Towards the Utilization of Wet Biomass Gasification in
Supercritical Water

On the energy efficiency and char formation

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ON THE ENERGY EFFICIENCY AND CHAR FORMATION

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SUMMARY

Wet biomass, which contains over 80 wt-% of water, is considered to be a cheap type of biomass with an abundant availability. Its utilization is beneficial since it can be converted into biofuels with a wide range of further applications, and can account toward reducing the problem of overflowing biowaste streams. The most used method to process wet biomass is to decompose it via biochemical conversion (i.e. using microorganism) to produce biogas. This biochemical method, however, is hindered by its most important limitation which is the long residence time necessary for complete conversion of the wet biomass. Taking this into consideration, the utilization of fast thermochemical conversion processes becomes very appealing. However, due to the high moisture content, the wet biomass requires a significant amount of energy for drying before it can be converted in conventional thermochemical processes (i.e. gasification, torrefaction, pyrolysis, combustion). This makes it hard to achieve an energy efficient process. Consequently, utilization of a hydrothermal conversion process, such as the Supercritical Water Gasification (SCWG), in which water is used as a reactant is preferred.

The SCWG process is typically done at temperatures above 773 K and pressures of 25 MPa. The SCWG process can be used to produce either hydrogen rich gas or methane rich gas, and its composition can be fine-tuned by altering the temperature of the gasification process to suit the targeted application. During the heating up of wet biomass, however, unwanted side reactions may occur leading to char formation. This char can deposit on the walls of the reactor or heat exchanger causing plugging of the system. One of the solution for char reduction is to develop a fast heating method of the wet biomass by e.g. mixing the relatively cold wet biomass stream with hot supercritical water via direct injection. The aim of this thesis is to gain a fundamental understanding of this process and reveal the key parameters that have a major impact on char reduction in the direct injection system. Additionally, the impact of applying this novel approach on the overall thermal efficiency of the process is also examined.

The investigation on the influence of the direct injection system on the thermal efficiency, is addressed by developing a system model using UniSIM. The UniSIM model is applied for both situations: the direct injection system and the conventional premixed SCWG system, while glycerol is used as feed for both systems. It is found that the implementation of direct injection significantly reduces the efficiency with approximately 8% - 23% in

comparison to the premixed system. Subsequently, the feedstock is then replaced with sewage sludge that is modelled by means of a surrogate fuel which incorporates three different compounds (i.e. acetic acid, diketene, propanone and benzene). Accordingly, it is found that a thermal efficiency of approximately 62% can be achieved when using a feedstock with 20 wt-% dry matter content. However, using a feedstock with 8 wt-% dry matter content leads to a thermal efficiency of only 10%. A further sensitivity analysis of several key operating parameters on the system efficiency has been carried out and this resulted in the proposal of an optimum operating window. Accordingly, the optimum reactor temperature is between 843 – 873 K. The ratio of the hot supercritical water flow to the total reactor feed stream is approximately 0.4 - 0.5. Furthermore, the total dry matter content contained in the reactor feed stream should not be more than 14 wt-%, due to expected difficulties in pumping. Based on this operating window, a pinch analysis is conducted for a further optimization of the system. The results show that when the system operates with a ratio of hot supercritical water to the total reactor feed stream of 0.4, the system can achieve a thermal efficiency of 22% and 50%, when the system operates with a total dry matter content of 8 wt-% and 12 wt-%, respectively.

The main objective of the present research is to gain insight in the effect of the biomass heating rate on the char formation. This is addressed by developing a Computational Fluid Dynamic (CFD) model of the SWG process. Three stages in the CFD modelling can be considered: 1) a single-phase model with glycerol feedstock; 2) a single-phase model with glucose feedstock; 3) and a multi-phase model with glucose feedstock. The first CFD model is developed to simulate the gasification of a non-char producing compound, i.e. glycerol. The gasification takes place in a straight tubular reactor with a tee connection near the two inlets (i.e. main tube with water and the feed injection tube). By mixing the relatively cold biomass with hot supercritical water, a fast heating rate of the feed can be obtained. The performance of the selected turbulence model and the expanded Arrhenius formulation to describe the kinetics are assessed via a validation with experimental data from literature. Subsequently, the CFD model is used to examine the flow behavior during the gasification process, showing that in cases where the mass flowrate is low, the gravitational force plays a major role in enhancing the mixing and heat transfer. Additionally, it is shown that this tranquil flow due to the low mass flowrate can lead to of flow recirculation in the tee connection, which may result in a gradual partial heating of the wet biomass that comes from the injection tube.

The second CFD model is developed for glucose gasification in a helical tubular reactor with a tee connection that bridges the two inlets (i.e. main tube and injection tube) together. The aim of this investigation is to examine the influence of several key operating parameters (e.g. the flowrate ratio of cold feed and hot supercritical water stream) on the char formation behavior of glucose. Initially, the CFD model has been developed with the assumption that glucose is directly converted into either gas or char via two different reaction path. Experimental validation of the numerical results showed that the model is capable of giving a good char yield prediction at low temperatures (i.e. 623K). However, at higher temperatures, noticeable discrepancies for the char yield prediction are noticed. Nevertheless, the trend of the char formation as function of temperature is well simulated. The third CFD model includes a Euler-Lagrange formulation and a complex five competing reactions scheme for the formation of gas and char. The implementation of the discrete phase approach is done to mimic the biomass particle behavior (evaporation and devolatilization) during gasification. The model proves to be very accurate in predicting the char yield at high temperatures (up to 693K), and it can also capture the general trend of the gas yield of the gasification process. The subsequent sensitivity analysis shows that implementing the direct injection of cold biomass into a hot supercritical water at a temperature of 723 K reduces the char yield with approximately 27% in comparison to the premixed system. Reducing the flow rate ratio of hot supercritical water and cold biomass from 4:1 to 1:1 (ratio of hot supercritical water to the total reactor feed stream of 0.8 to 0.5) leads to an increase in the char yield by 25%. This is mainly because of the fact that less energy is available to provide a fast heat-up of the cold biomass.

Finally, in an effort to account for realistic dimensions of a SCWG reactor, the model is applied to a reactor with a larger diameter (e.g. 8mm instead of 1 mm). Through this investigation, it is found that enlarging the reactor diameter significantly affects the char formation process. It is shown that increasing the reactor diameter to 8 mm may lead to an increase of the char yield with 107% for a temperature of 723 K. This char formation increase is mainly obtained due to the extended residence time of the biomass in the low temperature region. An optimum mixing of the feed and the preheated water is required to avoid a non-uniform temperature distribution inside the reactor tube is. Therefore an optimal injector geometry that can contribute to a more uniform temperature field and less char formation has been investigated. Three different injector designs are proposed (i.e. 90° wall injection, 45° wall injection and central injection). It is found that injecting the glucose feed in the middle of the reactor via central injection has the best performance in

comparison to the other designs. Central injection of glucose leads to a more prominent swirling pattern inside the reactor that enhances the mixing and heat transfer, and reduces the char yield with 25%. Additionally, a further char yield reduction can be achieved by preheating the relatively cold biomass feed to about 473 K.

The data and knowledge regarding the process obtained in this research provide reliable means to predict the gasification performance and therefore may facilitate the further development of this technology. The conversion of wet biomass via gasification in supercritical water can definitely be done reliable, safe and in an energy efficient manner. Further research is recommended to increase the energy efficiency of the SCWG system, to develop a laboratory set-up for detailed validation of the CFD model, and to further improve the CFD model with a discrete char particle model to describe the char or salts deposition on the wall.

SAMENVATTING

Biomassastromen die meer dan 80 gewichtsprocent water bevatten (zogenaamde natte biomassastromen) worden beschouwd als goedkope stromen die in overvloed beschikbaar zijn. Het gebruik van deze stromen is gunstig omdat ze omgezet kunnen worden in biobrandstoffen met een breed scala aan toepassingsmogelijkheden, wat bijdraagt aan het verminderen van het probleem van overvloedige bioafvalstromen. De meest gebruikte methode om natte biomassastromen te verwerken is het ontbinden via biochemische omzetting (d.w.z. met behulp van micro-organismen) om biogas te produceren. Deze biochemische methode wordt echter gehinderd door de lange verblijftijden die nodig zijn voor de volledige omzetting van de biomassa, in combinatie met lage opbrengsten. Hiermee rekening houdend wordt het gebruik van snelle thermochemische conversieprocessen erg aantrekkelijk. Vanwege het hoge vochtgehalte vereist de natte biomassa echter een aanzienlijke hoeveelheid energie voor een noodzakelijke droogstap, voordat deze kan worden omgezet in conventionele thermochemische processen (d.w.z. vergassing, torrefactie, pyrolyse, verbranding). Dit maakt het moeilijk om een energie-efficiënt proces te bereiken. Dientengevolge heeft het gebruik van een hydrothermisch omzettingsproces, zoals superkritische watervergassing (Supercritical Water Gasification, SCWG), waarbij water wordt gebruikt als een reactant, de voorkeur.

Het SCWG-proces wordt meestal uitgevoerd bij temperaturen boven 773 K en een druk van 25 MPa. Het SCWG-proces kan worden gebruikt om ofwel waterstofrijk gas ofwel methaanrijk gas te produceren, en de samenstelling ervan kan worden verfijnd door de temperatuur van het vergassingsproces aan te passen aan de beoogde toepassing. Tijdens het opwarmen van natte biomassa kunnen echter ongewenste nevenreacties optreden die leiden tot koolvorming. De gevormde kool kan zich afzetten op de wanden van de reactor of de warmtewisselaar waardoor het systeem verstopt raakt. Eén van de oplossingen om koolvorming tegen te gaan is om een snelle verwarmingsmethode van de natte biomassa te ontwikkelen door bv. het mengen van de relatief koude natte biomassastroom met heet superkritisch water via directe injectie. Het doel van dit proefschrift is om een fundamenteel begrip van dit proces te verkrijgen en de belangrijkste parameters te onthullen die een grote impact hebben op de vermindering van koolvorming door een directe injectiesysteem. Bovendien wordt de impact

van het toepassen van deze nieuwe benadering op het algehele thermische rendement van het proces onderzocht.

Het onderzoek naar de invloed van het directe injectiesysteem op de thermische efficiëntie wordt aangepakt door een systeemmodel te ontwikkelen met behulp van UniSIM. Het UniSIM-model wordt toegepast voor twee situaties: het directe injectiesysteem en het conventionele voorgemengde SCWG-systeem. Glycerol wordt gebruikt als invoerstroom voor beide systemen. Uit de resultaten van het onderzoek bleek dat de implementatie van directe injectie de efficiëntie aanzienlijk vermindert met ongeveer 8-23% in vergelijking met het voorgemengde systeem. In een volgende stap werd de invoerstroom vervangen door rioolslib dat is gemodelleerd door middel van een surrogaatbrandstof die vier verschillende verbindingen bevat: azijnzuur, diketeen, propanon en benzeen. De resultaten toonden aan dat een thermisch rendement van ongeveer 62% kan worden bereikt bij het gebruik van een invoerstroom met een drogestofgehalte van 20 gewichtsprocent. Wanneer het drogestofgehalte echter slechts 10 gewichtsprocent is, daalt het thermisch rendement tot slechts 10%. Een verdere gevoeligheidsanalyse van het effect van verschillende belangrijke bedrijfsparameters op de systeemefficiëntie resulteerde in een voorstel van een optimaal werkingsvenster. Dienovereenkomstig ligt de optimale reactortemperatuur tussen 843-873 K. De verhouding van de hete superkritische waterstroom tot de totale reactorvoedingsstroom is ongeveer 0.4–0.5. Verder zou het totale drogestofgehalte in de reactorvoedingsstroom niet meer dan 14 gewichtsprocent moeten zijn, vanwege verwachte moeilijkheden bij het pompen. Op basis van dit werkvenster werd een pinch-analyse uitgevoerd voor een verdere optimalisatie van het systeem. De resultaten laten zien dat wanneer het systeem werkt met een verhouding van heet superkritisch water tot de totale reactorvoedingsstroom van 0.4, het systeem een thermisch rendement van 22% en 50% kan bereiken, wanneer het systeem werkt met een totaal drogestofgehalte van respectievelijk 8 en 12 gewichtsprocent.

Het belangrijkste doel van dit onderzoek is om inzicht te krijgen in het effect van de verwarmingssnelheid van biomassa op de koolvorming. Dit wordt aangepakt door een numeriek stromingsleermodel (Computational Fluid Dynamics (CFD) model) van het SCWG-proces te ontwikkelen. Drie fasen in de CFD-modellering kunnen worden overwogen: 1) een enkelfasig model met glycerol-voeding; 2) een enkelfasig model met glucose-voeding; 3) en een meerfasig model met glucose-voeding. Het eerste CFD-model is ontwikkeld om de vergassing van een niet-koolvormende verbinding, in dit geval glycerol, te simuleren. De vergassing vindt plaats in een rechte

buisreactor met een T-verbinding nabij de twee inlaten (dat wil zeggen de hoofdbuis met water en de toevoerbuis). Door de relatief koude biomassa te mengen met heet superkritisch water, kan een snelle verwarmingsnelheid van de voeding worden verkregen. De prestaties van het geselecteerde turbulentiemodel en de uitgebreide Arrhenius vergelijking om de kinetiek te beschrijven, worden beoordeeld via een validatie met experimentele gegevens uit de literatuur. Vervolgens wordt het CFD-model gebruikt om het stromingsgedrag tijdens het vergassingsproces te onderzoeken. Het model toont aan dat in gevallen waarin het massadebiet laag is, de zwaartekracht een belangrijke rol speelt bij het verbeteren van de menging en warmteoverdracht. Bovendien wordt aangetoond dat deze rustige stroming als gevolg van het lage massadebiet kan leiden tot stroom-recirculatie in de T-verbinding, wat kan resulteren in een geleidelijke gedeeltelijke opwarming van de natte biomassa die uit de injectiebuis komt.

Het tweede CFD-model is ontwikkeld voor glucosevergassing in een spiraalvormige buisreactor met een T-verbinding die de twee inlaten (dat wil zeggen hoofdbuis en injectiebuis) overbrugt. Het doel van dit onderzoek is om de invloed van verschillende belangrijke bedrijfsparameters (bijvoorbeeld de stroomsnelheidsverhouding van koude voeding en hete superkritische waterstroom) op het koolvormingsgedrag van glucose te onderzoeken. Aanvankelijk is het CFD-model ontwikkeld met de aanname dat glucose via twee verschillende reactiewegen direct in gas of kool wordt omgezet. Experimentele validatie van de numerieke resultaten toonde aan dat het model in staat is om een goede voorspelling te geven van koolvorming bij lage temperaturen (dat wil zeggen 623 K). Bij hogere temperaturen worden echter opvallende verschillen opgemerkt voor de voorspelling van de koolopbrengst. Niettemin wordt de trend van de koolvorming als functie van temperatuur goed gesimuleerd. Het derde CFD-model omvat een Euler-Lagrange-formulering en een complex reactieschema met vijf concurrerende reacties voor de vorming van gas en kool. De implementatie van de discrete-fasebenadering wordt gedaan om het biomassa-deeltjesgedrag (verdamping en ontgassing) tijdens de vergassing na te bootsen. Het model blijkt zeer nauwkeurig te zijn in het voorspellen van de koolopbrengst bij hoge temperaturen (tot 693 K), en het kan ook de algemene trend van de gasopbrengst van het vergassingsproces vastleggen. De daaropvolgende gevoeligheidsanalyse toont aan dat de implementatie van de directe injectie van koude biomassa in heet superkritisch water bij een temperatuur van 723 K de koolopbrengst met ongeveer 27% vermindert in vergelijking met het voorgemengde systeem. Het verlagen van de stroomsnelheidsverhouding van heet superkritisch water en koude biomassa van 4:1 naar 1:1 (verhouding van

heet superkritisch water tot de totale reactortoevoerstroom van 0.8 tot 0.5) leidt tot een toename van de koolopbrengst met 25%. Dit komt vooral omdat er minder energie beschikbaar is om de koude biomassa snel op te warmen.

