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Developing the next generation of pyrolysis reaction models

Experimental and modeling studies on pyrolysis

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Dissertation submitted in partial fulfillment of a
Doctor degree in Chemical engineering

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Abstract

Municipal solid waste incineration has been identified as a major source of dioxins in the air, leading to the closure of many European incinerators. While gasification of waste and biomass has been considered a more environmentally friendly alternative, it is not always guaranteed to meet regulatory emission limits. Pyrolysis, a sub-section of the gasification process, is a sustainable technique used to produce biofuels and is known for its low-emission properties. This thesis evaluates the applicability of widely used wood pyrolysis models and two proposed models by conducting experiments on walnut shells and reviewing existing experimental data on woody material and plastic waste pyrolysis. The analysis suggests that conventional models are inadequate for predicting pyrolytic product yields at higher temperatures and additional reactions must be accounted for. This thesis makes a significant contribution to the field of woody/plastic pyrolysis by demonstrating that incorporating secondary tar and char reactions into the reaction scheme improves the accuracy and predictive capabilities of kinetic models. An understanding of the kinetic characterization of pyrolysis is fundamental to advancing the field. This study aims to assist researchers in conducting relevant research for improving and optimizing pyrolysis processes.

Útdráttur

Brennsla sorps frá sveitarfélögum hefur verið skilgreind sem ein helsta uppspretta díoxíns í andrúmsloftinu. Þetta hefur leitt til lokunar fjölmargra brennsluofna í Evrópu. Þrátt fyrir að gösun sorps og lífmassa hafi verið talin vera umhverfisvænni valkostur þá er ekki öruggt að gösunarferlið standist losunarreglugerðir. Pýrólýsa er ferli í gösunarferlinu. Hún er sjálfbær tækni sem notuð er til að framleiða lífeldsneyti og er þekkt fyrir að hafa litla losun eiturefna. Í þessu doktorsverkefni er lagt mat á næmni líkana sem eru oft notuð fyrir pýrólýsu á timbri og tveggja endurbættra líkana. Næmnin er metin útfrá pýrólýsu tilraunum á valhnetuskeljum og með því að greina tiltæk gögn frá pýrólýsu tilraunum á við og plastúrgangi. Niðurstöður greiningarinnar benda til þess að hefðbundin líkön eru ófullnægjandi þegar kemur að því að spá fyrir um magn brunaefna sem myndast við hátt hitastig. Þetta undirstrikar þörfina á endurbótum þar sem gerð er grein fyrir viðbótarhvörfum. Framlag doktorsverkefnisins á sviði pýrólýsu á við og plasti er umtalsvert. Framlagið felst í því að sýna fram á að aukin nákvæmni og forspárgeta fæst með því að bæta við kviku pýrólýsulíkönin hvörfum á tjöru og kolum sem myndast í ferlinu. Frekari framfarir á sviðinu munu byggja að stórum hluta á auknum skilningi á kvikum einkennum pýrólýsu. Eitt af markmiðum þessa verkefnis er að styðja við frekari rannsóknir og þróun á sviðinu.

Dedication

To my dad of blessed memory
my mom,
my brother,
and the love of my life

Preface

This thesis is submitted in candidacy for a Ph.D. degree from the University of Iceland. The work was carried out at the Faculty of Industrial Engineering, Mechanical Engineering, and Computer Sciences supervised by Prof. Runar Unnthorsson and Prof. Christiaan Richter.

Aysan Safavi

November 2023.

Table of Contents

List of Figures

List of Tables

List of Publications

This thesis is based on the following publications:

Book chapter:

I: Safavi, Richter and Unnthorsson. Dioxin and furan emissions from gasification. *IntechOpen*; 2021, https://doi:10.5772/intechopen.95475.

Journal Papers:

I: Safavi, Richter and Unnthorsson, Dioxin formation in biomass gasification: a review, *Energies*, 15(3), 700, 2022, https://doi.org/10.3390/en15030700.

II: Safavi, Richter and Unnthorsson, Mathematical modeling and experiments on pyrolysis of walnut shells using a fixed-bed reactor, *ChemEngineering* 2022, 6(6), 93, https://doi.org/10.3390/chemengineering6060093.

III: Safavi, Richter and Unnthorsson, Revisiting the reaction scheme of slow pyrolysis of woody biomass, *Energy* 2023, https://doi.org/10.1016/j.energy.2023.128123.

IV: Safavi, Richter and Unnthorsson, A Study of parallel and competitive reaction schemes in kinetic modeling of plastic pyrolysis, submitted to *ACS Omega* 2023, under review.

Peer-reviewed conference contributions (not appended to this thesis):

I: Safavi, Richter and Unnthorsson, Kinetic modeling of nutshells pyrolytic products, *American Institute of Physics Conference Proceedings,* 2023, submitted.

II: Nazemi, Safavi, Bonthonneau, Richter and Unnthorsson, Producing high-strength pellets from seaweed, sawdust, and hay for the purpose of gasification, *American Society of Mechanical Engineers*, 2022.

Abbreviations

GHG   Greenhouse gas

MSW   Municipal solid waste

PCDDs Polychlorinated dibenzo-p-dioxins

PCDFs Polychlorinated dibenzofluorans

TEQ   Toxic equivalent concentrations

RDF   Refuse derived fuels

PVC   Polyvinyl Chloride

A   Pre-exponential factor

E   Activation energy

R   Gas constant

T   Temperature

$f(\alpha)$ Conversion function

β Linear heating rate

$d\alpha/dT$ Non-isothermal reaction rate

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I am deeply grateful to the individuals who have significantly contributed to and enhanced my doctoral research, making it a truly enjoyable and rewarding experience. Their invaluable support and guidance have played a vital role in shaping the outcome of this work.

Foremost, I extend my sincerest appreciation to my esteemed advisors, Rúnar Unnþórsson and Christiaan Richter. Their unwavering commitment to my research and their invaluable guidance throughout this journey has been instrumental in its success. Their expertise, insightful comments, and continuous encouragement have greatly enriched the quality of this thesis. I would also like to express my heartfelt gratitude to Jorge Mario Marchetti, a member of my committee, for his constructive feedback and valuable input. His expert evaluation has immensely contributed to the refinement of this work, for which I am genuinely thankful. Furthermore, I am indebted to the distinguished opponents, Dr. Patricia Taboada-Serrano, and Dr. Timo Kikas, who willingly examined my research and provided valuable insights.

I am grateful for the help and support of all the people during my time at Queen Mary University of London. I would like to extend my appreciation to my friends, especially Iman. We have shared countless joyful moments and have provided each other with invaluable support, making this academic journey even more memorable.

I am also deeply indebted to my family, Farhad, Parvaneh, and Mahan, who have instilled in me the enduring value of education. Their unwavering love, encouragement, and support have been the cornerstone of my success. I am profoundly grateful for their faith in me and for being a constant source of motivation throughout this challenging process.

Lastly, I want to express my deepest gratitude to Younes, my beloved partner. Your unwavering love, endless support, and understanding have been the bedrock upon which I have built my academic pursuits. With you by my side, I feel invincible, and I am eternally grateful for everything you have done. You are, without a doubt, the most loving and supportive person in my life, and I cherish you with all my heart.

1 Introduction

The steady increase in greenhouse gas (GHG) emissions is a consequence of the rising energy demand due to population growth, industrialization, rising energy demand, and waste generation. Fossil fuel consumption accounts for about 80% of world energy consumption, contributing to the rise in GHG emissions (Ward & Løes, 2011). Furthermore, the increasing population and waste generation from human activities such as food and plastic waste are also major contributors to the increase in GHG emissions. The decomposition of waste in landfills releases methane, a potent GHG that is even more harmful than carbon dioxide.

Iceland has made significant commitments to reduce GHG emissions and transition away from fossil fuels. The government has set targets to achieve carbon neutrality no later than 2040 and to phase out fossil fuels completely by 2050 ("Iceland's message at COP26: We need to upgrade our pledges," 2021). To achieve these goals, emissions from all major sectors, including energy, industry, agriculture, and waste, will need to be reduced by 40% by 2030, as required by the Paris agreement (Keller et al., 2020). However, total GHG emissions in Iceland, excluding land use, land-use change, and forestry, have increased by approximately a third since 1990 (see Figure 1) (Keller et al., 2020). The energy sector is a significant contributor to GHG emissions, with fuel consumption for road transport and fisheries being the main sources of emissions. The transportation sector, in particular, is a major contributor to emissions, with the burning of fossil fuels in cars, trucks, and airplanes releasing significant amounts of carbon dioxide and other pollutants into the atmosphere.

Figure 1: Greenhouse gas emissions by energy, industry, agriculture, and waste sectors, from the year 1990 to 2019 in kt $CO_2 e$ (Keller et al., 2020).

Waste management activities, such as solid waste disposal and wastewater treatment, also play a significant role in GHG emissions. Municipal solid waste (MSW) management in

Iceland primarily relies on landfilling and incineration, both of which result in GHG and hazardous emissions. The decomposition of organic waste in landfills and the treatment of wastewater release methane and other GHGs into the atmosphere. The incineration of MSW is a significant contributor to hazardous air pollutants, such as dioxins and furans, which are among the most toxic pollutants known to humans. In fact, MSW incineration is one of the main sources of dioxin formation in the environment. As a result of the harmful effects of incineration, almost all of the incineration plants in Iceland were shut down due to their dioxin formation (Arnarson, 2015; Halldorsson et al., 2012; Umhverfisstofnun, 2011). Transitioning to renewable energy sources and implementing sustainable waste management practices are vital steps in mitigating the impacts of climate change. To date, no cost-effective and environmentally sound alternative plans have been found to treat waste as stated by the Environment Agency of Iceland (Keller et al., 2020).

The utilization of waste for energy production is a promising field of research and development, aimed at reducing dependence on fossil fuels and promoting sustainable practices. This involves using waste to produce heat, electricity, fuel, chemicals, and for agricultural purposes. By pursuing these options, the goal is to mitigate GHG emissions and promote regional economic and social growth (Demirbas & Demirbas, 2007). The chemical energy present in the waste can be transformed into practical forms of energy through diverse conversion techniques like biochemical (S. M. Safavi & Unnthorsson, 2017, 2018), and thermochemical (Monteiro Nunes, Paterson, Dugwell, & Kandiyoti, 2007; Ouadi, Brammer, Kay, & Hornung, 2013; Rollinson & Williams, 2016) processes.

Biochemical conversion involves techniques like fermentation, digestion, and enzymatic hydrolysis, which are widely used but have limitations and are slower compared to thermochemical conversion processes (Zhang, Yang, Jiang, Liu, & Ding, 2013). In addition to that biochemical and chemical methods can only convert selected waste types to biogas, biodiesel, etc., while most waste materials can be thermochemically converted.

Thermochemical conversion, on the other hand, focuses on producing thermal energy and involves four main processes: combustion, pyrolysis, liquefaction, and gasification. Combustion is the oldest method and involves burning biomass with oxygen. Pyrolysis, in contrast, breaks down large molecules into smaller ones without oxygen. Liquefaction uses water or solvent to generate liquid fuel from solid biomass. Gasification is burning with limited oxygen (Pollex, Ortwein, & Kaltschmitt, 2012).

Gasification/pyrolysis converts waste, such as MSW, agricultural residues, and non-recyclable plastics, into clean energy while minimizing the emission of harmful substances, such as dioxins. The ultimate goal of the proposed project is to adopt a small-scale gasification/pyrolysis plant to communities in Iceland as a state-of-the-art green solution with significantly less emission of toxic materials produced for solid waste disposal.

The objective of this project is to assess the feasibility of using gasification and pyrolysis techniques as sustainable alternatives to traditional landfilling and incineration methods. Additionally, aims to develop essential tools, such as validated models, to streamline the design and implementation of such technological solutions, with a particular focus on pyrolysis.

In this project, our initial objective was to assess the effectiveness of gasification/pyrolysis method in addressing the issue of dioxin emissions associated with waste incineration in Iceland. To gain a comprehensive understanding of dioxin formation in gasification, the available data on the levels of dioxins formed by gasifying different waste streams, such as MSW, plastics, wood waste, animal manure, and sewage sludge, from existing experimental work were reviewed. The results imply emissions of Polychlorinated dibenzo-p-dioxins (PCDD) and Polychlorinated dibenzofluorans (PCDF) will not always be below the regulatory or detection limits.

Therefore, pyrolysis was chosen for further examination due to its integral role in the gasification process and its distinct technological advantages compared to alternative treatment methods. Pyrolysis, as a standalone technology, offers several benefits. It is characterized by its simplicity and minimal requirements for preprocessing of feedstock, and it can be engineered to yield minimal quantities of unusable byproducts (Al-Haj Ibrahim, 2020). The pyrolysis study in this thesis encompasses a combination of experimental work and modeling. Theoretical investigations of biomass/plastic pyrolysis were conducted as understanding its kinetics is imperative for the advancement of process development, optimization, and reactor design.

1.1 Research questions

The objective of the project was to introduce sustainable waste management solutions in Iceland, with a focus on addressing the issue of dioxin emissions associated with waste incineration. Initially, the effectiveness of the gasification method was assessed. Subsequently, pyrolysis was chosen for further evaluation, which involved a combination of experimental work and modeling. Pyrolysis was preferred as it is a primary sub-process in the gasification process and also a distinct technology on its own. A comprehensive understanding of its kinetics is necessary for process development, optimization, and reactor design. The research was conducted to answer a set of interwoven research questions, ultimately leading to the achievement of the project's goals.

The research questions which the project aimed to answer were:

1) Can gasification assure reliable and consistent dioxin formation well below limits?

   The purpose of this question is to shed more light on dioxin formation and its sources in gasification technologies. A review that summarizes the evidence on when gasification would likely result in environmentally benign emissions with dioxins below legal limits, and when not, would be of scientific and practical interest.

2) Do the fixed-bed (hot-rod) reactors used for slow pyrolysis experiments by many authors have the right tar collection setup? Can they ensure complete tar capture?

   Pyrolysis experiments on walnut shells were conducted using a fixed-bed (hot-rod) reactor. Effort has been made to ensure the pyrolysis yields are correctly

measured as they were used to establish an appropriate reaction mechanism for woody biomass pyrolysis. Hot-rod reactors have commonly been utilized to conduct various biomass slow pyrolysis experiments. However, during the author's research tenure at the Queen Mary University of London, she was able to make improvements in the tar collection section of the pyrolysis setup at the laboratory for the complete tar condensation.

3) Can the existing reaction pathways in the literature predict the yields of woody material pyrolysis? If not, then can the pyrolysis reaction scheme for woody material pyrolysis be improved in order to be able to predict pyrolysis yields, and if so, how? Can woody biomass reaction schemes be used for the prediction of plastic pyrolysis yields?

    Widely used conventional reaction models from the literature were tested in a wide range of process conditions feedstock and temperature profiles and reactor types.
    Two new kinetic models were proposed in this study to answer this question as the existing models were incapable of predicting pyrolytic product yields of woody biomass and plastic pyrolysis. Experimental studies on walnut shell pyrolysis a long with data from the literature were used to validate the models.

1.2 Contributions

The answers to the research questions will be presented in detail across chapters 2, 3, and 4. Chapter 5, section 5.1, will provide a comprehensive summary of the overall answers and findings. In this section, I will outline the dissemination of the results, including how and where they have been shared.

The main contributions of this thesis are divided into three major categories that are responses to the above-mentioned research questions.

1) The contribution of this work lies in its ability to provide a comprehensive understanding of the formation of PCDD/Fs during gasification. This review consolidates the available evidence to determine under what conditions gasification is likely to yield emissions of PCDD/Fs that are environmentally acceptable, complying with legal limits, and when it is not. This information holds both scientific and practical relevance. The author performed a thorough study of all accessible articles that came into existence over the last 30 years in literature to be able to answer question 1 which answer was really missing from the field. The answer to the first question was published in a book chapter and in review paper I. The results were also presented at the NECS 2023 conference.

2) The author's suggestion to explore the hypothesis that achieving a cooling bath temperature below -27°C is essential for achieving full tar condensation stands as a key aspect of this experimental research. For the purpose of answering the second question, the author improved the tar collection section in the pyrolysis setup at the Queen Mary University of London. The answer to question 2 was published in

paper II in Chemengineering journal in section 3.1. The results were also presented at the Efnís 2022 conference.

3) Conventional models for woody biomass pyrolysis were evaluated to see if they accurately predict yields under different experimental conditions. Expanded kinetic models for pyrolysis of woody material were proposed. The purpose of the expanded model(s) was to predict pyrolysis behavior over a wide temperature range under non-isothermal heating conditions. This modeling study enhances the lumped kinetic modeling of woody biomass pyrolysis by demonstrating that the inclusion of secondary pyrolysis reactions in the reaction scheme improves the accuracy and overall predictive capacity of the kinetic models for pyrolytic product outcomes. Moreover, woody biomass reaction pathways were evaluated to study their performance in predicting plastic pyrolytic products. The response to the third question were published in paper II (in section 3.2), papers III and paper IV at the journal of Chemengineering, Energy and ACS Omega, respectively. The results were also presented at ENEFM 2022 conference and also published at American Institute of Physics Conference Proceedings.

An overview of the relation between the contributions and the publications can be found in Table 1.1.

Table 1: An overview of the relation between the research questions and the publications.

Research questions	Book chapter	I	II	III	IV
			Papers		
1	X	X			
2			X		
3			X	X	X

1.3 Outline

The thesis structure can be outlined as follows. It is comprised of five main chapters: Introduction, Literature Review, Experimental Work, Pyrolysis Modeling, and Conclusion. Additionally, references and papers are included at the end.

Chapter 1, the introduction chapter of this thesis establishes the motivation behind the research and provides an overview of the methodology used to address the research questions.

Chapter 2 is an extensive Literature Review that provides a comprehensive overview of dioxin formation during gasification processes.

Chapter 3 is dedicated to Experimental Work on pyrolysis. This chapter includes an introduction, methodology, and the results obtained from the experiments conducted.

Chapter 4 delves into Pyrolysis Modeling. It provides a detailed explanation of the kinetic models employed in this study, the method used for modeling, and the results obtained from the modeling.

Finally, Chapter 5, the Conclusion, presents a summary of the findings of the study, highlights the limitations of the thesis, and suggests future research opportunities.

In addition to the main chapters, the thesis includes a comprehensive list of references and papers at the end.

2 Literature review

This chapter's literature review centers on dioxin formation in gasification, which was the original focal point of this thesis before shifting the focus to pyrolysis experiments and modeling. Subsequent chapters will delve into their respective literature reviews for pyrolysis experiments and modeling.

2.1 Dioxins formation in gasification

Incinerators emit PCDD/Fs and their concentration often exceeds the legal limit, which calls for an alternative waste treatment technology. Gasification has come up to tackle these issues and improve energy efficiency. The amount of PCDD/Fs emissions produced by gasification operations is always within standard limits set by national and international laws (<0.1 ng TEQ/Nm^3). TEQ stands for Toxic equivalent concentrations.

> *There is a common belief that gasification of waste and/or biomass, unlike incineration, inherently and always achieves dioxins emission below regulatory and detectable limits.*

Testing the hypothesis

> *Finding of this literature study suggests that the belief that the substitution of incineration with gasification would always, or necessarily, reduce dioxins emissions to acceptable levels is overly simplistic. However, the dioxins formation in gasification and the operational parameters can be controlled during the process to minimize their formation.*

The contribution of this study is to offer a comprehensive picture of PCDD/Fs formation in gasification. This review summarizing the evidence on when gasification would likely result in environmentally benign emissions with PCDD/Fs below legal limits, and when not, is of scientific and practical interest. The study concludes that unburnt carbon, a chlorine source, and a metallic catalyst are the main ingredients for PCDD/Fs formation (McKay, 2002). The operational conditions of the process, such as high temperature, and oxygen deficiency along with maximizing the conversion of hydrocarbons that are being produced in pyrolysis, are possible approaches to reduce the formation of PCDD/Fs in gasification (Kamińska-Pietrzak & Smoliński, 2013).

2.2 Introduction

Energy generation via waste incineration has become an effective way of managing combustible waste, because it reduces the waste and the areas required for landfilling. Nevertheless, it contributes to the release of very toxic organic (Environment Australia, 1999; Huang & Buekens, 1995; Lavric, Konnov, & De Ruyck, 2004). MSW incinerations had historically been implicated as the major source of PCDD/Fs distributed by air. As a result of awareness and legislation most European MSW incinerators were either shut down or equipped with modern air pollution control systems necessary to achieve MSW

incineration with PCDD/Fs emissions within regulatory limits set by national and international laws (typically < 0.1 ng TEQ/Nm^3). A detailed explanation of the PCDD/Fs formation mechanism can be found in the author´s book chapter (S. M. Safavi, Richter, & Unnthorsson, 2021).

PCDD/Fs are a group of by-products coming from thermal processes. They are highly toxic and cause severe bronchitis, asthma, and strangulation of the lungs in humans (see Figure 2) (Jeno, Rathna, & Nakkeeran, 2021). Agricultural lands and livestock in the vicinity of incinerators can also be affected by dioxin that infects meat, dairy products, and so on (Martens et al., 1998; Sodhi, Kumar, Shree, Singh, & Singh, 2020; *Waste incineration and public health*, 2000). Consuming these products may destroy the human immune system, thyroid function, hormone dysfunction, and causes cancer. It has negative health condition in infants because of dioxin exposure through breast milk and uterine exposure (Altarawneh, Dlugogorski, Kennedy, & Mackie, 2009; Paladino & Massabò, 2017). PCDD/Fs emission from incinerators often exceeds the legal limit, which calls for an alternative waste treatment technology. Gasification processes usually emit PCDD/Fs within acceptable limits as determined by national and international organizations (Lopes, Okamura, & Yamamoto, 2015). The amount of pollutants in producer gas can be lower than that of the flue gas of an incinerator (Panepinto, Tedesco, Brizio, & Genon, 2014), and it is because of partial oxidation of waste with limited oxygen supply (Klein, 2002; Thakare & Nandi, 2015; Xu, Jin, & Cheng, 2017). However, small amounts of PCDD/Fs can result from deficient destruction of the PCDD/Fs present in the waste itself or from the existence of organic chlorinated compounds in the reactor (Seggiani, Puccini, Raggio, & Vitolo, 2012; Werther & Ogada, 1999).

Figure 2: The sources of dioxin formation are depicted on the left, while the right side showcases several examples of severe health conditions that can result from the consumption of dioxins (Jeno et al., 2021).

2.3 Method

To achieve the objectives of this study, an extensive review of the literature was conducted to provide a comprehensive overview of PCDD/Fs formation during gasification. This work explores existing experimental data on the levels of dioxins generated from various waste streams, including MSW, plastics, wood waste, animal manure, and sewage sludge. The potential of gasification technology to reduce PCDD/Fs emissions to levels that meet regulatory or detection limits is also emphasized. The author conducted a thorough assessment of all available articles published since 1990 to construct this review, which fills a critical gap in the field.

2.4 Results

Paper I provides the results obtained from the reviewed literature reporting experimental measurements of dioxin formation levels in gasification using various substrates and process parameters. The findings of this study are summarized below.

The correlation of the amount of dioxins that was measured with feedstock types and temperatures (process temperature) is illustrated in Figure 3. This figure shows that gasification does not necessarily result in PCDD/Fs formation below the acceptable limits (<0.1 ng TEQ/Nm^3). There are not enough studies measuring PCDD/Fs formation in gasification. It is evidenced, with the data gathered in this review, that there is a strong relation between high temperature and less dioxins formation for almost all feedstock types. It can be seen from the plot that the PCDD/Fs concentrations reported for refuse derived fuels (RDF) and textile tend to be more than an order of magnitude higher compared to other feedstock because of their high chlorine and sulfur content. Researchers (Borgianni, De Filippis, Pochetti, & Paolucci, 2002; Van Paasen, Cieplik, & Phokawat, 2006) showed that a high-temperature reactor and gas cooling, in the absence of oxygen, prevents PCDD/Fs formation by de novo synthesis reactions (Huang & Buekens, 2001; Ma, Wang, Tian, & Zhao, 2019). Thus, this resulted in dioxin-free high-calorie gas production when high chlorine level feedstock was used. Most of the chlorine in the waste was converted to hydrogen chloride in the off gas (Yamamoto et al., 2004). When gasifying wastes, especially for MSW and sewage sludge, with temperatures above 1000°C, PCDD/Fs concentrations are within acceptable limits.

The effect of using gas cooling methods and high temperatures on dioxin formation of different feedstock even for those with high chlorine contents is shown in Figure 4. Gas cooling suppressed dioxins emission to a very low level. Experiments showed the regeneration of PCDD/Fs occurring during slow gas cooling after high-temperature treatment (Yamawaki, 2003). The general trend in the field is that dioxin concentrations decrease as temperature increases. The trend lines for each case may not fit very tight, but the best-fit lines always slope downwards, showing the correlation between the PCDD/Fs concentrations and the temperatures. Figure 4 shows a strong correlation for MSW and sewage sludge with existing data. For other feedstock, it is not possible to look for a trend as there are not enough studies and thus data available in the literature.

For MSW, the most frequently studied feedstock, there is a correlation but also an outlier at temperatures below 1000°C. Researchers stated that they did not consider any treatment (such as cooling methods) for the product gases, which could be the reason for the dioxin concentration being above the standard limits (Lopes et al., 2015).

Figure 3: The scatter chart shows the PCDD/Fs concentrations for different feedstock versus temperature. Data points that are Scheme 0 (ng-TEQ/Nm^3) are those measurements with dioxin concentration below the detection limit or zero dioxin. As it is not possible to put zero values on a logarithmic axis, the red dashed line is the acceptable limit as determined by national and international organizations (<0.1 ng TEQ/Nm^3).

For sewage sludge as well as MSW, there are usually several parameters affecting dioxin formation, but above 1000°C, it is mainly the temperature that has the most dominant effect. Studies (Gang et al., 2007; Hu, Huang, Chi, & Yan, 2019) showed that that more than 99.9% of dioxins are de-composed during MSW gasification and that most heavy metals are solidified when the temperature is 1100°C.

For RDF, which is the high chlorine content feedstock, there are only three data points available. There are no data points for temperatures higher than 850°C, and thus it is not possible to talk about a trend here.

For plastics, there are several data points for high-temperature measurements but nothing for low-temperature measurements in the existing literature. In the high-temperature region, it seems a trend exists, but whether this trend extends into the low-temperature region is currently untested. Researchers studied the effect of chlorine content on dioxins formation by mixing plastic waste with polyvinyl chloride (PVC), as PVC is high in chlorine (Kikuchi, Sato, Matsukura, & Yamamoto, 2005; Yamamoto et al., 2004). Results showed that all PCDD/Fs concentrations were within the standard limits, which proves the effect of the high-temperature treatment and the gas cooling (Adlhoch, Sato, Wolff, & Radtke, 2000; Yamamoto et al., 2004; Yamawaki, 2003).

For wood waste, there is one measurement that is above the limit. This measurement was reported by the Energy Research Centre of the Netherlands, which implemented an oil-based gas washing (OLGA) process in a biomass gasifier in order to remove dioxins from the product gas (Zwart et al., 2009). The dioxin concentration of the product gas was 0.5 ng TEQ/Nm^3 where no OLGA was applied, while it was a factor 10 lower when the gas

was purified using the OLGA scrubber. Other measurements presented in the plot are within the acceptable limit, thanks to rapid gas cooling (Asikainen, Kuusisto, Hiltunen, & Ruuskanen, 2002).

For animal waste, very little data are available, one of which is hydrothermal gasification of chicken manure at 400°C under a pressure of 26~27 MPa, where PCDD/Fs were not detected (Bircan, Matsumoto, & Kitagaw, 2012). The other study shows the result of cogasification of biofermenting residue at 1300 to 1400°C. The dioxins emission was calculated to be 0.365 ± 0.23 ng-TEQ/Nm^3, which is far beyond the limits in the EU. This biofermenting residue contains starch, fish meal, yeast powder, etc., and is identified as a hazardous waste according to the national hazardous wastes classification, proposed by the Ministry of Environmental Protection of China (Du et al., 2014).

One might inquire about the statistical significance of the trend lines presented in Figure 4. Each plot within the figure depicts measurements of dioxin formation from the same substrate, albeit under varying experimental setups, operational conditions, and treatments. Notably, the available data in the literature are relatively scarce for most substrates, with the exception of MSW. The outliers in the data can be attributed to variations in experimental conditions and unique treatments applied in each study. For instance, the outlier in the case of MSW is a consequence of low-temperature gasification, specifically below 1000°C.

The formation of PCDD/Fs compounds in thermochemical processes is indeed the outcome of a complex set of competing chemical reactions. Specific operating settings result in PCDD/Fs formation involving deficient combustion of fuel, the presence of a chlorine source (Rollinson & Williams, 2016), oxidizing atmosphere between 10 and 15% oxygen in the cooling zone (Wu, Azharuddin, & Sasaoka, 2006), fly ash with degenerated graphical structures, fly ash surface acting as a carbon source, temperature range between 250 and 450°C, and the existence of catalytic metals such as copper, iron, manganese, and zinc (Behrend & Krishnamoorthy, 2017). However, in gasification, these conditions are not satisfied, or are less common or fleeting, and hence, the likelihood of detection of PCDD/Fs compounds in the producer gas is low. The specific conditions by which the gasifier runs the gasification process prevents the formation of free chlorine from HCl, thus confining the chlorination of any species in the producer gas (Prabhansu, Karmakar, Chandra, & Chatterjee, 2015).

