocellulose in crop wastes can provide feedstock for pyrolysis to create synthetic diesel fuel. Pyrolysis can also be used on plastic waste to produce fuel similar to diesel. In fact, many waste materials can be used as feedstock for pyrolysis. These include greenwaste, saw dust and waste wood, nut shells, straw, cotton trash, rice hulls, switch grass, poultry litter, cattle manure, waste paper, paper sludge, distillers grain, sewage sludge, and many more [4].

Hydrothermal carbonization is a relatively new variation of converting biomass into biofuel [5]. Moderate temperatures and pressures are used over an aqueous solution of biomass in a dilute acid for several hours. The resulting matter captures carbon for use as a solid fuel.

The transition from a fossil fuel-based economy to a more sustainable economy will not come quickly and without effort. It will require a solid foundation of ongoing scientific research. The articles included in this volume offer valuable building blocks to that foundation.

Elena Cristina Rada, PhD

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Chapter 1, by Le Gleau and colleagues, deals with the treatment of acid gases present in fumes from meat and bones meal and sewage sludge co-incineration. A new implementation of acid gas treatment consists in catalytic ceramic filters, which are able to simultaneously capture particles, neutralise acid gases by dry basic sorbent injection and catalyse the reduction of nitrogen oxides by NH₃. This work aims at evaluating the efficiency of an existing system of industrial flue gas treatment, involving two different processing pathways installed in parallel. The results presented here consist in a measured material balance of the main species present in the fumes, followed by a discussion on the real processes and yields gotten under industrial conditions.

Fly ashes both from municipal solid waste incinerator (MSWI) and medical waste incinerator (MWI) are classified as hazardous materials because they contain high amounts of heavy metals. In present these contaminant ashes have become a major environmental problem. In Chapter 2, Pan and Xie determine the ability of these contaminating heavy metals to be incorporated into a glass-matrix and in various mineral phases after a high temperature melting process using a direct current plasma torch. After the melting process, the leaching characteristics of heavy metals in

fly ash and vitrified slag were investigated using the toxicity characteristic leaching procedure (TCLP), and the products also were characterized by X-ray diffractometry (XRD) for crystal structure determination, and scanning electron microscopy (SEM) for microstructure/morphology observation. After vitrification, there were prominent changes in microstructures and crystalline phases between produced slags and raw ashes. TCLP results indicate the leaching level of heavy metals in slags decreases obviously and additives such as silica and liquid ceramic (LC) contribute to high effect on immobilization of heavy metals in a host glass matrix.

There is a growing recognition that conversion or valorization of wastes (municipal solid wastes (MSW) and agricultural wastes) is an environmentally responsible way of treating the increased volumes without occupying a large portion of land. Many companies are turning to gasification of MSW, biomass and mixtures of these to produce fuels and chemicals. In Chapter 3, Castaldi utilizes rapid heating rates (greater than or equal to $700^{\circ}\text{C min}^{-1}$) to gasify Clean Wood and two Refuse Derived Fuel (RDF) samples using thermogravimetric analysis coupled to gas chromatography (TGA/GC). Reaction atmospheres included Air, 5% O_2 /95% Argon (Ar), 10% O_2 /90% Ar, 100% Ar and steam and were used to produce gas evolution profiles for hydrocarbons ranging from H_2 to C_4H_{10} . While expected results were obtained using Air reaction atmospheres, some interesting results were observed using steam and Ar. Different concentration profiles and production rates of C_2H_6 compared to C_2H_4 and C_2H_2 enabled some understanding of the reaction sequence occurring during gasification under rapid heating conditions. Kinetic analysis showed pre-exponential factors of 8.00×10^{27} , 2.02×10^{29} and 3.71×10^{23} ($\text{sec}^{-1} \text{K}^{1/2}$) for samples Clean Wood, RDF C (Industrial Solid Waste basis) and A (Municipal Solid Waste basis), respectively. Furthermore the apparent activation energy was determined to be 22, 71, and 185 (kJ mol^{-1}) for Clean Wood, RDF C and A respectively indicating that the Clean Wood is slightly more reactive than RDF C and more reactive than RDF A. This study also demonstrates good potential for H_2 production through gasification of RDF (from Industrial and Municipal Solid Wastes) in comparison to Clean Wood gasification. These RDF preparations were not specifically formulated with the intent of being used as gasification feedstocks. However, the present results show that gasification performance can be greatly improved by adjust-

ing the feedstock formulation when employing RDF from Commercial, Industrial and Municipal Solid Wastes.