Ten slotte, in een poging om rekening te houden met realistische afmetingen van een SCWG-reactor, wordt het model toegepast op een reactor met een grotere diameter (bijvoorbeeld 8 mm in plaats van 1 mm). Door dit onderzoek is gebleken dat het vergroten van de diameter van de reactor het proces van koolvorming aanzienlijk beïnvloedt. Er wordt aangetoond dat een verhoging van de diameter van de reactor tot 8 mm kan leiden tot een toename van de koolopbrengst met 107% bij een temperatuur van 723 K. Deze toename van koolvorming wordt voornamelijk verkregen door de langere verblijftijd van de biomassa in de lage-temperatuurregio. Een optimale menging van de voeding en het voorverwarmde water is vereist om een niet-uniforme temperatuurverdeling binnen de reactorbuis te voorkomen. Daarom is een optimale injector-geometrie onderzocht die kan bijdragen aan een meer uniform temperatuurveld en minder koolvorming. Er worden drie verschillende injectorontwerpen voorgesteld (90° muurinjectie, 45° muurinjectie en centrale injectie). Het blijkt dat het injecteren van de glucosetoevoer in het midden van de reactor via centrale injectie de beste prestatie geeft in vergelijking met de andere ontwerpen. Centrale injectie van glucose leidt tot een prominenter wervelpatroon in de reactor dat het mengen en de warmteoverdracht verbetert en de koolopbrengst met 25% vermindert. Bovendien kan een verdere vermindering van de koolopbrengst worden bereikt door de relatief koude biomassavoeding voor te verwarmen tot ongeveer 473 K.

De gegevens en kennis met betrekking tot het proces verkregen in dit onderzoek bieden betrouwbare middelen om de vergassingsprestaties te voorspellen en kunnen daarom de verdere ontwikkeling van deze technologie mogelijk maken. De omzetting van natte biomassa via vergassing in superkritisch water kan zeker op een betrouwbare, veilige en energie-efficiënte manier gedaan worden. Verder onderzoek wordt aanbevolen om de energie-efficiëntie van het SCWG-systeem te verhogen, om een laboratoriumopstelling te ontwikkelen voor gedetailleerde validatie van het CFD-model, en om het CFD-model verder te verbeteren met een discreet kooldeeltjesmodel om de kool- of zoutenafzetting op de wanden te beschrijven.

TABLE OF CONTENTS

Chapter 1	Introduction	1
1.1	Global status and necessity of biomass utilization	1
1.2	Wet biomass and the possible conversion routes	2
1.3	An introduction to supercritical water gasification	5
1.4	Recent advances and process challenges	9
1.5	Research objectives	12
1.6	Thesis outline.	13
Chapter 2	An Energy Analysis on Gasification of Sewage Sludge by a Direct Injection in Supercritical Water	15
2.1	introduction	16
2.2	Methodology	17
2.2.1	Tools and Assumptions	18
2.2.2	Performance Indicators	18
2.2.3	Choice of property method	19
2.2.4	Process flow modelling	20
2.3	System Performance: Parametric Investigations	24
2.3.1	Thermal Efficiency of Real and Model Compounds	24
2.3.2	Effect of Direct Injection	25
2.3.3	Effect of Key operating Parameters in the DI System	26
2.3.4	Proposed Operating Window	30
2.4	System Optimization: Pinch Based Design	31
2.4.1	Targeting by Pinch Analysis	31
2.4.2	Optimized Flow Process	33
2.5	Conclusion	35
Chapter 3	Computational Fluid Dynamic Model for Glycerol Gasification in Supercritical Water in a Tee Junction Shaped Cylindrical Reactor	37

3.1	introduction	38
3.2	Modelling approach	40
3.2.1	Governing equations	40
3.2.2	Turbulence modelling	41
3.2.3	Fluid properties	42
3.2.4	Reaction kinetics	43
3.2.5	Experimental data, geometry and boundary	43
3.2.6	Numerical method	44
3.2.7	Data analysis	45
3.3	Results and Discussion	46
3.3.1	Mesh independency	46
3.3.2	Model validation	48
3.3.3	Sensitivity analysis	54
3.4	Conclusion	60
Chapter 4	Numerical Modelling of Char Formation during Glucose Gasification in Supercritical Water	63
4.1	introduction	64
4.2	Modelling approach	66
4.2.1	Fluid properties	66
4.2.2	Reaction kinetics	66
4.2.3	Geometry and boundary conditions	69
4.2.4	Numerical methods	70
4.2.5	Data analysis	71
4.3	Results and discussion	71
4.3.1	Mesh independency	71
4.3.2	Model validation	73
4.3.3	Sensitivity analysis	75
4.4	Conclusions	84

Chapter 5	Design of a supercritical water Reformer for Pilot Scale Wet Biomass Gasification: numerical study with model compound glucose	87
5.1	introduction	88
5.2	Modelling approach	89
5.2.1	Discrete phase model	90
5.2.2	Fluid properties and reaction kinetics	91
5.2.3	Experimental data, geometry and boundary	93
5.2.4	Numerical methods and data analysis	96
5.3	Results and discussion	96
5.3.1	Model validation	97
5.3.2	Sensitivity analysis	98
5.4	Effect of injector design for a pilot scale reformer	103
5.4.1	Geometry and boundary conditions	103
5.4.2	Influence of injection design and feed temperature	105
5.5	Conclusion	108
Chapter 6	Conclusions and recommendations	109
6.1	Conclusions	109
6.2	Recommendations	112
	Bibliography	115
	Nomenclature	127
	Acknowledgements	129
	Publications	133

CHAPTER 1

INTRODUCTION

1.1 GLOBAL STATUS AND NECESSITY OF BIOMASS UTILIZATION

In the past couple of decades the world has experienced incredible success that manifested in the tremendous boost in industrialization together with the economic growth, which are made possible largely due to the availability of large amounts of cheap fossil fuels reserves. This success in effect bolsters the worldwide growth in population [1-3]. Population growth, however, leads to the rise of challenges such as an increasing energy demand and generation of overflowing waste streams. It is forecasted that there will be a 56 % increase in energy demand and 26 % increase in natural gas consumption by 2040 worldwide [4].

The continuous use of fossil fuel to fulfill the current energy demand has already resulted in the reduction of the air quality and the rise of greenhouse gas emissions causing a global climate change [3, 5]. In the last couple of years from 1990 up to 2014, the world has seen an increase of CO₂ emissions from 21.5 to 33.5 billion metric tons [6]. Further use of the fossil fuels for the energy demand, will increase the CO₂ emission to 45.5 billion metric tons by 2040 [6]. In addition to that, the fossil energy sources are not endless. Though the proven reserves are sufficient for the coming years, it is inevitable that its price will soar along with the depletion of these reserves. Furthermore, the main reserves are concentrated in some (politically and economically unstable) regions in the world, which could lead to the risk of security of supplies for certain countries [7].

Branching out toward the use of renewable alternatives is a favorable means to cope with these issues. In 2014, renewables provided about 19.2 % of the global energy consumption [5]. Biomass is considered to be carbon neutral, so its conversion toward biofuels for efficient energy generation perfectly fits in the future energy system [8-15]. Development of novel technologies for biomass conversion is expected to increase its share among the renewable resources to approximately from 26 % to 60 % by 2030 [5, 16], and thus play a major role in the global energy mix toward the phasing out of fossil fuels [17, 18]. In addition to that, biomass has a widespread availability distribution throughout the globe that mitigates the risk of security of supply

[15]. Finally, adopting the emerging circular economy concept fits perfectly to account for the problem of overflowing waste streams. In this concept, the conversion of biowaste materials to energy, fuels, chemicals and materials helps to close the industrial ecosystem loops [19].

1.2 WET BIOMASS AND THE POSSIBLE CONVERSION ROUTES

Among the considerable amount of available biomass, a substantial part contains over 80 wt-% of water in it [20]. These highly aqueous biomass resources are referred to as wet biomass. Some examples of this wet biomass are sewage sludge, manure, black liquor and wastewater from paper mills, olive mill wastewater, wine distillery waste, fruit pulp and many others. This wet biomass is considered as a cheap type biomass and its availability is abundant. For example, there are approximately 11.5 dry million tons production of waste sewage sludge stream among the EU27 in 2017 [21]. In addition to that, Europe produced approximately 148 million tons of swine manure per year [22, 23], while in 2017 the United States is reported to produce a staggering amount of 120 million tons annually [24]. Furthermore, it is estimated that 190 dry millions tons of black liquor are annually produced from Kraft process in 2011 [25], which accounts for approximately 60 % of the overall paper pulp production globally [26].

The utilization of these wet biomass streams is not yet widespread, due to the challenge to develop an energy-efficient way of converting it into valuable products. This is due to the excessive energy requirement in the pretreatment step to remove the water from the wet biomass. The overall process efficiency of the system is negatively impacted as the energy contained in the conversion product is lower than what is used for the drying process [4, 27]. Conversion technologies that avoid the evaporation of water from the biomass are therefore very appealing. There are two main categories of such conversion technology: the biochemical and the thermochemical conversion routes. In the biochemical conversion, the wet biomass can be treated through either composting or anaerobic digestion or other methods [24, 28]. Whereas, the thermochemical conversion routes avoids the water phase change by operating at high pressures [29].

Composting uses aerobic microorganisms to convert biodegradable organic into a stable humus-like substance [24, 30]. This process eliminates pathogens in the biomass, produces a stable form of organic nitrogen from ammonia, reduces the odors and waste volume. In contrast to that, anaerobic

digestion uses bacteria to metabolize the organic materials into biogas (e.g. methane and carbon dioxide) under an oxygen-free environment [31]. In 2017, roughly 17.000 biogas plants and 459 biomethane plants were operating in Europe [32]. Among the European countries, Germany had 10.846 biogas plants, and among which 1.400 plants are operated using wet biomass (i.e. sewage sludge) [19]. This remarkable growth in biogas plant installation, however, leads to an excess of digestate (the byproduct of a biogas plant) in certain locations as there is not enough demand of this digestate for farmland's fertilizer. Moreover, digestate could have a negative effect on soil as components such as salts, residual organic matters or even pathogen bacteria may still remain in the digestate [33]. More importantly, these conversion processes (i.e. anaerobic digestion and composting) require a significant period of residence time. The anaerobic digestion process takes a period of approximately 20-30 days to be completed, while composting requires at most 12 weeks. These issues might become a major drawback on the further implementation and upscaling of these technologies.

The thermochemical method allows heat recovery from the hot water to take place in the system, as it is not necessary to evaporate water from the biomass. As water is involved in the conversion process, this method is often referred to as a hydrothermal conversion process that includes technologies such as [29, 34, 35]: a) Hydrothermal Carbonization (HTC); b) Hydrothermal Liquefaction (HTL); c) Hydrothermal Oxidation (HTO); d) Supercritical Water Gasification (SCWG). Figure 1.1 presents the simplified scheme of the available conversion routes.

Due to all of these issues with the biochemical route, especially related to residence time, the utilization of a quick hydrothermal conversion process can be very appealing. HTO is an example of such process and it is most often used to solely disposal of wet biomass. In this process, the organic components are dissolved in water and are oxidized with a pressurized oxidizer (e.g. pure oxygen, ozone, or hydrogen peroxide). In this manner, the compounds that are typically too resilient for microbial treatment or too difficult to break down with incineration can be rapidly degraded into basic molecules such as carbon dioxide and water [36, 37]. Wet biomass that is commonly treated with this method could be sewage sludge, toxic industrial waste and high-risk waste from military byproduct [38]. The HTO process that is done in subcritical water (i.e. temperatures of 125 – 320 °C and pressures of 0.5 -20 MPa) is often referred to as Wet Oxidation (WO). Whereas, when the conditions are supercritical (i.e temperature of above 374 °C and pressure of above 22.5 MPa), this process is referred to as

Supercritical Water Oxidation (SCWO). In relation to energy generation, utilizing SCWO for coal processing can lead to a higher efficiency in comparison to a conventional power plant [39].

Figure 1.1 Classification of wet biomass conversion routes, modified from [40]

With the exception of HTO, other hydrothermal technologies aim not only to the disposal of wet biomass, but also to produce materials for resources or for energy application. For example, the HTC process in principle aims to convert wet biomass into hydrochar using hot compressed water at temperatures of 180-260 °C within a period of 5 - 30 minutes. The hydrochar produced usually contains a reduced ash content from the original biomass since part of the inorganic components (e.g. alkali metals) dissolves in water [29, 34]. This hydrochar is suitable as an alternative for fossil coal since its heating value is similar to lignite, and it has been used for co-combustion with low rank coals [29]. Also, the conversion of microalgae to generate a product with bituminous coal quality through HTC has been done [41]. Such product has a wide range of applications such as for soil nutrient, raw materials to produce syngas or chemicals.

Similar to the production of char, wet biomass can also be converted through the HTL process into a liquid product using subcritical water at temperatures of 280-370 °C and pressures of 10-25 MPa within a time range of 3 – 120 minutes. This process for bioliquids uses subcritical water, as Supercritical Water (SCW) promotes the production of gaseous compounds. The main products of HTL are bio crude, char, aqueous organics and a CO₂ rich gas phase [29, 34]. The produced bio crude has a high heating value and reduced oxygen content compared to the original biomass. This reduced

amount of oxygen can still lead to some limitations in further application, and therefore, downstream hydrotreatment processing is required. In addition to this, the bio crude is quite viscous and consequently, and an upgrading hydrogenation process is necessary to increase the hydrogen content and reducing the viscosity. Nevertheless, the interest to use HTL to convert algae in a biorefinery concept is growing. This is driven by protein (i.e. amino acids) contained algae that are useful for feed additives, cosmetic and pharmaceuticals.

In addition to its conversion toward char and liquid, the wet biomass can also be converted into gaseous compounds rich in methane and hydrogen through SCWG. This technology is known to have the highest potential to convert wet biomass in an energy efficient manner [4, 42-45]. Utilization of a catalyst is required if the process is performed using water at subcritical condition (e.g. approximately temperature of 350 °C) [29]. Detailed information related to the basic principle, schematics, advantages and challenges of the SCWG process are presented in the next section.

1.3 AN INTRODUCTION TO SUPERCRITICAL WATER GASIFICATION

SCWG is a thermochemical process to convert wet biomass at a high pressure and a high temperature in water (i.e. SCW). The major advantage of this technology is that it eliminates the need for drying since the water fraction of wet biomass is used in the conversion reactions. A big challenge is the high energy requirement for heating the water to its supercritical state. The energy supplied for the heating, however, can be reduced by heat recovery and thus a thermochemical conversion system with a high thermal efficiency can be achieved [42-45].

In principle, the SCWG process is able to convert wet biomass into gaseous product within a very short residence time, in the range of a few minutes [4]. The aqueous stream byproduct of the process is cleansed from any possible pathogens (e.g. bacteria and biotoxin) that come from the original biomass source [46]. The SCWG process may achieve a complete carbon conversion without any catalyst when it is operated at high temperature (i.e 500 – 800 °C), although a lower operating temperature might be beneficial for the thermal efficiency and investment costs [46]. The resulting gaseous product is free from nitrogen (opposite to the product of normal air blown gasification), and its composition can be fine-tuned by altering the temperature of the gasification process to suit the targeted

application. For instance, by maximizing the composition of methane by using lower conversion temperatures and upgrading it afterwards, the gaseous product can be used as a replacement for natural gas [4, 46]. Furthermore, maximizing the hydrogen composition at higher conversion temperatures could be done if the intended purpose is to produce pressurized hydrogen. Whereas, a synthetic gas (syngas) can be obtained by minimizing the composition of methane [4, 46]. In addition, several renewable fuels (e.g. Fischer-Tropsch diesel and methanol) production can be performed without the need for an extra pressurization step, as the gaseous product from the SCWG process already has a high pressure.

The SCWG process is highly dependent on the thermophysical and transport properties of SCW as the reaction medium, as well as the peculiar solvent strength of SCW that is closely related to its dielectric constant. At standard temperature and pressure, the dielectric constant of water is 78.5 F/m and this makes it a very good solvent for ionic species such as inorganic salt. During water phase change from liquid to supercritical state, however, its hydrogen bond breaks down leading to the decrease of its dielectric constant to approximately 8 F/m. With this low value of the dielectric constant, SCW is able to dissolve non-polar compounds (e.g. biomass) and gases. Furthermore, as the organic compounds dissolve in water and become a homogenous solution, the phase boundaries between compounds are eliminated and thus an increase of the overall heat transfer during the conversion process can be achieved [47, 48]. The breakage of hydrogen bond also causes the drastic reduction of density as presented in Figure 1.2. Since the behavior of both density and dielectric constant are the results of the change in hydrogen bonds, the value of these two properties can often be directly related to each other.

Similar to the drastic reduction of density during the transition of water to SCW, the other thermodynamic and transport properties of water also experience a significant change. The viscosity largely decrease at this condition, see Figure 1.2, contributing to an improved mass transfer (diffusion of the reactant molecules to each other) [8, 40]. Furthermore, thermal conductivity is reduced and a significant variation of its specific heat capacity can also be observed from the figure [44, 45].