This chapter reviewed existing literature on dioxin formation in gasification technology, however, further investigations and research had been conducted on pyrolysis in the following chapters. Pyrolysis is an inevitable process in thermochemical conversions. It has several advantages compared to other treatment processes, especially gasification technology. It is a relatively simple technology that can be made compact and lightweight. It can be conducted as a batch, low-pressure process, with minimal requirements for feedstock preprocessing. Pyrolysis can be used for all types of solid and liquid products and can be easily adapted to changes in feedstock composition. It can be designed to produce minimal amounts of unusable byproducts. In comparison with gasification, pyrolysis generally produces fewer air emissions, lower emissions of nitrogen and sulfur oxides (Al-Haj Ibrahim, 2020), less CO_2 generation, less dust emission, and no emission of dioxin inside the pyrolyzer due to the pyrolysis with deoxidized hydrocarbon gas (Al-Haj Ibrahim, 2020).

Figure 4: The scatter chart shows the PCDD/Fs concentrations for each feedstock versus temperature. Since there is only one study experimenting with textile and hospital waste, they are not included in this figure. The symbols show if any cooling methods/rapid cooling were used and whether high-chlorine-level feedstock were used.

2.5 Summary

This chapter discussed the levels of PCDD/Fs measured in emissions during waste gasification. The literature contains limited studies examining and measuring dioxin formation in this process, all of which were reviewed in this study. It was found that PCDD/Fs formation during gasification can be regulated by implementing high temperature and gas cooling, as these parameters are the most effective at preventing dioxin formation even when working with feedstock that have a high chlorine content.

Next chapter presents experimental studies on woody biomass pyrolysis. It is concluded in this chapter that temperature has the most significant influence on dioxins formation in thermochemical processes. Hence the likelihood of dioxins formation in pyrolysis is high due to lower operational temperatures than that of gasification. The objective of the experimental study was to ensure complete tar capture, as dioxins and their related amounts correlates well with tar formation.

3 Pyrolysis experiments

Pyrolysis experiments on walnut shells was conducted to develop a suitable reaction model for woody biomass material. The atmospheric pressure hot-rod reactor previously developed at the Queen Mary university of London was used in this study for the pyrolysis experiments. The pyrolysis setup was used for several experimental studied (M. Volpe, D'Anna, Messineo, Volpe, & Messineo, 2014; R. Volpe, Menendez, Reina, Messineo, & Millan, 2017; R. Volpe, Messineo, Millan, Volpe, & Kandiyoti, 2015; R. Volpe, Messineo, Volpe, & Messineo, 2016). In this study, modification was made to the tar collection section in the setup in order to capture all the tars produced from the pyrolysis process. The term tar in this thesis used to denote the species that are condensable at room temperature (Dufour et al., 2007; Neves, Thunman, Matos, Tarelho, & Gómez-Barea, 2011).

The studies (M. Volpe et al., 2014; R. Volpe et al., 2017, 2015, 2016) *utilized a cooling bath to trap tars, and its temperature was set at -27°C, which was presumed to be sufficiently low to capture all condensable volatiles generated by the sample during pyrolysis. However, the investigation conducted by the author proposes that a much lower temperature for the cooling bath is necessary to ensure that the temperature at the tar trap is below room temperature for the complete tar condensation.*

Testing the hypothesis

The author's proposal to investigate the hypothesis that a cooling bath temperature lower than -27°C is necessary for complete tar condensation represents a key contribution of this experimental work. Improvements in the tar collection section of the pyrolysis setup were made, as there are no existing reports on temperature measurements of tar tubes using the same hot-rod reactor setup in the literature. Previous studies (M. Volpe et al., 2014; R. Volpe et al., 2017, 2015, 2016) *utilized a cold bath consisting of a mixture of ethylene glycol, dry ice, and water, and all of them reported a temperature of approximately -27°C. After conducting an investigation, it was determined that the temperature recommended in the literature for the tar cooling bath was insufficient for complete tar condensation at the trap and keeping the temperature of the tar tube below room temperature. As a result, it was necessary to significantly decrease the temperature of the tar cooling bath.*

3.1 Introduction

Pyrolysis is a high-temperature thermochemical process that involves the treatment of solid materials, such as coal, biomass, MSW, plastic waste, and even animal and human fecal waste, in an oxygen-free or inert atmosphere (Al-Haj Ibrahim, 2020). Typically, pyrolysis is performed at temperatures ranging from 200°C to 700°C (Gil & Sebastián, 2016). The rate of pyrolysis is temperature-dependent, with higher temperatures leading to increased rates of pyrolysis (Shi, Ronsse, & Pieters, 2016). During pyrolysis the molecules are subjected to very high temperatures leading to very high molecular vibrations at which the

molecules are stretched and shaken to such an extent that they start breaking down into smaller molecules. The solid material is thermally cracked into three main products: a gas product known as syngas, which consists of non-condensable gases; a liquid product called bio-oil or tar, which comprises condensed vapors; and a solid product called bio-char (Gil & Sebastián, 2016). Bio-oil can serve as a substitute for conventional fossil fuels or be used in chemical production. The gas fraction produced during pyrolysis can be used for heat and power generation, while char can be utilized as a soil amendment, as a precursor for making catalysts and contaminant adsorbents, or as a solid fuel (Shi et al., 2016).

Pyrolysis also is always the first step in other processes such as gasification and combustion where partial or total oxidation of the treated material occurs. As pyrolysis is an inevitable process in thermochemical biomass conversion, understanding pyrolysis kinetics is important for process development, optimization, and proper reactor design. Pyrolysis experiments on walnut shells were conducted for the purpose of developing a suitable reaction model for woody biomass material.

3.2 Method

A detailed explanation of the experimental procedure is published in paper II. The pyrolysis experiments were carried out on a fixed-bed (hot-rod) reactor at the Queen Mary University of London (shown in Figure 5). The schematic of the pyrolysis process is illustrated in Figure 6. The system consists of vertically positioned stainless steel tubes, where the pyrolysis of the biomass occurs, and a U-style tar trap connected to the reactor. Power was delivered via copper clamps attached to the outside of the stainless steel tube body at the top and bottom of the tube. The process was performed at different temperatures (300–600°C), with a heating rate of 0.25 $°C·s^{-1}$ and a holding time of 100 s.

Numerous attempts have been made to develop a tar collection method that did not involve solvents or rotary evaporators, as the high temperature of rotary evaporators could cause the loss of some tars (Nunes, Paterson, Herod, Dugwell, & Kandiyoti, 2008). To achieve this, the author modified the tar tube and tested different setups, with and without a cooling bath. Initially, several pyrolysis experiments were conducted without a cooling bath, during which the author experimented with different materials, lengths, and shapes of the tar tube. During the experiments, a thermocouple was placed at the top of the tar trap tube to monitor its temperature and ensure that it was cool enough to capture tars. They first used a glass tar tube and then switched to various lengths of stainless steel tubes, with or without placing quartz wool inside the tubes to capture tars, failed to capture and measure any tars (see Figure 7.a).

Figure 5: Hot-rod reactor setup for the pyrolysis process.

The authors then tested a cooling bath with different lengths of steel tube and different tube placements (see Figure 7.b). Attempts to avoid using a u-shaped steel tube, as it would result in weight differences that could cause errors, were unsuccessful. However, it was ultimately decided to use a u-shaped tube and place it in the cooling bath (see Figure 7.c). The first cooling bath was used contained dry ice with a temperature of -17°C, which was insufficiently cold. As the process temperature increased to the final temperatures of 300-600°C, the temperature of the tar tube rose to above 70°C, which was too high for volatile condensation. Therefore, the author experimented with different mixtures and compositions of dry ice and ethylene glycol to achieve better heat transfer and lower temperatures. The author was ultimately able to develop an effective cooling bath for pyrolysis vapor condensation. The bath consists of a mixture of dry ice and ethylene glycol, and is fully insulated to minimize heat transfer with the outside environment (see Figure 7.d). The temperature of the tar tube is maintained below 10°C throughout the process. The cooling bath temperature of -60°C was achieved through the use of volume fractions of 0.4 and 0.6 of dry ice and ethylene glycol, respectively (Jensen & Lee, 2000).

Figure 6: Schematic view of the pyrolysis setup.

Figure 7: Stainless steel tar tube without cooling bath (7.a), tar tube had placed on top of the cooling bath containing dry ice (7.b), U-shaped tar tube in the cooling bath (7.c), fully insulated cooling bath with U-shaped tar tube (7.d).

Figure 8: Pyrolysis process and tar trap temperatures versus time of pyrolysis.

3.3 Results

Figure 8 shows the data collected from the thermocouples, including the pyrolysis process and tar trap temperatures versus the time of the pyrolysis. The cooling bath exhibited good heat preservation performance with the right volume fractions of dry ice and ethylene glycol. During pyrolysis, the temperature of the tar trap gradually increased from −30°C to the final temperature of 2°C, which is well below the temperature limit (30°C) reported in the literature (Nunes et al., 2008). Wang et al. found the optimum condensing temperature to be in the range of 67 to 77°C, at which point the moisture in the pyrolysis oil decreased from 30% to 10% and the condensing efficiency was in the range of 0.4 to 0.2 (C. Wang, Luo, Diao, & Zhu, 2019).

$$\text{Condensing efficiency} = Liquid\ mass\ /\ Walnut\ shell\ mass - solid\ mass \quad (1)$$

Condensation efficiency in this study was calculated using Eq. 1 (C. Wang et al., 2019), and the result was around 0.25 for all the experiments, which is in the optimum range (C. Wang et al., 2019). Where liquid mass denotes the mass of condensed tar in the tar trap, walnut shell mass specifies the mass of raw materials (walnut shells) prior to pyrolysis, and solid mass represents the mass of char after pyrolysis.

The tar and char yields were measured after each test, and the results are shown in Figure 9. The gas yield was calculated as the percentage of the balance between the original sample weight and the weights of tar and char formed. Volatile yields (volatile yield is the sum of the gas and tar yields) increased as the temperature increased. The ideal pyrolysis temperature for maximum tar yields is reported to be between 400–600°C for most types of woody biomass (Bhoi, Ouedraogo, Soloiu, & Quirino, 2020). The tar yields increased

twofold, rising from 10% at 400°C to 20% at 500°C. There was a major increase in tar yields up to 500°C, but by 600°C the yield reached a maximum value of 19%. Efeovbokhan et al. (Efeovbokhan et al., 2020) observed that tar yields increased by more than double when the temperature was in the range of 400–500°C for pyrolyzing yam peels. The gas yields were high, with approximately half of the feedstock being converted to gas. The high char yields, measured at the low temperatures in the range studied, decreased up to 23% of the total biomass feed. This indicates that the optimum temperature range for char production from pyrolysis of walnut shells is up to 400°C. Temperature negatively affects char production yields (Dhar, Sakib, & Hilary, 2022). Sarkar et al. (Sarkar & Wang, 2020) studied the pyrolysis of coconut shells in the temperature range of 400–600°C and reported the char yield reduced while bio-oil yield was improved with the temperature increase.

Figure 9: Distribution of the products generated during pyrolysis at different temperatures. Each test was performed in duplicate.

3.4 Summary

The aim of this chapter was to investigate the slow pyrolysis behavior of walnut shells using a fixed-bed reactor and develop an appropriate reaction model for woody biomass materials. The experiments were conducted over a range of temperatures (300-600°C) with a heating rate of 0.25 °C·s^{-1} and a holding time of 100 s. Temperature is known to be a critical factor affecting the distribution and quantity of pyrolysis products, hence, the effect of temperature on the yield of walnut shells pyrolysis products was investigated.

This chapter focuses on the research methodology rather than the process economics. The author conducted experiments using various ratios of dry ice and ethylene glycol to achieve the desired temperature in the tar collection section. Previous studies (M. Volpe et al., 2014; R. Volpe et al., 2017, 2015, 2016) used a cooling bath with a temperature of -27°C to trap tars, assuming that it was low enough to capture all the condensable volatiles produced during pyrolysis. However, the author's investigation suggests that a much lower temperature for the cooling bath is required to fully condense the tar. The economics of tar removal methods for industrial pyrolysis and gasification plants remains a major challenge

for the commercialization of biomass and waste based processes. For example, in a recent (2023) comprehensive review, Cortazar et al. wrote: "Despite [that existing industrial tar removal] strategies prove effective for tar elimination, they are hardly economically feasible" (Cortazar et al., 2023; Lateh, Taweekun, Maliwan, & Ishak, 2020; Zeng et al., 2020).

In the following chapter, the experimental data obtained from this study and other relevant literature on woody biomass pyrolysis will be utilized to establish an appropriate reaction mechanism for woody biomass pyrolysis.

4 Pyrolysis modeling

Kinetics plays an important role in understanding the complex pyrolysis process and deriving mathematical models. Pyrolysis process involves a highly complex set of competitive and concurrent reactions, and the exact mechanism remains unknown. Numerous studies have investigated the kinetics of pyrolysis. Various lumped models have been developed and utilized a limited, yet sufficient number of sequential and parallel reactions to describe the pyrolysis process (Çepelioğullar, Haykiri-Açma, & Yaman, 2016; Di Blasi & Branca, 2001; Gouws, Carrier, Bunt, & Neomagus, 2022; Koufopanos, Lucchesi, & Maschio, 1989; Noszczyk, Dyjakon, & Koziel, 2021; Park, Atreya, & Baum, 2010; E. Ranzi, Dente, Goldaniga, Bozzano, & Faravelli, 2001; Vo et al., 2021; Wagenaar, Prins, & van Swaaij, 1993)(Chen, Liu, & Fan, 2006; Koufopanos, Papayannakos, Maschio, & Lucchesi, 1991; Mate, 2016; Eliseo Ranzi et al., 2008; Scott, Piskorz, & Radlein, 1985; Shafizadeh & Chin, 1977).

Although numerous studies exist on pyrolysis reaction schemes and kinetic modeling, no generally accepted model can predict the pyrolysis rate and final products of different materials over a range of experimental conditions. The hypothesis to be investigated is if a rate expression exists with more general predictive capability than current popular lumped kinetic models? By more general predictive capability, the author refers to the sufficiently accurate prediction of product yields across heating profiles, temperature ranges and feedstock variations by changing only model parameters, but not the form of the rate expression.

Testing the hypothesis

The contribution of the modeling work was to first evaluate the applicability of the widely used wood pyrolysis kinetic model on several sets of experimental data, over the wide range of temperature and feed type. Second, the author proposed two new kinetic models. Models proposed accounts for additional reactions not captured by conventional models that was found contributing nontrivially to the formation of secondary pyrolysis phases. This modeling work contributes to the lumped kinetic modeling of woody biomass pyrolysis by concluding that the addition of secondary tar and char reactions into the reaction scheme makes the kinetic models more accurate and broadly capable of predicting pyrolytic products. Proposed models further investigated and showed promising results for plastic pyrolysis yields prediction. The study findings have been reported in papers II, III and IV.

4.1 Introduction

Biomass pyrolysis involves numerous extremely complex reactions and end up with large number of intermediates and end products, devising an exact reaction mechanism and kinetic modeling for biomass pyrolysis is extremely difficult, hence, pyrolysis models are modeled on the basis of visible kinetics. There have been extensive studies on biomass

pyrolysis kinetics in the past decades for developing various kinetic models (Kersten, Wang, Prins, & van Swaaij, 2005; X. Wang, Kersten, Prins, & van Swaaij, 2005). Most of kinetic models are considered as lumped models because the kinetics are based on the yields of lumped products (i.e., char, tar and gas). Two methods are typically employed to determine the kinetic parameters of biomass pyrolysis experimentally: model-free and model fitting. The key difference between these methods is that model-free methods do not make any assumptions about the reaction scheme for calculating the kinetic parameters, whereas model fitting methods assume a reaction model and determine the kinetic parameters using a mass-dependent function. Model fitting methods can be further categorized into one-component or multi-component based on how the initial biomass is characterized (e.g., by specific type of biomass or by its components), and lumped or detailed reaction schemes based on how the products are defined (e.g., by lumped products such as gas, char, and tar, or by species in each lumped product) (Di Blasi, 2008).

Since pyrolysis is an extremely complex process resulting in the formation of a large number of intermediates and end products, it is difficult to devise a precise model including all the reaction mechanisms. The pyrolysis process is composed of three stages and is closely related to the pyrolysis temperature (Altantzis, Kallistridis, Stavropoulos, & Zabaniotou, 2021). Biomass moisture evaporates after it is heated to over 100°C to below 200°C (Glushkov, Nyashina, Shvets, Pereira, & Ramanathan, 2021). Then, primary pyrolysis takes place at temperatures of 200°C to 400°C (Fisher, Hajaligol, Waymack, & Kellogg, 2002; Leng et al., 2022), which is also considered to be the initial depolymerization reaction stage. At this stage, the dry biomass particles are decomposed into solid, condensable, and non-condensable products. As the temperature further rises, the primary products undergo secondary reactions. Secondary reactions such as tar cracking, reforming, dehydrogenation, and repolymerisation lead to the production of permanent gases, secondary chars, and secondary tars (Miller & Bellan, 1996; Vikram, Rosha, & Kumar, 2021). There is no clear border between primary and secondary pyrolysis since these pyrolysis stages generally take place simultaneously in different parts of the biomass (Guo et al., 2020; Vershinina, Nyashina, & Strizhak, 2022). For a more detailed discussion of the chemical nature of secondary tar and char, see section 4.2.

Despite extensive research on biomass pyrolysis reaction schemes and kinetic modeling, there is currently no widely accepted model capable of accurately predicting the pyrolysis rate and resultant products of various materials under a broad range of experimental conditions (Koufopanos et al., 1989). The initial aim of this study is to evaluate the applicability of the most famous wood pyrolysis kinetic models on different experimental data, then further investigate the addition of extra reactions to the pyrolysis reaction scheme until the modeling predictions match the experimental data. This work concludes whether adding extra reactions into the reaction mechanism and further determination of any kinetic parameter may make the model more accurate and precise in predicting pyrolytic products of different biomass materials. The author also aims to investigate whether the proposed reaction schemes can accurately predict the plastic pyrolysis product yields compared to the conventional models used in the literature (Chan, Kelbon, & Krieger, 1985; Di Blasi & Russo, 1993; Fakhrhoseini & Dastanian, 2013; Shafizadeh & Chin, 1977).

4.2 Method

4.2.1 General approach

The goal of the modeling studies in this thesis was to develop a kinetic model that could accurately predict pyrolysis yields under non-isothermal heating conditions, and fit the experimental data. Ideally, if reaction rates could be measured instantaneously during pyrolysis experiments, they could be compared with the model's rates. However, in the experimental part of this thesis, only final yield measurements were taken at the end of each batch. As a result, the reported measurements are the yields at the final temperature when the process was completed. Thus, we adopted an approach of fitting the models with the final experimental yields at each final temperature of 300, 400, 500, and 600ºC. This same approach was used in the experimental studies from the literature that were used for model validation.

4.2.2 Detailed discussion

In this study, the conventional reaction models (models I and II) (Di Blasi & Branca, 2001; Papari & Hawboldt, 2015; Shafizadeh & Chin, 1977) were compared with two expanded reaction models (models III and IV) to study their application and compare their applicability to woody biomass and plastic pyrolysis (see Figures 10, 11, 12 and 13). A large number of experimental studies conducting pyrolysis has been documented in the literature. In order to make a relevant comparison with the experimental data presented in the previous chapter, the authors examined previous studies (Monteiro Nunes et al., 2007; M. Volpe, Luz, & Messineo, 2021) that conducted pyrolysis using a hotrod reactor. The experimental data from various materials were used in the study, including walnut shells (which were conducted by the author), eucalyptus wood (Monteiro Nunes et al., 2007), pistachio shells (M. Volpe et al., 2021) and plastic (Monteiro Nunes et al., 2007).

Model I is the widely used competitive reaction model which is a common reaction scheme for representing the components of pyrolysis by simply lumping them into three groups of products (gas, tar, and char) (Di Blasi & Branca, 2001; Papari & Hawboldt, 2015). The reaction scheme for model I is shown in Figure 10.

Figure 10: The competitive reaction model (model I).

The results from paper II suggest that the competitive reaction model with three reactions needs to be expanded to include the secondary decomposition of pyrolysis products to accurately predict yields (Mate, 2016). Model II is the commonly used parallel and competitive reaction model developed by Shafizadeh and Chin (Shafizadeh & Chin, 1977), that indicates the primary degradation of biomass conjoining the secondary decomposition

of primarily tar and higher hydrocarbons to gas (Scott et al., 1985) and tar polymerization reactions to produce secondary char (Eliseo Ranzi et al., 2008). The reaction scheme for model II is shown in Figure 11.

Figure 11: The parallel and competitive reaction model with secondary tar cracking (model II).

Model III in this study proposes the addition of an extra reaction to model II. The added reaction competes with the decomposition of primary tar into secondary char and secondary gas to form instead more stable secondary tar that is subsequently not available to secondary gas and char formation. Although the addition of this term was suggested purely by the comparison of models I and II in papers II (A. Safavi, Richter, & Unnthorsson, 2022) and III (A. Safavi, Richter, & Unnthorsson, 2023a), respectively, this expansion of the reaction scheme has a rational motivation as well: This extra reaction can be ascribed to the successive conversion of primary tars into an ever more stable mixture of tars (condensable molecules) that could include oxygenates, aromatics & phenolic ethers, olefins and higher hydrocarbons like polycyclic aromatic hydrocarbons. In essence, all the chemical species frequently detected with gas chromatography/mass spectrometry analysis of secondary tars (Li & Suzuki, 2009; Pattanotai, Watanabe, & Okazaki, 2013; Serio, Peters, & Howard, 1987). As primary tar is cracked, dehydrogenated and deoxygenation at elevated pyrolysis temperature and/or accelerated by catalysts a reformed and refined secondary tar is progressively obtained and the fact that this process removes primary tar from secondary gas and char formation apparently need to be explicitly included in the reaction scheme if it is to be broadly predictive. Model III explicitly includes this feature of pyrolysis and is shown in Figure 12.

Figure 12: The parallel and competitive reaction model (model III).

A further expansion, model IV, is also proposed in this study. Model IV has a total of eight reactions. First, virgin wood decomposes into three major products: tar, char, and gas, by three primary reactions. And then, a portion of tar decomposes to secondary gas and secondary char and secondary tar by successive secondary reactions, respectively. In model IV it is then added that primary char can volatilize to produce additional gas by secondary reactions with an even more devolatilized solid carbon remaining (Anca-Couce,

Mehrabian, Scharler, & Obernberger, 2014; Lyon, 1998). The reaction scheme for model IV is shown in Figure 13.

Figure 13: The parallel and competitive reaction model (model IV).

For detailed explanations on the methodology section see papers II, III and IV. The rate of reaction of the solid phase under non-isothermal conditions is presented using Eq. 2 (Fogler, 2004). The reaction rate expressions for all the species in the models can be found in Appendix A.

$$\frac{d\alpha}{dT} = \frac{A_i}{\beta} exp\left(\frac{-E_i}{RT}\right) f(\alpha) \qquad (2)$$

where $d\alpha/dT$ is the non-isothermal reaction rate, $\beta = dT/dt$ is the linear heating rate ($^{o}C.s^{-1}$), A is the pre-exponential factor (s^{-1}), E is the activation energy ($kJ.mol^{-1}$), R is the universal gas constant ($kJ.K^{-1}.mol^{-1}$), and T is the absolute temperature (K), $f(\alpha)$ is the conversion function. In the kinetic models, the rate expression based on the first-order decomposition of the reactive solid is defined in terms of fractional conversion.

Nonlinear least squares fitting is employed to estimate Arrhenius parameters by fitting the experimental data. Model searched for values of the unknown parameters (Ai, Ei) that minimized the sums of the squares of the experimental data (final yields of gas, tar, and char at the final temperature) and determined the corresponding points of functions calculated (at the final temperature) by the model (see Eq. 3) (Anca-Couce, Berger, & Zobel, 2014; Várhegyi, Antal, Jakab, & Szabó, 1997). n represents the total number of experimental data.

$$sum = \sum_{i=1}^{n} \left(\left(\frac{d\alpha_i}{dt}\right)_{experiment} - \left(\frac{d\alpha_i}{dt}\right)_{model}\right)^2 \qquad (3)$$

The primary kinetic parameters used in models I, II, III, and IV are listed in Table 2. Primary kinetic parameters were obtained from studies using lumped model for wood pyrolysis (Chan et al., 1985; Liden, Berruti, & Scott, 1988; Morf, 2001; Park et al., 2010). A large number of estimated pyrolysis kinetic parameters have been reported in the literature. The author reviewed the studies that conducted kinetic modeling on batch woody biomass pyrolysis. Among those, the kinetic parameters obtained from one-component lumped models having primary and secondary first-order reactions were gathered presenting the activation energies ($kJ\cdot mol^{-1}$), pre-exponential factors (s^{-1}), and

the minimum and maximum of each parameter for all the reactions in woody biomass pyrolysis (see paper II, III and IV). The kinetic parameters in this study were fitted by minimizing the sum in Eq. (3) using nonlinear optimization with the generalized reduced gradient method, subject to the constraints obtained from the literature. The motivation for using these constraints was to ensure that all the parameters remained within the physically realistic range based on the existing literature. This variation in reported values is due to researchers´ use of different models, feeds, operation conditions, and heating profiles (Koufopanos et al., 1989).

Table 2: Primary kinetic data that are used in the models I, II, III, and IV.

Parameters	Woody biomass	Plastic
A_1 (s^{-1})	1.30×10^8	9.94×10^2
A_2 (s^{-1})	2.00×10^8	1.23×10^{16}
A_3 (s^{-1})	1.08×10^7	1.07×10^{13}
A_4 (s^{-1})	4.28×10^6	1.18
A_5 (s^{-1})	1.00×10^6	1.37×10^{-3}
A_6 (s^{-1})	1.00×10^4	1.24×10^{-1}
A_7 (s^{-1})	1.38×10^{10}	1.37×10^{-3}
A_8 (s^{-1})	1.38×10^{10}	1.18
E_1 (kJ.mol^{-1})	140^a,110	86
E_2 (kJ.mol^{-1})	133	268
E_3 (kJ.mol^{-1})	121	233
E_4 (kJ.mol^{-1})	107	386
E_5 (kJ.mol^{-1})	107	216
E_6 (kJ.mol^{-1})	76.6	230
E_7 (kJ.mol^{-1})	161	216
E_8 (kJ.mol^{-1})	161	386

[a] The primary activation energy value for the solid-gas reaction (E_1) is 140 for model I and 110 for all other models.

4.3 Results

4.3.1 Arrhenius kinetic parameters

The Arrhenius parameters were obtained by best fitting the measured conversion data by using a nonlinear least-squares regression. The best values of the estimated kinetic parameters for models I, II, III and IV are shown in Tables 3 and 4, respectively, for walnut shells and plastics experimental data. Reports on kinetic parameters obtained for pistachio shell and eucalyptus wood pyrolysis can be found in paper III. The subscripts 1, 2, 3, 4, 5, 6, 7, and 8 are the kinetic parameters of the reactions: solid to gas, solid to tar, solid to char, tar to gas, tar to char, tar to tar, chart to char, and char to gas respectively. The estimated kinetic parameters are within the predetermined physically realistic range based on the existing literature.

Parameters	Values (model I)	Values (model II)	Values (model III)	Values (model IV)

Parameters	Model I	Model II	Model III	Model IV
A_1 (s^{-1})	1.70×10^8	1.07×10^8	7.99×10^7	1.30×10^8
A_2 (s^{-1})	3.35×10^9	1.64×10^8	5.74×10^8	2.00×10^8
A_3 (s^{-1})	3.29×10^5	6.80×10^6	1.45×10^6	1.09×10^7
A_4 (s^{-1})		4.87×10^6	2.30×10^4	4.25×10^6
A_5 (s^{-1})		8.90×10^5	1.00×10^5	1.01×10^6
A_6 (s^{-1})			1.00×10^4	1.00×10^4
A_7 (s^{-1})				1.38×10^{10}
A_8 (s^{-1})				1.38×10^{10}
E_1 (kJ.mol^{-1})	114.14	110.4	108.6	150.3
E_2 (kJ.mol^{-1})	135.54	120.5	125.6	126.1
E_3 (kJ.mol^{-1})	87.32	99.8	92.6	105.9
E_4 (kJ.mol^{-1})		107	107	107
E_5 (kJ.mol^{-1})		139.9	139.9	101.2
E_6 (kJ.mol^{-1})			76.6	67.2
E_7 (kJ.mol^{-1})				160.4
E_8 (kJ.mol^{-1})				157.6

Table 3: Kinetic data obtained by models I, II, III, and IV for the walnut shell pyrolysis experiments.

Table 4: Kinetic data obtained by models II, III, and IV for the plastic pyrolysis experiments.

Parameters	Model II	Model III	Model IV
A_1 (s^{-1})	5.86×10^4	4.23×10^5	1.54×10^5
A_2 (s^{-1})	1.99×10^4	1.99×10^4	1.99×10^4
A_3 (s^{-1})	6.51×10^2	2.28×10^1	2.53×10^2
A_4 (s^{-1})	1.18	1.18	1.18
A_5 (s^{-1})	1.37×10^{-3}	1.37×10^{-3}	1.37×10^{-3}
A_6 (s^{-1})	-	1.24×10^{-1}	1.24×10^{-1}
A_7 (s^{-1})	-	-	1.37×10^{-3}
A_8 (s^{-1})	-	-	1.18
E_1 (kJ.mol^{-1})	82	96	92
E_2 (kJ.mol^{-1})	78	82	82
E_3 (kJ.mol^{-1})	56	43	55
E_4 (kJ.mol^{-1})	386	386	386
E_5 (kJ.mol^{-1})	216	216	216
E_6 (kJ.mol^{-1})	-	230	230
E_7 (kJ.mol^{-1})	-	-	386
E_8 (kJ.mol^{-1})	-	-	244

4.3.2 Pyrolysis reaction model for woody biomass

The present work combines experimental data and theoretical modeling on different woody materials (walnut and pistachio shells and eucalyptus wood) carried out over a range of pyrolysis conditions. The operative temperature range is from 300ºC to 500ºC, with a heating rate ranging from 15 ºC/min to 60 ºC/min. The purpose is to compare the

performance of conventional models with the expanded model(s) in predicting pyrolysis behavior over a wide temperature range under non-isothermal heating conditions.