Recycling and utilization of waste is one of the key parameters of environmental issue. Chapter 4, by Tilahun and colleagues, explored the capability of supercritical waste gasification to convert the waste into marketable by-product. Adding catalysts or oxidants to supercritical waste gasifier can further reduce operating costs by creating self-sustaining reactions under mild conditions with even shorter residence times. The hydrogen produced by this process will be utilized for generating electricity using fuel cell technology. Besides, alkaline fuel cells appear to be an important technology in the future as they can operate at a high efficiency. Therefore, the combination of biomass gasification through supercritical water with alkaline fuel cells represents one of the most potential applications for highly efficient utilization of biomass. The main aim of the study is to recover energy from waste using alkaline fuel cell. With the different operation conditions 88.8 % of hydrogen and 45 % of carbon dioxide, maximum power density 9.24 W/cm² was obtained.

Chapter 5, by Tanigaki and colleagues, evaluates municipal solid waste co-gasification technology and a new solid waste management scheme, which can minimize final landfill amounts and maximize material recycled from waste. Waste is processed with incombustible residues and an incineration bottom ash discharged from existent conventional incinerators, using a gasification and melting technology. The co-gasification system produced high quality slag with few harmful heavy metals, which was recycled completely without requiring any further post-treatment. As a consequence, the co-gasification system had an economical advantage over other systems. Sensitivity analyses of landfill cost were also conducted. The higher the landfill costs, the greater the advantage of the co-gasification system has. The co-gasification was beneficial for landfill cost in the range of 80 Euro per ton or more. These results indicate that co-gasification of bottom ash and incombustibles with municipal solid waste contributes to minimizing the final landfill amount and has great possibilities maximizing material recovery and energy recovery from waste.

Organic and inorganic contaminants in sewage sludge may cause their presence also in the by-products formed during gasification processes. Thus, Chapter 6, by Werle and Dudziak, presents multidirectional chem-

ical instrumental activation analyses of dried sewage sludge as well as both solid (ash, char coal) and liquid (tar) by-products formed during sewage gasification in a fixed bed reactor which was carried out to assess the extent of that phenomenon. Significant differences were observed in the type of contaminants present in the solid and liquid by-products from the dried sewage sludge gasification. Except for heavy metals, the characteristics of the contaminants in the by-products, irrespective of their form (solid and liquid), were different from those initially determined in the sewage sludge. It has been found that gasification promotes the migration of certain valuable inorganic compounds from sewage sludge into solid by-products which might be recovered. On the other hand, the liquid by-products resulting from sewage sludge gasification require a separate process for their treatment or disposal due to their considerable loading with toxic and hazardous organic compounds (phenols and their derivatives).

In Chapter 7, Zhao and colleagues investigate the pyrolysis of waste plastics separated from municipal solid wastes (MSW) and pyrolysis of whole combustibles in MSW together to compare their products and emissions with a purpose to improve the pyrolysis process for combustibles in MSW. The pyrolysis experiments were carried out with two substrates, namely the upper siftings from excavated aged MSW in landfill cell and waste plastics separated from the upper siftings. The upper siftings were indeed combustibles and their composition was also investigated. The characteristics of pyrolysis products were studied with special attention paid to mass distribution among gas, liquid and char products, composition of gas products and liquid products, quality of oil products and pollutants in gas products. Chars from the two pyrolysis processes were also investigated to check their possible applications and their leaching characteristics. The results obtained based on the tests carried out at lab scale proved that the pyrolysis process carried out for the separated waste plastics was preferred to pyrolysis process for the whole upper siftings. Those information can be very useful for the design of a pyrolysis process for combustibles or waste plastics from MSW.

The amount of plastic waste is growing every year and with that comes an environmental concern regarding this problem. The authors of chapter 8 explore pyrolysis as a tertiary recycling process as a solution. Pyrolysis can be thermal or catalytical and can be performed under different experi-

mental conditions. These conditions affect the type and amount of product obtained. With the pyrolysis process, products can be obtained with high added value, such as fuel oils and feedstock for new products. Zeolites can be used as catalysts in catalytic pyrolysis and influence the final products obtained.

A novel strategy of waste recycling of polypropylene plastics (PP) bags for generation of commercially viable byproducts using nanoforms of nickel as catalyst is presented in Chapter 9, by Mishra and colleagues. After pyrolysis of waste PP bags ($>20\ \mu\text{m}$) under continuous argon flow, 90% conversion efficiency to high petroleum oil was observed at 550°C . To assess the physicochemical attributes of formed oil, flash point, pour point, viscosity, specific gravity, heating value, and density were also measured and found to be very close to ideal values of commercial fuel oil. Moreover, GC-MS was used to resolve the range of trace mass hydrocarbon present in the liquefied hydrocarbon. This robust recycling system can be exploited as economical technique to solve the nuisance of waste plastic hazardous to ecosystem.