Figure 1.2 Properties of water during the transition from subcritical to supercritical condition

Another interesting effect is the ionic product of water which is the equilibrium constant of the self-ionization reaction of water. At room temperature, the ionic product of water is generally taken to be $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. This value can also be translated as a pH of 7, which indicates that it is neither acid nor base (neutral). The ionic product is related to the amount of ions present in the system, which governs the acid-base equilibria and the selectivity towards certain reaction pathway. As an example, for a relatively high ionic product (higher than $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$) the main reactions (e.g. self-ionization and dehydration reaction in SCWG) are ionic pathways and at the opposite condition, free radical reactions (initiation and termination reactions in SCWG) would be the main pathways. At a pressure of 25 MPa, the ionic product of water increases up to the value of $10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ at around 250 °C. It then decreases to around $10^{-23} \text{ mol}^2 \text{ dm}^{-6}$ at around 600 °C. It has to be noted that near the critical point, the ionic product experiences a dramatic decrease, and both ionic and radical reactions occur and compete with each other.

Following the dissolution of biomass in SCW, various decomposition and chemical transformation reactions will take place in the SCWG process. A brief description of the reaction pathways of cellulose is given here. The first step of the process is a hydrolysis of the cellulose into its monomer, which is glucose. Once it is produced, glucose can go through several different reactions. To simplify the possible intermediates produced from these reaction, Savage [49] adopted the lumped approach and assumed a generic intermediate compound. This intermediate compound will then experience steam reforming, char formation and also decomposes into gaseous compounds. Once the gaseous compounds are formed, water-gas shift and methanation reactions may occurs and alters the composition. Figure 1.3 presents the simplified scheme of the gasification reactions.

Figure 1.3 simplified schematic of decomposition and chemical transformation reactions of glucose

A generic process scheme of a continuous SCWG system is displayed in Figure 1.4. The system consists of a feed storage for the wet biomass. This wet biomass is delivered by a high pressure pump and to recover the heat from the hot gaseous products a heat exchanger is used. Subsequently, the feed enters the supercritical reactor where the gasification reactions occur. The resulting gaseous products are then cooled down, and then the two phase product stream is separated using a high-pressure and low-pressure separation system.

Figure 1.4 (A) Simple schematic of a continuous SCWG process.

1.4 RECENT ADVANCES AND PROCESS CHALLENGES

Many articles about experimental and numerical studies on wet biomass gasification in SCW have been published over the last decades. The experimental studies on SCWG are conducted either in a laboratory set-up (batch system and continuous system) or in pilot plants. The largest SCWG plant in the world (100 kg/h) currently operating is the VERENA plant in Germany. Other large operating pilot plants are one that is jointly owned by Chugoku Electric Power Company and the University of Hiroshima in Japan [50], and a SCWG plant in the Netherlands that is designed by SPARQLE B.V.

Wet biomass used for SCWG experimental studies can typically be categorized into three types: a) waste-based; b) plant-based; c) model compounds. Waste-based feeds include leftover materials from society or industry, such as livestock manure [51, 52], sewage sludge [53], olive mill wastewater, wine distillery waste [4, 51-63], fruit pulp [55] and fruit waste [63]. Chicken, swine and cattle manure gasification in SCW at 873 K at 25 MPa achieved a reasonably high Carbon Gasification Efficiency (CGE) equal to 80% [51], 84% and 81%, respectively [52]. Operating at a higher temperature of 893 K, chicken manure was gasified with a very high CGE of 99.2% [62]. Comparatively, gasification of sewage sludge in SCW at a temperature of 873 K and pressure of 25 MPa led to a CGE of 73 % [53]. Under similar operating conditions, the SCWG of fruit pulp yielded a CGE of 49% [55] and SCWG of fruit waste led to a CGE ranging from 24 % - 33 % [63].

The second category of plant-based feeds include non-food crops like artichoke, pine cone and sawdust [64] or specially engineered energy crops such as algae [54]. In relation to this, algae were successfully gasified with CGE of 53% with an operating temperature of 873 K and 24 MPa. The third category, which is the model compound feed, is investigated to understand the decomposition pathway of complex biomass feed. Examples of such model compounds are cellulose, lignin [49], glycerol [65, 66], glucose [67, 68], indole [69], acetic acids and hydroxyl acetone [70]. Glycerol was successfully gasified at an operating temperature of 873 K and pressure of 25 MPa [65] with a CGE of approximately 89%. Similarly, a CGE of approximately 67% was found for glucose gasification in SCW at a temperature of 873 K and a pressure of 28 MPa, and a residence time of 50 seconds. [71]. All of these experimental investigations are done at different operating conditions, so a difference in conversion level may be expected, but most of these authors noticed that char was produced during the gasification experiments.

Simulating the gasification process in SCW with numerical modelling is very beneficial as it is able to facilitate the prediction of the process performance and therefore overcome possible challenges that are related to equipment at high pressures and high temperatures. In essence, four general types of numerical modelling used for SCWG may be distinguished, which are: a) kinetic modelling; b) thermodynamic equilibrium modelling, c) system modelling; d) Computation Fluid Dynamic (CFD) modelling. On the contrary to the large number of articles on experimental investigation, only a few publications on CFD modelling of SCWG can be found in literature. SCWG investigations via CFD modelling that have been done recently can be classified in two categories: a) disregarding chemical reactions; b) considering chemical reactions.

CFD models of SCWG that disregard chemical reactions are typically developed to study the mixing or particle distribution in the reactor. Investigation of the mixing process for injection of n-decane into SCW in a cylindrical tee mixer was conducted by Raghavan and Ahmed [72]. Their main findings were that there was no change on the flow field within the reactor when mixing different fluids with less than a 100 K temperature difference. In addition to these, Caputo et al. [73] developed a model to observe the influence of the inlet configuration to the flow field. It was found that mixing pre-heated water with cold biomass can improve the reactor's performance. Similarly, Wei et al. [74] investigated the influence of the biomass feeding on the solid particle and residence time distribution. The

authors observed that a uniform feed distribution and long residence time was achieved using an injector with a 45° angle.

In contrast to these investigations, more complex CFD models that includes chemical reactions are developed to assess the gasification performance of the SCWG process. In relation to the study that was done by Wei et al [74], Su et al. [75] further improved the model by implementing three competing reactions for the SCWG of glucose in a fluidized bed reactor. Results from this study showed that the intensive mixing of glucose with pre-heated water in the fluidizing sections led to an almost immediate gasification reaction. In addition to this, Goodwin and Rorrer [76] modelled the gasification of xylose assuming constant thermal properties of water. It was found that the gas composition can be predicted accurately with the exception of CH₄. More recently, Hui et al. [77] developed a more detailed glycerol gasification model that uses 7 reactions to study the influence of the injector shape of the reactor. Authors observed that unwanted char producing reactions occurring in lower temperature regions, can be reduced with different injector angles.

Despite all this research progress that have been achieved and the advantages that this technology offers, the SCWG technology is not yet ready for industrial application [78]. This is due the fact that this process still faces some major technical challenges. One of the challenges is related to the capability to pump wet biomass in the system. Clogging problems may occur if the dry matter content of the wet biomass is too high. High dry matter content, however, is desired as this could increase the amount of gaseous product that affect the operational performance of the plant. As the process takes places at severe operating conditions, corrosion of the reactor material is another important challenge. This aspect could be a major problem for scaling up of the system, as the capital costs to use a high corrosion resistant material will be significant. Applying an anti-corrosion liner would be possible if the SCWG occurs at lower temperature (e.g. 400 °C). This, however, could lead to a low level of biomass conversion. Related to the scaling up of the system, an additional challenge would be to maintain a sufficiently high thermal efficiency of the process. The system should strive for a high thermal efficiency value as the feasibility of the gasification plant is dependent on its thermal efficiency.

Another important challenge for this technology would be the salt precipitation due to its low solubility in a SCW. These precipitated salts may stick to the reactor wall and thus plug the reactor, which is harmful from a practical point of view. Char deposition is another major challenge related to

the accumulated char formation as has been stated earlier. Char that is formed during the gasification process tends to deposit on the inner wall of the reactor [79] and might cause reactor plugging [64]. Char formation also represents a loss of useful carbon, reducing the overall process efficiency. The char formation is thus a major concern regarding SCWG process and it is investigated here in details with the help of numerical modelling.

1.5 RESEARCH OBJECTIVES

The work presented in this thesis has been supported by the AgentschapNL (RVO) TKI and is part of the Scarlet+ project. The main focus of this research is related to one of the major challenges of the SCWG technology, the char formation during the gasification process. As has been mentioned earlier, the produced char deposition might plug the reactor, which is harmful from a practical point of view [64]. Based on available literature research, a proposition was made that the unwanted char formation can be minimized through a fast heat-up of the feedstock [80, 81]. To increase the heating rate and reduce the char formation, a new system with direct injection has been developed. This system works by injecting the relatively cold biomass stream into a pre-heated supercritical water stream, and thus reduces the residence time during of the heat-up process. A process scheme of this direct injection SCWG system is shown in Figure 1.5.

Figure 1.5 (A) Simple schematic of a continuous SCWG process with injection system

The main objective of this thesis is to gain a deeper insight in the processes and key factors that have impact on char formation when fast heating-up of

biomass is implemented via direct injection of wet biomass in supercritical water. To get a better understanding, the effect of heat and mass transfer, as well as the reaction mechanism, and key parameters such as the reactor temperature are investigated in detail. Furthermore, the impact of this novel approach of direct biomass injection on the overall energy efficiency of the system is also studied. The following research questions are formulated:

1. What are the key parameters with respect to the energy efficiency of the novel direct injection system?
2. What are the main processes and key parameters that control the char formation during the gasification process?
3. What is the effect of scaling up of the direct injection system on the char formation process?

1.6 THESIS OUTLINE.

The research content of this thesis has been divided into four chapters followed by a final chapter containing conclusions and recommendations.

Chapter 2 describes an energy analysis of the direct injection system compared to the conventional system. The analysis was done using a flowsheet tool for both model compounds and real wet organics (imitated using lumped compound approach). A design based on pinch analysis and an optimum operating window for this system is proposed.

Chapter 3 discusses a CFD model developed for glycerol gasification in SCW. Flow patterns during the gasification are analyzed and the influence of parameters such as gravity and the flowrate ratio of biomass and water are investigated.

Chapter 4 is related to a CFD model for glucose gasification in SCW. This model describes the production of gas and char compounds using a simplified scheme. Several parameters related to char formation are investigated and the influence of a reactor scale up is explore shortly.

Chapter 5 presents a discrete phase CFD model for gasification of glucose droplets in SCW with a more detailed gasification scheme. Examination of several injector designs for a pilot scale application is conducted.

In chapter 6, conclusions and recommendations are formulated.

It has to be mentioned that the research chapters of this thesis (i.e. Chapters 2 – 5), are already or are in the process of being published in scientific journals. There might be some minor changes within the introduction and methodology sections of these chapters to avoid repetition.

CHAPTER 2

AN ENERGY ANALYSIS ON GASIFICATION OF SEWAGE

SLUDGE BY A DIRECT INJECTION IN SUPERCRITICAL WATER

Abstract

Supercritical Water Gasification is an efficient technology in converting wet biomass into H₂ and CH₄ in comparison to other conventional thermochemical processes. Char deposition, however, remains a major challenges in this technology. Char formation is the result of polymerization reactions that take place at sub-critical conditions. Directly injecting the relatively unheated wet biomass feed into supercritical water increases the heating rate and reduces the residence time of the feed in the sub-critical condition. This leads to a minimized char formation in the process. However, a non-isothermal mixing takes place during this direct injection that is less energy-efficient. In addition, the biomass feed stream experiences less pre-heating that means less heat recovery from the product gas. These two aspects might reduce the overall process performance. Parametric studies of key operating parameters, such as operating temperature, dry matter content, bypass water ratio and heat exchanger effectiveness, are carried out to investigate the influence of direct injection to the thermal efficiency of the system. Subsequently, optimization using pinch analysis is conducted to the system with direct injection. Finally, an operating window for optimum performance of the optimized direct injection gasification system is proposed.

The work presented in this chapter has been published in:

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2.1 INTRODUCTION

A substantial part of biomass available worldwide is not suitable for common conversion processes as it contains over 80 wt-% of water. SCWG is considered to be the most efficient technology to process this type of wet biomass [82]. Utilization this technology offers a promising solution to solve the challenges related to both energy demand and overflowing waste streams in the coming years. In spite of its attractive potentials, this technology still has a difficulty to find a place in the industrial market. This is due to several number of challenges that kept being addressed in the last couple of years [4]. Example of such challenges would be the char formation and overall thermal efficiency of the process.

The focus of this research is to offer a solution for the char formation, and its influence to the thermal efficiency of the system. Char that is formed during the gasification process tends to deposit on the inner wall of the reactor [79]. This char deposition might cause reactor plugging which is harmful from a practical point of view [64]. Chuntanapum and Matsumura [83] experience this in their reactor when investigating the gasification of 5-hydroxymethylfurfural. Chuntanapum and Matsumura [67] then observe that char is only formed at subcritical conditions due to the polymerization of reaction intermediates. It is also observed that there are few successful studies on gasification of wet biomass at moderate temperature (400°C – 450°C) [84]. Zöhrer et al. [81] then state that a fast heat-up of the wet biomass can minimize the unwanted char formation. A fast heating rate can be achieved by injecting a partially heated wet biomass feed directly into hot supercritical water.

The main objective of this research is to investigate and to optimize the performance of a SCWG system that employs a Direct Injection (DI) approach. A system model will be used to analyze the system performance. This research is a follow-up of previous work by Yukananto et al.[85] that investigate an ideal case flow process. The current study considers two types of processes that are based on VERENA pilot plant in Germany, the Reference Premixed (RP) system [86] and the DI system [87]. The RP system makes use of premixed biomass and water (both at room temperature) as its feed stream [88, 89]. This mixed stream is preheated using product gas before it enters the reactor. The DI system uses wet biomass and water as its feed streams. The water stream is heated up to its supercritical condition (approximately 420 °C and 25 MPa) using the product gas, and is

subsequently mixed with a partially heated wet biomass stream to reduce char formation.

The DI system experiences a non-isothermal mixing process which is known to reduce the energy efficiency of the system [90]. In addition to this, partial heating up of wet biomass in the DI system also increases the amount of residual heat in the product gas, which will significantly reduce the energy efficiency in comparison to the RP system. Bendig et al. [91] define waste heat into two types: a) avoidable waste heat; b) residual heat. Residual heat is any type of heat that should be released to the ambient condition using a cold utility (cooler). These two aspects make it important to study the influence of utilizing the DI system on the overall system performance. Furthermore, the flow process of the DI system should be optimized to enhance its performance. Several key operating parameters that give insights in this investigation are:

- i) Operating temperature;
- ii) Feed concentration (Dry Matter Content, DMC), which represents the total weight percentage of biomass in the system;
- iii) Bypass Water Ratio (BWR), which represents the ratio of bypass water to the total reactor feed steam;
- iv) Heat Exchanger (HE) effectiveness.

The following sections first present the methodology used to develop both RP and DI models using the flowsheet program UniSIM. After that, performance differences when utilizing glycerol and sewage sludge in the RP system are described. Next, the effect of utilizing the DI system and several of its key operating parameters are studied. Subsequently, optimization of the system using pinch analysis is introduced. This optimization is conducted based on the operating conditions of the DI system in the VERENA pilot plant [87]. Finally, an operating window to achieve the highest performance for the optimized DI system is proposed.

2.2 METHODOLOGY

This sections describes the tools and assumptions that are used to developed the model. The indicator that is used to determine the performance of the system is defined. Afterward, both the RP system and DI system are explained thoroughly. In addition to this, limitations of the system and the analyzed feedstocks are discussed

2.2.1 TOOLS AND ASSUMPTIONS

The system model for the SCWG process is developed using UniSIM. In this model, chemical equilibrium is assumed, as there is a lack of information on kinetics and reaction mechanisms for the lumped compounds used to imitate the sewage sludge. Minimization of Gibbs free energy is used and therefore the calculation is made based on the maximum possible theoretical yield [8, 92]. It should be taken into account that this may lead to an overestimation of the system's performance. This results, however, can be used to predict thermodynamic limits as a guide for evaluation and improvement of a process design [92, 93]. Furthermore, throughout the process, constant pressure is assumed. This is deemed reasonable as it is observed that pressure variations in the SCWG process are less significant for the gas yield compared to e.g. the effect of the temperature [94]. Adiabatic conditions are also assumed throughout the process. Due to the low concentrations of other gas components, only H₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆ are taken into account [95]. Finally, the separation of H₂ and CH₄ with the rest of the components is done at atmospheric temperature.

2.2.2 PERFORMANCE INDICATORS

Bendig et al. [90] describe several performance indicators that are commonly used, which are: a) Energy content indicator (thermal efficiency); b) Exergy content indicator; c) Thermal pinch (pinch analysis); d) Water pinch. Exergy indicator and water pinch are not in the scope of the investigation and will not be reviewed.