Figure 14 compares the model-predicted yields with the experimentally measured yields for walnut shell pyrolysis. The fit of the models I and II to the experimental data for the pyrolysis temperatures of 300 and 400°C was sufficiently good (see Figures 14a and 14b). At higher temperatures, there was less agreement with the models, which could indicate that some other reactions dominate at such temperatures. This kinetics scheme better represents the primary decomposition of biomass pyrolysis than the secondary decompositions.

Figure 14c shows the results of the model-predicted yields with the experimentally measured yields of walnut shell pyrolysis. By comparing the predicted results and experimental data, it is found that the existence of a secondary tar reaction for the pyrolysis reaction scheme is helpful to improve the reasonability of reaction models as compared to model II. With the increase in temperature (above 400°C), secondary pyrolysis is taking place simultaneously with primary pyrolysis resulting in the production of secondary gas, tar, and char (Guo et al., 2020; Leng et al., 2022). Pattanotai et al. (Pattanotai et al., 2013) conducted an experimental study on secondary reactions of tar during the slow pyrolysis of Japanese cypress wood. They found that the tar decomposition progresses between 400 and 500°C, and showed that the secondary reactions of tar play an important role in the pyrolysis of wood particles. The fit of the model to the experimental data for the pyrolysis temperatures was good, except for the highest temperatures. This indicates that there are still some other reactions involved in the secondary pyrolysis phase. Hence this kinetics scheme further improved to be able to reproduce the observed behavior of woody biomass pyrolysis experiments. Computed gas, tar, and char yields for model IV is illustrated in Figure 14d. The model fits well with the experimental data. The good agreement with experimental results indicates that model IV is successful in developing a quantitative understanding of woody biomass pyrolysis. This model includes secondary char reactions to the pyrolysis reaction scheme in model III. During the secondary pyrolysis phase, primary char can be activated as a catalyst to convert organic vapors into light gases and form secondary char by polymerization reactions (Neves et al., 2011).

The conventional reaction schemes primary and secondary pyrolysis reactions (model II) and two extended reaction models proposed in this study also used to predict pyrolysis yields of pistachio shells (M. Volpe et al., 2021) and eucalyptus wood pyrolysis (Monteiro Nunes et al., 2007). Similar trend is seen for model-predicted yields as compared to the experimental data for all the models II, III and IV (see Figure 15). Model II fits the experimental data well at low temperatures, but not at higher temperatures. It is proven in this study that this reaction scheme is not a suitable scheme for the slow pyrolysis of every woody biomass at high temperatures. The fit of model III to the experimental data for the pyrolysis temperatures was good, except for the highest temperatures. This indicates that there are likely still more additional reactions, in addition to "stable" secondary tar formation, that are active at the high end of pyrolysis temperatures. This finding suggests that the reaction scheme should also explicitly include terms for these reactions if a model is to be broadly predictive at the higher end of pyrolysis temperatures. By adding rate expressions for the secondary further degassing of char, and the accompanying formation of devolatilized secondary char, the resulting model IV sufficiently accurately predicted the pyrolysis yields of various types of woody biomass across all common pyrolysis temperature ranges.

Figure 14: Figures 14a, 14b, 14c and 14d present data for distribution of the products generated during walnut shells pyrolysis experiments at different temperatures and model-predicted yields of walnut shells pyrolysis from model I, II, III and IV, respectively.

Figure 15: Distribution of the products generated during pyrolysis experiments at different temperatures and model-predicted yields. Figures 15a, 15b, and 15c present data for eucalyptus wood pyrolysis for models II, III, and IV, respectively. Figures 15e, 15f, and 15g present data for pistachio shell pyrolysis for models II, III, and IV, respectively.

4.3.3 Pyrolysis reaction model for plastics

The applicability of three kinetic models (models II, III and IV) for plastic pyrolysis was evaluated by using plastic pyrolysis experimental data from the study conducted by Nunes et al. (Monteiro Nunes et al., 2007). The simulated concentration distributions of products, namely gas, tar, and char, during plastic pyrolysis under non-isothermal conditions are shown in Figure 16.

Figure 16a illustrates the comparison of model-predicted yields and experimentally measured yields for model II. The results demonstrate that the model's accuracy is satisfactory only at 300°C, with less agreement at higher temperatures. This reaction scheme is not an ideal pathway for plastic pyrolysis, especially at high temperatures, indicating the involvement of other reactions in the secondary pyrolysis phase. Consequently, the kinetics scheme necessitates further refinement to replicate the observed behavior of plastic pyrolysis experiments.

Figure 16b displays the predicted yields from model III. The comparison of the predicted results and experimental data suggests that including a secondary tar reaction in the pyrolysis reaction scheme improves the reasonability of reaction models compared to models II and IV. At temperatures above 400°C, secondary pyrolysis occurs concurrently with primary pyrolysis, producing secondary gas, tar, and char (Guo et al., 2020; Leng et al., 2022). The model's good agreement with experimental results for all temperatures indicates that model III is successful in developing a quantitative understanding of plastic pyrolysis.

Computed gas, tar, and char yields from model IV are shown in Figure 16c. The model fits well with the experimental data for temperatures up to 400°C. This kinetics scheme is more appropriate for representing the primary decomposition of biomass pyrolysis than the secondary decompositions. Including secondary char reactions does not improve the accuracy of predicting the products of plastic pyrolysis.

The kinetic scheme of Model IV most accurately predicts the decomposition of biomass pyrolysis (A. Safavi et al., 2022; A. Safavi, Richter, & Unnthorsson, 2023b). Compared to the biomass pyrolysis modeling previously investigated by the authors (A. Safavi et al., 2022, 2023b), the behavior of plastic pyrolysis is different. The results here suggest that in plastic pyrolysis there is the presence of secondary tar reactions, whereas primary char once formed subsequently acts as an inert substance.

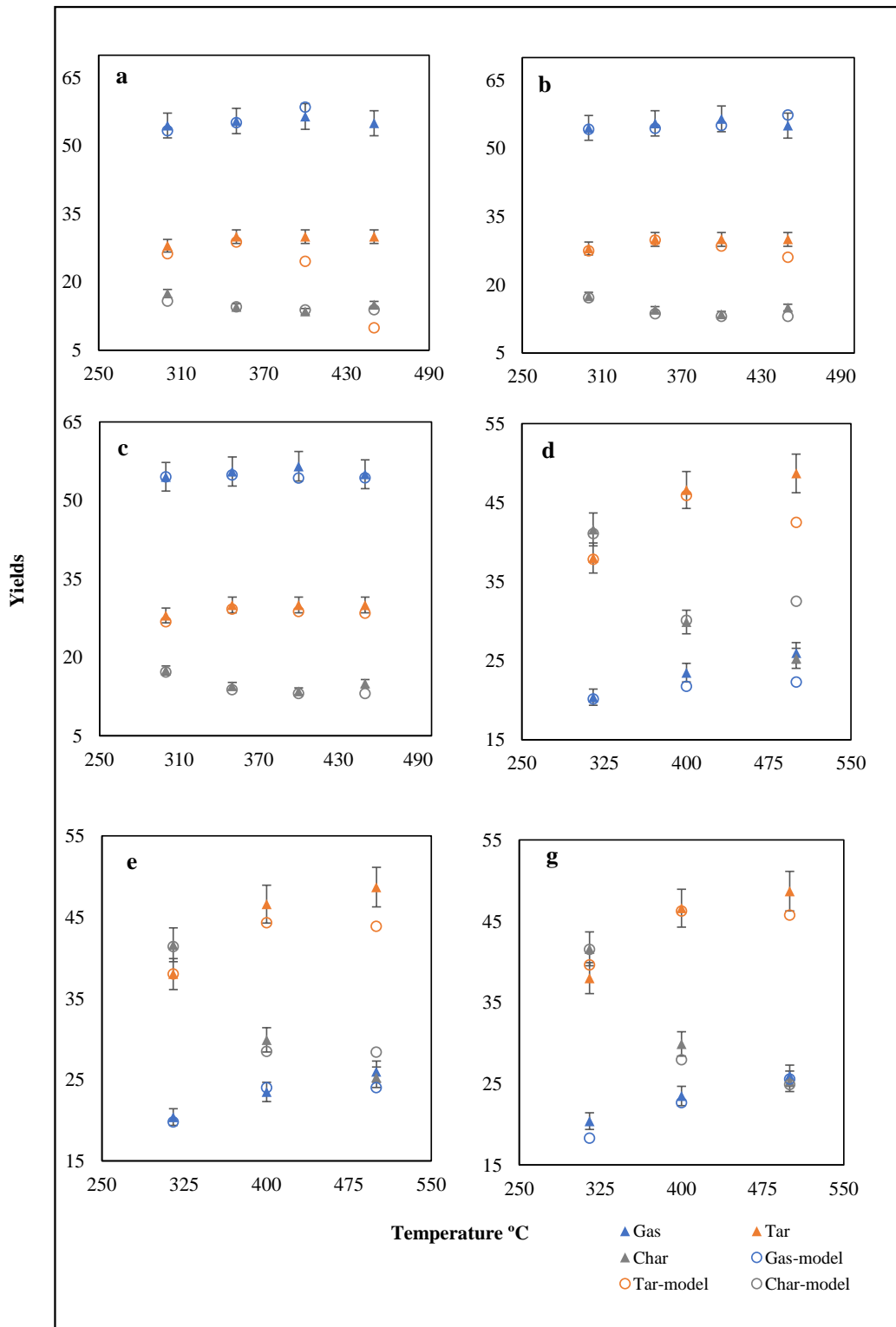*Figure 16: Distribution of the products generated during plastic pyrolysis experiments at different temperatures and model-predicted yields from models. Figures 16a, 16b, and 16c present data for model II, model III, and model IV, respectively.*

4.3.4 Validation and sensitivity analysis

The standard deviation was determined by applying Eq (4) (Babu & Chaurasia, 2003). The outcomes of Model IV exhibited a minor deviation of 0.3 from the experimental data of walnut shell, and a deviation of 0.1 from the experimental data of eucalyptus wood and pistachio shell. In the case of plastic pyrolysis, Model III showed a deviation of 0.1 from the experimental data of plastic. These results suggest that Models III and IV perform optimally for plastic and woody biomass, respectively, and are therefore validated.

$$Standard\ deviation = \sqrt{\frac{\sum_{i=1}^{n}(\frac{data_{experiment}-data_{model}}{data_{experiment}})^2}{n-1}} \qquad (4)$$

Sensitivity analysis was carried out to examine the importance of extra reactions addition to the models III and IV. As explained in section 4.2, a "physically realistic range" was determine for the kinetic parameters whenever possible, based on a broad survey of the literature. This "physically realistic range" was then used as a constraint for the kinetic parameters of a given model when the kinetic parameters were adjusted to best simulate the experimental data.

One can ask if the constraint window designed to keep all parameters physical, i.e. to avoid purely mathematical artifacts, could possibly have been too narrow or too wide during this fitting procedure. To explore the question of a too narrow window the following sensitivity analysis was performed: The constraint windows for $A_{4,5}$ and $E_{4,5}$ were broadened by 20% and the kinetic parameters were re-fitted to the experimental data with these relaxed constraints.

The effect of this relaxation on the best fit kinetic parameters reported in Table 3 for the models III and IV can be seen in table 5 below. As expected, there is an effect, however, the absolute deviation only ranges from -0.09% to 0.04%. This deviation is not large enough to reverse or invalidate any of the conclusions of this thesis.

Table 5: Results of the sensitivity analysis (effect of constraint window size on experimentally fitted kinetic parameters)

Parameter	Value with original constraint window	Value with constraint window ± 20%	Percent change*
Model III			
A_4	23000	22996.70	-0.00%
A_5	100000	99751.73	-0.00%
E_4	107	107	0%
E_5	139.88	139.88	0%
Model IV			
A_4	4247776.64	3872785.66	-0.09%
A_5	1011079.80	982167.96	-0.03%
E_4	107	107	0%
E_5	101.22	125.66	0.04%

4.4 Summary

We conducted a study to develop a suitable reaction model for woody biomass material and plastic pyrolysis. The aim was to evaluate and validate existing reaction models from literature, as well as to propose and evaluate two new models. The study analyzed different models' performance in predicting pyrolytic yields, using experimental data from literature and walnut shell pyrolysis experiments.

In paper II, a classical lumped kinetic model with a three-competitive reaction scheme was tested to determine its accuracy in predicting walnut shell pyrolysis product yields. Paper III evaluated the applicability of the most famous wood pyrolysis kinetic model from literature, along with two new reaction models, on the walnut shell pyrolysis experiment. These models were further evaluated using different experimental data from literature to predict pyrolytic products of woody biomass pyrolysis and compare them to experimental data. Finally, paper IV aimed to explore the possibility of using existing woody material pyrolysis reaction models to predict plastic pyrolysis yields and assess their accuracy.

5 Conclusions and Discussions

MSW management in Iceland primarily involves landfilling and incineration, both of which result in GHG and hazardous emissions. As regulations on organic waste disposal become stricter in the European Union and Iceland, the long-term goal is to eliminate the use of landfills for organic waste. In addition, incinerators were shut down in Iceland due to their negative impact on air quality. It is necessary to establish an efficient waste management system to improve the environment and explore economic development opportunities. However, no cost-effective and environmentally sound alternative plans have been identified so far, according to The Environment Agency of Iceland (Keller et al., 2020).

This project proposed gasification/pyrolysis as a waste management method. Pyrolysis is a crucial sub-section of the gasification process that can convert waste and/or biomass to energy, chemicals, and fuels. Unlike previous waste management methods (landfilling and incineration), pyrolysis is a sustainable method that can significantly reduce GHG emissions. It can also promote renewable energy while achieving other environmental goals, such as improving air quality and promoting a circular economy. These benefits align well with Iceland's Waste Management Plan and Waste Prevention Program, which aim to promote a circular economy.

The primary goal of this project was to evaluate the viability of employing gasification and pyrolysis methods as eco-friendly alternatives to conventional landfilling and incineration practices. Furthermore, it sought to create crucial tools, including validated models, to facilitate the efficient design and adoption of these technological solutions, with a specific emphasis on pyrolysis. The ultimate goal (future plan) of the proposed project is to adopt small-scale pyrolysis as a state-of-the-art green solution with significantly less emission of toxic materials produced for solid waste disposal in Iceland. Pyrolysis is a relatively simple process that is suitable for operation at small scales, making it an attractive option for municipalities in Iceland.

This thesis delved into the issue of dioxin formation resulting from thermochemical technologies, with a particular focus on comprehensively reviewing the existing literature regarding dioxin formation in gasification processes. The findings suggested that emissions of PCDDs and PCDFs may not consistently remain within regulatory or detection limits. Given the pivotal role of pyrolysis in the gasification process, substantial research efforts were undertaken, comprising both experimental and modeling approaches. Due to the complexity of the pyrolysis process, there is no universally accepted method for accurately characterizing solid pyrolysis. Consequently, this thesis endeavored to develop a simple and accurate model for describing the decomposition rate of solids during pyrolysis, a critical factor for the scalability and optimization of pyrolysis processes.

The government and energy sectors benefit from implementing pyrolysis plants, as the pyrolysis process is the pathway to carbon-negative energy production. Carbon-negative energy is achieved by combining net carbon removal from the atmosphere with the production of energy or other revenue-generating products beyond sequestered carbon.

Pyrolysis biomass can produce both energy and carbon sequestration agents in the form of bio-char, bio-oil and biogas. Municipalities in Iceland can replace their old waste management techniques with small-scale waste pyrolysis plants. Pyrolysis is attractive for its relative simplicity and suitability for operation at scales more aligned with the distributed nature of biomass resources. Energy recovery from waste, depletion of fossil fuel prevention, landfilling, and GHG emission reduction can all be achieved through pyrolysis. Pyrolysis makes possible a waste-free future and transitions to the circular economy (see Figure 17).

Figure 17: Sustainable bio-refinery approaches towards a circular economy for conversion of waste to value-added materials. Reprinted from (Chew et al., 2021) *with the permission of Elsevier.*

5.1 Answers to the research questions

The goal of this proposed project is to introduce sustainable waste management solutions in Iceland by considering pyrolysis technology as a state-of-the-art green solution for solid waste disposal. This technology has the potential to significantly reduce emissions of toxic materials and produce renewable energy. The study addressed the research questions that were intertwined with the conducted research, ultimately leading to the project's goals.

Here are the answers to the research questions in this project:

1) Can gasification assure reliable and consistent dioxin formation well below limits?
   The prevailing belief is that waste gasification consistently yields emissions below regulatory limits (<0.1 ng TEQ/Nm^3) in contrast to incineration. However, the findings of this extensive literature study indicate that such a belief is overly simplistic. Although gasification holds promise for reducing dioxin emissions, it does not always guarantee the attainment of acceptable levels.
   To address the research question on PCDD/Fs formation during gasification,

an extensive literature review was conducted to provide a comprehensive overview. The author thoroughly assessed all available articles published since 1990, resulting in a book chapter and a review paper (paper I). This work examined the levels of dioxins generated from various waste streams, including MSW, plastics, wood waste, animal manure, and sewage sludge. The potential of gasification technology to reduce PCDD/Fs emissions to levels that meet regulatory or detection limits was also highlighted.

The formation of PCDD/Fs during gasification is influenced by operational parameters and the presence of unburnt carbon, a chlorine source, and a metallic catalyst. To minimize their formation, the process should be controlled by maximizing the conversion of hydrocarbons produced during pyrolysis, high temperature, and oxygen deficiency.

The contribution of this study is to offer a comprehensive understanding of PCDD/Fs formation during gasification. This review provides evidence on when gasification can result in environmentally benign emissions with PCDD/Fs below legal limits and when it cannot. This information is of scientific and practical interest.

2) Do the fixed-bed (hot-rod) reactors used for slow pyrolysis experiments by many authors have the right tar collection setup? Can they assure complete tar capture?

Upon investigation, it was determined that the previously specified temperature for the tar cooling bath was insufficient to achieve complete tar condensation at the trap and maintain the temperature of the tar tube below room temperature. Consequently, a substantially lower temperature was found to be necessary for the tar cooling bath.

To answer this question an experimental work on pyrolysis was conducted and the results can be found in the section 3.1 of paper II. To develop a reaction model suitable for woody biomass, the author conducted pyrolysis experiments on walnut shells using the atmospheric pressure hot-rod reactor, which had been previously developed at Queen Mary University of London. To capture all the tars produced during the pyrolysis process, the author made modifications to the tar collection section of the setup.

The author developed an effective cooling bath for pyrolysis vapor condensation. This bath consists of a mixture of dry ice and ethylene glycol, which is fully insulated to minimize heat transfer with the outside environment. By using volume fractions of 0.4 and 0.6 of dry ice and ethylene glycol, respectively, a cooling bath temperature of -60°C was achieved. As a result, the temperature of the tar tube was maintained below 10°C throughout the process.

3) Can the existing reaction pathways in the literature predict the yields of the woody material pyrolysis? Does the pyrolysis reaction scheme for woody material pyrolysis needs improvement in order to be able to predict pyrolysis yields? Can woody biomass reaction schemes be used for the prediction of plastic pyrolysis yields?

The author conducted a comprehensive evaluation of the applicability of commonly employed wood pyrolysis kinetic models, along with two newly proposed models. Multiple sets of experimental data from woody biomass and

plastic pyrolysis were utilized for this analysis. The findings indicated that the existing models lacked accuracy in their predictions and failed to match the experimental data. It was evident that additional reactions were necessary to enhance the modeling predictions. Notably, the conventional models demonstrated limited effectiveness in predicting pyrolytic product yields, particularly at higher temperatures.

The proposed models accounted for additional reactions that were not considered by the conventional models, and these reactions were found to contribute significantly to the formation of secondary pyrolysis phases. The first model introduced a secondary tar formation term that describes the production of more stable tar that forms at elevated pyrolysis temperatures, possibly accelerated by catalysts. The second model included terms that modeled secondary gas and char formation reactions, making it more accurate and capable of predicting pyrolytic products from various types of woody biomass. The analysis showed that the first reaction model was suitable for plastic pyrolysis, while the second model was better suited for pyrolysis of woody materials.

5.2 Thesis limitations

There were a number of limitations that had to be considered during this research. One of the main challenges was the lack of a suitable pyrolysis laboratory in Iceland, which required the author to conduct the experimental work outside the country. This made it difficult to collect the necessary data on pyrolyzing different materials under varying experimental conditions. While it would have been beneficial to have more experimental data, the author was constrained by a limited amount of time to collect the required information.

Moreover, the original plan to conduct dioxin measurements and analysis on gasification had to be abandoned due to technical problems with the gasification unit at the university, which could not be resolved during the course of this thesis work. This was a setback, as it would have provided valuable insight into the potential environmental impact of the gasification/pyrolysis process.

Given the lack of experimental data, especially for plastic pyrolysis investigations, the author was only able to find one paper containing experimental results on plastic pyrolysis, which provided a detailed explanation and information on the experimental conditions, temperature profile, and pyrolysis results at different temperature ranges.

Despite the limitations encountered during this research, the study has successfully put forward a sustainable waste management solution for Iceland. With further research and development, this approach could greatly aid small Icelandic communities and contribute to reducing the adverse environmental effects of waste disposal.

5.3 Future work

In order to facilitate the achievement of Iceland's waste disposal industry's 2030 goals, it is recommended that a laboratory or bench-scale pyrolysis unit or a modified thermogravimetric analysis unit be established at University of Iceland. This would enable the pyrolysis of various types of Icelandic waste and facilitate optimization of the system under different conditions.

In addition, improvements to the pyrolysis setup can be made by modifying the bio-oil and gas collection sections. Specifically, a gas analysis system could be incorporated to detect the chemical components of the syngas. Furthermore, to increase the knowledge of the chemical processes involved in pyrolysis, additional tests and analyses could be conducted, such as evolved gas, bio-oil, and solid residue analysis. This would lead to an enhanced reaction kinetics models in pyrolysis.

Moreover, to improve the pyrolysis modeling, it is suggested that mass and heat transfer be taken into account. While a reaction rate expression is a necessary component of a pyrolysis reactor model, it is insufficient on its own. Therefore, it is recommended that heat and mass transfer models be used in conjunction with the developed kinetic expressions to produce a more comprehensive pyrolysis model.

Overall, these recommendations would enhance the current research on waste disposal management in Iceland and potentially lead to further developments in the field.

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Paper I

Review

Dioxin Formation in Biomass Gasification: A Review

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Abstract: The amount of PCDD/F emissions produced by gasification operations is often within standard limits set by national and international laws (<0.1 ng TEQ/Nm^3). However, a recent assessment of the literature indicates that gasification cannot always reduce PCDD/Fs emissions to acceptable levels, and thus a common belief on the replacement of incineration with gasification in order to reduce PCDD/Fs emissions seems overly simplistic. A review that summarizes the evidence on when gasification would likely result in environmentally benign emissions with PCDD/F below legal limits, and when not, would be of scientific and practical interest. Moreover, there are no reviews on dioxin formation in gasification. This review discusses the available data on the levels of dioxins formed by gasifying different waste streams, such as municipal solid wastes, plastics, wood waste, animal manure, and sewage sludge, from the existing experimental work. The PCDD/Fs formation in gasification and the operational parameters that can be controlled during the process to minimize PCDD/Fs formation are reviewed.

Keywords: biomass gasification; dibenzo-p-dioxins; dibenzofluorans; syngas

1. Introduction

Incineration of municipal solid waste (MSW) increased during the 1960s. The process recovers energy from waste and decrease the areas required for landfilling. Nevertheless, it contributes to the release of very toxic organic [1]. Incineration causes fly and bottom ashes, which release leachable toxic heavy metals, polychlorinated diben-zo-p-dioxins (PCDDs) and polychlorinated dibenzofluorans (PCDFs), and volatile organic compounds [2], especially for MSW incineration [3–5].

PCDD/Fs are a group of toxic by-products coming from thermal processes that have serious carcinogenic and mutagenic effects [6,7]. After PCDD/Fs enter the atmosphere, dioxins are deposited onto soil/plant surfaces. Most plants uptake soil-deposited dioxins. Dioxins enter the animal food chain when animals consume these contaminated plants. Therefore, food sources serve as a primary intake of dioxin in humans [8–10]. Therefore, controlled measurement of PCDD/Fs emissions has received much attention as it is one of the most important aspects affecting public acceptance. The release of PCDD/F from incineration processes was first spotted in the late 1970s, and since then, researchers have been evaluating the emission of this compound produced from a series of thermal processes [11].

Due to their high toxicity, the dioxins emissions limit, determined by national and international organizations, is 0.1 ng I-TEQm^3, where I-TEQ (international toxic equivalent) is a single figure resulting from the product of the concentration and individual toxic equivalency factor values of each congener [12]. Incinerators emit PCDD/Fs and their concentration often exceeds the legal limit, which calls for an alternative waste treatment technology.

Waste gasification is a feasible alternative to incineration, tackles PCDD/Fs formation, and improves energy efficiency, which found application in the late 1990s [13]. In a gasifier, MSW, industrial waste, and biomass/wood [14], at 800 to 1400 °C in the presence of a

gasifying agent (typically air, steam, nitrogen, carbon dioxide, oxygen, or a combination of these), can be converted into producer gas (a mixture of H_2, CO, etc.). Utilizing producer gas to generate electrical and thermal energy is the most dominant process in gasification; however, chemicals and liquid fuel may also be produced from the producer gas [15]. Residual carbon (mainly char), which results from incomplete conversion of the biomass, can be utilized for soil enhancement [12].

The measured amount of PCDD/Fs originating from gasification processes is usually within acceptable limits [16]. The producer gas can contain a lower amount of pollutants compared to the pollutants coming from the flue gas of an incinerator [17] thanks to fractional waste oxidation at high temperatures and a limited oxygen environment [18–20]. However, organic chlorinated compounds in the reactor and incomplete destruction of the PCDD/Fs present in the waste itself can result in some amounts of PCDD/Fs [15,21,22].

This current study offers a more comprehensive picture of PCDD/F formation in gasification. This review discusses the available data on the levels of dioxins formed by gasifying different waste streams, such as municipal solid wastes, plastics, wood waste, animal manure, and sewage sludge, from the existing experimental work. This article highpoints the prospect of using gasification technology in order to reduce the emission of PCDD/Fs to levels below regulatory or detection limits. We tried to cover all accessible articles that have been published since 1990 and perform a thorough assessment to frame this review, which is really missing in the field.

2. Dioxin Formation in Gasification

Assessing the environmental impacts of gasification technology is crucial to ensure the feasibility of the process. The real challenge/concern is the formation of harmful chemicals, especially PCDD/Fs. From the environmental perspective, it is the topmost priority to reduce PCDD/Fs formation and increase their capture. The following industries are among those producing high amounts of dioxins: plastic-coated wire incineration in which the burning of Cu electrical wiring that is treated with chlorine-containing PVC could be a driving force for dioxin formation. High-temperature and metal-containing processes, such as the sintering of Fe ore taking place in the steel industry, melting the Cu ore, splicing of electrical cables, and the process of reviving the catalyst in the petroleum refining industry, are other examples [23].

An organic material, a chlorine source, and a metallic catalyst (such as Cu, Fe, etc.) are the main ingredients for dioxin/furan formation. Dioxins form by the precursor route via reactions between aromatic rings containing chlorine (chlorophenols (CPs) and chlorobenzenes (CBs)) in the gas phase or by the de novo synthesis route in the post-combustion zone (reactions between unburnt carbon and chlorine sources with metallic catalysts) [24]. The temperature windows for the formation of PCDD/Fs are defined as 200–800 °C [5,25], where the reaction rate is maximized from 350 to 400 °C [26]. A detailed explanation of the PCDD/Fs formation mechanism can be found in our previous study [24]. In combustion processes, a low combustion temperature, humidity, poor turbulence and short residence time in the combustion zone, oxygen availability, and slow cooling process of flue gas in the critical temperature range could be the reasons for the formation of PCDD/F, as well as the presence of residual carbon, chloroaromatics, and polycyclic aromatic hydrocarbons (PAHs) [1,12,27]. Humidity has been shown to influence the product distribution more, driving it towards highly chlorinated congeners [27].

Halogens in the feed [28,29] and catalytic metals (Cu, Fe, Zn, etc.) [16] in fly ash boost formation of PCDD/Fs are present in thermal processes [5,30]. Additionally, the reaction of dioxins with chlorine and unburned carbon in the presence of these metals can contribute to the de novo synthesis of PCDD/Fs and promote the formation of other organic chlorinated compounds [16,31–33]. The catalytic effect of the metal ions facilitates the reaction of HCl with O_2 and release of Cl_2 for chlorinating the aromatic rings that result in dioxin formation. Copper halides, such as CuCl and $CuCl_2$, are known to be strong catalyst, acting as both a catalyst and chlorine source at once. These catalysts enhance the precursor route via the

chlorination process, and the de novo synthesis route via chlorination of carbon as well as oxidative breakdown of carbonaceous material [34].