Chapter 10, by Sun and colleagues, describes a kinetic study of the decomposition of waste printed circuit boards (WPCB) under conventional and microwave-induced pyrolysis conditions. We discuss the heating rates and the influence of the pyrolysis on the thermal decomposition kinetics of WPCB. We find that the thermal degradation of WPCB in a controlled conventional thermogravimetric analyzer (TGA) occurred in the temperature range of 300°C – 600°C , where the main pyrolysis of organic matter takes place along with an expulsion of volumetric volatiles. The corresponding activation energy is decreased from $267\ \text{kJ/mol}$ to $168\ \text{kJ/mol}$ with increased heating rates from 20°C/min to 50°C/min . Similarly, the process of microwave-induced pyrolysis of WPCB material manifests in only one stage, judging by experiments with a microwave power of $700\ \text{W}$. Here, the activation energy is determined to be only $49\ \text{kJ/mol}$, much lower than that found in a conventional TGA subject to a similar heating rate. The low activation energy found in microwave-induced pyrolysis suggests that the adoption of microwave technology for the disposal of WPCB material and even for waste electronic and electrical equipment (WEEE) could be an attractive option.

In Chapter 11, by Sarkar and colleagues, newspaper waste was pyrolysed in a 50 mm diameter and 640 mm long reactor placed in a packed bed pyrolyser from 573 K to 1173 K in nitrogen atmosphere to obtain char and pyro-oil. The newspaper sample was also pyrolysed in a thermogravimetric analyser (TGA) under the same experimental conditions. The pyrolysis rate of newspaper was observed to decelerate above 673 K. A deactivation model has been attempted to explain this behaviour. The parameters of kinetic model of the reactions have been determined in the temperature range under study. The kinetic rate constants of volatile and char have been determined in the temperature range under study. The activation energies 25.69 KJ/mol, 27.73 KJ/mol, 20.73 KJ/mol and preexponential factors 7.69 min^{-1} , 8.09 min^{-1} , 0.853 min^{-1} of all products (solid reactant, volatile, and char) have been determined, respectively. A deactivation model for pyrolysis of newspaper has been developed under the present study. The char and pyro-oil obtained at different pyrolysis temperatures have been characterized. The FT-IR analyses of pyro-oil have been done. The higher heating values of both pyro-products have been determined.

Chapter 12, by Lam and colleagues, presents an extensive review of the scientific literature associated with various microwave pyrolysis applications in waste to energy engineering. It was established that microwave-heated pyrolysis processes offer a number of advantages over other processes that use traditional thermal heat sources. In particular, microwave-heated processes show a distinct advantage in providing rapid and energy-efficient heating compared to conventional technologies, and thus facilitating increased production rates. It can also be established that the pyrolysis process offers an exciting way to recover both the energetic and chemical value of the waste materials by generating potentially useful pyrolysis products suitable for future reuse. Furthermore, this review has revealed good performance of the microwave pyrolysis process when compared to other more conventional methods of operation, indicating that it shows exceptional promise as a means for energy recovery from waste materials. Nonetheless, it was revealed that many important characteristics of the microwave pyrolysis process have yet to be raised or fully investigated. In addition, limited information is available concerning the characteristics of the microwave pyrolysis of waste materials. It was thus concluded that more work is needed to extend existing understanding of

these aspects in order to develop improvements to the process to transform it into a commercially viable route to recover energy from waste materials in an environmentally sustainable manner.

In Korea, municipal solid waste (MSW) treatment is conducted by converting wastes into energy resources using the mechanical-biological treatment (MBT). The small size MSW to be separated from raw MSW by mechanical treatment (MT) is generally treated by biological treatment that consists of high composition of food residue and paper and so forth. In Chapter 13, Kim and colleagues apply the hydrothermal treatment to treat the surrogate MT residue composed of paper and/or kimchi. It was shown that the hydrothermal treatment increased the calorific value of the surrogate MT residue due to increasing fixed carbon content and decreasing oxygen content and enhanced the dehydration and drying performances of kimchi. Comparing the results of paper and kimchi samples, the calorific value of the treated product from paper was increased more effectively due to its high content of cellulose. Furthermore, the change of the calorific value before and after the hydrothermal treatment of the mixture of paper and kimchi can be well predicted by this change of paper and kimchi only. The hydrothermal treatment can be expected to effectively convert high moisture MT residue into a uniform solid fuel.