Figure 2.1-A and B show the process flowsheets of the RP and DI system. In these flowsheets the thermal efficiency is described as energy produced by the process (H₂ and CH₄ gas) minus the energy consumptions within the system, divided by the energy input [96]. The remaining burnable species (e.g. CO) are not included in the calculation as their energy contents are insignificant in comparison to either H₂ or CH₄ (e.g. CO contributes to less than 2% of the total energy). The fuel required by the methane burner is one of the energy consumptions within the system. The other energy consumption is the pump's duty, which is usually low as water is an incompressible substance. The energy input is the Low Heating Value (LHV) of the provided feed. Accordingly, the thermal efficiency (η) of the system is defined as follows:

$$\eta = \frac{(LHV_{H_2} \times \dot{m}_{prod,H_2}) + (LHV_{CH_4} \times \dot{m}_{prod,CH_4}) - Q_{pump} - (LHV_{CH_4} \times \dot{m}_{burner,CH_4})}{(LHV_{biomass} \times \dot{m}_{biomass})} \quad \text{Eq 2.1}$$

With $\dot{m}$ representing mass flow rate (m/kg). The amount of produced gases that is used in Eq 2.1 is obtained from the “*cold product*” stream in accordance to Figure 2.1-A. The fuel requirement for the burner is largely influenced by the heat recovery within the system. Therefore, HE effectiveness for recovering heat plays an important role in determining the thermal efficiency of the system. The HE effectiveness is defined as the ratio of the actual heat transferred by the HE and the maximum heat that could possibly be transferred from one stream to the other [88]. During the SCWG process, the specific heat capacity of water can change dramatically. Therefore, it is preferable to calculate the effectiveness of the HE using the enthalpy method, as follows:

$$\varepsilon = q/q_{max} = \frac{(\dot{m} \times h)_{cold,out} - (\dot{m} \times h)_{cold,in}}{(\dot{m} \times h)_{hot,in} - (\dot{m} \times h)_{cold,in}} \quad \text{Eq 2.2}$$

With q representing heat flow (kW) and h representing specific enthalpy (kJ/kg). Pinch analysis is a technique to improve the performance of a system by increasing the process to process heat exchanges. There are three important points that should be followed when optimizing the system: a) heat transfer across the pinch point should not take place; b) no hot utility should be used below the pinch point; c) no cold utility should be used above the pinch point. Related to this, Bendig et al. mention several methods that are generally used to enhance the energy usage in a process system. These methods are: internal heat recovery; water reutilization; elimination of non-isothermal mixing; condensate recovery; energy conversion and energy upgrading using a heat pump. Methodologies such as grand composite curve or the shifted combine composite curves can be used to visualize the target of the optimization [91].

2.2.3 CHOICE OF PROPERTY METHOD

SCWG usually takes place at a temperature of 400 – 650 °C and a pressure above 22.4 MPa. At such a high pressure, ideal gas assumptions can no longer be used to describe its thermodynamic and transport properties as the real gas behavior deviates significantly. In addition to this, chemical equilibrium assumptions are highly dependent of the fugacity (effective partial pressure)

value of the mixture. Therefore, it is important to select the best method to approximate the values of these properties accurately.

The Equation of State (EoS) is a common method to approximate the above mentioned properties. Valderrama mentions that Soave Redlich-Kwong (SRK), Peng-Robinson (PR) and Patel-Teja-Valderrama (VPT) cubic EoS provide a good approximation for high pressure processes between polar and non-polar mixtures [97]. Subsequently, mixing rules have to be used in order to relate the EoS parameters of each component in the mixture. Valderrama also states that mixing rules such as Van der Waals, Wong-Sadler or Panagiotopoulos-Reid, can be used, but those that are proposed by Soave and Twu give better results for calculations in the supercritical region [97]. In this research, the SRK with the Twu mixing rule (SRK-Twu) is selected. This method is already tested and the results are similar in comparison to other work related to SCWG process modelling [88].

2.2.4 PROCESS FLOW MODELLING

2.2.4.1 PROCESS FLOWSHEET

Two different flow processes are described in this subsection. The RP configuration can be categorized into 5 different stages, shown in Figure 2.1-A. In the first stage the DMC of the overall feed stream is regulated by mixing a specified amount of water with biomass. Then the “*initial stream*” is brought to its operating pressure. Subsequently, the “*high pressure feed*” is sent to the HE so that it can recover some heat from the hot “*product*” gases to reduce the residual heat. The “*heated feed*” has already reached supercritical state when it exits the HE.

Afterwards, the “*heated feed*” is preheated even further and is then supplied to the reactor where the gasification reaction occurs. Both the heat required for the preheating and for the reactor originate from the hot “*exhaust gas*” from a methane burner. The Gibbs reactor employs an infinite residence time for the incoming feed stream. The energy in the hot “*product gas*” is recovered in the HE to preheat the “*high pressure feed*”. Separation of CH₄ and H₂ from the water-CO₂ mixture can easier be performed at ambient temperature, therefore a cold utility is used to cool down the “*product gas*” to the “*cold product*”. The water-CO₂ mixture is then expanded to ambient pressure and is further separated into CO₂-rich gas and tail water. Tail water might be recycled back into the system or might need further mineral processing.

The DI configuration is designed so that the biomass compound can be injected directly into hot supercritical water to experience a fast heat-up that leads to a reduction of char formation. Figure 2.1-B presents the flowsheet of this DI system. The DI system differs from the RP system because of the existence of a mechanical separator at the start of the process, and different locations of HEs to recover heat from the hot “*product gas*”. The overall DMC in the system is regulated by mixing the biomass compound with water. The “*temporary mixture*” enters the mechanical separator that separates the mixture into: i) “*concentrated biomass*” that consists of hot biomass compound and water; ii) “*bypass water*” which is purely water. This step is performed to accommodate an easier comparison between feed flowrate and concentration in reference to the RP system. Both of these streams are then pressurized to the operating pressure.

Subsequently, the “*HP bypass water*” is then heated to its supercritical state by sending it to a HE to recover some heat from the hot “*product gases*”. In addition to that, this “*supercritical water*” stream is heated up further using the hot exhaust gas from the methane burner. The “*HP concentrated biomass*” is also preheated to just below the critical point by using the “*warm product gas I*”. These two streams are mixed together and are then referred to as “*reactor feed*”. This mixing is carried out to achieve a fast heat-up of preheated injected-biomass (“*heated HP concentrated biomass*”). In doing so, injected biomass will have a shorter residence time in the near-critical region, which is presumed to reduce char formation. This “*reactor feed*” that enters the reactor is heated up to its operating temperature and the gasification process will then occur. The hot “*product gas*” leaves the reactor into the two HEs. The “*product gas*” is then cooled down and is separated in the same way as done in the RP system.

2.2.4.2 DIRECT INJECTION SYSTEM LIMITATION

The RP system is modified into the DI system to minimize char formation that might lead to plugging. In his investigation, Knezevic et al. observe that both decomposition and char formation already occur at 250 °C. The rate of these reactions, however, are still low at this temperature as this is implied by the low conversion rate of glucose itself [79].

Chuntanapum and Matsumura show that the kinetics of char formation increases intensively at 300-370 °C, and reduce dramatically at temperatures higher than 400 °C [67]. It is also found that char formation kinetics at 300 °C is comparable to the kinetics of gas formation. Taking this into

consideration, the “*heated HP concentrated biomass*” temperature in this model is chosen to not exceed 300 °C and be limited to 280 °C as a safety measure.

Zöhrer et al. also state that a fast heat-up of the wet biomass can minimize the unwanted char formation [81]. Chuntanapum and Matsumura observes that the char formation rate is reduced dramatically above the critical point [67]. Therefore, the temperature of the resulting mixture from the “*heated HP concentrated biomass*” and the “*heated SCW*”, which is referred to as “*reactor feed*”, should exceed 375 °C. Finally, it is assumed that the pinch temperature in the HEs is 15 °C. The pinch temperature is the minimum temperature difference in a HE, and the location at which this takes place is referred to as the pinch point.

Related to the pumping capability of wet biomass (slurry), Yakaboylu et al. state that in a laboratory environment, it is possible to pump wet biomass of up to 40 wt-% dry matter content [4]. Stolten et al. state that depending on the type of wet biomass, only biomass that has up to 20 wt-% dry matter content is pumpable [98]. This statement is also supported with a demonstration by the pilot plant in Verena [87]. The pinch based optimization should take these information into consideration.

Figure 2.1 (A) Reference Premixed [RP] system flowsheet, (B) Direct Injection [DI] system flowsheet

2.2.4.3 ANALYZED FEEDSTOCK

In the present research firstly a simple model compound in the RP configuration will be used to represent the wet organic compound. Afterwards, a real wet organic compound is simulated using the lumped component approach. The molecular formula that is chosen for sewage sludge

is $\text{CH}_{1.498}\text{O}_{0.413}$ with an HHV of 22.4 MJ/kg [99]. The amount of C-H-O molecules is the most important factor to be considered when implementing the Gibbs reactor. The molecular formula of sewage sludge is obtained by mixing acetic acid, diketene, propanone and benzene with various proportions. The surrogate weight percentages of each compound are 30, 45, 15 and 10, respectively. These compounds are used since they are possible compounds found in real sewage sludge. Differences of the other thermodynamic properties due to utilizing these compounds are assumed to be negligible.

2.3 SYSTEM PERFORMANCE: PARAMETRIC INVESTIGATIONS

This section presents the performance differences when utilizing two different biomass feeds. Next, the influence of directly injecting the relatively cold biomass into supercritical water to the system's performance is investigated. Subsequently, the influence of key operating parameters to the performance of the DI system is looked into. Finally, an optimum operating window for the DI system is proposed.

2.3.1 THERMAL EFFICIENCY OF REAL AND MODEL COMPOUNDS

Two different compounds (glycerol and sewage sludge) are used with RP operating at 575°C and 25MPa. A comparison of thermal efficiency of these two compounds with varying DMC is presented in Figure 2.2-A. Increasing the DMC leads to an increase in thermal efficiency for both glycerol and sewage sludge. It can also be seen that usage of glycerol leads to a system with a lower efficiency. Approximately 19% difference of thermal efficiency can be seen at 8 wt-% DMC, and approximately 5% difference at 20 wt-% DMC.

The difference in thermal efficiency occurs due to the fact that glycerol produces a significantly lower amount of CH_4 and slightly less H_2 in comparison to sewage sludge. Glycerol, having a 4.54 C:H ratio, is theoretically expected to produce more CH_4 and H_2 in comparison to sewage sludge that has a C:H ratio of 7.9. However, Louw stated that oxygen content significantly affects the yield when a feedstock's C:H ratio is lower than 10 [100]. Accordingly, glycerol, which has an oxygen content higher than 50 wt-%, produces less yield in comparison to sewage sludge, which has an oxygen

content of approximately 30 wt-%. A prediction of the maximum yield can be used as a guideline to improve the process design. Therefore, all of the subsequent cases are investigated using sewage sludge as a feedstock.

2.3.2 EFFECT OF DIRECT INJECTION

Non-isothermal mixing and partial heating of “concentrated biomass” stream are expected to reduce the thermal efficiency of the system. The thermal efficiency comparison of the RP and DI systems, at 575 °C, 25 MPa and 0.4 BWR, is visualized in Figure 2.2-B. BWR represents the ratio of “bypass water” to the “reactor feed” in Figure 2.1-B. Both systems operate with a maximum HE effectiveness, which represents the highest realizable effectiveness while maintaining 15 °C difference in the HE. This value can be different in every system, depending on the mass flowrate in the HE.

Figure 2.2-B shows that at 8 wt-% DMC, the thermal efficiency of the DI system reduces by approximately 23% points compared to the RP system. When it is operated at 20 wt-% DMC, the difference in thermal efficiency is approximately 10% points. These are directly related to the fact that the DI system operates with several limitations mentioned in subsection 2.2.4.2. (e.g. the maximum biomass preheating temperature of 280 °C). These limitations cause the non-optimal heat transfer configuration in the system, which leads to a reduction of the thermal efficiency. Aside from that, the non-isothermal mixing process that is introduced in the DI system also reduces the thermal efficiency of the system.

The reduction of thermal efficiency is less significant when a higher DMC is used. With an equal BWR, a higher DMC leads to lower amounts of water in the “heated HP concentrated biomass”. This reduces the energy required by the reactor and hence the fuel consumption for the methane burner. The following subsection will investigate in more detail the key operating parameters that cause this reduction of thermal efficiency.

Figure 2.2 (A-B) Thermal efficiency comparison at 575 °C, 25 MPa. (A) RP system using glycerol and sewage sludge, (B) RP and DI system using sewage sludge.

2.3.3 EFFECT OF KEY OPERATING PARAMETERS IN THE DI SYSTEM

Several key operating parameters have been investigated: temperature, DMC, BWR and HE effectiveness. The requirements that are mentioned in subsection 2.2.4.2. have to be satisfied for every variation of these key parameters. The proposed optimum operating window for the DI system is made based on these results.

The first key parameter is the reactor operating temperature. The investigation is done at 12 wt-% DMC, 25 MPa, and a BRW of 0.4. The influence of operating temperature on the thermal efficiency at constant HE effectiveness is illustrated in Figure 2.3-A. Figure 2.3-A. also indicates the influence of the operating temperature on the “*reactor feed*”, which has to be above 375 °C.

It can be seen that the thermal efficiency of the system reduces as the operating temperature increases. This reduction of efficiency is caused by the increase of residual heat in the “*warm product gas*” and “*cooled exhaust gas*”. Figure 2.3-B. demonstrates the effect of operating temperature on the amount of residual heat and the gas yield in the product gas stream. Even though the H₂ yield increases with operating temperature, its energy contribution is less than the energy loss by residual heat and reduction of CH₄ produced in the product gas.

Figure 2.3-A also shows that operating with reactor temperatures below 650 °C will lead to a reactor feed temperature of less than 375 °C. Figure 2.3-C shows the reactor feed temperature at maximum HE effectiveness. Figure 2.3-C illustrates that the requirement mentioned in subsection 2.2.4.2 is

satisfied when operating at a temperature higher than 575 °C. The sharp increase at the beginning of Figure 2.3-C occurs due to the limited amount of thermal energy in the product gas at a temperature of 450 °C to transform “*HP bypass water*” into its supercritical state. This changes the pinch point location to the center of “*HE I*”, and thus the outlet temperature of the SCW is far below the inlet temperature of the hot product gas. This results in a lower reactor feed temperature after mixing of the SCW stream and the injected-feed stream. In contrast to what is taking place at 450 °C, the pinch point location at higher operating temperature (e.g. at 600 °C) is located near the outlet of “*HE I*”. These pinch point locations inside “*HE I*” with different operating temperatures are shown in Figure 2.3-D.

The second key parameter is the DMC. Figure 2.4-A presents the thermal efficiency of the DI system for various DMCs. The DI system is operating at 575 °C and 25 MPa at constant HE effectiveness, and has a BWR of 0.4. It can be seen that the increase of thermal efficiency (inclination) is higher at a DMC below 14 wt-% in comparison to the gradient at a DMC above 14 wt-%. The curve going flatter with the increase of DMC means that the increase of this parameter is less significant at higher value. At a DMC-range of 8 ~ 14 wt-%, any increase in feed concentration will increase both the methane and hydrogen yield in the product gas stream. When the system operates at a DMC of 14 ~ 20 wt-%, any increase in feed concentration will increase the methane yield and decrease the hydrogen yield. This can be seen in Figure 2.4-B. The changes in the (cooled) product gas temperature are not significant enough to affect the overall thermal efficiency.

Figure 2.3 (A-C) Influence of operating temperature for DI system using sewage sludge at 12 wt-% DMC, 25 MPa and 0.4 BWR. (A) Influence on thermal efficiency and reactor feed temperature at constant HE effectiveness. (B) Influence on waste gas temperature and H₂ yield at constant HE effectiveness. (C) Reactor feed temperature at maximum HE effectiveness. (D) Pinch point locations inside “HE 1” at various operating temperatures.

The third key parameter is the BWR. The investigation is conducted at 575 °C, 25 MPa and 12 wt-% DMC. Influence of the BWR on the thermal efficiency, reactor feed temperature and waste gas temperature is displayed in Figure 2.4-C. It can be seen that the increase of this ratio results in a significant increase of the thermal efficiency. An increase of this ratio physically means that the system delivers a higher bypass water flowrate in comparison to the injected feed flowrate. This makes it possible for “HE 1” to recover more heat from the hot product gases, and in turn leads to a decrease of the residual heat in the cooled product gas and less fuel consumption in the burner.

A higher flowrate of hot bypass water (“heated SCW”) means that the stream contains more sensible energy. Mixing of this stream with the “heated

HP concentrated biomass” will increase the sensible energy in the reactor feed. This leads to a decrease of the required energy by the reactor to reach the designed operating temperature. These two reasons lead to the steep increase of thermal efficiency.