Zhang et al. [35] considered the influence of temperature and extrinsic and intrinsic oxygen on the formation of chloroaromatics, which are prerequisites for the synthesis of PCDD/Fs. This study provides useful information when designing the syngas combustion zone of gasification-combustion processes for MSW disposal. The results revealed that at low temperatures, intrinsic oxygen affects inhibition of chloroaromatics formation. At high temperatures, extrinsic oxygen had a strong inhibition effect on the formation of chloroaromatics [35]. Studies have shown that Cl radicals can be transformed to HCl over a designed homogeneous conversion, which inhibits PCDD/Fs formation in syngas. Nevertheless, HCl can simultaneously be oxidized and regenerate Cl radicals during the syngas combustion process. The presence of these radicals and hydrocarbon fragments could be a key path for the formation of chloroaromatics via chlorination reactions under an oxidative atmosphere. The results concluded that O_2 has a considerable effect on the formation of chloroaromatics, and this depends on the competition between oxidation and chlorination [35].

Calcium-based chemical looping gasification is composed of an air reactor and gasifier. The system uses calcium oxide (CaO) as a carrier between two reactors. The dioxin precursors available in biomass are attacked by CaO via absorption and decomposition. This hampers the PCDD/Fs formation. In addition, CaO could also absorb HCl and prevent the formation of Cl_2 from HCl [36–38]. The effectiveness of calcium-based chemical looping gasification on dioxin emissions and from heavy metal contamination wastes was studied by Cai et al. [39]. The results showed that the availability of steam and calcium-based sorbent can minimize PCDD/Fs formation. The presence of catalytic metals in the process is more effective in the synthesis of dioxin compared to chlorine and residual carbon. The catalytic activity of metals is in the following order: Cu > Fe > Cr > Zn. Calcium-based chemical looping gasification outcomes prove that the high H_2 concentration in the process stimulates HCl formation instead of $CuCl_2$; thus, this is favorable in hampering the formation of dioxins. At operating temperatures of 600 to 750 °C, the valences of Pb, Cr, and Cu decreased; therefore, the process had a positive effect on the stabilization of heavy metals [39].

The operational conditions of the process, such as high temperature, oxygen deficiency along with maximizing the conversion of hydrocarbons that are being produced in pyrolysis, are possible approaches to reduce the formation of PCDD/Fs in gasification as compared to that of combustion [40]. The oxygen content in a gasification reactor is much lower than the theoretical oxygen content required for fuel combustion, resulting in much lower PCDD/Fs synthesis. Thus, the atmosphere of a gasification reactor is a reducing atmosphere [41].

Zwart et al. [42] analyzed the dioxin formation from refuse-derived fuel (RDF), wood, and sewage sludge gasification in a broad temperature range. The results showed that dioxins levels were different to the gasification feedstock's chlorine content and temperature. High chlorine amounts in the feedstock caused dioxin formation, mainly at below 800 °C. Above 800 °C, dioxins levels were significantly reduced, along with corresponding tar levels [42]. The minimum concentration of dioxins set by most current European legislation is 0.1 ngm^3 expressed in I-TEQ units [43]. It can be concluded that high-temperature gasification depresses dioxin PCDD/F formation when high-chlorine content fuels are used [40]; however, PCDD/F is formed at high temperatures but under an insufficient oxygen environment [44].

Another important effective measure is syngas rapid cooling by water immersion, which impedes the synthesis of PCDD/Fs [45]. During wood gasification, dioxin compounds remain on the surface and then are removed by fly ash particles [46]. This signifies the importance of emission control measurements to successfully alleviate this part of the PCDD/Fs emission in the producer gas. Utilizing high quality wood fuel, optimizing

combustion conditions, and precipitating the fly ash at temperatures below 200 °C should be taken into consideration [47].

Multi-step absorption filters are effective in removing dioxins from the gas or cooling effluent [48–54]. Volatile organic compounds, such as dioxins and other organics, are effectively eliminated in the gaseous and liquid phases due to the high-temperature reactor and shock cooling [16,55].

The quality of char, and syngas produced from the gasification of solid wastes degrades in the presence of chlorinated compounds and leads to dioxin formation. In gasification, the majority of the chlorine content is captured as HCl and KCl into the syngas, but some organic chlorinated compounds will be formed in oil/tar and char [56]. Gasification is known to decrease corrosion and emission by preserving alkali and heavy metals (apart from mercury and cadmium), sulfur, and chlorine in the process residues, impeding PCDD/Fs formation and decreasing the formation of thermal NOx as a consequence of lower temperatures and reducing conditions [57].

3. Overview of Experimental Measurements of Dioxin Formation Levels in Pyrolysis and Gasification

A brief description of pyrolysis, gasification experiments, and reports on dioxin formations is provided here and also in Table 1.

Figure 1 shows a summary of the dioxin measurements, based on different substrates that have been gasified and the operational temperature, in the literature reviewed. The pie charts show what feedstock and temperatures have been investigated with experimental measurements and how often in relation to the presence of dioxin. Any publication that reported sampling and analysis of PCDD/Fs and subsequently either detected PCDD/Fs (which includes zero results) or did not detect any measurable level down to 0.1 ng-TEQ/Nm^3 is counted.

Figure 1. Dioxin measurements, based on different substrates that have been gasified and the operational temperature in the reviewed literature. Dioxin measurements from gasification of different substrates in lab-, pilot-, and full-scale studies (papers from 1990–2021). The pie-charts illustrate the number of times that researchers tried to measure dioxin for each substrate type (chart on the right); and the number of times that dioxin was measured for each substrate. type gasified based on the temperature. The total number of occurrences is greater than the number of articles because several articles discuss more than one substrate type. The selections cover all the reports in the literature measuring dioxin in gasification.

Figure 2 indicates what conditions (temperatures or feedstock) more frequently result in the presence of dioxin. For example, for MSW, the first measurement (light blue bar) was done at 1400 °C and the corresponding measured dioxin is 0.0059. Clustered bar charts are used to show how frequently an attempt was made to detect dioxin, how often it was found, and how much was found. It is noted that RDF (RDF is industrial waste with a high chlorine content) and textiles (waste with a high sulfur content coming from vulcanized material) as feedstock generally result in relatively high dioxin levels, while the gasification of plastics generally results in low dioxin levels independent of the gasification temperature. Wood and paper waste as feedstock also typically result in relatively low dioxin levels except in one report. Dioxin emissions from the gasification of MSW have been the most frequently studied because its formation from MSW incineration has always been the main concern. In particular, reports measuring dioxin formation over a wide range of gasifier operating temperatures (600–1400 °C) exist for MSW. For RDF, however, dioxin formation has only been studied for gasifiers operating around 800 °C. Studies on textiles, hospital waste, animal waste, and wood and paper waste are relatively limited as well. It is expected that dioxin formation decreases at higher temperatures as most of the literature states. This is the case when the substrate is sewage sludge, but there is no difference in the dioxin concentration at different temperatures when the feedstock is MSW or plastics.

Figure 3 illustrates the correlation of the amount of dioxins that was measured with feedstock types and temperatures (process temperature). Since the reported dioxin levels differ, a log plot was created to show the correlation. This figure shows that gasification does not necessarily result in PCDD/Fs formation below the acceptable limits (<0.1 ng TEQ/Nm^3). There are not enough studies measuring PCDD/Fs formation in gasification. It is evidenced, with the data gathered in this review, that there is a strong relation between high temperature and less dioxins formation for almost all feedstock types. It can be seen from the plot that the PCDD/Fs concentrations reported for RDF and textile tend to be more than an order of magnitude higher compared to other feedstock because of their high chlorine and sulfur content. Researchers [58,59] showed that a high-temperature reactor and gas cooling, in the absence of oxygen, prevents PCDD/F formation by de novo synthesis reactions [60]. Thus, this resulted in dioxin-free high-calorie gas production when high chlorine level feedstock was used. Most of the chlorine in the waste was converted to hydrogen chloride in the off gas [61]. When gasifying wastes, especially for MSW and sewage sludge, with temperatures above 1000 °C, PCDD/Fs concentrations are within acceptable limits.

The correlation of the amount of dioxins that was measured with feedstock types and temperatures (process temperature) based on the type of gasification technology used is shown in Figure 4. The effect of using gas cooling methods and high temperatures on dioxin formation of different feedstock even for those with high chlorine contents (such as RDF and plastics) is shown in Figure 5. Gas cooling suppressed dioxins emission to a very low level. Experiments showed the regeneration of PCDD/Fs occurring during slow gas cooling after high-temperature treatment [62]. The general trend in the field is that dioxin concentrations decrease as temperature increases. The trend lines for each case may not fit very tight, but the best fit lines always slope downwards, showing the correlation between the PCDD/Fs concentrations and the temperatures. Figures 4 and 5 show a strong correlation for MSW and sewage sludge with existing data. For other feedstock, it is not possible to look for a trend as there are not enough studies and thus data available in the literature.

For MSW, the most frequently studied feedstock, there is a correlation but also an outlier at temperatures below 1000 °C. Researchers stated that they did not consider any treatment (such as cooling methods) for the product gases, which could be the reason for the dioxin concentration being above the standard limits [16].

Figure 2. The bar chart on the top shows the temperature at which the dioxin was measured (**A**). The bar chart at the bottom shows the dioxin concentration based on the feedstock used in the literature (**B**). There is one cluster of bars for each substrate. Each one of these clusters has a few thin bars right next to each other, meaning that every measurement reported has its own bar, even the ones that measured zero dioxin or below the detection limit (empty space between bars). Since the measured concentration of PCDD/Fs reported for different substrates varies a lot, the Y axis has to be broken more than once. To make it easier for readers, the real values of measured PCDD/Fs were added on top of some of the bars for which a higher amount of PCDD/Fs has been reported. The dashed black lines are for ease of reading and separating the substrates from each other.

Figure 3. The scatter chart shows the PCDD/Fs concentrations for different feedstock versus temperature. Data points that are Scheme 0 (ng-TEQ/Nm^3) are those measurements with dioxin concentration below the detection limit or zero dioxin. As it is not possible to put zero values on a logarithmic axis, the red dashed line is the acceptable limit as determined by national and international organizations (<0.1 ng TEQ/Nm^3).

For sewage sludge as well as MSW, there are usually several parameters affecting dioxin formation, but above 1000 °C, it is mainly the temperature that has the most dominant effect. Studies [63,64] showed that that more than 99.9% of dioxins are decomposed during MSW gasification and that most heavy metals are solidified when the temperature is 1100 °C.

For RDF, which is the high chlorine content feedstock, there are only three data points available. There are no data points for temperatures higher than 850 °C, and thus it is not possible to talk about a trend here.

For plastics, there are several data points for high-temperature measurements but nothing for low-temperature measurements in the existing literature. In the high-temperature region, it seems a trend exists, but whether this trend extends into the low temperature region is currently untested. Researchers studied the effect of chlorine content on dioxins formation by mixing plastic waste with PVC (as PVC is high in chlorine) [61,65]. Results showed that all PCDD/Fs concentrations were within the standard limits, which proves the effect of the high-temperature treatment and the gas cooling [61,62,66].

For wood waste, there is one measurement that is above the limit. This measurement was reported by the Energy research Centre of the Netherlands, who implemented an oil-based gas washing (OLGA) process in a biomass gasifier in order to remove dioxins from the product gas [42]. The dioxin concentration of the product gas was 0.5 ng TEQ/Nm^3 where no OLGA was applied, while it was a factor 10 lower when the gas was purified using the OLGA scrubber. Other measurements presented in the plot are within the acceptable limit, thanks to rapid gas cooling [67].

For animal waste, very little data are available, one of which is hydrothermal gasification of chicken manure at 400 °C, where PCDDs and PCDFs were not detected [68]. The other study shows the result of cogasification of biofermenting residue (BR) at 1300 to 1400 °C. The dioxins emission was calculated to be 0.365 ± 0.23 ng-TEQ/Nm^3, which is far beyond the limits in the EU. This BR contains starch, fish meal, yeast powder, etc., and is

identified as a hazardous waste according to the national hazardous wastes classification, proposed by the Ministry of Environmental Protection of China [69].

Figure 4. The scatter chart shows the PCDD/Fs concentrations for each feedstock versus temperature. As the number of data points is not enough in the existing literature, it is not possible to say how temperature and PCDD/Fs concentrations correlate for any specific feedstock type, except for MSW, which are the most studied feedstock. Since there is only one study experimenting with textile and hospital waste, they are not included in this figure.

Figure 5. The scatter chart shows the PCDD/Fs concentrations for each feedstock versus temperature. Since there is only one study experimenting with textile and hospital waste, they are not included in this figure. The symbols show if any cooling methods/rapid cooling were used and whether high-chlorine-level feedstock were used.

The formation of PCDD/F compounds in thermochemical processes is indeed the outcome of a complex set of competing chemical reactions. Specific operating settings result

in PCDD/F formation involving deficient combustion of fuel, the presence of a chlorine source [45,70], oxidizing atmosphere between 10 and 15% oxygen in the cooling zone [71], fly ash with degenerated graphical structures, fly ash surface acting as a carbon source, temperature range between 250 and 450 °C, and the existence of catalytic metals such as copper, iron, manganese, and zinc [72]. However, in gasification, these conditions are not satisfied, or are less common or fleeting, and hence, the likelihood of detection of PCDD/Fs compounds in the producer gas is low. The specific conditions by which the gasifier runs the gasification process prevents the formation of free chlorine from HCl, thus confining the chlorination of any species in the producer gas [73]. In conclusion, high temperature and gas cooling are by the most effective parameters eliminating dioxins formation in gasification even for feedstock with a chlorine content, while gasifier types play a less important role in dioxin formation prevention as shown in Figures 4 and 5.

Table 1. Emission of dioxins from various combustion, pyrolysis, and gasification sources.

Technology	Feedstock	Reactor Type	Temperature (°C)	PCDD/F Emission (ng-TEQ/Nm^3)	Syngas Info.	Note	Ref.
Gasification	MSW	Moving grit gasifier	877.82	0.28	-	dioxin concentration below the allowed value set by the Brazilian legislation (0.5), USA (0.1 to 0.3 for new plants and 0.3 to 0.8 for existing plants), Canada (0.5).	[16]
Combustion	Different types of wood chips and waste wood	Moving grate, Grate burner, Fluidized bed	Temperature is not reported, burners vary in power from 500 kW to 10 MW	0.0027–9.57	-	Emissions from grate burners when using wood pellets goes below allowed value.	[3]
Gasification	Torrefied wood pellet	Downdraft GEK gasifier	850	Lower than the limit	-	-	[70]
Gasification	Sewage sludge with wood pellets	Fixed-bed updraft	1010–1394	0.043	-	PCDD/Fs were completely destroyed at temperatures above 600 °C.	[21]
Gasification	MSW	Thermoselect	1200–1600	0.03	CO 25–34% H$_2$ 28–38% HHV of syngas varies from 10.88–14.65 MJ/Nm^3	-	[55]
Gasification	MSW	Fixed bed Thermoselect	1200	0.03	CO 27–40% H$_2$ 36–40% Heating value 8–10.2 MJ/Nm^3	-	[74]
Pyrolysis and combustion	Animal wastes	Horizontal furnace	600–1100	The highest for pyrolysis at 850 °C was 20.2 and for combustion was 43	-	-	[75]

Table 1. *Cont.*

Technology	Feedstock	Reactor Type	Temperature (°C)	PCDD/F Emission (ng-TEQ/Nm^3)	Syngas Info.	Note	Ref.
Pyrolysis and combustion	Cotton textile, polyester textile, Polyvinyl chloride (PVC), sewage sludge, waste lube oils, meat and bone meals, and paper waste.	Batch laboratory scale Horizontal tubular reactor	850	Combustion: 14.8 14 4500 55 80 40 17 Pyrolysis: - - 215 81 - 21 -	-	Some data is not present in pyrolysis for materials such as polyester textiles, waste lube oil, waste paper.	[76]
Gasification	Sewage sludge	Fluidized bed	750–850	At 750 °C was 1.98 and at 850 °C was 0.38	CO 16.8% H$_2$ 14.9% CO$_2$ 13.5% CH$_4$ 4.1% N$_2$ 47%	-	[58]
Gasification	RDF	Fluidized bed	725–820	At 725 °C was 74.2 and at 820 °C was 4.5	CO 12.1% H$_2$ 7.1% CO$_2$ 13.7% CH$_4$ 6.4% N$_2$ 53%	-	[58]
Co-gasification	Coal and MSW	Fluidized bed	600–950	In raw gas was 0.012. In flue gas was 0.002. In exhaust gas was 0.005	CO 37% H$_2$ 34% CO$_2$ 25% CH$_4$ 5%	Flue gases from the same plant, contained 0.03 ng-TEQ/Nm^3 PCDD/F because of the fraction of plastic waste from sorting. The PCDD/F stream derived with the slag during an hour is equal to the stream of these compounds in the raw gas.	[66]
Gasification	MSW	Direct melting system	1000	In flue gas was 0.0059–0.0082. In fly ash was 0.18–0.037	LHV of syngas MJ/m^3 was 4.4–5.9	-	[77]
Gasification	Chicken manure	Hydrothermal gasification	200–400	PCDD/Fs were not detected	Without the additive 0.1943 mmol H$_2$, 0.2617 mmol CO, 0.0244 mmol CO$_2$, 0.0024 mmol CH$_4$ With the additive the yields of gasses were decreased.	The alkaline additive Ca(OH)$_2$ enhances the reaction rate of the hydrothermal gasification at low reaction temperature.	[68]
Gasification	WEEE plastics	-	1200	0.014–0.59	-	The allowed limit by Japan legislation is (0.1 to 0.5 ng-TEQ/Nm^3).	[62]

Technology	Feedstock	Reactor Type	Temperature (°C)	PCDD/F Emission (ng-TEQ/Nm^3)	Syngas Info.	Note	Ref.
Gasification	Pelletized and loose straw	Fluidized bed	792–826	Small negligible	For pelletized straw CO 13–14% H$_2$ 17–18% CO$_2$ 16–18% CH$_4$ 3–4% N$_2$ 49–50% For loose straw CO 14–17% H$_2$ 8–9% CO$_2$ 16–17% CH$_4$ 5% N$_2$ 51–54%	Higher amount of tars in experiments with loose straw. PAHs were present in large amounts in the fly ash especially for loose straw.	[67]
Gasification	Biofermenting residue with coal-water slurry	Multicomponent slurry pressure gasifier	1300−1400	0.365	CO 43.7% H$_2$ 34.2% CO$_2$ 18.2% CH$_4$ 0.3%	It meets the PCDD/F concentration limit of China (0.5 ng-TEQ/Nm^3) but is far beyond the limits in the EU.	[69]
Gasification	Carpet and textile waste	Plasma gasification	1600	14.061	CO 11.7% H$_2$ 8.1% CO$_2$ 3.1% CH$_4$ 1.1% O$_2$ 1.1%	Presence of Cl elevates dioxin formation and the gas cools down in 200 to 400 °C where secondary dioxin formation occurs.	[78]
Gasification	MSW Plastic waste PVC refuse	-	1000	0.0035–0.014	-	The measured values were converted assuming 12% oxygen.	[65]
Gasification	MSW	Drying, pyrolysis, gasification, combustion, and ash vitrification in one step	600–1200	0.076	-	-	[79]
Gasification	Alfalfa stem	-	-	Total chlorinated dioxin compounds were 0.1–0.6 µg/kg	-	The concentrations both in fly and bottom ash were as following: TCDD was 0.1 µg/kg, 2, 3, 7,8 trichlorodioxyfuran was 0.08 µg/kg	[80]
Gasification	RDF and PVC	-	600–1000	Lower than the limits	CO 11.4% H$_2$ 69.6% CO$_2$ 13.5% CH$_4$ 5.5% Heating value of 10.92 (MJ/m^3)	-	[59]

Table 1. *Cont.*

Technology	Feedstock	Reactor Type	Temperature (°C)	PCDD/F Emission (ng-TEQ/Nm³)	Syngas Info.	Note	Ref.
Gasification	MSW	High temperature gasification and smelting system	1070	Less than 0.01 ng-TEQ/Nm³	-	Gasification and smelting system with O₂ blowing and drying waste, and rapid gas cooling system in high-temperature reduction atmosphere are effective for dioxin removal.	[81]
Gasification	Plastic waste and PVC	Sumitomo Metals gasification and smelting system	1070	Less than 0.01 ng-TEQ/Nm³	-	-	[61]
Gasification	Plastic waste	Chemical looping gasification	900	too small to detect by using GC-MS	CO 21.9% H₂ 12.7% CO₂ 7.8% CH₄ 5.9% N₂ 50.7%	-	[82]
Gasification	Hospital waste	Drying, pyrolysis, gasification, combustion, and ash vitrification in one step	600–1200	0.0861	-	-	[83]
Gasification	MSW	Industrial-sized power plant	1400	In clean fuel gas was 0.00003 to 0.0059 and in exhaust gas was 0.0000082 to 0.0031	CO 15.6% H₂ 11.9% CO₂ 15.3% CH₄ 1.1% N₂ 55.1% Heating value of 3700 (kJ/m³ N)	-	[84]

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Gasification	Hospital waste	Drying, pyrolysis, gasification, combustion, and ash vitrification in one step	600–1200	0.0861	-	-	[83]
Gasification	MSW	Industrial-sized power plant	1400	In clean fuel gas was 0.00003 to 0.0059 and in exhaust gas was 0.0000082 to 0.0031	CO 15.6% H_2 11.9% CO_2 15.3% CH_4 1.1% N_2 55.1% Heating value of 3700 (kJ/m^3 N)	-	[84]

4. Conclusions

Dioxin formation/emission via combusting waste is of great public concern. Gasification offers a sustainable substitute approach for waste treatment and energy generation. Gasification is an environmentally friendly technology that enables operation within current regulatory restrictions.

In the presence of organic carbon, oxygen, and chlorine, all combustion processes can result in the formation of PCDD/F in the temperature range 200–800 °C. However, dioxins formation is significantly reduced if a high-temperature reactor is used at above 800 °C and shock cooling of gases is combined, without the presence of oxygen. Dioxin formation can be reduced with the aid of high-temperature gasification even in the problematic case of having fuels with a high content of chlorine.

PCDD/Fs formation in gasification has not been well investigated in the literature. In this review, the levels of PCDD/Fs measured in emissions during gasification of wastes were discussed. There are only few studies available in the literature considering and measuring dioxin formation in waste gasification, and all were reviewed in this paper.

More research should be carried out regarding dioxin formation in gasification. Topics could include:

- Gasification of wastes other than those mentioned in this review;

- The inhibitors of dioxin formation in gasification, such as sulfur- or nitrogen-containing agents.

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Paper II

Article

Mathematical Modeling and Experiments on Pyrolysis of Walnut Shells Using a Fixed-Bed Reactor

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Abstract: Pyrolysis is a low-emission and sustainable thermochemical technique used in the production of biofuels, which can be used as an alternative to fossil fuels. Understanding the kinetic characterization of biomass pyrolysis is essential for process upscaling and optimization. There is no accepted model that can predict pyrolysis kinetics over a wide range of pyrolysis conditions and biomass types. This study investigates whether or not the classical lumped kinetic model with a three-competitive reaction scheme can accurately predict the walnut shell pyrolysis product yields. The experimental data were obtained from walnut shell pyrolysis experiments at different temperatures (300–600 °C) using a fixed-bed reactor. The chosen reaction scheme was in good agreement with our experimental data for low temperatures, where the primary degradation of biomass occurred (300 and 400 °C). However, at higher temperatures, there was less agreement with the model, indicating that some other reactions may occur at such temperatures. Hence, further studies are needed to investigate the use of detailed reaction schemes to accurately predict the char, tar, and gas yields for all types of biomass pyrolysis.

Keywords: biomass to fuel; pyrolysis; fixed-bed reactor; walnut shells; pyrolysis oil; model-based method; competitive reaction scheme; lumped model

1. Introduction

Due to worldwide energy concerns, the depletion of fossil fuels, as well as environmental problems associated with their use, renewable energy sources are receiving increased attention. Biomass has been recognized as an alternative to fossil fuels due to its global availability and environmental benefits, which provide the main motivation for the conversion of biomass into fuels. This conversion can be achieved through biochemical conversion (anaerobic digestion [1,2], fermentation [3]), and thermochemical conversion (combustion [4], pyrolysis [5], and gasification [6,7]). Unlike biochemical transformation, the thermochemical method can convert various types of biomass into fuels or chemicals in an efficient, sustainable, and quick way [8]. However, the use of biomass in traditional combustion processes is limited due to its low energy density and release of toxic organic compounds, such as dioxins [9,10].

Pyrolysis is a low-emission and sustainable thermochemical technique that can be used to thermally degrade biomass into a range of useful products, including bio-char (solid), pyrolysis oil/tars, and fuel gas products (volatiles) [11]. In addition to being an independent technology, biomass pyrolysis is the main sub-process in combustion and gasification processes. As pyrolysis is an inevitable process in thermochemical biomass conversion, understanding pyrolysis kinetics is important for process development, optimization, and proper reactor design.

Kinetics plays an important role in understanding the complex pyrolysis process and deriving mathematical models. Numerous studies have investigated the kinetics of pyrolysis processes [12,13]. Pyrolysis of biomass involves a highly complex set of competitive and concurrent reactions, and the exact mechanism remains unknown. There is no conventional

model that can predict the pyrolysis rate or provide initial information about final conversion yields over a varied range of biomass types, pyrolysis conditions, and reactors types [14]. Hence, simple models that can describe pyrolysis kinetics are very beneficial.

This paper investigates the use of a simple lumped model to mathematically simulate the reaction kinetics of the slow pyrolysis of walnut shells. While lumped models do not necessarily represent the complex physicochemical mechanism of the process, they are able to predict the overall yields [15,16]. A lumped model is acceptable for determining the kinetic parameters of reactions involving pyrolysis, combustion, and gasification [17]. In such models, biomass components and their reaction products are categorized into three product groups: solid (char), non-condensable volatiles (gas), and liquid (tar) [18].

There are two main mathematical approaches to experimentally determine the kinetic parameters of biomass pyrolysis: iso-conversional (model-free) [19–21] and model-based (model-fitting) [22] methods. Model-fitting methods can be categorized as one-component or multi-component depending on the initial biomass characterization (biomass type or its components) and as lumped or detailed reaction mechanisms according to how the products are defined (by products or by species in each product) [23]. The present work combines experimental and theoretical studies on walnut shell pyrolysis. Nutshells as potential materials can be used as an alternative fuel. While studies have evaluated the kinetics of nutshell thermal decomposition [24,25], many have used different reaction mechanisms and kinetic models [26].

Sheth et al. [27] validated the model previously proposed by Koufopanos [28] to optimize the kinetic parameters of the hazelnut shell pyrolysis experiments conducted by Demirbas [29], which involved thermogravimetry experiments on hazelnut shells at heating rates of 0.5, 2, 10, 25, and 40 K/s. Noszczyk et al. [26] conducted thermogravimetric analyses at three different heating rates (5, 10, and 20 °C·min^{-1}) on walnut, hazelnut, peanut, and pistachio shells. The kinetic parameters were determined by Coats and Redfern [30] using the isothermal model-fitting method. Their results showed that an increase in the heating rate caused an increase in the activation energy of nut shell pyrolysis. They concluded that there is a significant difference in the kinetic parameters of different feed materials, even those from the waste classes (e.g., nutshell wastes). They recommended characterizing specific nutshell residues to improve the modeling of thermal processes and reactor design for thermal waste treatment [30].

So far, few studies have been conducted on the pyrolysis of walnut shells using a fixed-bed reactor. To the best of our knowledge, no research has been performed on lumped kinetic modeling of nut shells, especially walnut shells. Therefore, the aim of this work was to apply the lumped kinetic model proposed by many authors [15,16,31] to accurately determine the kinetic parameters of walnut shells pyrolysis. The objectives of this research were as follows: (1) conduct slow pyrolysis experiments on walnut shells in a fixed-bed reactor, (2) estimate the kinetic parameters of the walnut shell pyrolysis. Then, based on a comparison of the modeling and experimental results, we will study whether the existing three-reaction competitive scheme has sufficient prediction power for gas, tar, and char yields across the temperature range of 300 to 600 °C.

2. Materials and Methods

2.1. Pyrolysis Experiment

Walnut shells were chosen as the pyrolysis material. The samples were chopped up and sieved into small particles with sizes ranging from 1 to 2 mm, dried in an oven at 105 °C for 48 h to remove any moisture, and then kept in a desiccator prior to the experiments to ensure that they remained dry. Based on the proximate analysis of the samples, walnut shells had 37.9% fixed carbon and 59.3% volatile matter on a dry and ash-free basis [32]. It is assumed that any moisture uptake that might have occurred during the handling of the samples prior to the experiments would have been eliminated due to the slow heating rate of the process (0.25 °C·s^{-1}), as thermal decomposition starts at around 180–200 °C.