Figure 2.4 (A-B) Influence of DMC on DI system using sewage sludge at 575°C, 25 MPa and 0.4 BWR. (A) Influence on thermal efficiency. (B) Influence on H_2 and CH_4 yield. (C) Influence of BWR on DI system using sewage sludge at 12 wt.-%, 575°C and 25 MPa. (D) Influence of BWR [575 °C] and operating temperature [0.4 BWR] on HEs effectiveness using sewage sludge at 12 wt.-% and 25 MPa.

The slope of the graph, however, changes after it reaches a BWR of 0.5. As the BWR is further increased, the “*HP bypass water*” stream requires more heat to achieve its supercritical state. This leads to the relocation of pinch point to the center of the “*HE 1*”, similar to what is described in Figure 2.3-D. This reduces the temperature of the “*heated SCW*” and also the “*heated HP concentrated biomass*” stream, which leads to a less significant increase in thermal efficiency, as demonstrated in the graph. It also has to be considered that increasing the BWR means that the amount of DMC in the

pumped slurry is increased. Taking into account that pumpability of the wet biomass is a challenge by itself, it is advisable not to use a high BWR.

The fourth key parameter is the effectiveness of “*HE 1*” and “*HE 2*”. It has been mentioned above that the “reactor feed” temperature and the “*warm product gas 2*” temperature have a significant effect on the thermal efficiency of the system. Subsequently, these two variables are changing dramatically with the variation of operating temperature and BWR. Figure 2.4-D visualizes the maximum effectiveness of “*HE 1*” and “*HE 2*”, as a function of these two variables. This system is operated at: a) 575 °C, 25 MPa and with 12 wt-% DMC; b) 0.4 BWR, 25 MPa, and with 12 wt-% DMC.

Effectiveness of both HEs are below 60% at any BWR value. The effectiveness of “*HE 1*” increases along with the increase of the BWR, whereas the effectiveness of “*HE 2*” remains almost constant until a BWR of 0.5 and then it decreases. The effectiveness of “*HE 1*” increases significantly because it is able to recover more sensible energy due to its higher flowrate. As the BWR increases, the outlet temperature of hot gas at “*HE 1*” decreases even further. At a BWR of 0.5, this temperature approaches the designed preheated-injected feed temperature (280 °C). To maintain the 15 °C pinch, “*HE 2*” is not able to recover any more heat, which in effect reduces its effectiveness.

At operating temperature higher than 450 °C, the HE effectiveness reduces along with the increase of operating temperature. The decrease of effectiveness of “*HE 2*” is due to the fact that the “*warm product gas 1*” still contains a significant amount of heat, while the “HP concentrated biomass” is only allowed to be heated up to 280 °C. The low value of the HE effectiveness means that the location of heat transfer is not optimal for the DI system. This phenomenon reduces the thermal efficiency of the system dramatically. Therefore, it is suggested to target the optimal heat transfer using the Heat Exchanger Network (HEN) configuration approach. HEN is a visual representation of the overall heat transfer of both hot and cold streams in a system, and can be used for energy integration analysis.

2.3.4 PROPOSED OPERATING WINDOW

Based on the analysis shown above, an operating window that takes into account the process limitations is proposed. Figure 2.3-C shows that the minimum operating temperature to satisfy the supercritical reactor-feed after non-isothermal mixing is 570 °C. It is also shown that any further increase of the operating temperature will only result in a lower thermal efficiency.

Figure 2.4-D shows that the slope of the “*HE 1*” effectiveness reduction is getting steeper at operating temperatures above 600 °C. It also shows that the gradient of the “*HE 2*” effectiveness is constant at temperatures above 500 °C. Therefore, the system is suggested to operate between reactor temperatures of 570-600 °C.

Figure 2.4-A shows that it is best to operate with DMC below 14 wt-%. Increasing the DMC will further increase the thermal efficiency, however, this alters the trend of the inclination of the upward curve. It has to be noted that this value is also limited by external factors such as pumpability. Figure 2.4-C shows that the rate of increase of the thermal efficiency of the system is the highest at a BWR of 0.4 - 0.5. A less significant increase of thermal efficiency can be obtained when increasing the BWR further.

2.4 SYSTEM OPTIMIZATION: PINCH BASED DESIGN

This section puts forward the optimization of the DI system based on the pinch analysis. It starts with the determination of the operating conditions that are used for the case study. Then the optimization is conducted using the HEN design method. Finally the performance of the optimized DI system is compared to the DI and RP system, and an operating window for this optimized system is proposed.

2.4.1 TARGETING BY PINCH ANALYSIS

The main objective of this analysis is to optimize the system by increasing the process to process heat transfer capacity to reduce the residual heat. As was stated in 3.4., it is suggested to operate the system with operating temperature of 570-600 °C, and with a BWR of 0.4 ~ 0.5. Pinch analysis is then conducted to a system that operates at 575 °C with 0.4 BWR. A large increase of the thermal efficiency is obtained when increasing the BWR up to 0.6 and therefore this condition is also analyzed for optimization. The DMC for both analyses is set to be 12 wt-%. A total flowrate of 100 kg/hour, which corresponds to the VERENA pilot plant configuration [87], is used.

Figure 2.5-A presents the combined composite curves when the DI system operates with a BRW of 0.4. A combined composite curves is a tool that visualizes heat availability and demand for both hot and cold stream in a system. In a combined composite curves graph, the area in between the curves represents the possible amount of heat that can be recovered. The cold pinch of the system is found to be located at the temperature of 365°C. A steep

increase in the cold composite curve can be seen in the range of 280–365 °C, after which the slope comes closer to the original trend goes quite flat. This steep increase shows that the injected feed is only preheated up to a temperature of 280 °C. The trend above 360 °C exhibits the high variation of specific heat of water when it transforms into its supercritical state. The slope of the graph goes flat at a temperature above 376 °C. This shows that there is an increase of heat flow demand to heat up the cold flow, which emerges from the reactor feed stream after mixing.

Figure 2.5 (A & C) Shifted combined composite curves of DI system using sewage sludge at 12 wt-% DMC, 575 °C and 25. (A) With 0.4 BWR. (C) With 0.6 BWR. (B & D) Heat exchanger network design for system using sewage sludge at 12 wt-% DMC, 575 °C and 25. (B) With 0.4 BWR. (D) With 0.6 BWR

Pinch optimization is done by considering guidelines and methods mentioned in subchapter 2.2. Figure 2.5-B displays the HEN design of the optimized system. The dashed line in the figure represents the hot stream and the solid lines represent the cold stream. The hot stream above its pinch transfers 23.5 kW of its heat to let cold stream 1 (pure water stream) reach a

temperature of 378 °C and thus become supercritical. The remaining 18.7 kW of heat is used to heat up cold stream 3 (reactor feed stream). The hot stream 2 (burner's exhaust gas) provides 9.05 kW of heat to supply the reactor's heat duty. Aside from that, 18.88 kW of its heat is also used to superheat the cold stream 1 until it reaches the temperature of 720 °C. The reactor feed stream is obtained by mixing the pure water stream and cold stream 2 (cold injected feed). The hot stream below the pinch transfers a total of 33.7 kW of heat to preheat both the cold pure water stream and the cold injected feed. The hot stream is split to match the heat flow requirement from the cold streams. In addition to this, 3.9 kW of the heat required by the cold stream below the pinch is extracted from the hot stream 2. In this way, no hot utility is necessary to heat up the cold stream. Cold utility is used to release the heat from the hot stream until its ambient condition. The hot stream is then sent to the separator.

A different configuration for the system that operates at 575 °C with a BWR of 0.6 is found. Figure 2.5-C presents the combined composite curves for the DI system with these operating conditions. The cold pinch of the system is found to be located at a temperature of 350°C. Figure 2.5-C demonstrates a less steep increase in the cold composite curve in the range of 280 °C ~ 365 °C, in comparison to Figure 2.5-A. This is due to a larger amount of heat flow requirement to heat up the pure water stream, which has higher flowrate. In the range of 376 °C ~ 392 °C, a sharper increase in the cold composite can be seen in Figure 2.5-C in comparison to Figure 2.5-A. Less heat flow requirement in that range occurs because the reactor feed after mixing has a temperature of 392 °C. This behavior relocates the cold pinch location in comparison to the previous operating conditions.

The optimized HEN design for this operating condition at a BWR of 0.6 is visualized in Figure 2.5-D. It can be seen that the hot stream above its pinch releases all of its energy to form the supercritical water up to a temperature of 492 °C. The reactor feed stream is heated up to its operating temperature using purely energy provided by hot stream 2 (burner's exhaust gas). The heat recovery below the pinch is treated similarly to the previous situation at a BWR of 0.4. Different split ratio in the hot stream is used to conform with the heat demands from cold stream 1 and 2.

2.4.2 OPTIMIZED FLOW PROCESS

Both of the designs presented in Figure 2.5-B and Figure 2.5-D are tested in accordance to their operating conditions. Figure 2.6 presents the result of the optimization with respect to the thermal efficiency of the system that

operates with 8 wt-% feed at a 0.4 and a 0.6 BWR, which are referred to as case (1) and case (2) respectively. Figure 2.6 also shows the result for the system that operates with 12 wt-% at a 0.4 and a 0.6 BWR, which are referred to as case (3) and case (4) from further on.

It can be seen that in case (1), the DI system suffers an efficiency loss of 21% points in comparison to the RP. This efficiency reduction can be decreased to 12% points with a higher DMC as can be seen in case (3). After the pinch analysis is applied, the efficiency decrease changes to 12% and 5% points for case (1) and case (3), respectively. The reduction in efficiency is not significant when the system operates with 0.6 BWR. The DI system in case (2) experiences an efficiency reduction of 6% points in comparison to the RP. After it is optimized, the difference in efficiency is reduced to 4% points. The effect of pinch optimization is even less pronounced at higher DMC. This slight effect of the pinch optimization can be explained due to the fact that the efficiency reduction of the DI in comparison to the RP is not that large at all. Therefore, pinch optimization could not play a big role in this condition.

However, as mentioned in subsection 2.2.4.2, it should be noted that the maximum DMC a system can handle because of the pumpability is around 20 wt-%. It means that the amount of biomass in the injected-feed stream should be at most 20 wt-%. The 20 wt-% pumped biomass in the injected-feed stream corresponds to case (3) (a wt-% DMC with a 0.4 BRW) or case (2) (an 8 wt-% DMC with a 0.6 RBW). This means that the optimized system that operates at a 0.4 BWR has a 50 % efficiency and the system that operates at a 0.6 BWR can only achieve 28 % efficiency. This value can be found in case (2) and case (3) in Figure 2.6. Taking this into consideration it is suggested to operate in accordance to the optimized system that uses a 0.4 BWR.

It should also be noted that Figure 2.5-B and D suggest that the product gas temperature is still higher than 250 °C. There are a lot of potential applications for this residual heat, such as process heating for paper industry, district heating or for heat supply of an organic Rankine cycle system. The influence of combining any of these options with the SCWG technology to improve the utilization factor for the process will be dealt in future studies.

Figure 2.6 (Case 1-4) Thermal efficiency comparison for system using sewage sludge at 575 °C and 25 MPa. (Case 1) With 8 wt-% DMC and 0.4 BWR. (Case 2) With 8 wt-% DMC and 0.6 BWR. (Case 3) With 12 wt-% DMC and 0.4 BWR. (Case 4) With 12 wt-% DMC and 0.6 BWR.

2.5 CONCLUSION

Implementing a direct injection system at reactor conditions of 575 °C and 25 MPa, a 0.4 bypass water ratio and an equal total dry matter content decreases the efficiency by approximately 8% ~ 23% points, in comparison to the reference system with only premixed biomass. Direct injection system has to operate at a temperature above 570 °C to minimize char formation. In order to avoid unnecessary loss of thermal efficiency and heat exchanger effectiveness, the upper limit of the operating temperature should be 600 °C.

The ratio of bypass water to feed mixture should be around 0.4-0.5 in order to have the most efficient system. The inclination of the upward curve is going flatter with further increase of this ratio.

An increase of the thermal efficiency is obtained after the implementation of the pinch analysis result at 575 °C and 25MPa. In case the system operates at a 0.4 bypass ratio, an improvement of thermal efficiency from 9.8% to 22% for a total of 8 wt-% and from 41% to 50% for a total of 12 wt-% dry matter content, are possible. When the system operates at a 0.6 bypass ratio, a very slight improvement in thermal efficiency is obtained. Literature states that currently pump can pumped a feed stream with a maximum of 20 wt-% dry matter content. If the direct injection system operates at 0.4 bypass ratio, then 12 wt-% dry matter content in the total feed stream is divided and a stream with 20 wt-% dry matter content will be pumped. The 12 wt-% value is translated into 8 wt-% dry matter content in the total feed stream if the direct injection system operates at a 0.6 bypass ratio. Taking this into consideration, it is more beneficial to operate with a bypass water ratio of 0.4 with a total feed concentration of 8-12 wt-%.

CHAPTER 3

COMPUTATIONAL FLUID DYNAMIC MODEL FOR GLYCEROL GASIFICATION IN SUPERCRITICAL WATER IN A TEE JUNCTION SHAPED CYLINDRICAL REACTOR

Abstract

Gasification in supercritical water is a very promising technology to process wet biomass into a valuable gas. Providing insight of the process behavior is therefore very important. In this research a computational fluid dynamic model is developed to investigate glycerol gasification in supercritical water, which takes place in a cylindrical reactor with a tee junction. The performance of the developed model is validated against experiment, and it shows that the model is able to describe the process very well. The experimental validation shows that the model slightly overestimates the outlet temperature on average by 6% and underestimates the carbon gasification efficiency on average by 16%. The flow behavior in the supercritical water gasification process is successfully described and a sensitivity analysis is conducted. It is revealed that the flow pattern of the process is heavily influenced by gravitational forces which significantly influences mixing and heat transfer.

The work presented in this chapter has been published in:

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3.1 INTRODUCTION

Wet biomass is an attractive, abundant and cheap type of biomass, and the SCWG conversion process is known to have a high potential to convert it in an energy efficient manner [42-45]. This technology, however, still faces some challenges (e.g. plugging due to char formation) before it can be utilized in industrial application [4, 44, 45]. Several studies indicate that char formation during the (slow) heating up of the biomass may be an important cause of plugging in the process [4, 67, 81]. Therefore, it is of major importance to be able to provide insight into flow and reaction behavior during SCWG of biomass with a numerical model.

Several numerical investigations of pure Supercritical Water (SCW) flow in a vertical, horizontal and an inclined pipe are done recently [101-106]. Earlier work of Cheng et al. [101] investigate the influence of mesh structures on the heat transfer in a turbulent SCW flow. It is observed that the performance of the ω -turbulence model strongly depends on the first dimensionless wall distance to the first mesh (y^+). In a study of an upward SCW flow in a vertical pipe, Palko and Anglart [102] states that buoyancy plays a small effect in a high mass flow rate. Whereas Wen and Gu [103] find that significant density variation near the pseudo-critical temperature region causes a deformation of the velocity profile and a weakening of turbulence production. This results in a weakening of heat transfer, which is termed a Heat Transfer Deterioration, in their investigation of an upward and downward SCW flow in a vertical pipe. In relation to this study, Zhang et al. [104] study a supercritical fluid flow in a vertical and horizontal pipe, and concludes that an anisotropic model is recommended to model the flow of a supercritical fluid. In parallel like investigations, Jaromin and Anglart [105] observes that heat transfer deterioration can be caused by either the thickening of the viscous sublayer or the influence of buoyancy, and this depends on the fluid flow rate. These results are also summarized in the review article of Huang et al [106].

Supercritical fluid flow in combination with another compound is investigated by various authors [72, 75-77, 84, 107]. Raghavan and Ahmed [72] investigates a mixing process of n-decane and SCW in a cylindrical tee mixer in a laminar flow. The mixer is comprised of a main tube for the SCW and an injection tube for the cold n-decane. Peng-Robinson Equation of State (EoS), Chung's formula, and Silva's formula are used to approximate the fluid density, thermal conductivity and viscosity, and the diffusivity of the compound. They observe that the mixing of different fluids with less than a

100 K temperature difference will not impact the flow field, but a larger temperature difference might. In addition to this study, Moussiere et al. [107] study the influence for both the Arrhenius law and the Eddy Dissipation concept in describing the kinetics for oxidation of dodecane in SCW. They observe that both the Arrhenius law and the Eddy Dissipation Concept are able to give a good prediction in comparison to experimental data. Moreover, Goodwin and Rorrer [76] look into the gasification of xylose in a laminar flow using a generic binary diffusion coefficient and constant thermal properties of water. They observe similar gas compositions, with the exception of CH_4 , compared to their experimental study. Another investigation by Yoshida and Matsumura [84] then assesses carbon particles deposition in a vertical reactor for oxidation in SCW. They observe the case that particles with the size of 1-10 μm are entrained in a SCW flow. Xiaohui et al. [75] examine the SCWG of glucose in a fluidized bed reactor assuming a uniform wall temperature and 3 competing kinetics. They are able to obtain a similar Carbon Gasification Efficiency (CGE) and gas yield trend compared to their experimental results, though the absolute values are much higher (approximately 40% difference). Recently, Hui et al. [77] implement 7 competing kinetics and investigate the influence of several turbulence models as well as the shape of the injector for glycerol SCWG in a cylindrical tee mixer. They conclude that mixing of the glycerol with the SCW flow prompts the side reaction in a region with low temperature, and that a different injector angle can reduce this effect.