The pyrolysis experiments were carried out on a fixed-bed reactor, as shown in Figure 1. The system consists of vertically positioned stainless steel tubes. A tube (350 mm and 8 mm ID) was connected to the reactor tube (50 mm and 6 mm ID), where the pyrolysis of the biomass occurs, and a U-style tar trap (6 mm ID) was connected to the reactor. The tar trap was submerged in the cooling bath for the duration of the experiment to condense and collect tar. Power was delivered via copper clamps attached to the outside of the stainless steel tube body at the top and bottom of the tube. The tube body acted as a resistance heater. The samples were held in place between two stainless steel wire meshes, placed in the middle of the reactor tube, and kept constant for all the tests. A layer of quartz wool was placed on top of the tar tube in order to separate the tar from other pyrolysis gases. The controller, the power supply, and the K-type thermocouple were arranged in a loop. The controller modulated the direct current onto the stainless steel tube, which was resistively heated to regulate the heating rate and control the temperature. The required experimental parameters, such as the heating rate, holding time, and temperature, were entered in the control program. Holding temperatures of 300 °C, 400 °C, 500 °C, and 600 °C were used in this study. A heating rate of 0.25 °C·s^{-1} and a holding time of 100 s were used for all of the experiments. A K-type thermocouple was used to measure and control the temperature. The thermocouple was introduced through a fitting connection at the top of the tube. The cooling bath used for pyrolysis vapor condensation contained a mixture of dry ice and ethylene glycol (the temperature of the bath was −60 °C). In order to achieve the desired temperature, volume fractions of 0.4 and 0.6 of dry-ice and ethylene glycol were used, respectively [33]. Another thermocouple was placed at the top of the tar trap to measure the temperature during the experiment and to ensure the trap was cool enough to capture tars. Argon (Ar) was used as a carrier gas, at a 3 L/min flow rate, from the top of the stainless steel tube to sweep away pyrolysis products. Argon was selected as the carrier gas, as it does not condense at a temperature of −60 °C.
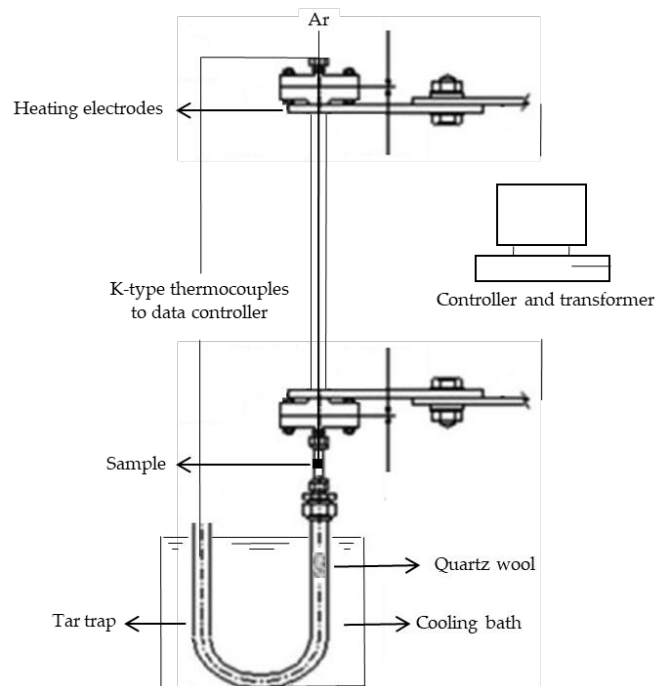

Figure 1. Fixed-bed reactor setup for the pyrolysis process.

Product Yield Calculations

At the end of the run, the reactor was left to cool naturally to room temperature, and products were collected to calculate char and tar yields. The tar collection method using solvents and rotary evaporators was avoided due to concerns of losing some tars due to the relatively high temperature of the rotary evaporators [34]. The difference in weight of the reactor tube and tar trap before and after the experiments was calculated as the mass of chars and tars, respectively. Gas yields were calculated by difference to close the mass balance. The experiments were repeated two times for each condition and then the mean values were obtained. The product yields were calculated using Equations (1)–(3):

$$Char\ yield\ (wt\%) = \frac{m_{char}}{m_{initial\ sample}} \times 100 \tag{1}$$

$$Tar\ yield\ (wt\%) = \frac{m_{tar}}{m_{initial\ sample}} \times 100 \tag{2}$$

$$Gas\ yield\ (wt\%) = 100 - Char\ yield - Tar\ yield \tag{3}$$

2.2. Mathematical Modeling

Model-based methods are the most common methods used for evaluating solid-state kinetics, especially in non-isothermal conditions. With these methods, a reaction scheme must be proposed first (see Figure 2). This study used the competitive model, which is a common reaction scheme for representing the components of pyrolysis by simply lumping them into three groups of products (gas, tar, and char) [15,35].

Figure 2. The competitive model with three reactions in the reaction scheme.

The rate of reaction of the solid phase under non-isothermal conditions (Equation (4)) is determined by multiplying $k(T)$, a process rate constant that obeys the Arrhenius law, and $f(\alpha)$, the conversion function depending on the reaction mechanism [36]. This study used first-order reaction $f(\alpha) = 1 - \alpha$. $i = 1, 2, 3$.

$$\frac{d\alpha}{dt} = k_i(T)f(\alpha) \tag{4}$$

The degree of conversion (α) represents the sample decomposition amount at time t and is defined in terms of the sample's mass change (Equation (5)), where m_0 is the initial mass, m_t is the mass at an arbitrary time, and m_∞ is the mass at the end of the process.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{5}$$

The rate constant is described by the Arrhenius equation (Equation (6)), where A is the pre-exponential factor (s^{-1}), E is the activation energy ($kJ \cdot mol^{-1}$), R is the universal gas constant ($kJ \cdot K^{-1} \cdot mol^{-1}$), and T is the absolute temperature (K).

$$k_i(T) = A_i \exp\left(\frac{-E_i}{RT}\right) \tag{6}$$

The linear heating rate under non-isothermal conditions β is calculated using Equation (7), where dT is a temperature change (K) and dt is a time change (s).

$$\beta = \frac{dT}{dt} \tag{7}$$

Nonlinear least squares fitting is commonly employed to estimate Arrhenius parameters by fitting the experimental data. Differential measurements are suggested for this method for better demonstration of solid de-volatilization [37]. We searched for values of the unknown parameters (A_i, E_i) that minimized the sums of the squares of the experimental data (final yields of gas, tar, and char at the final temperature) and determined the corresponding points of functions calculated (at the final temperature) by the model (see Equation (8)) [38]. n represents the total number of experimental data.

$$sum = \sum_{i=1}^{n} (\left(\frac{d\alpha_i}{dt}\right)_{experiment} - \left(\frac{d\alpha_i}{dt}\right)_{model})^2 \tag{8}$$

A large number of estimated pyrolysis kinetic parameters have been reported in the literature. Reported activation energies (kJ·mol^{-1}) vary from 112.7 to 140 for E_1, 84 to 133 for E_2, 106.5 to 121 for E_3, and pre-exponential factors from (s^{-1}) 4.1×10^6 to 1.48×10^{10} A_1, 1.43×10^4 to 2×10^8 for A_2 and 7.4×10^5 to 2.66×10^{10} for A_3 [31,39,40]. The kinetic parameters (A_i, E_i, in total 6 parameters) in this study were fitted by minimizing the sum in Equation (8) using nonlinear optimization with the generalized reduced gradient method, subject to the constraints obtained from the literature mentioned above. The motivation for using these constraints was to ensure that all the parameters remained within the physically realistic range based on the existing literature. This variation in reported values is due to the fact that the researchers used different models, feeds, operation conditions, and heating profiles. [14]. Table 1 presents the primary kinetic parameters and other constants used in the model. Primary kinetic parameters were obtained from a study using lumped model for wood pyrolysis [39].

Table 1. Primary kinetic data and other constants that are used in the model.

Parameters	Values
A_1 (s^{-1})	1.30×10^8
A_2 (s^{-1})	2.00×10^8
A_3 (s^{-1})	1.08×10^7
E_1 (kJ·mol^{-1})	140
E_2 (kJ·mol^{-1})	133
E_3 (kJ·mol^{-1})	121
R (kJ·mol^{-1})	8.314×10^{-3}
Heating rate (°C·s^{-1})	0.25

3. Results and Discussion

3.1. Pyrolysis Experiments

Pyrolysis of walnut shells was conducted using a fixed-bed reactor. The process was performed at different temperatures (300–600 °C), with the heating rate of 0.25 °C·s^{-1} and a holding time of 100 s.

3.1.1. Vapor-Condensing Temperature and Condensing Efficiency

Figure 3 shows the data collected from the thermocouples, including the pyrolysis process and tar trap temperatures versus the time of the pyrolysis. The cooling bath exhibited good heat preservation performance with the right volume fractions of dry ice and ethylene glycol. During pyrolysis, the bath temperature gradually increased from −30 °C to the final temperature of 2 °C, which is well below the tar trap limit (30 °C) temperature reported in the literature [34]. Wang et al. found the optimum condensing temperature to be in the

range of 67 to 77 °C, at which point the moisture in the pyrolysis oil decreased from 30% to 10% and the condensing efficiency was in the range of 0.4 to 0.2 [41].

Figure 3. Pyrolysis process and tar trap temperatures versus time of pyrolysis.

Condensation efficiency in this study was calculated using Equation (9) [41], and the result was around 0.25 for all the experiments, which is in the optimum range [41].

$$Condensing\ efficiency = \frac{Liquid\ mass}{Walnut\ shell\ mass - solid\ mass} \qquad (9)$$

where liquid mass denotes the mass of condensed tar in the tar trap, walnut shell mass specifies the mass of raw materials prior to pyrolysis, and solid mass represents the mass of char after pyrolysis.

3.1.2. Pyrolysis Products and the Effect of Temperature

The effect of temperature (in the range of 300–600 °C) on the quantity of pyrolysis products formed from walnut shells has been studied, as it is the most significant factor related to the pyrolytic product distribution and yield.

The tar and char yields were measured after each test, and the results are shown in Figure 4. The gas yield was calculated as the percentage of the balance between the original sample weight and the weights of tar and char formed. Volatile yields (volatile yield is the sum of the gas and tar yields) increased as the temperature increased. The ideal pyrolysis temperature for maximum tar yields is reported to be between 400–600 °C for most types of woody biomass [42]. The tar yields doubled when pyrolysis was carried out between 400–500 °C. There was a major increase in tar yields up to 500 °C, but by 600 °C the yield reached a maximum value of 19%. Efeovbokhan et al. [43] observed that tar yields increased by more than double when the temperature was in the range of 400–500 °C for pyrolyzing yam peels. The gas yields were high, with approximately half of the feedstock being converted to gas. The high char yields, measured at the low temperatures in the range studied, decreased up to 23% of the total biomass feed. This indicates that the optimum temperature range for char production from pyrolysis of walnut shells is up to 400 °C. Temperature negatively affects char production yields [44]. Sarkar et al. [45] studied the pyrolysis of coconut shells in the temperature range of 400–600 °C and reported the char yield reduced while bio-oil yield was improved with the temperature increase.

Figure 4. Distribution of the products generated during pyrolysis at different temperatures. Each test was performed in duplicate.

3.2. Pyrolysis Modeling

The simple lumped kinetic model was chosen to evaluate the accuracy of pyrolysis reaction kinetics and product yield prediction. The kinetic parameters of each reaction in the reaction scheme of the competitive model were determined with a least squares method by fitting experimental data at different temperatures. The kinetic parameters from Chan et al. [39] were employed as the primary values. The initial values for the fitting were the kinetic parameters determined for the case of a first-order reaction. The best values of the estimated kinetic parameters (3 activation energies and 3 pre-exponential factors) are shown in Table 2. The subscripts 1, 2, and 3 are the kinetic parameters of the reactions: solid to gas, solid to tar, and solid to char, respectively. The estimated kinetic parameters are within the range of values reported in the literature. Sheth et al. [46] conducted kinetic modeling on woody biomass decomposition to volatiles and char. Their chosen reaction scheme used two competing reactions for each biomass component. Sheth et al. then applied the least squares method to find the optimum kinetic parameters. They described this approach to modelling biomass decomposition as a failure since the kinetic parameters (A_i, E_i) they obtained with their model and methodology were not within the predetermined physically realistic range.

Table 2. Kinetic data obtained by the model.

Parameters	Values
A_1 (s^{-1})	1.70×10^8
A_2 (s^{-1})	3.35×10^9
A_3 (s^{-1})	3.29×10^5
E_1 (kJ·mol^{-1})	114.14
E_2 (kJ·mol^{-1})	135.54
E_3 (kJ·mol^{-1})	87.32

Figure 5 compares the model-predicted yields with the experimentally measured yields. The model used the best-fit parameters in Table 2. The modeling data confirmed that the solid yield dropped while the tar and gas yields enhanced during the experiments in the temperature range of 300 to 400 °C. The fit of the model to the experimental data for the pyrolysis temperatures of 300 and 400 °C was sufficiently good. At higher temperatures, there was less agreement with the model, which could indicate that some other reactions dominate at such temperatures. The first-order Arrhenius kinetics focus on the primary pyrolysis process; consequently, the kinetics scheme better represents the primary

decomposition of biomass pyrolysis [47]. In pyrolysis processes, biomass moisture loss occurs at temperatures below 100 °C; primary pyrolysis reactions occur at 200–600 °C, where biomass decomposes into the primary char, primary tars, and non-condensable gas; and secondary pyrolysis reactions occur at 300–800 °C [48]. This study found that the one-component mechanism with three competing reactions is not a suitable scheme for the slow pyrolysis of walnut shell at high temperatures. As one-component kinetic mechanisms are mostly used for describing pyrolysis under fast heating rates or/and high temperatures, the disagreement could be eliminated if a different reaction mechanism was chosen [49].

Figure 5. Comparison between experimental data and yields predicted by the model during pyrolysis as a function of maximum pyrolysis temperature.

The average percentage error from the experimental data was calculated using Equation (10) [50]. At low temperatures, the model and experimental results agreed well, with an average percentage error of 3% for the low-temperature data. This indicates the model performs well in the temperature range of 300 to 400 °C. Based on this result and the studies on lumped kinetic modeling in the same temperature range, average percentage error typically achieves results within 5%.

$$Average\ percentage\ error = \frac{\sum_{i=1}^{n} \left(\frac{data_{experiment} - data_{model}}{data_{experiment}} \right) \times 100}{n} \qquad (10)$$

In Figure 6, we plot the temperature-dependent rate constants $k_i(T)$ over different temperature ranges. We show these somewhat unconventional plots because the plots reveal how reactions 1, 2, and 3, responsible for the formation of the three phases (gas, liquid, solid), take over or dominate in different temperature ranges. For example, one might expect that the solid formation (char) would dominate at the lowest temperatures, liquid formation (tar) would dominate in the central (pyrolysis) range, and gas formation would take over at the high end as it approaches gasification temperatures. This trend does hold for char $k_3(T)$, but according to our model and data $k_2(T)$ is dominant up to 600 °C. This suggests that $k_1(T)$ largely corresponds to volatilization. In a sense, we may have averaged out or missed the effect of gasification reactions at higher temperatures.

Figure 6. The reaction rate constants (s^{-1}) versus temperature (K): (**a**) for the temperature range 100 °C to 300 °C; (**b**) for the temperature range 150 °C to 400 °C; (**c**) for the temperature of range 200 °C to 500 °C; and (**d**) for the temperature range 200 °C to 600 °C.

4. Conclusions

Pyrolysis experiments and mathematical modeling of walnut shells were conducted. No previous studies have investigated the application of lumped-kinetic modeling to simulate walnut shell pyrolysis product yields. The experimental work was conducted at different temperatures (300–600 °C) in a fixed-bed reactor. According to the experiments, char yields dropped from 37% to 23% with the temperature increase, while volatile yields (tar and gas) increased from 64% to 77%, respectively. We used the nonlinear least squares fitting method to determine the kinetic parameters of the reactions involved. The conventional competitive reaction scheme with three reactions fit our experimental data well at low temperatures, where the primary degradation of biomass occurred (300 and 400 °C), but not at higher temperatures. The results here suggest that the competitive reaction model with three reactions needs to be expanded to include the secondary decomposition of pyrolysis products to accurately predict yields as gasification temperatures are approached. This will be explored in a future work that will be published soon.

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Paper III

Revisiting the reaction scheme of slow pyrolysis of woody biomass

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A R T I C L E I N F O

A B S T R A C T

Existing lumped kinetic models have limited accuracy in predicting the pyrolysis behavior of different materials. There is currently no universally accepted model capable of accurately predicting pyrolysis rates and final product yields for various materials under different experimental conditions. This study aims to address this limitation by assessing the sensitivity of a widely used wood pyrolysis kinetic model across multiple sets of experimental data. The analysis reveals that the existing model falls short in accurately predicting the yields of woody biomass at higher temperatures. To overcome this, two new kinetic models were proposed that incorporate additional reactions not accounted for in conventional models. These additional reactions have impact on the formation of secondary pyrolysis phases. The first proposed model introduces a term for secondary tar formation, which takes into account the production of more stable cracked, dehydrogenated, and deoxygenated tars that typically occur at elevated pyrolysis temperatures, possibly influenced by catalysts. The second proposed model expands on this concept by incorporating terms that represent the formation of secondary gases and chars arising from the primary chars. By including these additional reactions, the model enhances its accuracy and predictive capacity for determining the pyrolytic products of various types of woody biomass.

1. Introduction

One of the major limitations of existing lumped kinetic models is their applicability to specific materials only. To address this issue, the present study combines experimental data and theoretical modeling of various woody materials under different pyrolysis conditions. The temperature range investigated is from 300 °C to 500 °C, with heating rates ranging from 15 °C/min to 60 °C/min. In this study, expanded kinetic models are proposed to predict the pyrolysis behavior of woody materials across a wide temperature range under non-isothermal heating conditions. The main hypothesis to be investigated is whether a rate expression exists that possesses more general predictive capabilities compared to the currently popular lumped kinetic models. By more general predictive capability we refer to the sufficiently accurate prediction of product yields across heating profiles, temperature ranges, and feedstock variations by changing only model parameters, but not the form of the rate expression.

Biomass can be converted into bio-fuel using different technologies, including biochemical [1,2] and thermochemical methods. Among these methods, gasification and pyrolysis are considered highly efficient and environmentally friendly, provided that operational parameters are carefully controlled during the process [3,4]. Pyrolysis, in particular, is

advantageous as it produces a liquid product that can be economically stored and transported. Pyrolysis involves the thermal degradation of biomass through heat in the absence of oxygen, resulting in the formation of solid (char), liquid (tar), and gas products [5]. Kinetic modeling plays a crucial role in understanding the thermal decomposition process and optimizing the pyrolysis process and reactor design for scale-up studies [6].

Wood pyrolysis is a complex process involving a multitude of competitive and concurrent reactions, leading to the formation of numerous intermediate products [7]. Due to this complexity, pyrolysis of wood is often modeled using relatively simple lumped kinetic models. These models lump the biomass constituents and reaction products into three categories: char, gas, and tar [7]. Numerous studies have been conducted to investigate the kinetics of pyrolysis, resulting in the development of various lumped models that employ a limited number of sequential and parallel reactions to describe the pyrolysis process [8–11].

The classical lumped kinetic model is based on competitive reactions, where three reactions represent the conversion of biomass into gas, tar, and char using first-order kinetics. Previous research [12] has applied this conventional competitive reaction scheme with three reactions to evaluate the accuracy of reaction kinetics and predict product

yields during walnut shell pyrolysis. The model showed good agreement with experimental data at lower temperatures where primary biomass degradation occurred (300 °C and 400 °C). However, the model's accuracy diminished at higher temperatures, indicating the need to expand the model to include secondary decomposition reactions for accurate yield predictions [13].

To address the limitations of the competitive reaction model, researchers have proposed multi-reaction models or competing and parallel reaction models [6,8–11,13–22]. These models consider the primary degradation of biomass, along with secondary decomposition of tar and higher hydrocarbons into gas [14], as well as tar polymerization reactions leading to secondary char formation [15]. There are studies that have focused on wood pyrolysis, developing reaction models that encompass both primary and secondary pyrolysis processes. Koufopanos et al. [16] developed a reaction model for wood pyrolysis which describes the process of pyrolysis. The model involves biomass decomposition to volatile, gases and char. Volatile and gases may further react with char and produce also volatile, gases and char of different compositions. Chen et al. [17] applied a kinetic model, considering a two-step consecutive reaction, to explain the decomposition of Chinese forest fuels using non-isothermal thermogravimetric analysis in an oxidative atmosphere at low heating rates. After the kinetic parameters calculation and their comparison with the literature, they suggested that the reaction scheme can describe the thermal decomposition process well.

Despite the numerous studies on biomass pyrolysis reaction schemes and kinetic modeling, there is no universally accepted model capable of predicting pyrolysis rates and final products for different materials under a range of experimental conditions [19]. Furthermore, compared with primary reactions, secondary reactions are less investigated.

The aspect of pyrolysis that is least understood pertains to the interaction between the hot pyrolysis vapors and the decomposing solid, which the vapors must pass through to escape into the environment. This process is known as secondary decomposition. When exposed to high temperatures for extended periods, secondary reactions of primary tar vapors also come into play [23]. These secondary reactions involve cracking, partial oxidation, re-polymerization, and condensation, resulting in the production of permanent gases, secondary chars, and secondary tars [24,25]. Although there is a comprehensive understanding of the chemical composition of these products, the commonly cited reaction mechanism simply consists of two competing reactions, as described in the existing literature [18,20,26]. Shafizadeh [18] developed the most well-known model for wood pyrolysis, which propose that biomass thermally decomposes into gases, tar, and char. The tar is then assumed to undergo two competing reactions, leading to the formation of permanent gases and char.

This study aims to investigate the inclusion of additional reactions in the secondary pyrolysis zone. The proposed models account for supplementary reactions that are not considered in conventional models, and we find that these additional reactions significantly contribute to the formation of secondary pyrolysis phases. It is challenging to determine whether more complex reactions yield more accurate predicted results, as it requires estimating a greater number of input kinetic parameters. In particular, when incorporating tar or immediate solid and their subsequent reactions, the relevant kinetic properties of tar are sourced from the literature, which are difficult to measure at the current experimental level. Consequently, the validation of these intricate models must rely on the limited experimental data available [7].

Thus, the objective of this paper is to validate and compare three kinetic models: the existing model [18], along with two new lumped-kinetic models. The evaluation is conducted using the authors' previous experimental data and experimental studies from the literature. The initial aim is to assess the sensitivity of the widely used wood pyrolysis kinetic model to various experimental data. Additionally, the study aims to explore the inclusion of additional reactions in the pyrolysis reaction scheme to improve the model's predictive capabilities

and align its predictions with experimental data. The ultimate goal is to determine whether the incorporation of extra reactions and refinement of kinetic parameters can enhance the accuracy and precision of the model when it comes to predicting pyrolytic products derived from diverse biomass materials. The outcomes of this research have the potential to provide significant benefits to the field of pyrolysis modeling.

2. Materials and methods

2.1. Experimental method

In this study, walnut shells, eucalyptus wood, and pistachio shells were selected as representatives of woody biomass. Detailed information on the experimental method and data regarding walnut shell pyrolysis can be found in our previous study [12]. Nunes et al. [27] and Volpe et al. [28] conducted the pyrolysis experiments on eucalyptus wood and pistachio shells, respectively.

For the slow pyrolysis process, hot-rod (fixed-bed) reactors were employed operating within a temperature range of 300 °C–500 °C. The heating rates were set at 0.25, 1, and 0.84 (°C s^{-1}), and the corresponding holding times were 100, 900, and 1800 s for walnut shells, eucalyptus wood, and pistachio shells, respectively. Throughout the experiments, the pyrolysis was conducted under different gas atmospheres: argon for walnut shells, helium for eucalyptus wood, and nitrogen for pistachio shells. Data from these experimental studies will be used for comparison with our predicted results to validate the validity of three reaction kinetic models in this study.

2.2. Modeling method

Model-fitting methods are the most common methods used for evaluating solid decomposition. With these methods, a reaction model must be proposed first. This study used competing and parallel reaction models, one of which is the Shafizadeh model [18], along with two new reaction models (see Fig. 1). The thermal decomposition of biomass is composed of three stages and is closely related to the pyrolysis temperature [29]. Biomass moisture evaporates after it is heated to over 100 °C to below 200 °C [30]. Then, primary pyrolysis takes place at temperatures of 200 °C–400 °C [31,32], which is also considered to be the initial depolymerization reaction stage. At this stage, the dry biomass particles are decomposed into solid, condensable, and non-condensable products. As the temperature further rises, the primary products undergo secondary reactions. Secondary reactions such as tar cracking, reforming, dehydrogenation, and repolymerisation lead to the production of permanent gases, secondary chars, and secondary tars [24,25]. There is no clear border between primary and secondary pyrolysis since these pyrolysis stages generally take place simultaneously in different parts of the biomass [33,34].

Model I is the widely used reaction scheme for wood pyrolysis developed by Shafizadeh and Chin [18]. The reaction scheme explicitly models biomass thermal decomposition into gases, tar, and char, and then the tar further decomposes into char and gases. Model II in this study proposes the addition of an extra reaction to model I. The added reaction competes with the decomposition of primary tar into secondary char and secondary gas to form instead more stable secondary tar that is subsequently not available to secondary gas and char formation. Although the addition of this term was suggested purely by the comparison of model I and data described in section 3.1 here and in Ref. [12], this expansion of the reaction scheme has a rational motivation as well: This extra reaction can be ascribed to the successive conversion of primary tars into an ever more stable mixture of tars (condensable molecules) that could include oxygenates, aromatics & phenolic ethers, olefins and higher hydrocarbons like larger PAH compounds. In essence, all the chemical species frequently detected with GC/MS analysis of secondary tars [35–37]. As primary tar is cracked, dehydrogenated and deoxygenation at elevated pyrolysis temperature
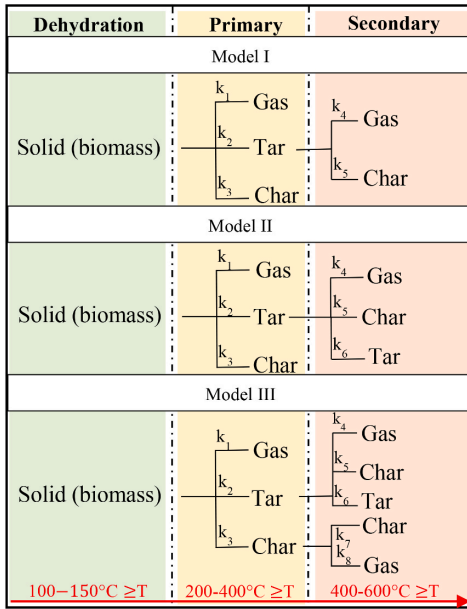
Fig. 1. Thermal decomposition of biomass with three different reaction schemes used in this study to predict pyrolytic products.

Table 1
Primary kinetic data and other constants that are used in the model.

Parameters	values
A_1 (s^{-1})	1.30×10^8
A_2 (s^{-1})	2.00×10^8
A_3 (s^{-1})	1.08×10^7
A_4 (s^{-1})	4.28×10^6
A_5 (s^{-1})	1.00×10^6
A_6 (s^{-1})	1.00×10^4
A_7 (s^{-1})	1.38×10^{10}
A_8 (s^{-1})	1.38×10^{10}
E_1 (kJ.mol^{-1})	110
E_2 (kJ.mol^{-1})	133
E_3 (kJ.mol^{-1})	121
E_4 (kJ.mol^{-1})	107
E_5 (kJ.mol^{-1})	107
E_6 (kJ.mol^{-1})	76.6
E_7 (kJ.mol^{-1})	161
E_8 (kJ.mol^{-1})	161
R (kJ.mol^{-1})	8.314×10^{-3}

heating rate ($^\circ$C.s^{-1}), A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ.mol^{-1}), R is the universal gas constant (kJ.K^{-1}. mol^{-1}), and T is the absolute temperature (K), f(α) is the conversion function. In the kinetic models, the rate expression based on the first-order decomposition of the reactive solid is defined in terms of fractional conversion f(α) = 1- α.

The differential equations related with kinetic model are solved simultaneously by ode45 tool in MATLAB. Nonlinear least squares fitting is employed to estimate Arrhenius parameters by fitting the experimental data, using nonlinear optimization with the generalized reduced gradient method. Model searched for values of the unknown parameters (A_i, E_i, in total 10, 12, and 16 parameters for model I, II, and III respectively) that minimized the sums of the squares of the experimental data (final yields of gas, tar, and char at the final temperature) and determined the corresponding points of functions calculated (at the final temperature) by the model [45,46]. The kinetic parameters in this study were fitted by minimizing the sum in Equation (2), subject to the constraints obtained from the range between the minimum and maximum presented in Table 2 n represents the total number of experimental data. The reaction rate expressions for all the species in the models can be found in the supplementary material.

$$sum = \sum_{i=1}^{n} \left(\left(\frac{d\alpha_i}{dt} \right)_{experiment} - \left(\frac{d\alpha_i}{dt} \right)_{model} \right)^2 \qquad (2)$$

A large number of estimated pyrolysis kinetic parameters have been reported in the literature. The authors reviewed the studies that conducted kinetic modeling on batch woody biomass pyrolysis. Among these, the kinetic parameters obtained from one-component lumped models having primary and secondary first-order reactions are gathered and illustrated in Table 2. The table presents the activation energies (kJ·mol^{-1}), pre-exponential factors (s^{-1}), and the minimum and maximum of each parameter for all of the reactions in woody biomass pyrolysis. The motivation for using these constraints was to ensure that all the parameters remained within the physically realistic range based on the existing literature. This variation in reported values is due to researchers' use of different models, feeds, operation conditions, and heating profiles [19].

3. Results and discussion

The Shafizadeh model [18], a common wood pyrolysis kinetic reaction scheme, along with two new lumped-kinetic models were proposed. Models belong to one solid-phase component reaction scheme, namely all the reactants are lumped as 'Wood' and the products are divided into solid-phase char, liquid-phase tar, and gas-phase volatiles.

and/or accelerated by catalysts a reformed and refined secondary tar is progressively obtained and the fact that this process *removes primary tar* from secondary gas and char formation apparently need to be explicitly included in the reaction scheme if it is to be broadly predictive. Model II explicitly includes this feature of pyrolysis.