Currently, there is limited literature published on numerical methods that addresses the gasification of biomass in SCW. In addition to that, there are no numerical studies that have been performed with the use of a simple global reaction kinetic. A global reaction kinetics is readily available, see [54, 65, 71, 108, 109] for more information, and can be utilized in Computational Fluid Dynamics (CFD). On the contrary, detailed reaction kinetics for SCWG is more difficult to obtain.

In this research, a CFD model is developed to investigate the flow pattern, mixing and heat transfer during SCWG of biomass. The gasification takes place in a cylindrical tee mixer with a main line for SCW and an injection line to provide fast heating to the biomass. Furthermore, the proposed CFD model uses glycerol as a simple model compound of biomass and it implements a global reaction kinetics.

The following section presents the methodologies to approximate the fluid properties, the implemented reaction kinetics, the detailed geometry and operating condition of the model. Subsequently, the performance of the model

is assessed, the influence of global reaction kinetics to the carbon conversion is analyzed and the process flow behavior is looked into. Finally, the use of an expanded Arrhenius model [110], the influence of gravity and flow velocity in the injector are also studied with a sensitivity analysis.

3.2 MODELLING APPROACH

A chemically reacting turbulent flow can be modelled and solved at each point in space and time by specifying its pressure, mass, temperature, velocity, and species concentration. The commercial CFD code ANSYS Fluent 16.0 is used to simulate the gasification of glycerol in supercritical water. The following section briefly presents the mathematical description of equations that govern this system and the relevant turbulence models. Selection of fluid properties, reaction kinetics, and discretization scheme are also presented here.

3.2.1 GOVERNING EQUATIONS

The simplest form of mass, species, momentum and energy conservation equations are given in the following equations [111]. The mass conservation is described as the product of local flow velocity and density without considering gravity. Species conservation takes into account that formation and consumption of species take place during chemical reactions. The momentum conservation equation contains the convective momentum transfer, its pressure tensor and the effect of gravity. Together with the mass conservation equation, it leads to the often used Navier-Stokes equation. The energy conservation considers the conductive and convective energy transfer, energy change due to pressure, viscous dissipation and chemical reactions. These equations are shown in Eq 3.1 - Eq 3.4 respectively.

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \vec{u}) = 0 \quad \text{Eq 3.1}$$

$$\frac{\partial \rho_i}{\partial t} + \nabla(\rho_i \vec{u}) + \nabla \vec{J}_i = M_i \omega_i \quad \text{Eq 3.2}$$

$$\frac{\partial(\rho \vec{u})}{\partial t} + \nabla(\rho \vec{u} \otimes \vec{u}) + \nabla \vec{p} = \rho \vec{g} \quad \text{Eq 3.3}$$

$$\frac{\partial(\rho h)}{\partial t} - \frac{\partial p}{\partial t} + \nabla(\rho \vec{u} h + \vec{J}_q) + \vec{p} : \nabla \vec{u} = q_r \quad \text{Eq 3.4}$$

$$\vec{p} = p \delta_{ij} + \tau_{ij} \quad \text{Eq 3.5}$$

3.2.2 TURBULENCE MODELLING

Continuous fluctuation of velocity is a defining feature in a turbulent flow and this leads to a fluctuation of other flow properties. The Reynold-Averaged Navier-Stokes (RANS) method splits the flow properties of the Navier-Stokes equations and subsequently implements the Favre averaging, and finally implements a model that can describe its *Reynold stresses* term [111].

Literature shows that to model a flow of a supercritical fluid, it is recommended to use either the Shear Stress Transport (SST) k- ω model or the Reynold Stress Model [102-104, 112, 113]. In relation to this, Zhang et al. [104] state that the Reynold Stress Model provides less error when predicting heat transfer in comparison to RNG k- ϵ model. On the other hand, Wang et al. [113] report that the SST k- ω model gives an improved heat transfer prediction for supercritical fluid in comparison to the RNG k- ϵ model. In addition, Jaromin and Anglart [105] show that the k- ω SST model give a very accurate heat transfer and flow prediction in an upward flow in a cylinder whereas Wen et al [103] prove that this model also performs well in a downward flow in a cylinder. Furthermore, Dutta et al. [112] observe that the SST k- ω in some cases outperforms the RSM model. The SST k- ω is therefore selected for this research. SST k- ω is a two equations RANS model that uses the turbulent kinetic energy and specific dissipation and defines its turbulence viscosity to solve the RANS equations [Eq 3.6-Eq 3.8] [110]. Results of investigations on turbulence models for SCW flows are summarized in a review article of Huang et al. [106].

It has to be noted that the flowing fluid is subjected to centrifugal force when flowing in a helical reactor, and this can completely change the flow structure. In some cases, centrifugal and viscous forces interact and create a swirl (secondary flow) on the pipe cross section. The selected turbulence models are expected to be able to capture such behavior.

$$\frac{\partial(\rho k)}{\partial t} + \frac{\partial(\rho k u_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left(\Gamma_k \frac{\partial k}{\partial x_j} \right) + G_k - Y_k + S_k \quad \text{Eq 3.6}$$

$$\frac{\partial(\rho \omega)}{\partial t} + \frac{\partial(\rho \omega u_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left(\Gamma_\omega \frac{\partial \omega}{\partial x_j} \right) + G_\omega - Y_\omega + S_\omega \quad \text{Eq 3.7}$$

$$\mu_t = \frac{\rho k}{\omega} \frac{1}{\max \left[\frac{1}{\alpha^*}, \frac{SF_2}{\alpha_1 \omega} \right]} \quad \text{Eq 3.8}$$

A flow of supercritical fluid usually involves a high heat transfer from the wall and a large property variation of the fluid near the wall. Therefore, one of the most important aspects when solving the supercritical fluid flow is to resolve the flow near the boundary properly. In the case of implementing the SST $k-\omega$ model, strong influences of the first mesh size on the overall heat transfer were observed [101, 102]. Palko and Anglart [102] states that the y^+ value has to be lower than 1.

3.2.3 FLUID PROPERTIES

As has been mentioned in section 1.3 and visualized in Figure 1.2, properties of water (e.g. density, viscosity, thermal conductivity and specific heat capacity) undergo a significant change during its transformation to supercritical condition. For an accurate calculation of density, specific heat capacity and enthalpy of water, the usage of IAPWS-IF97 is recommended [114]. This method divides the properties of water into 5 separate regions and calculates its properties based on different sets of equations respectively for each region [115]. Similarly, the viscosity of water is calculated using the IAPWS 1985 formulation revised in 2003 and its thermal conductivity is calculated with the IAPWS 1985 formulation revised in 1998 [115].

Several authors recommended to approximate the properties of the other compounds with the Peng-Robinson EoS [72, 116]. The values of thermal conductivity and viscosity of other compounds are approximated using the method proposed by Chung et al., see [117] for further information. The real gas specific heat capacity and enthalpy are calculated using the method proposed by Aungier, see [118, 119] for further information. The coefficients used to calculate the specific heat capacity and enthalpy at STP are obtained from the NASA thermodynamic database, see [120] for further information.

In high temperature range, the SCW is able to dissolve organic compounds [47, 48]. The diffusion coefficient of an organic compound in water at normal conditions is enhanced by a factor of 100 when the water is in its supercritical condition. There are two methods available to approximate the temperature-dependant diffusivity of compound in SCW, the He's method and the Tracer Liu-Silva-Macedo (TLSM) method, see [121, 122]. Since the He's method does not provide an accurate prediction at the lower temperature range, thus, the TLSM method is chosen, and further information can be found in [122].

All the above mentioned properties are calculated at a constant pressure and incorporated as tabulated data into a User Defined Function (UDF). In

these tables, the properties are reported for every 5 °C. In the region near the supercritical point (i.e. 50 °C above and below), all properties are reported for every 1 °C. The CFD solutions are then interpolated between these points. A constant pressure assumption is used to calculate all of the properties mentioned above. This is deemed acceptable as the flow velocity is relatively slow and the pressure losses due to friction are minor. In addition to this, the overall density of the mixture is calculated with volume-weighted-mixing-law, while its specific heat capacity is calculated with mixing-law. Subsequently, thermal conductivity and viscosity of mixture are calculated using mass-weighted-mixing-law

3.2.4 REACTION KINETICS

Due to the excess of water, it is assumed that the gasification reaction proceeds with a pseudo first-order kinetic behavior, see [4, 71] for further information. Experimental investigations show that no char is produced during SCWG of glycerol [54, 109]. Simao et al. [65] show that the pre-exponential factor (A) and the activation energy (Ea) for the kinetics of glycerol gasification are $10^{5.9 \pm 1.3} \text{ s}^{-1}$ and $104.5 \pm 20.3 \text{ kJ/mol}$ respectively. During the experiment, a plug flow condition was assumed and the research was conducted applying isothermal condition, which implies that it is a kinetically-limited reaction rate. The empirical reaction stoichiometry was derived from the experimental results done by Simao et al. [65]. Calculation formulas for the kinetics and reaction stoichiometry are shown in Eq 3.9 and Eq 3.10 respectively.

$$k_r = A \exp \frac{Ea}{RT} \quad \text{Eq 3.9}$$

3.2.5 EXPERIMENTAL DATA, GEOMETRY AND BOUNDARY

This investigation is done to simulate gasification of glycerol in supercritical water as was experimentally investigated by Simao et al. [65]. The experimental investigation is done in a reactor that has a shape of a cylindrical tee mixer. This consists of a main cylindrical tube with an inner diameter of 10.85 mm and a small injection tube with an inner diameter of 4 mm. The main tube delivers supercritical water that provide a fast heat-up to the biomass feed that comes from the injection tube. The main tube is positioned horizontally and the injection tube enters it perpendicular to the

flow. The injection tube is located at a distance of 0.125 m from the inlet of the main tube. The overall length of the tube is 1.368 m and only the 1.24 m of tube wall after the injection point is heated. The schematic of the reactor is visualized in Figure 3.1.

Figure 3.1 Half domain schematic of the reactor

The experiments are performed at a flow rate of 4 kg/h with an inlet temperature of 699 K in the main tube and a flowrate of 1 kg/h with an inlet temperature of 288 K in the injection tube. The injection tube delivers a flow containing 50 wt-% glycerol that corresponds to a total of 10 wt-% glycerol in the overall system. The experiments are done at a pressure of 25 MPa.

3.2.6 NUMERICAL METHOD

Volumetric reaction with a laminar-finite rate is used for the turbulence chemistry interaction. Input for both the reaction and the stoichiometry are stated in section 2.4. For the calculation, the “Coupled” pressure and velocity coupling method is used. The conservation equations are discretized and are solved with second order upwind scheme interpolation. The residual criteria for convergences are set to be 10^{-4} for the continuity and 10^{-6} for the rest of the equations. The BCG stabilization method is used for all equations.

3.2.7 DATA ANALYSIS

Both outlet temperature and CGE are used to validate the model. CGE represents the ratio of the total converted carbon at the end of the process to the fed carbon. This definition is shown in Eq 3.11.

$$CGE = 1 - \frac{C_{f,e}}{C_{f,s}} \quad \text{Eq 3.11}$$

The natural convection plays an important role in a supercritical flow with low mass flux, see [102, 123, 124] for further information. The Grashof number can be applied to quantify the influence of buoyancy to the flow field. The Grashof number approximates the ratio of buoyancy force that might happen because of the temperature gradient to the viscous force, and is shown in Eq 3.12. This dimensionless parameter is commonly used in conjunction with the Reynolds number [124]. A ratio of the Grashof number to the square root of the Reynolds number that is higher than unity represents a significant influence of the flow field due to buoyancy.

$$Gr = \frac{g \beta_b D^3 (\nabla T)}{v_b^2} = \frac{(\rho_w - \rho_b) \bar{\rho}_b g D_h^3}{\bar{\mu}_b^2} \quad \text{Eq 3.12}$$

Density variations due to the major temperature difference that takes place near the pseudo-critical point can lead to a non-unity density ratio. This can modify the flow field as eddies in the flow move toward the denser fluid and hence, the entrainment pattern is changed favoring the denser fluid [125, 126]. Depending on the flow condition, this flow entrainment pattern can be transmitted upstream of the flow and significantly affect the flow characteristic. The Froude number can be used here to identify the type of flow and it is defined in Eq 3.13. A Froude number below unity represents a slow or tranquil flow and any disturbances in the flow will be transmitted upstream.

$$Fr = \frac{u}{\sqrt{g D}} \quad \text{Eq 3.13}$$

3.3 RESULTS AND DISCUSSION

This section presents the flow behavior inside the reactor during the gasification. To begin with, the mesh independency is checked. Then the performance of the model is assessed based on a comparison between the predicted temperature and the CGE level against the experimental data from Simao et al. [65]. Finally, a sensitivity analysis of the model is presented.

3.3.1 MESH INDEPENDENCY

A mesh independency study is done in order to verify that the chosen mesh provides adequate spatial resolution and it does not influence the result. Each mesh is refined by doubling the number of the elements in the radial direction. The three meshes comprise of: 1) 2.9 million elements; 2) 6.5 million elements; 3) 13.3 million elements. The mesh independency study is done for non-reacting flow, since preliminary investigation showed that the velocity and temperature flow fields do not vary considerably for a flow with and without reactions.

The inlet flow rate of the SCW is equal to 4 kg/h and it enters the reactor at a pressure of 25 MPa and a temperature of 699 K. The mixture of water and glycerol is injected with a temperature of 288 K and a mass flow rate equal to 1 kg/h. Figure 3.1 shows the geometrical dimensions, injection location and coordinate system. Figure 3.2 presents the velocity and temperature distributions in the vertical and horizontal direction inside the tube.

The velocity profile in the horizontal direction shown in Figure 3.2-A does not seem to change significantly with different mesh sizes. A peak velocity profile near the injection can be observed in this figure. This peak takes place due to a movement of the SCW fluid from the main tube into the injection tube. The velocity profile in the vertical direction shown in Figure 3.2-B indicates that by decreasing element sizes there is a minor velocity change near the injection point. This, however, does not result in a significant temperature change as visualized in Figure 3.2-C and D. The maximum difference in temperature obtained from these three different meshes amounted to does not exceed 10 K.

Figure 3.2 (A-D) Flow field profile at axial coordinate of 0.12 m, 0.125 m, 0.13 m, 0.5 m, 1.368 m. (—) Mesh 1: 2.86 M elements; (—) Mesh 2: 6.49 M elements (—) Mesh 3: 13.3 M elements. (A-B) Horizontal and vertical velocity profile. (C-D) Horizontal and vertical temperature profile.

The vertical velocity profiles for positions of 0.12 m up to 0.13 m show that the peak velocity in the bulk flow is moving downward along the axial direction. This takes place due to the density difference between the SCW fluid and the injected fluid. The colder (denser) injected fluid goes to the bottom of the tube and creates a swirling motion upstream of the injection location. This swirling motion pushes the incoming SCW to flow to the top of the tube. Subsequently, at the injection point, SCW that flow on the top of the tube will move downward to fill the void left by the swirling injected fluid.

Visualization of these phenomena is also shown in Figure 3.3 that presents the streamline coming from the main inlet (grey line) and injection inlet (colored line). The minor differences between the investigated meshes for velocity and temperature profiles suggest that the result are mesh independent

and the mesh with the biggest element size provides sufficient spatial resolution and therefore can be used for final research.

Figure 3.3 Streamline for non-reacting flow with reactor wall temperature of 873 K. (—) Streamline of SCW; (—) Streamline colored with temperature of injected glycerol and water.

3.3.2 MODEL VALIDATION

The study is done for several different outer reactor wall temperatures, namely: 773 K, 823 K, 873 K, 923 K and 963 K, and in combination with the operating conditions that are mentioned in section 3.3.1. Experimental values used for the validation are obtained from the work of Simao et al. [65] and Hui et al. [77]. Figure 3.4-A shows a comparison of numerical and experimental outlet temperature for various wall temperatures. It can be seen that the simulations slightly overestimate the outlet temperature by approximately 6%. This can be due to two things: a) heat transfer deterioration causes the non-uniformity of the experimentally investigated inner reactor wall temperature whereas the developed model imposes a uniform wall temperature [105]; b) wall thickness of the tube, which is not considered in the model, might play an important role to reduce the overall heat transfer. It should also be noted that the numerical results may in fact be in agreement with the experimental data as the measurement error in [65, 77] was not given.