A further expansion, model III, is also proposed in this study. Model III has a total of eight reactions. First, virgin wood decomposes into three major products: tar, char, and gas, by three primary reactions. And then, a portion of tar decomposes to secondary gas and secondary char and secondary tar by successive secondary reactions, respectively. In model III it is then added that primary char can volatilize to produce additional gas by secondary reactions with an even more devolatilized solid carbon remaining [38,39]. The primary kinetic parameters and other constants used in models I, II, and III are listed in Table 1. Kinetic parameters (A_1, A_2, A_3, A_4, A_5, E_1, E_2, E_3, E_4, E_5) used in model I were obtained from Chan et al. [40] and Liden et al. [41]. Kinetic parameters for the primary tar to secondary tar reaction (A_6, E_6) in model II were obtained from Morf [42]. Kinetic parameters for the primary char to secondary char reaction (A_7, E_7) in model III were obtained from Park et al. [8], and for the primary char to secondary gas reaction (A_8, E_8) the same kinetic parameters as primary char to secondary char were used, with the assumption of these two reactions having the same conversion rates. Ahuja et al. [43] studied the kinetics of acacia and eucalyptus wood pyrolysis and proposed a model in which secondary char and gases are both produced from primary char with the same reaction rates.

The rate of reaction of the solid phase under non-isothermal conditions is presented using Eq. (1) [44]:

$$\frac{d\alpha}{dT} = \frac{A_i}{\beta} exp\left(\frac{-E_i}{RT}\right) f(\alpha) \qquad (1)$$

where dα/dT is the non-isothermal reaction rate, β = dT/dt is the linear
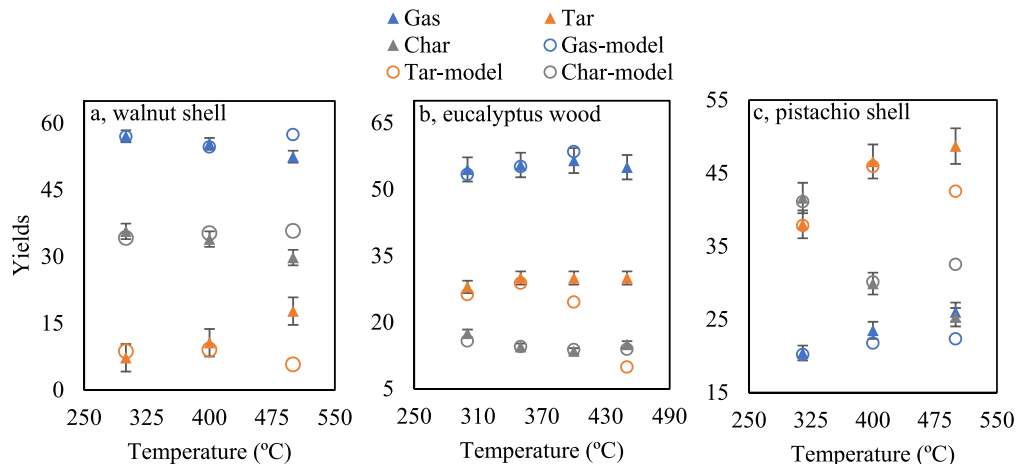
Fig. 2. Distribution of the products generated during pyrolysis experiments at different temperatures and model-predicted yields from model I. Fig. 2a, b, and 2c present data for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively.

Data from three experimental studies, walnut shell [12], eucalyptus wood [27], and pistachio shell [28] pyrolysis is used for comparison with our predicted results to evaluate the accuracy of pyrolysis reaction kinetics and product yield prediction. Arrhenius kinetic treatment, as the most common formula, is applied to represent the pyrolysis reaction rates of the models illustrated in Fig. 1. Taking model I as an example, the proposed kinetic model that needs to be parametrized is 10 by providing appropriate values of A_i, and E_i. The total number of kinetic parameters that need to be optimized is 38 for each experimental study.

The Arrhenius parameters were obtained by best fitting the measured conversion data by using a nonlinear least-squares regression. The kinetic parameters from the literature were employed as the primary values [8,40–42]. The initial values for the fitting were the kinetic parameters determined for the case of a first-order reaction. The best values of the estimated kinetic parameters for models I, II, and III based on the experimental data are shown in Tables 3–5, respectively. The subscripts 1, 2, 3, 4, 5, 6, 7, and 8 are the kinetic parameters of the reactions: solid to gas, solid to tar, solid to char, tar to gas, tar to char, tar to tar, chart to char, and char to gas respectively. The estimated kinetic parameters are within the predetermined physically realistic range based on the existing literature (Table 2).

The applicability of three kinetic models for the pyrolysis of woody biomass was evaluated by using experimental data from the literature [12,27,28]. The simulated concentration distributions of products, namely gas, tar, and char, during woody material pyrolysis under non-isothermal conditions are shown in Figs. 2–4.

3.1. Model I

Fig. 2a, b, and 2c show the results of the model-predicted yields with the experimentally measured yields of walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively, developed by Shafizadeh [18]. The model used the best-fit parameters in Table 3. The modeling data confirmed that the solid yield dropped while the tar and gas yields enhanced during the experiments in the temperature range of 300–500 °C [12,51]. The fit of the model to the experimental data for the pyrolysis temperatures of 300 and 400 °C was sufficiently good for all three studies. At higher temperatures (above 400 °C), there was less agreement with the model, which could indicate that some other reactions dominate at such temperatures. This kinetics scheme better represents the primary decomposition of biomass pyrolysis than the secondary decompositions. This reaction kinetic model originally adapted well to

the experimental data from cottonwood pyrolysis conducted by Shafizadeh et al. [18] and also to other studies in the literature [49,52]. However, it is proven in this study that this reaction scheme is not a suitable scheme for the slow pyrolysis of every woody biomass at high temperatures.

3.2. Model II

Fig. 3a, b, and 3c show the results of the model-predicted yields with the experimentally measured yields of walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively. The model used the best-fit parameters in Table 4 and shows the results of the proposed model with the secondary reactions of tar. By comparing the predicted results and experimental data, it is found that the existence of a secondary tar reaction for the pyrolysis reaction scheme is helpful to improve the reasonability of reaction models as compared to model I. With the increase in temperature (above 400 °C), secondary pyrolysis is taking place simultaneously with primary pyrolysis resulting in the production of secondary gas, tar, and char [32,34]. Pattanotai et al. [36] conducted an experimental study on secondary reactions of tar during the slow pyrolysis of Japanese cypress wood. They found that the tar decomposition progresses between 400 and 500 °C, and showed that the secondary reactions of tar play an important role in the pyrolysis of wood particles. Since the tar produced in the pyrolysis zone is transported toward exterior particles through micropores in the char layer which acts as a catalyst, a portion of the tar is decomposed or polymerized to form secondary gas, secondary tar, and secondary char during this transportation. Moreover, these reactions have the potential to achieve tar reduction in biomass gasification without any additional tar removal process. The fit of the model to the experimental data for the pyrolysis temperatures was good, except for the highest temperatures for all three studies. This indicates that there are still some other reactions involved in the secondary pyrolysis phase. Hence this kinetics scheme requires further improvements to be able to reproduce the observed behavior of woody biomass pyrolysis experiments that are investigated in this study.

3.3. Model III

Computed gas, tar, and char yields for the model are illustrated in Fig. 4. Fig. 4a, b, and 4c show the results of the model-predicted yields with the experimentally measured yields of walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively. The model used the

best-fit parameters in Table 5 and shows the results of the proposed model with the secondary reactions of tar and char. The modeling results confirmed that the solid yield declined while the liquid and gas yields increased. As can be seen in Fig. 4, the model fits well with the experimental data for all three studies at all temperatures. The good agreement with experimental results indicates that model III is successful in developing a quantitative understanding of woody biomass pyrolysis. This model includes secondary char reactions to the pyrolysis reaction scheme in model II. During the secondary pyrolysis phase, primary char can be activated as a catalyst to convert organic vapors into light gases and form secondary char by polymerization reactions [53].

3.4. Validation and sensitivity analysis

The standard deviation was calculated using Equation (3) [54]. The modeling results showed a small deviation of 0.3 from the walnut shell experimental data, and 0.1 from both eucalyptus wood and pistachio shell experimental data. This indicates the model III performs well and thus it is validated.

$$Standard\ deviation = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{data_{experiment}-data_{model}}{data_{experiment}}\right)^2}{n-1}} \tag{3}$$

Sensitivity analysis was carried out to examine the importance of extra reactions addition to the models II and III. As explained in section 2.2, a "physically realistic range" was determine for the kinetic

Table 2
Kinetic parameters of woody biomass pyrolysis studies in the literature [7,8,23,40–42,47–50].

Reactions		KP	Wood (pine, birch)	Wood	Wood	Wood	Wood	Rice husk	Beechwood	Beechwood	Wood	Wood fir and spruce	Wood	Min	Max
								Feedstock							
Solid to gas	A_1	1E+08	5E+06	4E+09	4E+09	1E+08	-	-	3E+08	3E+08	5E+09	-	1E+08	5E+06	5E+09
Solid to tar	A_2	2E+08	1E+10	1E+10	1E+10	2E+08	-	-	1E+08	3E+08	9E+09	-	1E+07	1E+01	1E+10
Solid to char	A_3	1E+07	3E+10	3E+06	3E+06	1E+07	-	-	7E+04	2E+04	4E+06	-	2E+08	2E+04	3E+10
Tar to gas	A_4	2E+04	4E+06	4E+06	4E+06	4E+06	-	-	6E+10	7E+10	4E+06	-	1E+06	2E+04	7E+10
Tar to char	A_5	-	1E+06	1E+05	1E+05	1E+06	-	-	3E+08	1E+09	1E+05	-	-	1E+05	1E+09
Tar to tar	A_6	-	-	-	-	-	-	1E+05	-	-	4E+04	1E+04	5E+05	1E+04	5E+05
Char to char	A_7	-	-	-	1E+10	-	-	-	-	4E+10	-	-	1E+10	1E+10	4E+10
Char to gas	A_8	-	-	-	-	-	-	-	-	-	-	-			

Ref.	Feedstock (KP)	Solid to gas E_1	Solid to tar E_2	Solid to char E_3	Tar to gas E_4	Tar to char E_5	Tar to tar E_6	Char to char E_7	Char to gas E_8
[47]	Wood (pine, birch)	140	133	121	80	-	-	-	-
[48]	Wood	89	113	107	108	108	-	-	-
[8]	Wood	153	148	112	108	108	-	161	-
[8]	Wood	153	148	112	108	108	-	-	-
[40,41]	Wood	140	133	121	107	107	-	-	-
[49]	Rice husk	-	-	-	-	-	105	-	-
[7]	Beechwood	120	112	92	156	134	-	-	-
[7]	Beechwood	121	116	87	157	140	-	244	-
[50]	Wood	56	93	112	108	108	-	-	-
[42]	Wood fir and spruce	-	-	-	-	-	77	-	-
[42]	Wood fir and spruce	-	-	-	-	-	136	-	-
[42]	Wood fir and spruce	-	-	-	-	-	100	-	-
[23]	Wood	140	121	133	114	107	-	161	-
Min		56	93	87	80	107	77	161	-
Max		153	148	133	157	140	136	244	-

Table 3
Kinetic data obtained by model I for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis experiments.

Parameters	Values (walnut)	Values (eucalyptus)	Values (pistachio)
A_1 (s^{-1})	1.07×10^8	6.26×10^6	5.16×10^6
A_2 (s^{-1})	1.64×10^8	1.40×10^7	4.19×10^7
A_3 (s^{-1})	6.80×10^6	3.34×10^5	6.32×10^4
A_4 (s^{-1})	4.87×10^6	1.50×10^7	2.30×10^4
A_5 (s^{-1})	8.90×10^5	1.00×10^5	1.00×10^5
E_1 (kJ.mol^{-1})	110.4	104.4	112.3
E_2 (kJ.mol^{-1})	120.5	111.6	119.4
E_3 (kJ.mol^{-1})	99.8	96.3	87.3
E_4 (kJ.mol^{-1})	107	157.2	157.2
E_5 (kJ.mol^{-1})	139.9	139.9	139.9

parameters whenever possible, based on a broad survey of the literature. This "physically realistic range" was then used as a constraint for the kinetic parameters of a given model when the kinetic parameters where adjusted to best simulate the experimental data.

One can ask if the constraint window designed to keep all parameters physical, i.e. to avoid purely mathematical artifacts, could possibly have been too narrow or too wide during this fitting procedure. To explore the question of a too narrow window the following sensitivity analysis was performed: The constraint windows for $A_{4,5}$ and $E_{4,5}$ were broadened by 20% and the kinetic parameters were re-fitted to the experimental data (walnut shell) with these relaxed constraints.

The effect of this relaxation on the best fit kinetic parameters reported in Tables 4 and 5 for the models II and III can be seen in Table 6 below. As expected, there is an effect, however, the absolute deviation

Table 4

Kinetic data obtained by model II for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis experiments.

Parameters	Values (walnut)	Values (eucalyptus)	Values (pistachio)
A_1 (s^{-1})	7.99×10^7	2.30×10^7	3.55×10^8
A_2 (s^{-1})	5.74×10^8	5.98×10^7	4.17×10^8
A_3 (s^{-1})	1.45×10^6	8.21×10^4	9.59×10^4
A_4 (s^{-1})	2.30×10^4	6.61×10^6	3.47×10^6
A_5 (s^{-1})	1.00×10^5	1.00×10^5	1.00×10^5
A_6 (s^{-1})	1.00×10^4	5.48×10^4	2.12×10^4
E_1 (kJ.mol^{-1})	108.6	108.6	131.4
E_2 (kJ.mol^{-1})	125.6	116.3	128.9
E_3 (kJ.mol^{-1})	92.6	87.3	87.7
E_4 (kJ.mol^{-1})	107	157.2	119.9
E_5 (kJ.mol^{-1})	139.9	139.9	139.9
E_6 (kJ.mol^{-1})	76.6	100.2	76.6

Table 5

Kinetic data obtained by model III for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis experiments.

Parameters	Values (walnut)	Values (eucalyptus)	Values (pistachio)
A_1 (s^{-1})	1.30×10^8	1.78×10^7	3.55×10^8
A_2 (s^{-1})	2.00×10^8	4.10×10^7	4.17×10^8
A_3 (s^{-1})	1.09×10^7	8.35×10^4	9.59×10^4
A_4 (s^{-1})	4.25×10^6	4.28×10^7	3.47×10^6
A_5 (s^{-1})	1.01×10^6	1.00×10^5	1.00×10^5
A_6 (s^{-1})	1.00×10^4	3.91×10^5	2.12×10^4
A_7 (s^{-1})	1.38×10^{10}	1.38×10^{10}	1.38×10^{10}
A_8 (s^{-1})	1.38×10^{10}	1.37×10^{10}	1.37×10^{10}
E_1 (kJ.mol^{-1})	150.3	107.7	132.4
E_2 (kJ.mol^{-1})	126.1	115	129.4
E_3 (kJ.mol^{-1})	105.9	87.8	88.3
E_4 (kJ.mol^{-1})	107	157.2	119.9
E_5 (kJ.mol^{-1})	101.2	139.9	139.9
E_6 (kJ.mol^{-1})	67.2	90.6	76.6
E_7 (kJ.mol^{-1})	160.4	232.3	232.4
E_8 (kJ.mol^{-1})	157.6	253.3	212.5

only ranges from −0.09% to 0.04%. This deviation is not large enough to reverse or invalidate any of the conclusions of this work.

The kinetic parameters of woody biomass, under different pyrolysis conditions, are different as biomass is lead to the breaking of different bonds resulting in the extraction of a slightly different kinetic equation each time. As shown in Table 5, E values ranged from 67 to 158, 88–253, and 77–232 (kJ mol^{-1}) for the walnut shell, eucalyptus wood, and

pistachio shell pyrolysis, respectively. The minimum A values were 1×10^4, 8×10^4, and 2×10^4 (s^{-1}) for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively, and the maximum was 1.4×10^{10} (s^{-1}) for all three studies. The lowest E and A values are observed at primary tars conversion to secondary tars for the walnut and pistachio shell pyrolysis while for the eucalyptus wood pyrolysis, the lowest E and A values belong to primary solid decomposition to char. Pyrolysis reactions with low E and A values are easier to initiate, as the required energy is smaller. Woody biomass has different biochemical compositions (cellulose, hemicelluloses, lignin, and extractives) [55] and they behave differently even under the same heating conditions of the pyrolysis process. The main decomposition zone of cellulose is at around 300–400 °C, hemicellulose decomposes at a lower temperature range from 220 to 315 °C, while the pyrolysis of lignin starts relatively earlier at 150 °C [56]. Feedstock with high cellulosic composition has high activation energies, while feedstock with high lignin content decomposes easier as they require lower activation energies [29]. In this study, eucalyptus wood and pistachio shell have higher activation energies, as a result of their high cellulosic compositions being 41.6% [57] and 42% [58], respectively. Walnut shell contains 50.3% lignin [59], consequently, has the lowest activation energies. In addition to different chemical compositions, heat and mass transfer happening in the pyrolysis reactors of woody biomass studied here imply different activation energy requirements [29].

4. Conclusion

In this study, the conventional Shafizadeh model was compared with two expanded lumped-kinetic models to study their application and compare their sensitivity to woody biomass pyrolysis. The study used experimental data from different woody biomass pyrolysis to find an appropriate kinetic model valid for non-isothermal heating conditions. The kinetic parameters of each reaction in the reaction scheme of the three models were determined with a least squares method by fitting experimental data at different temperatures. Model I showed good agreement with the experiments for the temperatures of 300 °C and 400 °C for all three studies. Less agreement with the model at higher temperatures (above 400 °C), was attributed to the inability of the conventional scheme (model I) to model high-temperature pyrolysis. That indicated that some other reactions contribute nontrivially at such temperatures. The fit of model II to the experimental data for the pyrolysis temperatures was good, except for the highest temperatures for all three studies. This indicates that there are likely still more additional
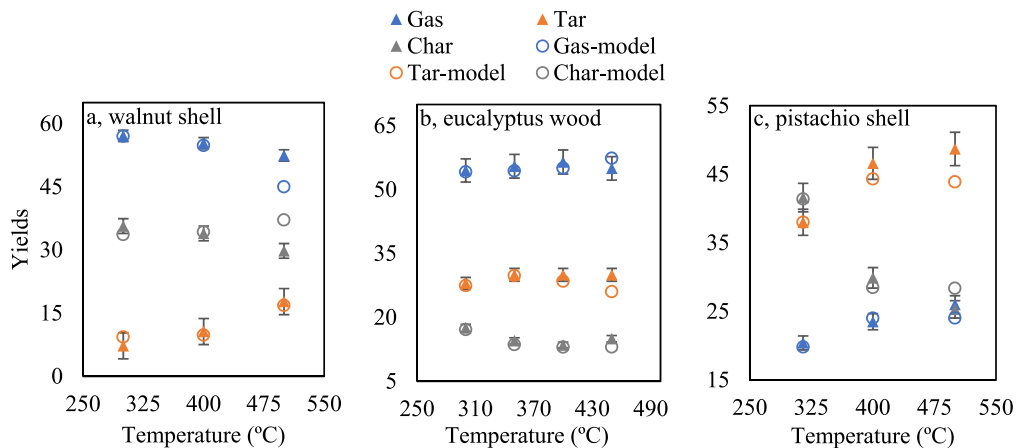

Fig. 3. Distribution of the products generated during pyrolysis experiments at different temperatures and model-predicted yields from model II. Fig. 3a, b, and 3c present data for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively.
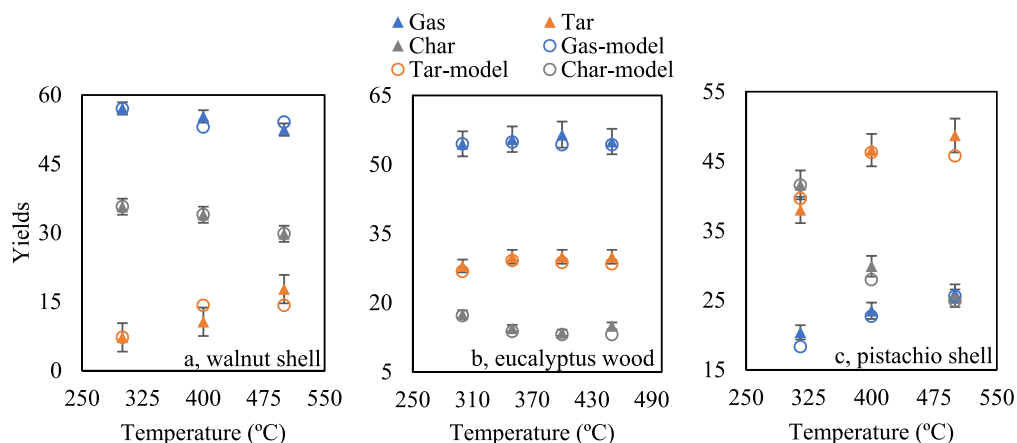
Fig. 4. Distribution of the products generated during pyrolysis experiments at different temperatures and model-predicted yields from model III. Fig. 4a, b, and 4c present data for the walnut shell, eucalyptus wood, and pistachio shell pyrolysis, respectively.

Table 6
Results of the sensitivity analysis (effect of constraint window size on experimentally fitted kinetic parameters).

Parameter	Value with original constraint window	Value with constraint window ± 20%	Percent change
Model II			
A_4	23000	22996.70	−0.0001%
A_5	100000	99751.73	−0.0025%
E_4	107	107	0%
E_5	139.88	139.88	0%
Model III			
A_4	4247776.64	3872785.66	−0.0882%
A_5	1011079.80	982167.96	−0.0286%
E_4	107	107	0%
E_5	101.22	125.66	0.0439%

reactions, in addition to "stable" secondary tar formation, that are active at the high end of pyrolysis temperatures. This finding suggests that the reaction scheme should also explicitly include terms for these reactions if a model is to be broadly predictive at the higher end of pyrolysis temperatures. By adding rate expressions for the secondary further degassing of char, and the accompanying formation of devolatilized secondary char, the resulting model III sufficiently accurately predicted the pyrolysis yields of various types of woody biomass across all common pyrolysis temperature ranges. This paper contributes to the lumped kinetic modeling of woody biomass pyrolysis by concluding that the addition of secondary tar and char reactions into the reaction scheme makes the kinetic models more accurate and broadly capable of predicting pyrolytic products.

Credit author statement

Aysan Safavi.: Conceptualization, formal analysis, validation, investigation, methodology, writing—original draft. Christiaan Richter: supervision, writing—review and editing. Runar Unnthorsson: funding acquisition, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Paper IV

A Study of Parallel and Competitive Reaction Schemes in Kinetic Modeling of Plastic Pyrolysis

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A Study of Parallel and Competitive Reaction Schemes in Kinetic Modeling of Plastic Pyrolysis

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Abstract

Pyrolysis is a technology capable of harnessing energy from challenging-to-recycle plastics, thus mitigating the necessity for incineration or landfill disposal. To optimize the plastic pyrolysis process, reliable models for product yield prediction are imperative. This study endeavors to determine the suitability of lumped models, a widely-used approach for modeling biomass and coal pyrolysis, in accurately estimating product yields in the context of plastic pyrolysis. To address this question, three lumped models with parallel and competitive reaction mechanisms will be compared and fitted to experimental data collected across a broad temperature range. The aim is to identify which models can elucidate the most appropriate reaction pathway for the plastic pyrolysis process. The first model in this study assesses whether the commonly employed wood pyrolysis kinetic models can effectively fit the experimental data from plastic pyrolysis. Subsequently, the final two models introduce additional reactions into the pyrolysis process, prompting the authors to investigate the necessity of these supplementary reaction pathways for accurately predicting plastic pyrolysis outcomes. This investigation seeks to pinpoint the essential terms and discern which ones may be safely omitted from the models. The results of the study reveal that the model incorporating secondary tar reactions with gas, tar, and char is the most precise in predicting the products of plastic pyrolysis, surpassing all other combinations evaluated in this research.

1   Introduction

Plastics, with their widespread and often fleeting use, low cost, and often low recyclability and recycle rates and very slow biodegradability are an environmental issue of wide concern [1–3]. Thermochemical technologies are the leading method to eliminate from the environment the many polymers that are hard or impossible to recycle or even down-cycle mechanically or chemically. Combustion, as a thermochemical method, does still in many cases where pollution control is not strict enough result in the release of pollutants into the environment which impact human health and result in air pollution [4–6]. Pyrolysis can recover more than just heat energy by extracting from plastic waste valuable products in the form of solid (e.g. char), liquid (e.g. pyrolysis oil), or gaseous fuels (e.g. hydrogen and/or syngas) that may be used in case of pyrolysis oil or syngas as a feedstock to produce alternative fuels or even in chemical synthesis to produce new plastics or chemicals and materials [7–9]. In short, pyrolysis of plastic is a versatile process with a flexible product range that can be easily varied with process parameters like reaction temperature profile and residence time [10].

Pyrolysis involves numerous reactions that involve a large number of intermediates and end products. As a result, devising a kinetic model for pyrolysis that includes all molecular species and their reactions is not only difficult but inevitably involves extensive approximations and parameter fitting [11]. Therefore, model-free and model-fitting methods that lump molecular species into groups, typically solids (with subgroups feed and char or chars), liquid (tar or tars), and gaseous product yields, as opposed to detailed molecular composition, are typically employed to determine the reaction rates and to practically model the yields of solid pyrolysis (see Figure 1). The key difference between these two modeling approaches is that model-free methods [12] do not make any assumptions about the reaction scheme between groups for calculating the kinetic parameters, whereas model-fitting methods assume a specific reaction model (parameterized rate expressions) and then determine the kinetic parameters typically by fitting experimental data [13]. Model fitting methods can be further categorized into one-component or multi-component based on how the initial feed is characterized (e.g., by a specific type of feed or by its components), and lumped or detailed kinetic models based on how the products are defined (e.g., by lumped products such as gas, char, and tar, or by representative or model species in each lumped product) [14]. A parallel reaction scheme involves primary and secondary reactions occurring simultaneously. On the other hand, in a competitive reaction scheme, solid mass reactions leading to the formation of gas, tar, and char are in competition with one another. This study employed both parallel and competitive reaction schemes

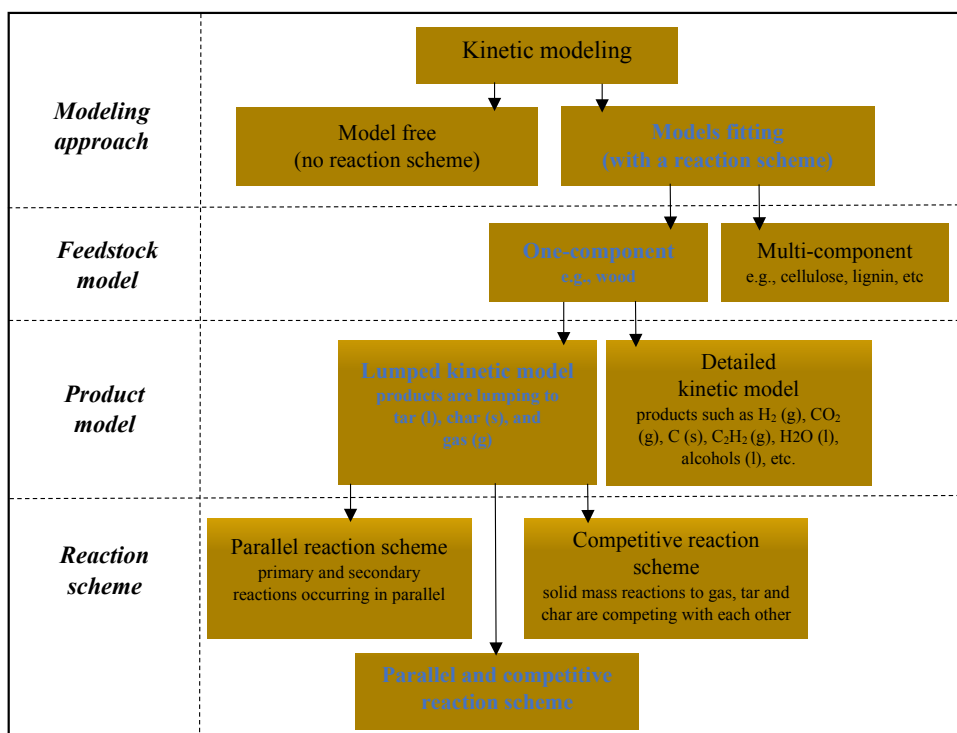*Figure 1: kinetic modeling approaches. This study used one-component model fitting approach, with parallel competitive reaction scheme lumping the products to tar, gas and char. Those selected in this study are in blue.*

Some studies investigate the degradation behavior of plastics pyrolysis with lumped kinetic approaches [3,6,9,15–19]. The majority of kinetic work utilizes lumped models because the kinetics are based on the

yields of lumped products (i.e., char, tar, and gas) [6,9,15–18]. The conventional parallel competitive reaction model with three primary pyrolysis reactions developed by Agrawal [20] was studied by many authors to predict plastic pyrolysis products [1,21,22]. This model is only suitable where the primary degradation of solid mass occurred (300 and 400°C), but not at higher temperatures [21–23]. The authors [23] previously studied using this reaction scheme to investigate its accuracy in predicting pyrolysis products. They concluded that the competitive reaction model with three reactions needs to be expanded to include the secondary decomposition of pyrolysis products to accurately predict yields. Costa et al. [24] used a lumped model with nine reactions to model batch pyrolysis of polyethylene at different temperatures. The pyrolysis products were lumped into lower molecular weight polymer, gas, light, and heavy oil. Ding et al. [25] conducted pyrolysis of polymers at temperatures of 360, 380, 400, and 420 °C. They also developed a four-lump kinetic model to describe the production distribution of the light fractions, middle distillates, and heavy fractions. Their results showed that the model reasonably fitted the experimental data in each reaction of operation conditions. Jiang et al [26] defined products of polyolefin pyrolysis lumping into wax, oil, and gas. Kinetic parameters obtained by their model were validated by using isothermal and non-isothermal experimental data. They concluded that calculated data are only in agreement with the isothermal experimental data. Koo et al. compared five different lumped models with first-order irreversible reactions to evaluate plastic pyrolysis. In all of the models, the pyrolytic products were lumped into char, tar, and gas. According to Koo et al. [22], models with secondary pyrolysis resulted in more accurate predictions.

Despite the research on plastic pyrolysis reaction schemes and kinetic modeling, there is currently no widely accepted model capable of accurately predicting the pyrolysis rate and resultant products of various materials under a broad range of experimental conditions [27]. In addition, there are no studies that considered secondary char reactions in the plastic pyrolysis reaction pathway. In prior work, it was demonstrated that by expanding the reaction scheme of the conventional lumped kinetic model with only a few specific terms a new expanded model can predict biomass pyrolysis yields not just for a limited temperature range and a given type of biomass, but the new model can predict biomass pyrolysis yields across various different biomass feedstock and broader temperature ranges [28]. This work investigates whether the previously proposed reaction schemes for pyrolysis of biomass [28] can also accurately predict the product yields of plastic pyrolysis. The same methodology will be followed as in the prior work on biomass [28]. Namely three lumped models with different primary and secondary reactions will be fitted to experimental data including variations in pyrolysis temperatures (300, 400, 450°C) [29]. The experimental study by Nunes et al. [29], is the only study that has delved into investigating the pyrolysis of the same feedstock under non-isothermal conditions, while maintaining consistent experimental parameters across all trials and providing comprehensive data on pyrolytic yields and temperature profiles. Based on experimental data the authors will estimate the Arrhenius parameters (frequency factor, activation energy) for the reactions by numerical modeling. The ability of the parallel competitive reaction model predominantly used in the literature [30–33] along with two lumped-kinetic models previously proposed by authors [28] will be compared to see which, if any of the selectively added reactions, is necessary or non-negligible when modelling plastic pyrolysis.

2   Materials and methods

Slow pyrolysis of plastic was conducted in a hot-rod (fixed-bed) reactor operating at different temperatures up to 450 °C. The heating rate was set at 1 ($^{\circ}$C s^{-1}), and the corresponding holding time was 900. Throughout the experiments, the pyrolysis was conducted under helium atmosphere. The detailed experimental methods and data on plastic pyrolysis experiments were conducted by Nunes et al. and is published elsewhere [29]. The type of plastic was not reported in Nunes et al. [29], but the ultimate analysis provided is consistent with polymethyl methacrylate (PMMA). The oxygen level is 34.7 wt% and C/H mass ratio is 7.4.

Data from this experimental study will be compared with the predictions of the three reaction kinetic models tested in this study. This study used competing and parallel reaction models (Fig. 1). The first model to be tested (denoted here as Model I) is an existing model developed and modified by many authors [30–32]. This first model can be considered a state-of-the-art baseline and has been use as such by the current authors in a previous study in search of a more universal model for biomass pyrolysis [28]. Model I (in black color in Fig. 2) simulates that solid converts into gases, tar, and char; subsequently the tar can further decompose into char and gases. Model II is a simple expansion of Model I with the addition of the possibility that primary tar can also convert to an inert secondary tar (the added reaction is illustrated in red). Model III is a further expansion of Model II that includes the addition of the possible formation of an inert secondary char and additional gas from primary char (the added reactions are illustrated in blue). The primary kinetic parameters and other constants used in models I, II, and III are listed in Table 1. The subscripts 1, 2, 3, 4, 5, 6, 7, and 8 are the kinetic parameters of the reactions: solid to gas, solid to tar, solid to char, tar to gas, tar to char, tar to tar, chart to char, and char to gas respectively. The typical or reported values for these kinetic parameters (A_i E_i) for Model I listed in Table 1 were obtained from the kinetic modeling of plastic pyrolysis conducted by Till et al. [18]. To obtain typical values for the kinetic parameters for the secondary char reactions in Model III it was assumed that the reactions have the same kinetic parameters as secondary tar reactions to char and gas. [18,34].
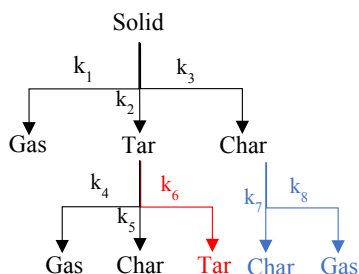

Figure 2: Thermal decomposition of solid with three different reaction schemes used in this study to predict pyrolytic products. Model I in black color, model II in black and red colors, and model III in black, red, and blue colors.

Table 1: Primary kinetic data, as well as, minimum and maximum values of the Arrhenius parameters of plastic pyrolysis studies in the literature that are used in this modeling study.

Parameters	Values	Min	Max
A_1 (s^{-1})	9.94×10^2	3.60×10^1	2.23×10^9
A_2 (s^{-1})	1.23×10^{16}	1.99×10^4	7.62×10^{19}
A_3 (s^{-1})	1.07×10^{13}	1.18×10^1	1.07×10^{13}
A_4 (s^{-1})	1.18	1.18	1.18×10^1
A_5 (s^{-1})	1.37×10^{-3}	1.37×10^{-3}	6.95
A_6 (s^{-1})	1.24×10^{-1}	1.24×10^{-1}	7.20
A_7 (s^{-1})	1.37×10^{-3}	-	-
A_8 (s^{-1})	1.18	-	-
E_1 (kJ.mol^{-1})	86	45	187
E_2 (kJ.mol^{-1})	268	71	319
E_3 (kJ.mol^{-1})	233	16	233
E_4 (kJ.mol^{-1})	386	9	386
E_5 (kJ.mol^{-1})	216	48	394
E_6 (kJ.mol^{-1})	230	32	230
E_7 (kJ.mol^{-1})	216	-	-
E_8 (kJ.mol^{-1})	386	-	-

The rate of reaction of the solid phase under non-isothermal conditions is presented using Eq. 1 [35]:

$$\frac{d\alpha}{dT} = \frac{A_i}{\beta}\exp\left(\frac{-E_i}{RT}\right)f(\alpha) \qquad (1)$$

where dα/dt is the non-isothermal reaction rate, β = dT/dt is the linear heating rate (ºC.s^{-1}), A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ.mol^{-1}), R is the universal gas constant (kJ.K^{-1}.mol^{-1}), and T is the absolute temperature (K), f(α) is the conversion function. In the kinetic models, the rate expression based on the first-order decomposition of the reactive solid is defined in terms of fractional conversion.

The objective is to minimize the difference between experimental data (final yields of gas, tar, and char at the final temperature) and model calculated yields (at the final temperature), by nonlinear least squares method to estimate Arrhenius parameters (Ai, Ei) [36]. A well-proven strategy to avoid mathematical artifacts, and ensure physically relevance of fitted kinetic parameters, is to identify a physically plausible range (expected lower and upper bounds) based on experiments or a survey of experimental work [28]. The authors reviewed the studies that conducted lumped kinetic modelling on plastic pyrolysis and gathered the kinetic parameters in Table 1 [18,21,26,37]. The table presents the minimum and maximum activation energies (kJ·mol^{-1}), and pre-exponential factors (s^{-1}) for all of the reactions in plastic pyrolysis. The variance in the reported values can be attributed to the diverse utilization of models, feedstock, operational conditions, and heating profiles by different researchers. The kinetic parameters optimized using the non-linear generalized reduced gradient method, subject to the constraints obtained from the range between the minimum and maximum presented in Table 1. The motivation for using these constraints was to ensure that all the parameters remained within the physically realistic range based on the existing literature.

3   Results and discussion

Arrhenius kinetic parameters

In this context, the predictive capabilities of Model I (the existing baseline model [30–32]) will be compared with two potential extensions of Model I, as previously investigated by the authors in their pursuit of a more universally predictive model for biomass pyrolysis [28].

Unfortunately, plastic pyrolysis data that include trials with widely varying temperature profiles are much rarer than what is available with biomass [28]. Ideally data should also be available for different polymers, analogous to the wide range of biomass types for which pyrolysis data is available. Upon a review of the literature available on plastic pyrolysis, it became evident that the experimental conditions employed in these studies varied significantly, rendering the utilization of their reported data a challenging endeavor. Specifically, some studies conducted isothermal pyrolysis experiments, while others implemented non-isothermal conditions, albeit with varying heating rates. Additionally, disparities were observed in reactor lengths and associated temperature profiles. Furthermore, some studies solely reported mass loss without reporting the other pyrolytic yields. Discrepancies in the categorization of pyrolytic yields, as compared to our study, further complicated data synthesis. Moreover, some studies exhibited insufficient information regarding the temperature profiles during the pyrolysis process, hindering a comprehensive understanding of their methodologies. Lastly, certain publications presented results exclusively in graphical formats, making data replication virtually impossible due to the absence of numerical values. Based on this review of plastic pyrolysis data, the experiments of Nunes et al. [29] was selected as the best available data on plastic pyrolysis to be used to compare the predictive power of the Models to be tested here across broad temperature ranges.

The objective of all models are merely to accurately predict product yields of the feedstock into the three product categories (char, tar and gas) as a function of the pyrolysis temperature profile. The widely used Arrhenius kinetic equation is used to represent the pyrolysis reaction rates of the models illustrated in Figure 2. The proposed kinetic models optimized 38 kinetic parameters in total for all three models.

Table 2: Kinetic data obtained by models I, II, and III for the plastic pyrolysis experiments.

Parameters	Model-I	Model-II	Model-III
$A_1\,(s^{-1})$	5.86×10^4	4.23×10^5	1.54×10^5
$A_2\,(s^{-1})$	1.99×10^4	1.99×10^4	1.99×10^4
$A_3\,(s^{-1})$	6.51×10^2	2.28×10^1	2.53×10^2
$A_4\,(s^{-1})$	1.18	1.18	1.18
$A_5\,(s^{-1})$	1.37×10^{-3}	1.37×10^{-3}	1.37×10^{-3}
$A_6\,(s^{-1})$	-	1.24×10^{-1}	1.24×10^{-1}
$A_7\,(s^{-1})$	-	-	1.37×10^{-3}
$A_8\,(s^{-1})$	-	-	1.18
$E_1\,(kJ.mol^{-1})$	82	96	92
$E_2\,(kJ.mol^{-1})$	78	82	82
$E_3\,(kJ.mol^{-1})$	56	43	55
$E_4\,(kJ.mol^{-1})$	386	386	386
$E_5\,(kJ.mol^{-1})$	216	216	216
$E_6\,(kJ.mol^{-1})$	-	230	230
$E_7\,(kJ.mol^{-1})$	-	-	386
$E_8\,(kJ.mol^{-1})$	-	-	244

Values for the Arrhenius parameters were obtained by fitting the measured conversion data by using a nonlinear least-squares regression. The kinetic parameters from the literature were employed as the initial guess value [18,21,26,37]. The initial values for the fitting were the kinetic parameters determined for the case of a first-order reaction. The best values of the estimated kinetic parameters for models I, II, and III based on the experimental data is shown in Table 2. The estimated kinetic parameters are within the predetermined physically realistic range based on the existing literature (Table 1).

The authors previously evaluated the performance of these three models on eucalyptus wood pyrolysis conducted by Nunes et al. [29]. For the eucalyptus wood pyrolysis, activation energies ranged from 88–158, 88–140, and 88–232 (kJ.mol^{-1}) for models I, II, and III, respectively. While in this study on PMMA like plastic with the same pyrolysis setup and operational conditions, the activation energies ranged from 56–386, 43–386, and 55–386 (kJ.mol^{-1}) for models I, II, and III, respectively. This suggests that polymers could have a wider range of temperature sensitivity compared to biomass that can be both higher or lower. The frequency factors obtained for plastic pyrolysis were also lower compared to eucalyptus wood pyrolysis. This indicates that plastic (specifically PMMA in this study) pyrolysis reactions are slower compared to eucalyptus wood pyrolysis at a given temperature.

3.1 Pyrolytic product yields

The applicability of three kinetic models for plastic pyrolysis was evaluated by using plastic pyrolysis experimental data from the study conducted by Nunes et al. [29]. The simulated concentration distributions of products, namely gas, tar, and char, during plastic pyrolysis under non-isothermal conditions are shown in Figure 3. In an ideal scenario, the reaction rates would be measured instantaneously during pyrolysis experiments and could be directly compared with the model's rates. However, the experimental design

employed in the models only permitted the collection of final yield measurements at the conclusion of each batch. Consequently, the reported measurements represent the yields achieved at the final temperature when the process concludes. Particularly when integrating tar or immediate solids and their subsequent reactions, the pertinent kinetic properties of tar were sourced from the literature, as they are challenging to measure at the current experimental level. Consequently, the validation of these intricate models necessarily relies on the limited available experimental data [11]. Hence, an approach of calibrating the models with the final experimental yields at three final temperatures: 300°C, 400°C, and 450°C was adopted. The models computed the yields for each of the reactions and subsequently reported the combined results for Gases, Tars, and Chars.

The experimental data shows that the solid yield drops monotonically with maximum process temperature, while the tar and gas yields increase with maximum process temperature for any experiments in the temperature range of 300 to 500 °C [23,38]. The modeling results from all three models confirmed that with an increase of maximum pyrolysis temperature the final product volume of tar will increase at first and then reach an approximate plateau level for processes that peat at around 400 to 500 °C.

Figure 3a shows the results of the model-predicted yields compared to the experimentally measured yields for Model I. The model prediction shown is that with the best-fit parameters in Table 2. The fit of the model to the experimental data was only accurate for trials with a maximum pyrolysis temperature of 300 °C . For pyrolysis runs with maximum temperatures above 300 °C, best fits of Model I achieved less agreement between Model I and experimental data, which could indicate that additional reactions not captured by Model I dominate at temperatures above 300 °C. The results prove that the conventional reaction scheme of Model I is not capable of accurate yield predictions for higher temperature plastic pyrolysis. Apparently additional conversion pathways are activated above 300 °C not captured by Model I.
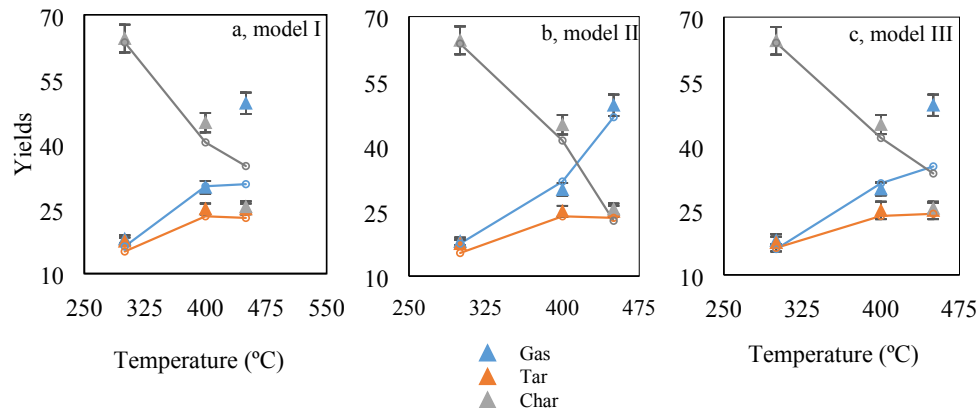

Figure 3: Distribution of the products generated during plastic pyrolysis experiments at different maximum process temperatures and model-predicted yields from models. Figures 3a, 3b, and 3c present data for model I, model II, and model III, respectively.

In Model II of this study, an additional reaction is introduced to enhance Model I. The predicted yields by Model II are depicted in Figure 3b. The model's predictions utilize the best-fit parameters from Table 2 and showcase the results of the proposed model, accounting for secondary (inert) tar formation reactions. This supplementary reaction competes with the primary tar's decomposition into secondary char and secondary gas, favoring the creation of a more stable secondary tar. Consequently, this secondary tar is no longer available for the formation of secondary gas and char. The extra reaction involves converting primary tars into a more stable mixture of tars, including various compounds. This conversion process, facilitated by

high temperatures and catalysts, progressively generates a refined secondary tar while separating it from secondary gas and char formation [39,40]. Model II explicitly incorporates this aspect. By comparing the predicted results with experimental data, it becomes apparent that the inclusion of a secondary tar reaction in the pyrolysis reaction scheme enhances the accuracy of reaction models when compared to Models I and III. Other researchers have suggested that at temperatures exceeding 400°C, secondary pyrolysis occurs concurrently with primary pyrolysis, resulting in the production of secondary gas, tar, and char [41,42]. The modeling work and the results presented in Figure 3 support this hypothesis. The fit of Model II is consistent across all maximum process temperatures tested in this study. The strong agreement with experimental results implies that Model II could provide a solid foundation for a quantitative understanding of plastic pyrolysis. Naturally, this outcome must be validated for various polymer types and reactor configurations to be considered more universally applicable.

Model III builds upon this by introducing the concept that primary char can undergo volatilization, leading to additional gas generation through secondary reactions. This results in a more devolatilized solid carbon residue [43]. Computed gas, tar, and char yields from Model III are displayed in Figure 3c. The model employs the best-fit parameters from Table 2 and exhibits the outcomes of the proposed model, considering the secondary reactions of tar and char. As evident in Figure 3c, the model aligns well with the experimental data for temperatures up to 400°C. The results demonstrate that including secondary char reactions does not enhance the precision of predicting plastic pyrolysis products (at least for the PMMA-like polymer examined here) to the same extent as it did for biomass. The kinetic scheme of Model III most accurately predicts the decomposition of biomass pyrolysis [23,28]. Compared to the biomass pyrolysis modeling previously investigated by the authors [23,28], the behavior of plastic pyrolysis is different. The results here suggest that in plastic pyrolysis there is the presence of secondary tar reactions, whereas primary char once formed subsequently acts as an inert substance. Therefore, the addition of secondary char reactions to char and gas (Model III) did not enhance the reaction scheme or improve the accuracy of yield predictions.

3.2 Validation and sensetivity analysis

The standard deviation between model predictions and experimental data was calculated using Equation (2) [44]. The modeling results showed a small deviation of 0.1 from plastic experimental data for model II.

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{data_{experiment} - data_{model}}{data_{experiment}}\right)^2}{n-1}} \qquad (2)$$

A sensitivity analysis was undertaken to evaluate the significance of incorporating additional reactions into Model II. It is worth considering whether the constraint window, designed to maintain all parameters within physically plausible values and prevent purely mathematical artifacts, may have been either too restrictive or too lenient during the fitting process. To explore the possibility of a narrow window, a sensitivity analysis was performed by expanding the constraint windows for $A_{4,5}$ and $E_{4,5}$ by 20% and subsequently recalibrating the kinetic parameters to the experimental data within these more relaxed constraints. The model was then executed to assess the impact of this relaxation on the optimal-fit kinetic parameters presented in Table 2 for Model II. The consequences of this relaxation on the best-fit kinetic parameters in Table 2 for Model II are shown in Table 3 below. As anticipated, there was an effect, but the absolute deviation was found to be 0%. This deviation is not substantial enough to overturn or invalidate any of the conclusions reached in this study. This study provided valuable insights into a plausible reaction scheme for plastic pyrolysis, primarily relying on the available experimental data. However, to establish its universal applicability, broader validation is essential.

Table 3: Results of the sensitivity analysis (effect of constraint window size on experimentally fitted kinetic parameters)

Parameter	Value with original constraint window	Value with constraint window ± 20%	Percent change*
Model II			
A_4	1.18	1.18	0%
A_5	1.37×10^{-3}	1.37×10^{-3}	0%
E_4	386	386	0%
E_5	216	216	-3.9×10^{-6} %

4 Conclusion

Pyrolysis is a technology that offers a means of harnessing energy from plastics that are traditionally challenging to recycle. The development of dependable models for predicting product yields is imperative, as it underpins the optimization of plastic pyrolysis process parameters, the assessment of its economic viability, and the quantification of its potential environmental advantages. Basing the exploration on the understanding that the pyrolysis process encompasses primary and secondary stages, the goal was to expand the pyrolysis reaction pathway. In prior studies, established models from existing literature, along with various experimental data for wood pyrolysis, were rigorously examined. The results strongly indicated the necessity for an expanded reaction scheme, offering a logical foundation for the previously proposed models (models II and III). To validate these models, earlier experimental data on wood pyrolysis were utilized. Moreover, experimental data from two other studies were incorporated to demonstrate the capability of the proposed model to predict pyrolysis yields across a broader spectrum of experimental conditions and feedstock types.

The aim of the modeling research in this study was to establish a viable reaction pathway for the plastic pyrolysis process within a kinetic model. This model was intended to provide accurate predictions of pyrolysis yields under conditions of non-isothermal heating while fitting the experimental data. The authors employed plastic pyrolysis experimental data obtained from Nunes et al.'s study, which utilized identical experimental conditions and equipment for both plastic and biomass pyrolysis. Previously, the authors had utilized biomass pyrolysis experimental data to develop a model in their earlier study.

Model I exhibited a satisfactory degree of agreement with experimental results, but only for pyrolysis runs conducted at a maximum temperature of 300°C. Model III, on the other hand, offered a good fit for most pyrolysis temperatures, with the exception of the highest temperature of 450°C. Nevertheless, it was Model II that excelled in terms of accuracy and precision when predicting the product outcomes of plastic pyrolysis. Hence, based on the dataset, it is proposed that the secondary tar reaction plays a significant role in plastic pyrolysis, particularly at temperatures exceeding 300°C, while primary char, once formed, behaves as an inert substance up to 450°C. Furthermore, the incorporation of secondary char reactions into both char and gas, as observed in Model III, did not yield an improvement in yield predictions within this reaction scheme.

Given the limited availability of experimental data, particularly concerning plastic pyrolysis investigations, it is noteworthy that the author identified only a single paper that presented comprehensive experimental results on plastic pyrolysis. This paper furnished an in-depth explanation of the experimental conditions, temperature profiles, and pyrolysis outcomes across various temperature ranges. This highlights the potential for future research endeavors within the field of plastic pyrolysis to conduct comprehensive

experimental studies covering a wide spectrum of plastic types, operating temperatures, and process conditions.

Author Contributions

Aysan Safavi.: Conceptualization, formal analysis, validation, investigation, methodology, writing—original draft. Christiaan Richter: supervision, writing—review and editing. Runar Unnthorsson: funding acquisition, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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Book Chapter

Dioxin and Furan Emissions from Gasification

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Abstract

PCDD/Fs are a 75-member family of toxic chemicals that include congeners (members) that have serious health effects including congeners that are classified group 1 carcinogens, endocrine disruptors and weakening or damage to the immune system. Municipal solid waste (MSW) incinerations had historically been implicated as the major source of PCDD/Fs distributed by air. As a result of awareness and legislation most European MSW incinerators were either shut down or equipped with modern air pollution control systems necessary to achieve MSW incineration with PCDD/F emissions within regulatory limits set by national and international laws (typically <0.1 ng TEQ/Nm^3). There is a common belief that gasification of waste and/or biomass, unlike incineration, inherently and always achieve emission below regulatory and detectable limits. However, a review of the literature suggests that the belief that the substitution of incineration with gasification would always, or necessarily, reduce PCDD/Fs emissions to acceptable levels is overly simplistic. This chapter discusses the mechanisms of PCDD/Fs formation, the operational measures and parameter ranges that can be controlled during gasification to minimize PCDD/Fs formation, and methods for post-formation PCDD/F removal are reviewed. The purpose of this chapter is to assist researchers and practitioners in formulating waste management policies and strategies, and in conducting relevant research and environmental impact studies.

Keywords: gasification, dioxins, furans, dioxin formation mechanism, PCDD/F removal technologies

1. Introduction

Due to industrialization and improved living standards, global energy consumption is on the rise. Simultaneous population growth and per capita energy demand led to increased fossil fuel production and consumption accounting for about 80% of world energy consumption, while nuclear, biomass, and hydroelectric energy accounting for the remaining 20%. This trend of fossil fuel use as the largest portion of the growing global energy mix results in a steady increase in CO_2, NO_2 and SO_2 emissions, leading to environmental threats. Therefore, seeking sustainable solutions is urgent. Biomass is defined as biological and carbon-containing material derived from living or recently living organisms. Biomass is one of the biggest sources of energy and is a renewable, possibly efficient, and an attractive alternative to fossil fuels. Biomass when compared to fossil fuels contains much less

carbon, more oxygen, and less heat in the range of 12–16 MJ/kg [1]. Its average net greenhouse gas emissions are lower than fossil fuels, an environmental advantage that may be a key driver for biomass and waste energy extraction. Biomass is the predominant source of energy in many developing countries, but in some industrialized ones it also plays an important role. Biomass-based options for energy production are widely researched and developed to replace fossil fuels in heat and electricity production, chemicals formation, agriculture, moving towards sustainability, regional economic and social development in order to alleviate the emission of greenhouse gas [2].

1.1 General overview: thermochemical biomass conversion methods

Through biochemical, chemical, and thermochemical conversion techniques, the chemical energy that is contained in biomass is converted to heat, electricity or fuel. Biochemical and chemical methods can only convert selected biomass to biogas, biodiesel, etc., while most biomass materials can be thermochemically converted. Thermochemical biomass conversion is one of the most energy-efficient, flexible, and high-energy yield methods for extraction of energy from biomass and organic waste, and therefore one of the most promising pathways with many environmental benefits. This thermal treatment can be divided into different processes depending on the supply of oxygen: (1) combustion; direct biomass burning using excess oxygen, (2) gasification; biomass burning with a limited oxygen supply, and (3) pyrolysis; biomass burning without oxygen [3], where gasification is the most efficient energy extraction process [4, 5].

Given its economic and environmental benefits, gasification has attracted worldwide attention. Many agricultural and industrial waste streams that are currently problematic can be used sustainably through gasification. Industrial waste (e.g., from the food and pulp and wood industries), municipal waste (e.g., household waste), or agricultural waste (e.g., gardening and animal manure) [6] and energy products can be all converted into a mixture of non-combustible gas in a gasifier (producer gas) via gasification. Gasification is the conversion of solid carbon to a gas under a limited oxygen supply at high temperatures (400–1000°C [7]). Producer gas is a mixture of CO, H_2, CH_4, slight amounts of other light hydrocarbons, steam, CO_2, N_2, in addition to impurities like char, ash, tar, and oil particles. The producer gas can simply be stored and combusted at a later time to produce heat and/or steam. The producer gas can also produce electricity when used in gas turbines or to power and engine-generator combo. Syngas is the purified producer gas that can be used as fuel or as feedstock to produce higher value fuel or chemicals [8].

Although the main feedstock for gasification can be any hydrocarbons; the acceptable range of feedstock properties is practically very narrow for most existing real world gasifiers. This is a major disadvantage compared to incineration. The reaction chemistry and fluid-dynamics within gasifiers tend to be highly sensitive to changes in the composition of raw materials, their reactivity, density, particle size, moisture, and ash content. The beneficial output in combustion plants is power and possibly heat, while the output in gasification can also be chemicals, liquid fuels or hydrogen in addition to power and heat. Due to the presence of acid gases, tar particles, and other impurities that exist in the gas produced by the gasifier, the producer gas should be treated properly for optimal production of chemicals, liquid or hydrogen fuels and internally-fired cycles (internal combustion engines, gas turbines) [8].

Biomass conversion efficiency varies based on the gasifier itself, purpose of use, type of treated material, its particle shape and size, and the gas flow. The process

of gasification which occurs in gasifiers can be divided into five groups: (1) the calorific heat of the producer gas is high when it is between 10 to 40 MJ/Nm^3; it is medium if it is between 5 to 10 MJ/Nm^3; and it is low when below 5 MJ/Nm^3; (2) nature of gasification agents (air, O2, steam, H$_2$); (3) the direction in which consuming material and gasifying agents move (updraft, downdraft; cross draft or fluidized bed); (4) operating pressure (atmospheric or high pressures of up to 6 MPa); (5) type of feedstock (municipal solid waste (MSW), industrial waste, biomass/wood). There are only a few processes that do not fall into these categories, namely molten iron bath gasification, in situ gasification (underground gasification), plasma gasification or hydrogasification and rotary kiln gasification [8, 9].

1.2 Gasification vs. combustion

Combustion has been a viable method for waste management with drawbacks such as harmful process residues and hazardous emissions. Gasification has come up to tackle these issues and improve energy efficiency. Gasification reduces corrosion and emission by preserving alkali and heavy metals (excluding Hg and Cd), sulfur and chlorine in the process residues, greatly inhibiting dibenzo-p-dioxins (PCDDs) and chlorinated dibenzofluorans (PCDFs) formation and decrease the formation of thermal nitrogen oxides (NO$_x$) owing to lower temperatures and reducing conditions [10]. Slag gasification can destruct dangerous compounds, however, S and Cl species such as H$_2$S and HCl might remain present in the producer gas. When producer gas volume is small, lower dimensioned gas cleanups is needed. This can save the cost of investment while using O2 raises both the costs and the producer gas calorific value. Producer gas can be used in different applications energetically or as raw material which has a higher efficiency [9, 11]. Some of the potential benefits of gasification versus combustion and their corresponding potential drawbacks are summarized in **Figure 1**, using reference [12] with the permission of Elsevier.