Figure 3.4 (A-C) Comparison of results obtained from numerical and experimental [65] result with SCW flow at 699K with 4kg/h and 50 wt-% injected glycerol at 288K with 1kg/h at 25 MPa. (A) Wall temperature vs outlet temperature. (B) Wall temperature vs CGE. (C) Gas yield at: $\blacklozenge$ 823 K, $\bullet$ 873 K, $\blacksquare$ 923 K, $\blacktriangle$ 963 K. (—) H_2 , (—) CO_2 (—) CO (—) CH_4 .

The discrepancies of the CGE between numerical and experimental range from 3% to 16 % as is visualized in Figure 3.4-B, except at reactor wall temperature of 773 K where about 50% can be observed. The main reason for such behavior is the reaction kinetics that is described in section 3.2.4. It provides a significant difference in reaction speed at temperatures lower than 780 K. Since the model predicted higher temperature for this condition than the experiment (by ± 30 K), consequently the CGE is also enhanced. Therefore, it is important to perform a CGE comparison based on the outlet temperature. This will be discussed in section 3.3.3.1.

A comparison of gas yield obtained from numerical and experimental results are presented in Figure 3.4-C. Neglecting a minor difference for H_2 yield, the overall predicted values are very similar. It can be concluded that a model that assumes a single phase flow in combination with the SST k- ω turbulence model is able to provide an accurate behavior of glycerol

gasification in SCW. Moreover, it is revealed that the implementation of a global kinetics with simple reaction stoichiometry is able to provide a similar result to the values obtained from experimental investigation.

Figure 3.5 (A-C) Streamline for flow with reactor wall temperature of 873 K. (A) Streamline colored with axial velocity and (B-C) Streamline colored with local temperature.

It was mentioned in section 3.3.1 that the SCW flow may experience a swirling motion near the injection point. Figure 3.5-A shows the streamline colored with the axial velocity of a flow with a reactor wall temperature of 873 K. It can be seen that some part of the injected glycerol/water mixture experiences a negative velocity, which means that this flow moves upstream toward the inlet of the main tube. Figure 3.5-B presents the streamline colored with local temperature from the top view of the reactor. It can be noted that there is a flow separation after the injection. This is further confirmed in

Figure 3.5-C where the streamline colored with local temperature from the front view of the reactor is depicted. Another flow separation that creates a left and right swirling motion as the injected fluid flows along the axial direction is presented there.

Figure 3.6 (A-D) Flow with reactor wall temperature of 873 K. (A-B) Front view of velocity vector colored with temperature variable at 0.125 m and 0.5 m. (C) Contour plot of Froude number near injection. (D) Velocity vector flow field near injection.

Figure 3.6-A presents a front view of the velocity vector colored with temperature field at the injection point. This figure suggests that the first swirling motion arises as the injected fluid, that has high density and is slower, moves to the bottom of the tube due to gravity. Figure 3.6-C shows that the Froude number near the injection is below 1, which means that this is a tranquil (unforced) flow. This means that the fluid movement in the axial direction is so slow that it cannot suppress the swirling motion. Because of that, the swirl pattern is moved upstream and creates even bigger swirls (eddies) near the inlet of the main tube. This swirling motion of the fluid is illustrated in Figure 3.6-D. Furthermore, the swirling motion acts together

with the gravitational force to drag the incoming SCW down. This generates the diagonal fluid movement shown in the Figure 3.6-A.

Subsequently, the fluid at the top of the tube at downstream location, which has been heated up by the hot reactor wall, is forced to swirl backward. This results in a minor temperature increase near the top of the tube. This concept is supported by the result presented in Figure 3.7-A and B. These illustrate the ratio of Grashof and Reynolds number, which are a measure of the buoyancy influence on the flow pattern, along the horizontal and vertical direction respectively. Value above one that indicates an intense buoyancy effect, can be observed on the injection location at an axial distance of 0.125 m in Figure 3.7-A. The sharp drop near a radial distance of -1 is due to the fact that temperature (density) is almost constant there while the velocity is increasing significantly. Figure 3.7-B also shows that the influence of buoyancy is significant for both the bottom and the top of the pipe near the injection.

Figure 3.7 (A-B) Ratio of the Grashof number to the square root of the Reynolds number for horizontal and vertical radial direction for a flow with reactor wall temperature of 873 K.

The second swirling motion in Figure 3.6-B, which takes places downstream of the pipe, occurs due to the difference of fluid density near the wall and in the bulk flow. It can be discerned that the fluid near the tube wall has a high temperature, and thus a low density. This fluid moves then quickly upward due to the buoyancy effect. After it reaches the top, it is dragged by the incoming flow in the middle of the tube and then slowly moves downward due to the gravity. After it reaches the bottom of the tube, the same cycle is repeated. Also according to Figure 3.7-A and B at an axial distance of 0.5 m, the Gr / Re^2 above 1 near the tube wall can be noted. Taking this into account,

it can be concluded that buoyancy indeed plays an important role in facilitating the swirling motions. It can also be concluded that the overall heat transfer in the tube is significantly improved due to the mixing induced by these swirling motions.

Figure 3.8-A and B present the temperature contour of a flow with a reactor wall temperature of 873 K from the top and side view respectively. It can be seen that in the vertical direction, the bulk flow has a higher temperature near the top of the tube and this is gradually reduced as it gets closer to the bottom tube. The reaction rate in the vertical direction shown in Figure 3.9-B is bound to portray a similar behavior, as reaction rate is highly dependent on temperature. The reaction rate at an axial distance of 0.125 m in Figure 3.10-B, however, does not show this behavior. The reaction rate temporarily decreases and then increases again as it proceeds toward the bottom tube. This milder reaction in the middle of the tube takes place due to the fact that glycerol does not have sufficient time and has not yet diffused from the bottom tube to the top region.

Figure 3.8 Temperature contour in a middle XZ plane (A) and XY plane (B).

In contrast, the temperature distribution of the bulk flow along the reactor as presented in Figure 3.8-A is uniform, except for the flow near the tube wall. Consequently, the rate of reaction near the wall is almost 5 times bigger than the reaction rate in the bulk flow, as is depicted in Figure 3.9-A. This figure also shows that the gasification reaction has already started to take place at an axial distance of 0.125 m at location closest to the injection (dimensionless radial distance of -1). This implies that the injected fluid has a sufficiently high temperature to start the reaction at that location. Therefore, it can be concluded that some part of the SCW from the main tube enters the injection

tube, and consequently it recirculates at that location and partially heats up the injected flow.

Figure 3.9 (A-B) Rate of reaction for horizontal and vertical radial direction for a flow with reactor wall temperature of 873 K

3.3.3 SENSITIVITY ANALYSIS

Influence of the kinetic description to the obtained result is investigated in this section. In addition to this, the importance of the imposed gravitational force and the injection velocity to the flow behavior is looked into.

3.3.3.1 INFLUENCE OF TEMPERATURE DEPENDENT ARRHENIUS FORMULA

Section 3.3.2 showed that there are some inconsistencies in the outlet temperature obtained from simulations and experiments. It is also observed that at a low temperature range, there is a significant CGE difference from the results that are obtained from simulations and experiments. To account for this, a CGE comparison that uses the corresponding outlet temperature is displayed in Figure 3.11.

In Addition to this comparison, an extended model that uses an expanded Arrhenius formula is investigated and the results are presented using the corresponding outlet temperature in Figure 3.11. This expanded Arrhenius formula is shown in Eq 3.14. This formula is used to account and correct for the deviation of predicted and the experimental data as is shown in Figure 3.10-A. The deviation of kinetics value obtained from the experimental data and the Arrhenius formula is fitted into a 4th order polynomial curve as can

be seen in Figure 3.10-B. The equation used to describe this curve is shown in Eq 3.15 and is used as an expansion factor in Eq 3.14. This expansion factor is only activated at the temperature of 760 – 840 K, since here the reaction occurs intensely.

$$k_{r,expanded} = A T^{\beta} \exp \frac{Ea}{RT} \quad \text{Eq 3.14}$$

$$\beta = 0.03898 T^4 + 0.0175 T^3 - 0.1213 T^2 - 0.02756 T + 0.05055 \quad \text{Eq 3.15}$$

As it can be seen from Figure 3.4-A, wall temperatures of 773 K, 823 K and 873 K corresponds to outlet temperatures of 752 K, 793 K and 834 K respectively. Observing the comparison made in Figure 3.11, numerical results with standard Arrhenius formula demonstrates CGE underestimation of about 18%, 34% and 20% respectively, based on the above mentioned outlet temperatures. Moreover, a noticeable difference of CGE at outlet temperature of 793 K is revealed. In contrast to this, utilizing the expanded Arrhenius formula leads to CGE underestimation of only 10%, 23% and 15% for the respective outlet temperature

Figure 3.10 (A) Kinetics of SCWG of glycerol from Simao et al. [65] and Chakinala et al. [54] (B) Fitted 4th order polynomial for the deviation of kinetic

The average accuracy of the CGE predictions using the standard and expanded Arrhenius formula are 24% and 16% respectively. Implementing the expanded Arrhenius formula is shown to improve the prediction accuracy of approximately 8%. However, Figure 3.11 also indicates that only minor improvement follows for the reaction that takes place in higher temperature region.

The discrepancies of the CGE comparison might be due to the fact that the kinetics that is used was obtained through experiment that assumes a

uniformly distributed glycerol with an isothermal condition [65]. However, Figure 3.5-C showed that concentration and temperature field inside the reactor does not follow these assumptions. This non-uniformity might lead to an Arrhenius formula (the pre-exponential factor and activation energy) that predicts lower kinetics value than what is occurring during the experiment. Therefore, a sensitivity analysis related to the pre-exponential factor and activation energy might be useful. Additional reason for these discrepancies might be due to the lack of phase-mass boundary interaction, which can be obtained through a multiphase flow modelling.

Figure 3.11 Comparison of CGE versus outlet temperature for results obtained from numerical and experimental for flow a with a reactor wall temperature of 873 K.

3.3.3.2 EFFECT OF DIRECTION OF GRAVITATIONAL FORCE

Several studies stated that char formation can take place during SCWG of biomass due to polymerization reactions that occur at subcritical conditions and that a fast heat up of wet biomass can reduce this effect [67, 81]. It has been discussed in section 3.3.2 that gravity promotes the swirling motions which in consequence improves both the heat transfer due to mixing enhancement and the residence time of the injected glycerol. Therefore, several different cases that use different gravitational forces are investigated and are listed in Table 3.1. The flow behaviors of these cases are presented in Figure 3.12-A to E respectively.

Table 3.1 List of investigated cases

Case	Name and properties					
	Reference	A	B	C	D	E
Gravitation	y-positive	x-positive	x-negative	z-positive	z-negative	non

It can be noticed that simulation based on case A, D and E provides a similar flow pattern. At these conditions, however, the back swirling motion near the injection point is eliminated.

Figure 3.12-H also shows that the outlet temperatures obtained from case A and D are very similar to the reference case. Even though the flow patterns obtained from simulations based on case A and E are almost identical, the x-direction gravitational force in case A induces a swirling motion from the SCW flow that comes from the inlet of the main tube and case E does not possess this behavior, as are portrayed in

Figure 3.12-F and G respectively. This swirling motion occurs due to faster fluid movement near the tube wall, i.e. along its axial direction and also slightly ahead of the injection location, compared to the bulk flow. This leads to significant outlet temperature differences from case A and E.

Simulation that is based on case B generates an extremely intense back swirl motion, because the tranquil flow essentially attempts to go upward against gravity. In contrast to this, simulation based on case C experiences a slight back swirl near the injection point. In addition to this, further down the tube, there will be a similar flow separation reference case and was shown in Figure 3.5-C. This creates top and bottom swirling motions along the length of the tube. These different flow patterns obtained from case A-D only lead to a minor difference in outlet temperature of up to approximately 5 K as is shown in

Figure 3.12-F. Case E, however, predicted lower temperature of approximately 50 K in comparison to the other cases.

Figure 3.12-I presents the residence time of the injected flow from these five different conditions. These residence times are obtained from the “Time” variable in the streamline provided in ANSYS CFD-Post, discounting streamlines that are stuck in a continuous swirl or flowing with a creeping motion on the tube wall. It can be seen that simulations that use gravitational force in the x-positive and x-negative direction have the shortest and longest residence time, respectively. It has to be noted that the latter also leads to an everlasting continuous swirl for some of its streamlines, and therefore is not recommended. Taking all of this into account, it is advised that the reactor tube is located horizontally with the injection tube entering from either the side or the bottom part of the main tube (y-positive or z-negative gravitational force).

Figure 3.12 (A-G) Flow with reactor wall temperature of 873 K. (A-E) S for case A, B, C, D and E respectively. (F-G) Front view of streamline colored with local temperature for case A and E respectively. (H-I) Comparison of outlet temperature and residence time from 6 different gravitational forces.

3.3.3.3 EFFECT OF GLYCEROL INJECTION SPEED

Figure 3.5-C in section 3.3.2 shows that a part of the SCW flow that comes from the inlet of the main tube enters the injection tube and recirculates there. This leads to a gradual partial heating of the injected glycerol. This is a disadvantages when gasifying a biomass compound as slow heating can lead to char formation [81]. This is especially true for flow condition with low mass flux as is commonly done in a laboratory scale investigations. Therefore, two additional geometries, one with a 2.8 mm inner diameter injection tube and the other with a 5.6 mm inner diameter of injection tube, are investigated. The same injection flowrate of 1 kg/h is used for both cases.

The latter is tested due to the fact that a higher injection velocity creates a more forceful flow that will not transmit the disturbance near the injection point upstream to the injection tube. The former is tested due to a premise that lower injection velocity creates a smaller disturbance near the injection point, thus reducing the swirls adjacent to it and consequently reducing the SCW flow that comes into the injection tube. The streamlines colored with temperature for both geometries are visualized in Figure 3.13-A and B, respectively.

These figures show that the case with a larger injection tube leads to a more intense recirculation inside the injection tube that causes a longer partial heating of the incoming flow. This can be deduced from the high temperature shown in the streamlines inside the injection tube. On the other hand, the second case reduces the recirculation inside the injection tube and thus reduces the partial heating. This, however, leads to a decrease in residence time as is shown in Figure 3.13-D. The changes of the injection geometry provides almost no changes to the outlet temperature, see Figure 3.13-C. Therefore, it is suggested to reduce the inner diameter of the injection tube or to increase the flowrate of the injection tube, as these options can reduce the partial heating induced by the flow recirculation.

Figure 3.13 (A-D) Flow with a reactor wall temperature of 873 K. (A-B) Streamlines colored with temperature for injection tubes with inner diameter of 2.8 mm and 5.6 mm. (C-D) Comparison of outlet temperature and residence time for simulation with different injection tube sizes.

3.4 CONCLUSION

The model developed in this research assumes a single phase flow with a global kinetics mechanism. Several different operating conditions were studied using this model. The model slightly overestimates the outlet temperature in average 6%, which might be due to neglecting the influence of the tube wall thickness. There is also discrepancy in the predicted carbon gasification efficiency in comparison to experimental data on average by 24%. This discrepancy is reduced to 16% when implementing the expanded Arrhenius formula.

Numerical results show that the process experiences several flow swirls that create non-uniform concentration and temperature distribution. Therefore, implementing the reaction kinetics that is derived from

experimental investigation that assumes a plug flow reactor with isothermal condition might be the reason of the discrepancies in the carbon gasification efficiency. Another possible reason might be due to the influence of a phase-mass boundary interaction, which is not considered in the model. In general, it can be concluded that the model provides good estimation of the processes occurring during supercritical water gasification.

In addition to model validation, a sensitivity analysis was performed taking into account the influence of gravity and biomass injection velocity. It was observed that the gravitational force induces swirling motions along the flow in the reactor which significantly affect its mixing and heat transfer. Neglecting the gravitational force is demonstrated to underestimate the outlet temperature by approximately 6 % in comparison to the standard case (gravity in y positive direction). The research shows that the best position for the reactor tube reactor is horizontal while the injection tube is placed in either the side or the bottom part of the main tube. This can lead to a flow with the most optimum residence time and sufficient swirling to promote the glycerol mixing and heat transfer. It is also revealed that a flow recirculation might take place inside the injection tube, which results in a gradual partial heating of the injected flow that can subsequently lead to char formation. Therefore, it is suggested to utilize a smaller injection tube or to increase the injection flow rate, as these can forcefully reduce this flow recirculation inside the injection tube.