PCDD/Fs are a group of unwanted by-products and pollutants coming from thermal and combustion processes. The toxicological and chemical properties of compounds of this sort depend on the number and position of the chlorine atoms that are bound to the two aromatic rings [13]. PCDDs and PCDFs are composed of 75 and 135 homologs, respectively. Specific isomers of PCDD/F have been recognized for their toxicological properties that have serious carcinogens [14]. They are highly toxic and cause severe bronchitis, asthma, and strangulation of the lungs in

Potential advantages of gasification vs. combustion	Related issues that hinder the benefits of gasification
• the combustible gas generated by gasification is easier to handle, meter and control than waste • the homogenous, gas-phase combustion of syngas can be carried out under conditions more favorable than those achievable with waste	• since syngas is highly toxic and explosive, its presence raises major security concerns and requires sophisticated control equipment • since feedstock is oxidized/converted in two steps (gasification + syngas combustion/conversion) plants tend to be more complex and costly, more difficult to operate and maintain, less reliable
The reducing conditions in the gasifier: • improve the quality of solid residues, particularly metals • reduce the generation of some pollutants (dioxins, furans and NO$_X$)	The actual production of pollutants depends on how syngas is processed downstream of the gasifier; if syngas is eventually oxidized, dioxins, furans and NO$_X$ may still be an issue • Required syngas treatment is costly and causes significant energy consumption/losses
Syngas can be used, after proper treatment, in highly efficient internally-fired cycles	• Due to the consumption/losses of gasification and syngas clean-up, overall energy conversion efficiency is typically lower than that of combustion plants • At the small scale typical of waste treatment plants, efficiency of internally-fired systems are low (especially if gas turbine- based) • Required syngas treatment very demanding and costly
Syngas can be used, after proper treatment, to generate high-quality fuels (diesel fuel, gasoline or hydrogen) or chemicals	• At the small scale typical of waste treatment plants, synthesizing quality fuels or chemicals can entail prohibitive costs
Gasification at high pressure enhances the opportunities to increase energy conversion efficiency and reduce costs gasification	Pressurized waste gasification poses formidable challenges and has not been attempted by any technology developer

Figure 1.
Comparison of waste gasification and combustion.

01 humans. Agricultural lands and livestock in the vicinity of incinerators can also be
02 affected by dioxin that infects meat, dairy products, and so on. Consuming these
03 products may destroy the human immune system, thyroid function, hormone
04 dysfunction, and causes cancer. It has negative health condition in infants because
05 of dioxin exposure through breast milk and uterine exposure. Scientists have
06 conducted numerous experimental studies on experimental animals (rats and
07 mice) to investigate the effects of dioxin contamination that lead to carcinogenic-
08 ity, liver toxicity, and immune toxicity. 2,3,7,8,8-tetrachlorodibenzo-p-dioxin
09 (TCDD), considered to be very toxic and assigned a toxic equivalence factor (TEF)
10 value of 1 [10, 15, 16], and commonly used as a test substance in toxicity tests. In
11 immunotoxicity experiments, 2,3,7,8-TCDD caused thyroid atrophy, cellular and
12 humoral immune abnormalities, constrained host resistance to viral infections, and
13 inhibited antibody formation [17].
14 In 1977, the release of PCDD/F from incineration processes was first observed.
15 Since then, researchers have evaluated emission of this compound by a series of
16 thermal processes that include integrated combustion and gasification [16]. The
17 main reason for the negative environmental reputation of waste incineration is the
18 emission of PCDD/F and other pollutants during the process [18], especially for
19 MSW incineration [19–21]. After PCDD/F enters the atmosphere, they are exposed
20 to chemical, physical, and biological changes and eventually contaminate soil, body
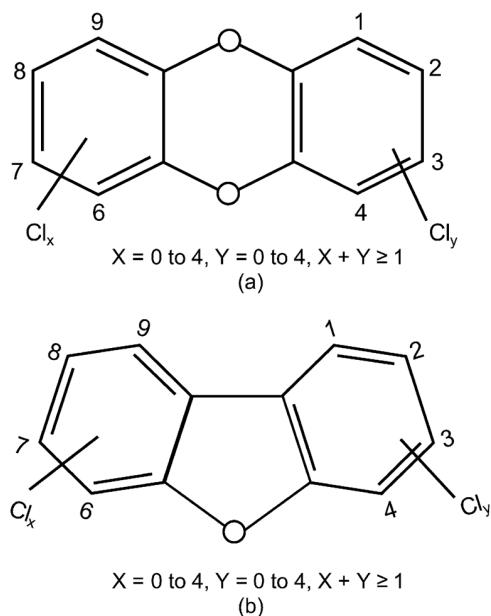21 and sediment [22].
22 The purpose of this chapter is to shed more light on PCDD/F formation and
23 their sources in combustion. The main objective is to review the PCDD/F forma-
24 tion in gasification as there is no review on formation and emission of dioxins from
25 processes based on gasification know-hows. This chapter highlights the likelihood
26 of reducing the emission of PCDD/Fs to well below regulatory limits or even detec-
27 tion limits, by using gasification technology. We have done a thorough study of all
28 the accessible articles came into existence over the last 30 years in literature to be
29 able to frame this review which is really felt missing in the field.

2. Dioxin formation

31 In the 1950s and 1960s, incinerating organic waste from chemical plants and
32 releasing greenhouse gases into the atmosphere became common practice. Its exten-
33 sion to incineration of solid waste, especially MSW, increased during the 1960s and
34 1970s and enabled these processes to recover the energy generated by waste inciner-
35 ation, reduce the waste by 80–90% of volume, and consequently decrease the areas
36 required for landfilling. Nonetheless, the release of very toxic organic compounds
37 from waste incineration, recognized as dioxins, was not known back then [23].
38 Actually, the toxic effects of PCDD/F were not materialized until around the end of
39 1980s. Due to maximum enforcement of available control technology regulations,
40 the release of "toxic equivalent" dioxin (TEQ) from US power plants was lessened by
41 three orders of magnitude to less than 12 g of TEQ per year by 1987 [24]. It has been
42 widely acknowledged that combustion processes lead to the formation or emission
43 of by-products such as NO_x, SO_x, HCl, TOC, CO, HF, and CO_2 into the atmosphere.
44 Moreover, small quantities of toxic substances such as metals and PCDD/F are
45 released into the atmosphere [23]. **Figure 2** shows the structure of PCDD/Fs [25].

2.1 Dioxin formation during combustion

47 The formation and emission of dioxin - group of chlorinated poly-nuclear
48 aromatic compounds - from waste combustion is of prodigious public concern.

X = 0 to 4, Y = 0 to 4, X + Y ≥ 1
(a)

X = 0 to 4, Y = 0 to 4, X + Y ≥ 1
(b)

01 **Figure 2.**
Molecular structure of polychlorinated dibenzo- p-dioxins (a) and dibenzofurans (b). Reprinted from [25]
with the permission of Elsevier.

02 Dioxin is released in small quantities from combustion sources mainly in the
03 process of municipal waste incineration, which is one of the most important sources
04 of PCDD/Fs formation in the environment. Therefore, dioxin control measurement
05 from combustion sources has become vital and the mechanisms of dioxin formation
06 have been comprehensively investigated because of its carcinogenic and mutagenic
07 effects.

08 *2.1.1 Mechanism of PCDD/F formation*

09 PCDD/Fs can be formed when reaction of hydrocarbons and chlorine takes
10 place in vicinity of O2 and metals like Cu at high temperatures of 200 to 800°C.
11 There are many theories regarding the mechanism of dioxin formation. PCDD/F
12 formation proceed via: (1) homogeneous (gas phase) reactions at high tempera-
13 tures (500 to 800°C), and the main mechanism of the reaction process is via
14 chlorination precursors like chlorophenol (CP) and chlorobenzene (CB) in the gas
15 phase. This high-temperature homogeneous path is known as "precursor route" in
16 which a smaller subset of PCDD/Fs is formed in the gas phase. (2) heterogeneous
17 (surface-catalyzed) reactions at lower temperatures (200 to 400°C) in the post-
18 combustion zone [21, 26]. This low temperature heterogeneous path is called the
19 "de novo route" (for the PCDD/Fs subset of carbon, oxygen, hydrogen and chlorine
20 in the cooling flue gas). In the heterogeneous mechanism, the formed PCDD/Fs
21 may also come from CPs or CBs or from carbon in fly ash. The catalytic effect of fly
22 ash or soot is the main factor in the latter case, and this is a well-known example
23 of a de novo process. It is said that the two pathways of dioxin formation occur
24 simultaneously and independently. It is still debated whether the carbon in the
25 heterogeneous PCDD/F mainly comes from gas precursors or from carbon in fly
26 ash [25, 27]. Dickson et al. [28] disclosed that under similar conditions, the rate of
27 PCDD/Fs precursor formation is 72–99000 times higher than the rate of carbon
28 formation in fly ash. Luijk et al. [29] thought that the formation of PCDD/Fs from

01 precursors was about 3,000 times faster than the de novo process of activated
02 carbon. The precursors were found to be the major source of PCDD/Fs formation
03 by Tuppurainen et al. [30]. **Figure 3** is a stylized illustration of the mechanisms
04 by which PCDD/F is formed in combustion systems. The surface shows a particle
05 of ash, and the arrows depict both the reaction and absorption processes. Thick
06 arrows indicate the relative importance of pathways in the formation of PCDD/F.
07   The emission of PCDD/Fs is directly related to the amount of carbon used.
08 Along with CP, CBs, polycyclic aromatic hydrocarbons (PAHs), and residual car-
09 bon, there are also key elements that influence the formation of PCDD/Fs including
10 residence time, precursors, combustion temperature, PCDD and chlorine in the
11 feed, feed processing, supplemental fuel and oxygen availability [31, 32].
12   Dioxin formation happens in a temperature range of 200 to 800°C with a
13 maximum reaction rate reached between 350 to 400°C [33]. Data from the litera-
14 ture show that the rate is very slow in the range of 200 to 250°C. Under optimum
15 combustion conditions (such as adequate oxygen, mixing, and airflow), virtually
16 all organic compounds including PCDD/F are destroyed above 800°C. However,
17 PCDD/F is formable at high temperatures, but under less optimum conditions like
18 insufficient oxygen [34]. Dioxin formation correlates well with access to organic
19 precursors, CO, unburned carbon or combustion products (even soot particles),
20 metal salts and hydrogen chloride/chlorine. Dioxins are formed during the cooling
21 cycles of the flue gas in combustion systems. This formation process goes via one of
22 the two mechanisms mentioned above [21, 35]. The main mechanism of dioxin for-
23 mation in combustion systems appears to be de novo synthesis where morphology
24 of the carbon from deteriorated graphical configuration is critical for dioxin forma-
25 tion. Therefore, such carbon morphologies have been investigated. It was found
26 that the soot particles from gas phase combustion reactions including deteriorated
27 graphical configurations are a potential source of de novo dioxins synthesis.
28   The formation of PCDD/F in combustion processes can be described in a two-
29 step route: (1) formation of carbon: carbon particles comprised of deteriorated
30 graphical configurations in the combustion region. (2) oxidation of carbon: the

31 **Figure 3.**
The pathway for formation of PCDD/F is illustrated in this diagram. Reprinted from [25] with the permission of Elsevier.

6

01 carbon particles that have not been properly burnt can still be oxidized in low
02 temperatures after combustion. PCDD/Fs are by-products of oxidative degrada-
03 tion of the graphical structure of carbon particles. There are several steps and
04 chemical reactions involved in these routes. Here are at least three known steps for
05 carbon formation: nucleation, agglomeration and particle growth. Here are four
06 steps involved in carbon oxidation: oxidant adsorption, complex intermediate
07 formation with metal ion catalysts, interaction with graphitic carbon structure,
08 and product desorption. The nature of these chemical reactions is complex and
09 heterogeneous [21].

10   Since the reactants for the formation of PCDD/Fs are inadequate during
11 combustion, the combustion conditions are likely to have a major influence on the
12 formation of PCDD/F. There are some conditions in the combustion process that
13 can cause a favorable formation of PCDD/F. These conditions are: low combus-
14 tion temperature, poor turbulence in the combustion chamber, short residence
15 time in the combustion zone, low O2 content resulting in deficient combustion,
16 sluggish flue gas cooling process in the critical temperature range [23]. Moreover,
17 existence of metals (Cu, Fe, Pb and Zn) [35] in fly ash catalytically increase
18 formation of PCDD/F. Also in presence of these metals, PCDD/F can react with
19 chloride and unburned carbon and contribute to the so-called de novo synthesis
20 of PCDD/F [35–37].

21   Chlorine content in raw materials is one reason for PCDD/Fs formation during
22 combustion [21, 38]. When combusting wood, for example, presence of phenol,
23 lignin or carbon and chlorine particles can contribute to emission of PCDD/Fs
24 [39]. Since the concentration of chlorine in uncoated natural wood is low [40],
25 the combustion of this feedstock yields a much lower emission rate of PCDD/Fs
26 compared to when combusting straw, coal, and sewage sludge [41]. Contrarily,
27 during combustion of wood, PCDD/Fs compounds can remain on the surface and
28 thus be removed by fly ash particles. Thus, primary and secondary emission control
29 measurements are vital to effectively mitigate this part of the PCDD/FS emission in
30 the flue gas. Some example of these control measurements are: usage of high quality
31 wood fuel, optimizing combustion conditions, and try to precipitate the fly ash at
32 low temperatures (less than 200°C) [42].

33   There is a review on dioxin emission from wood combustion by Lavric et al.
34 [19] emphasizing on the fact that the combustion conditions and fuel properties
35 are the most dominant considerations on the dioxin release rate. They concluded
36 that using flue gas cleaning systems when combusting non-contaminated natural
37 wood, lowers the level of dioxin emission below the legitimate levels. The minimum
38 concentration of dioxin in greenhouse gas emissions prescribed by most current
39 European legislation is 0.1 ng m^3 expressed in I-TEQ units [43].

40 **2.2 Dioxin formation in gasification**

41   The formation of harmful chemicals, especially PCDD/Fs, is the most serious
42 problem. It is important to reduce the formation of polychlorinated compounds and
43 increase their capture due to their environmental emissions. Although there is an
44 increasing trend of well-designed gasifiers with a broad range of raw materials that
45 are essentially used in gasifiers, not all materials should necessarily be gasified in
46 a given setup. Processed plastic, rubber, and tanned leather [44] as well as vari-
47 ous animal biomasses (such as food waste) and sewage sludge [45] contain large
48 amounts of chlorine.

49   Solid waste segment is commonly treated at incinerators. Energy generation
50 via waste incineration has become an effective way of managing combustible
51 waste, because it reduces the volume and mass of waste. Nevertheless, perilous

emissions and detrimental process residues are among the drawbacks of incinera-
tion. Incineration causes fly and bottom ashes, and thus release leachable toxic
heavy metals, PCDD/Fs, and volatile organic compounds. Therefore, it is possible
to replace incinerators with gasifiers. Incinerators emit PCDD/Fs and their con-
centration often exceeds the legal limit, which calls for a different technology for
waste treatment. Gasification processes usually emit PCDD/Fs within acceptable
limits as determined by national and international organizations [35]. The amount
of pollutants in producer gas can be lower than that of the flue gas of an incinera-
tor [46], and it is because of partial oxidation of waste with limited oxygen supply
[47]. Gasification benefits from numerous advantages in comparison of traditional
waste combustion. It occurs in a low oxygen environment (where the equivalence
ratio varies between 0.25 to 0.50) which limits the formation of PCDD/Fs and large
amounts of SO_x and NO_x [48]. Gasification reduces the emission of acidic gases due
to higher temperatures and reduction conditions [49]. However, small amounts of
PCDD/Fs can result from deficient destruction of the PCDD/Fs present in the waste
itself or from the existence of organic chlorinated compounds in the reactor [50, 51].

It is evident that the mechanisms of dioxin formation and its related amounts to
producer gas correlate well with tar formation, and is therefore a relatively compa-
rable parameter for all gasifiers in which tar is partly converted to producer gas [52].
Zwart et al. scrutinized the formation of dioxin from refuse derived fuel (RDF),
sewage sludge, and untreated wood pellets gasification in an extensive range of
temperatures. The outcome revealed that the level of dioxins was very different in
terms of gasification temperature and feedstock quality (chlorine content). Their
conclusion was that high amounts of chlorine in the feedstock cause dioxin forma-
tion, especially at temperatures below 800°C. At temperatures above 800°C, dioxins
levels are drastically reduced, along with corresponding tar levels. At temperatures
above 850°C, the PCDD/Fs concentration in the producer gas was within the range
of 0.5 ng TEQ/Nm^3 for clean wood pellets and sewage sludge. However, PCDD/Fs
concentrations became lower in higher temperatures for RDF, it was still above the
allowed limit [52].

3. PCDD/Fs removal

Assessing the environmental impacts of gasification know-how is vital to ensure
the practicality of the process. An occasional misconception that gasification plants
are only minor variations of incinerators is the cause of gasification processes to
still face environmental community resistance. One important distinction is that
gasification can be an intermediary process for the production of producer gas in a
broad range of applications. Utilizing syngas to generate on-site electrical and ther-
mal energy is the most dominant process in gasification, however, the production of
chemicals and fuel may be the ideal goal for the near future. Gasification contrib-
utes to air pollution control and make it less complex and costly compared to that
needed for incineration. Although cleaning exhaust gases from non-combustion
thermochemical conversion processes could be simpler than that of incineration,
proper design and emission control systems are critical to satisfy health and safety
requirements. Products of gasifiers must be controlled before discharging into the
air as they can comprise several air pollutants. These include particles, hydrocar-
bons, CO, tars, N_2, SO_x, and small amounts of PCDD/Fs.

Lonati et al. [53] evaluated the risk of human carcinogenicity owing to the
release of PCDD/Fs and Cd from a waste gasification plant using a probabilistic
method. Probability density functions were used to define emission rates and risk
model parameters of pollutants via Monte Carlo simulations. This gave a probability

distribution estimation with involvement of epistemic uncertainty and aleatory variability. The results showed that Cd emissions are much higher than PCDD/Fs despite their higher toxicity. PCDD/Fs concentrations were well below the current permissible limit of 0.1 ngTEQ m^3. They indicated that 95% of carcinogenic risk is due to Cd exposure.

To control greenhouse gas emissions from gasification processes different strategies can be adapted, depending on plant configuration, the requirements of specific energy conversion equipment or reactors and catalysts for downstream fuel synthesis. In any case, there is the advantage that it can be possible to control the air pollution of the reactor and the exhaust gas output in numerous cases using a combined method [9]. Coal filters were the first dioxin-reducing technologies, which were installed in the backend of an air pollution control system in many wastes to energy plants, in the late 1980s.

Filters also helped to absorb other organic compounds and mercury, but their bulky volume and probability of ignition were their pitfalls. For the sake of safety, inorganic sorbents such as zeolites were used for monitoring and inertisation of CO [54]. It was also found in the 1980s that oxidative catalysts have high degradation potential for dioxins [55]. Those catalysts were initially operational at 300 to 350°C, and then they were further developed to reach higher destruction efficiency of 99% at temperatures of about 230°C [56].

The high operating temperature (> 1000°C) along with oxygen deficiency eliminates any PCDD/Fs that may be present in the raw material and eradicates potential formation of PCDD/Fs. Thus, operating the gasification process at high temperature or maximizing the conversion of hydrocarbons that are being produced in pyrolysis are possible approaches to reduce the formation of dioxins [57]. For example, high-temperature gasification lowers dioxin formation when high-chlorine content fuels are used [57]. Another effective and easily applicable measure is the rapid cooling of the syngas by a water immersion that inhibits the synthesis of PCDD/Fs [58]. The capture of PCDD/Fs by a special multi-step absorption filter is the most effective method of removing dioxins from the residual burst stage and/or the gas or cooling effluent, regardless of technology used. Volatile organic compounds such as PCDD/F and other organics are effectively eliminated in the gaseous and liquid phases due to the high temperature reactor and shock cooling [35, 59].

As an example, Andersson et al. who got inspired by Griffin's theory [60] were successful to lower the concentration of dioxins [61]. They increased the concentration of SO_2 in the flue gas and adjusted the Cl/S ratio in a way that lowered the concentration of dioxin to around 0.1 ng(TE)/m^3 in the raw gas. As another example, Pařízek et al. applied the REMEDIA technology in a MSW incinerator, and they varied the operational temperature from 180–260°C. They saw that the degradation efficiency can be extended to 99–97% while dioxin emission can be lowered below 0.1 ng. (TEQ)/m^3 [62]. REMEDIA technology benefits from catalytic substrates that are overlaid on a two-layer polytetrafluoroethylene (PTFE) membraned material to filter and eliminate PCDD/F.

Off-gas cleaning system is vital for both incineration and gasification processes in thermal waste treatment plants, as it keeps the amount of pollutants being released into the environment lower than that legislated. PCDD/F can be cleaned using $DeNO_x/DeDio_x$ technologies such as sodium bicarbonate or PCDD/F removal using catalytic filtration or adsorption materials such as activated carbon [63].
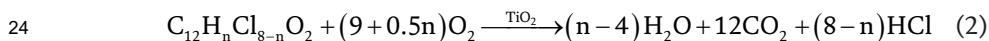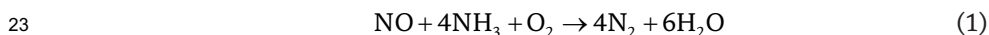
3.1 Catalytic filtration of PCDD/F

On the basis of applied applications it has been found that the method of dioxin removal by catalytic filtration REMEDIA [64] is highly effective. A GORE-TEX is

a special fabric filter bags usually used in catalytic filtration by which particles of
solid fly ash are well separated via instantaneous removal of dioxins in flue gases.
The filtration efficiency of the gas can be elevated to around 96.6% due to a PTFE-
type membrane used in the external filtration layer. This refined gas is then driven
inward the internal filtration layer comprised of catalytically active compounds
that can eliminate dioxins further to reach 98.8% efficiency. The external filtration
layer is periodically revived with the help of a usual pulse jet cleaning system. In
the gasification process, catalytic filtration is usually placed immediately after a
mechanical cleaning of the flue gases [65].

The Japanese government enforced the guideline of dioxin emission via Waste
Management and General Purification Act (WMGPA) in 1997. After this WMGPA
enforcement, the industrial sector was obliged to install catalytic reactors and
bag filters in the new facilities. Following this enforcement, not only the adjusted
values for the combustion temperature, the cooling temperature of the exhaust gas
from the furnace, and the CO concentration in the exhaust gas from the stack were
satisfactory at almost all facilities, but also the concentration of dioxin, acidic gases,
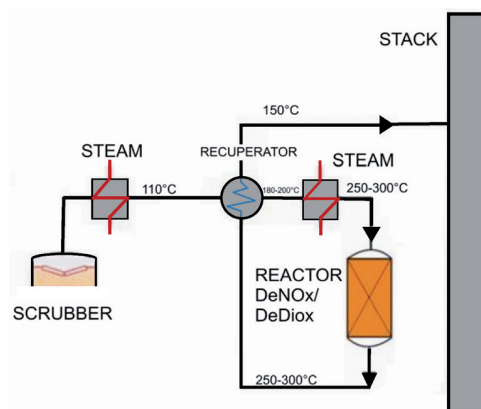and NOx in the discharged gases was significantly lower than those made before
1997 [66].

3.2 Technology $DeNO_x/DeDio_x$

One proficient approach to remove Dioxin is to combine its catalytic degrada-
tion with selective reduction of NO_x according to the following stoichiometric
equations [67]:

$$NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

$$C_{12}H_nCl_{8-n}O_2 + (9 + 0.5n)O_2 \xrightarrow{\text{TiO}_2} (n-4)H_2O + 12CO_2 + (8-n)HCl \tag{2}$$

In order to selectively reduce NO_x, ammonia can be injected prior to the
catalytic reactor. Simultaneous removal of NO_x and dioxins ($DeNO_x/DeDio_x$) can
be carried out in a catalytic reactor at 200 to 300°C [56]. Although the NO_x and
dioxins removal via this method is a highly efficient process, catalyst poisoning
is one of the main detriments. In addition to mechanical and chemical clean-
ing, the reactor in this setup needs to be installed after dust removal from flue
gases (**Figure 4**). This means that re-heating of the flue gases to 200–300°C is
required [68].

Parizek et al. [69] analyzed the economical balance of catalytic filtration versus
DeNOx/DeDiox technology. They used a computer-based system for simulation
calculations making solution more approachable. The annual economic balance of
the operation of the catalytic filtration REMEDIA is composed of: cost of the filtra-
tion bags (for this study the guaranteed lifespan and real lifespan of the filtration
tube was 4 and 8 years, respectively), energy cost of the fan drive, cost required to
spray the flue gases before entering the filter. Also the annual economic balance of
the operation of DeNOx/DeDiox technology is composed of: catalyst costs (a 4-yar
life-time operation was considered), energy costs of the fan drive, and cost for
heating of flue gases. Results showed that the operating cost of the DeNOx/DeDiox
technology rises due to the reheating of flue gases to the required temperature of the
reaction and the cost was linked with the increased pressure drop. Catalytic filtra-
tion does not require heating of flue gases and the cost of the filtration bags falls due
to their real lifespan.

Figure 4.
Scheme of DeNOx/DeDiox technology [69].

4. Experimental evidence of PCDD/Fs in gasification and reliable mitigation

In an upcoming article [70] we will publish and extensive review of experimental measurements and evidence of PCDD/F emissions from gasifiers of various types and sizes, varying operating conditions and feedstocks.

The main findings are:

- Although PCDD/F emissions from gasification are in general lower than those from incinerators without modern emission control of the same feedstock it is not correct to assume that PCDD/F emission from a gasifier will *necessarily* be safe or below regulatory limits. PCCD/F can be produced in gasification above safe and regulatory limits.

- The two main factors that can widely and reliably reduce PCCD/F emissions to very low levels in gasification are

  1. peak operating temperature (> 1000°C) in the combustion and cracking zone together with oxygen deprivation

  2. rapid cooling of syngas by for example a water quench which prevents de novo synthesis

  3. high amounts of chlorine in the feedstock cause dioxin formation, especially at temperatures below 800°C. At temperatures above 800°C, dioxins levels are drastically reduced.

5. Future work or guidelines

The main purpose of this chapter is to assist researchers in making primed decisions when adopting waste management policies and conducting relevant research and environmental impact studies. There is a need to establish more information on PCCD/F formation in gasification by experimentation of different feedstock when using different operational parameters and removal technologies;

in order to be able to choose an appropriate PCCD/F mitigation method when
gasifying different waste streams.

6. Conclusions

Dioxin formation and emission from the incineration of waste have been
reduced in Europe and North America by either decommissioning plants or other-
wise installing of air pollution control systems [71–73]. However, given the severity
of the health impacts and continued unknowns (like emissions during start-up,
shut-down and other peak events) the topic continues to be of great public concern
both in Europe and North America [73–75] and the developing world [73, 76, 77].
Gasification can offer a substitute approach for waste treatment and energy genera-
tion that may indeed more consistently achieve lower toxic PCDD/F emission levels
compared to combustion.

All combustion processes can result in formation of PCDD/F at temperature
range of 200 to 600°C in case organic carbon, oxygen, and chlorine become acces-
sible. The formation of dioxins is effectively reduced due to the high temperature
reactor (in special cases >1000°C) and shock cooling of gases combined, with an
absence of available oxygen.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Nomenclature

PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
PCBs	Polychlorinated biphenyls
TEF	Toxic equivalence factor
TEQ	Toxic equivalent
CPs	Chlorophenols
CBs	Chlorobenzenes
PAHs	Polycyclic aromatic hydrocarbons
SOx	Sulfur oxides
NOx	Nitrogen oxides
DeNOx/DeDiox	Removal of nitrogen oxides and dioxins
RDF	Refuse derived fuel
MSW	Municipal solid waste
WEEE	Waste electrical and electronic equipment
PVC	Polyvinyl chloride
BR	Cogasified biofermenting residue

01	iGCLC	In-situ gasification chemical looping
02	GEK	Gasifier's experimenter's kit
03	LHV	Low heating value (MJ/m^3)
04	HHV	High heating value (MJ/m^3)

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Appendix I

Reactions:

1 Biomass→Gas
2 Biomass→Tar
3 Biomass→Char
4 Tar→Gas
5 Tar→Char
6 Tar→Tar
7 Char→Char
8 Char→Gas

Main equations:

$$\frac{d\alpha}{dt} = k_i(T)f(\alpha)$$

$$k_i(T) = A_i \exp\left(\frac{-E_i}{RT}\right)$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}$$

$$\beta = \frac{dT}{dt}$$

Species rate expressions:

$$\frac{\partial mbiomass}{\partial t} = -mbiomass\,(k1 + k2 + k3)$$

$$\frac{\partial mgas1}{\partial t} = mbiomass\,(k1)$$

$$\frac{\partial mtar1}{\partial t} = k2 \times mbiomass - mtar1\,(k4 + k5 + k6)$$

$$\frac{\partial mchar1}{\partial t} = mbiomass\,(k3) - mchar1(k7 + k8)$$

$$\frac{\partial mgas2}{\partial t} = mtar1\,(k4)$$

$$\frac{\partial mchar2}{\partial t} = mtar1\,(k5)$$

$$\frac{\partial mtar2}{\partial t} = mtar1\,(k6)$$

$$\frac{\partial mchar3}{\partial t} = mchar2\,(k7)$$

$$\frac{\partial mgas3}{\partial t} = mchar2\,(k8)$$