CHAPTER 4

NUMERICAL MODELLING OF CHAR FORMATION DURING GLUCOSE GASIFICATION IN SUPERCRITICAL WATER

Abstract

Supercritical water gasification is an efficient thermochemical conversion process to convert wet biomass into a high grade fuel. However, char formation during the conversion might influence the process efficiency and operational stability. Providing insight into char formation behavior during the gasification process will facilitate the utilization of this technology. Computational fluid dynamic modelling is used to study the supercritical water gasification of glucose in a tubular helical reactor, which includes an injector tube to mix glucose feed with pre-heated water to provide fast heating. Validation against experimental data confirms that the developed model performs well. An average discrepancy of 4% is obtained for the total feed conversion whereas the gas yield at high temperature is computed with 15% difference. The char yield trend is also captured well. Sensitivity analysis reveals that the presence of low temperature zone at the injection point plays a significant role in char formation.

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4.1 INTRODUCTION

A substantial part of biomass such as pig manure and sewage sludge is not suitable for conventional conversion process due to its high water content. Gasifying these in supercritical water is considered to be an attractive option, as there is an absence of drying requirement which is a highly energy-intensive process [82]. Despite all the interest, SCWG process still faces some major technical challenges, including char formation [4], which possibly plug the SCWG reactor [4, 67, 68]. Therefore, prediction of the char formation during the SCWG of biomass will be a necessary step towards process improvement.

A number of investigations related to biomass gasification in SCW were recently done [4]. Several real biomass compound such as algae [54], chicken manure [51] and sewage sludge [53] were gasified at 873 K and 24 ~ 25 MPa, and Carbon Gasification Efficiencies (CGE) of about 53%, 90% and 75%, respectively were obtained. These authors noticed that char was produced during the gasification experiments. In addition to that, the SCWG of lignin [49], cellulose, artichoke, pine cone and sawdust [64] were investigated, revealing that char was also produced for these feedstocks. To understand the decomposition pathway of the biomass, detailed investigations were done using model compounds. Glycerol was frequently used as the main feedstock [65, 66] for SCWG processes as it does not produce any char when used. Additionally, glycerol used as co-solvent [127] tends to reduce the char production during the gasification process. Glucose was investigated by Lee et al. [71] as a model compound for cellulose gasification. The results showed no char formation at temperature above 957 K and a very small amount of char was found at lower temperatures. Other authors [67, 68] working with glucose, however, experienced plugging of the experimental test-rigs due to char formation, when operating at temperature of 673 K ~ 823 K. Furthermore, an investigation of catalytic glucose gasification in SCW by Zhang et al. [128] also resulted in reactor plugging. In relation to this, Chuntanapum and Matsumura [67] observed that during glucose gasification, reaction intermediates polymerize and form char only at subcritical condition. Similarly, researchers using indole [69], acetic acids and hydroxyl acetone [70] stated that longer residence time at lower temperature enhance char production. Correspondingly, Hendry et al. [80] implemented a faster heating by injecting glucose into pre-heated water right before it enters the gasification reactor. It was observed that char formation and reactor plugging appear only in cases without fast heating. Consequently, Zöhrer et al. [81] then proposed that a

fast heat-up of the feedstock is required to minimize the unwanted char formation.

In addition to several investigations that have been described in section 3.1, there are only a few more publications that addressed SCWG with numerical modelling. The work of Wei et al. [74] were focused on the influence of the biomass feeding on the solid particle and residence time distribution. An Euler-Euler model disregarding any chemical reaction was used for that purpose. The authors proposed that a 45° angle allows a uniform feed distribution in the fluidized bed reactor. More recently, Yukananto et al. [18] investigated glycerol gasification using a simplified reaction kinetic in a tee junction shaped reactor. The gas compositions of the process were accurately predicted. The authors concluded that gravity plays a significant role in the mixing and heat transfer near the injection area. Furthermore, Caputo et al. [73] studied the influence of the inlet configuration on the flow field in a SCWG reactor without considering any reactions. The performance of the investigated reactor was improved by pre-heating of the water that mixes with the cold biomass.

To the best of authors' knowledge, among the numerical investigations that are currently published, there is not yet any model that could predict char formation during SCWG. In this research, a Computational Fluid Dynamic (CFD) model is developed to investigate biomass gasification in SCW by taking the competing char formation reaction into account. The gasification process takes place in a helical coil reactor that uses a tee junction shaped entrance. This tee junction consists of a main line for pre-heated water flow and an injection line to deliver the biomass. This is referred to as the injector tube from further on. Glucose is used as a simple model compound. Furthermore, two competing reactions that represent gas and char formation are implemented into the numerical model.

The following section describes the methodology to estimate the fluid properties, the employed reaction kinetics, the detailed reactor geometry and operating condition of the model. The performance of the model and the influence of pre-heated water temperature on the char formation in the gasification process are evaluated. Finally, the effect of the flowrate ratio of the pre-heated water, biomass mixture and the importance of the reactor diameter are investigated.

4.2 MODELLING APPROACH

This sections briefly describes the relevant conservation equations that govern the system and the selected turbulence model. These are solved using the commercial CFD code ANSYS Fluent 16.0. Subsequently, an approximation of the fluid properties, the kinetics of gasification reactions, the domain of the system and the discretization scheme are presented.

The governing equations and turbulence model that is used in this study are discussed in section 3.2.1 and section 3.2.2, respectively.

4.2.1 FLUID PROPERTIES

Part of the explanation in this section are discussed in section 3.2.3

In addition to the information from section 3.2.3, the approximation of the densities of glucose and gaseous compounds are done using Peng-Robinson EoS [72, 116]. The method proposed by Aungier [118-120] is applied to calculate the real gas specific heat capacity and enthalpy of glucose and gaseous compounds while the values of the thermal conductivity and viscosity are calculated using the method proposed by Chung et al. [117] accordingly. The temperature dependent diffusivity of compounds in SCW are approximated using the Tracer Liu-Silva-Macedo method [122].

In contrast to this, char is represented as pure carbon that has a constant density and thermal conductivity. Its value of specific heat capacity is in accordance to [129] and the mass diffusivity is considered to be very low. An important consideration is that char compounds are treated as an additional species dissolved in the supercritical phase, and is therefore assigned with a high viscosity value.

4.2.2 REACTION KINETICS

Glucose decomposition that occurs in the presence of excess water is assumed to have a pseudo first-order kinetic behavior [4, 71]. In the current study a CFD model is developed that proposes a competitive reaction between gas and char formation, similar to the proposition of Broide-Shafizadeh for biomass pyrolysis [130]. Here, however, glucose is assumed to directly decompose into gas and char as is shown in Figure 4.1.

Glucose reaction rates applied in the CFD model are obtained from extensive investigation conducted by Promdej and Matsumura [131]. The pre-exponential factor and the activation energy for the kinetics of gas

formation (k_1), are equal to 55.6 s^{-1} and 49.52 kJ/mol , respectively. These values are taken from the limiting reaction that produces gas in accordance to the proposed pathway. In addition, kinetics of char formation (k_2) is obtained by combining the data points of two reactions that lead to char formation. These reactions represent the char formation at lower temperature range (573 K - 623 K) and at higher temperature range (673 K - 733 K), see [131] for further detail. This is done to include different rates of char formation at different temperature ranges in a single kinetics. The pre-exponential factor and the activation energy for char formation are $4.903 \times 10^{-06} \text{ s}^{-1}$ and -32.45 kJ/mol , respectively.

Figure 4.1 Glucose decomposition pathway that is used in the CFD model

The negative value for the activation energy of char formation reaction is not a physical value but a mathematical expression to account for deactivation of reaction at high temperature (i.e. no char is formed at high temperature). Similar procedure is used e.g. in [132-134]. Kinetics of reactions are calculated in accordance with Eq 4.1, and are shown in Figure 4.2-A and B for gas and char formation, respectively.

$$k_r = A \exp \frac{Ea}{RT} \quad \text{Eq 4.1}$$

Figure 4.2 (A-B) Gas and char formation kinetics from Promdej and Matsumura [131].
(C) Fitted 3rd order polynomial for the deviation of char formation kinetics.

An expanded Arrhenius formulation, see [18] and Eq 4.2, is used to calculate the final char formation kinetics. This is done, in order to account for the deviation between predicted char kinetics using the standard Arrhenius and the experimental kinetics. The deviation of kinetics values are thus fitted into a 3rd order polynomial curve as presented in Figure 4.2-C. This polynomial formula is used to correct the kinetics at the temperature of 570 – 740 K and is given in Eq 4.3.

$$k_{r,expanded} = A T^{\beta} \exp \frac{E_a}{RT} \quad \text{Eq 4.2}$$

$$\beta = (7.70022 \times 10^{-7}) T^3 - 0.00154 T^2 + 1.03115 T - 2.27941 \quad \text{Eq 4.3}$$

The empirical stoichiometry for the gas formation reaction (Eq 4.4) is derived from the experimental results of Lee et al. [71], whereas the char formation stoichiometry (Eq 4.5) follows the proposed reaction in SCWG by Sustani et al. [48]. Both reactions stoichiometry, which determine the gaseous product composition, are assumed to be independent on feed concentration.

4.2.3 GEOMETRY AND BOUNDARY CONDITIONS

The developed CFD model is used to simulate the experimental investigation of glucose gasification in SCW done by Promdej and Matsumura [131]. The experimental set-up consists of a 1 mm inner diameter and 20 m long helical shaped tubular reactor equipped with an injector tube. This injector tube has two inlets that resemble a tee junction. Via the main inlet, pre-heated water that provides a faster heating of the glucose feed coming from the injection inlet is delivered. Feed that comes from the injection inlet contains 7.5 wt-% glucose. The mass ratio of flows between the main inlet to the injection inlet is equal 4:1. The experiments were conducted for several different operating temperatures (e.g. 623 K, 698 K and 733 K) at 25 MPa

The geometry used for the numerical investigation in this current study is shortened from 20 m to approximately 5 m due to the impractical computational power requirement. To account for the difference in length, the flow velocity is varied such that the residence time of the feed in the simulation matches the residence time in the experiments of Promdej and Matsumura [131]. The influence of different flow velocity, in the experiment and simulation, to the overall heat transfer that occurs in the tube is very small. This is confirmed by the Richardson number which is lower than 0.087 in the simulation. Thus the natural convection in comparison to the forced convection can be neglected in the system. Furthermore, the Nusselt number is found to be much higher than 1 for both simulation and experiment, which represents a very high heat transfer coefficient for both cases. The small diameter of the reactor (1 mm) and high wall temperature lead to very rapid heating up the feed to the operational temperature (i.e. wall temperature). Taking all these into account, the final amount of char produced is mainly influenced by the residence time, which is kept the same for simulations and experiments. The schematic overview of the whole reactor with the injector tube is presented in Figure 4.3. This geometry is then discretized with an unstructured mesh method, using tetrahedral elements in the core and hexahedral prism in the wall boundary.

Figure 4.3 (A) Schematic of the helical reactor (B) Schematic of the injector tube

Based on the experimental data of [135], it is assumed that isothermal conditions are achieved right after the injection and the temperature of pre-heated water is equal to operating temperature (i.e. 573 K ~ 733 K depending on the investigated case). The constant wall temperature is imposed as the wall boundary condition, and the value is equal to the investigated operating temperature. Simulations are conducted for a residence time of about 7 s for every operating temperature. This is achieved by varying the mass flowrate at both inlets. The flow rate of pre-heated water ranges from 2.6×10^{-4} kg/s to 4.31×10^{-5} kg/s, for operating temperature of 623 K to 723 K whereas the feed is injected at a constant temperature of 300 K and flow rates of 6.54×10^{-4} kg/s to 1.08×10^{-5} kg/s. Finally, the pressure outlet boundary condition is used to impose an operating pressure of 25 MPa.

4.2.4 NUMERICAL METHODS

Turbulence chemistry interaction is solved assuming a volumetric reaction (homogenous reaction) together with a laminar-finite rate. Reaction kinetics and stoichiometries used are described in section 4.2.2. Velocity and pressure calculation are solved with the “Coupled” scheme. A second order upwind scheme is used to solve the relevant conservation equations. The influence of buoyancy is often minimal for a very small diameter tube due to the small Richardson number (i.e. below unity) [124]. A Richardson number of lower than 0.087 is observed for the investigated cases, and therefore, the gravitational force can be neglected. Simulations are considered to be fully converged when the continuity residual is below 10^{-4} and the remaining residuals reach the value of 10^{-6} . The BCG stabilization method is used for all computations.

4.2.5 DATA ANALYSIS

Validation of the model with the experimental data of Promdej and Matsumura [131] is done by comparing the results for unconverted feed, carbon gas yield and char yield. Unconverted feed represents the ratio of the remaining carbon in the glucose and intermediates at the end of the process to the inlet carbon. The value of unconverted feed, carbon gas yield and char yield, can be obtained by assigning the carbon content found in each products in accordance to the Eq 4.6.

$$yield = \frac{(Carbon\ content\ in\ product)\ [mol\ C / litre]}{0.083\ [mol / litre] \times 6\ [mol\ C / mol]} \quad Eq\ 4.6$$

The value of 0.0083 [mol/L] represents the molar concentration of glucose in the mixture and 6 [mol C/mol] represents the amount of atom C in glucose. In the literature [67, 131], apart from carbon and char, the glucose feed is converted into intermediates such as total-organic-compound, 5-HMF, fructose and furfural. This numerical study, however, assumes that glucose directly decomposes into gas and char. This is considered as an acceptable solution since all of the intermediates produced by glucose decomposition are further decomposed into gas and char, see [131] for further detail. Therefore, the unconverted feed values are validated against the sum remaining glucose and these intermediates found from the experimental data. Whenever possible the numerical data is validated against experimental results, otherwise it is compared with the trend lines fitted to the experimental data, see for details [67, 131].

4.3 RESULTS AND DISCUSSION

This section presents the analysis of numerical investigations for glucose gasification in SCW. First, mesh independency is verified. Subsequently, the performance of the model is compared to the experimental results obtained from literature [67, 131]. Finally, a sensitivity analysis of several parameters influencing char formation is presented.

4.3.1 MESH INDEPENDENCY

This section provides a verification that the chosen mesh provides an acceptable spatial resolution and that the results are no longer affected by the

element size. Due to the significant computational power resources required for the computations, the mesh refinement is performed only to the injection tube that as shown in Figure 4.3-B. This method is acceptable as it is known from the experiment that isothermal condition is achieved very rapidly. Each mesh is refined by doubling the number of the elements. The three meshes of the injector tube comprise of: 1) 2.7 million elements; 2) 3.8 million elements; 3) 6.2 million elements. The mesh independency study is done for an operating temperature of 693 K. The pre-heated water and glucose mixture enter the reactor at flow rate of 5.27×10^{-5} and 1.38×10^{-5} kg/s, respectively.

Figure 4.4 displays the velocity and temperature profiles at different axes positions inside the reactor. Only minor changes between the three investigated meshes can be noted. It can also be observed that the isothermal condition is achieved near the end of the injection tube, i.e. at axial location of 0.22 m. This verifies the assumption used for the mesh independency study. Taking all of these into account, it is concluded that the mesh with 2.7 million elements inside the injector and 10.2 million elements in total, provides sufficient spatial resolution and therefore is chosen for further research.

Figure 4.4 (A-B) Horizontal and vertical velocity. (C-D) Horizontal and vertical temperature profile for (—) Mesh 1: 2.7M elements; (---) Mesh 2: 3.8 M elements (····) Mesh 3: 6.2 M elements.

4.3.2 MODEL VALIDATION

The developed model is validated at the following operating temperatures: 623 K, 693 K, 723 K and 733 K. An average discrepancy of the unconverted feed values of 4% is observed from Figure 4.5-A that displays a comparison between numerical and experiment results. It can be noted that at higher operating temperatures (i.e. 733K), the model tends to overestimate the unconverted feed. However, a majority of the experimental data that is reported in [67, 131] do not provide a complete carbon balance (i.e. ranging from 0.94 - 1.05), which might be the reason for the noticeable discrepancies at this temperature.

Figure 4.5 (A-C) Comparison of numerical and experimental result at 623 K, 693 K, 723 K and 733 K. (A) Unconverted feed. (B) Carbon gas yield. (C) Char yield.

In relation to the feed conversion, operating at a temperature of 693 K results in the lowest overall value. This is due to two reasons: a) char formation rate is already suppressed at this temperature; b) gas formation rate is still quite slow at this temperature. Since neither high rate of char nor gas formation takes place, a low primary feed conversion is then observed. The behavior of char and gas formations can be observed from the reaction kinetics shown in Figure 4.2-A and B.

At operating temperature equal to or higher than 693 K (i.e. at 693 K, 723 K and 733 K), the numerical model slightly over predicts the gas yield by an average difference of 15%, as presented in Figure 4.5-B. In contrast, at temperature of 623 K, which is low for SCWG, the gas yield is approximated by 55% higher than the experimental data. This can be a consequence of char formation reaction that occurs intensively at this temperature, as it is observed in Figure 4.5-C. Since this char formation reaction also produces carbon-containing-gas, it significantly increases the discrepancy between the measured and predicted gas yield.

An opposite trend is observed for char formation. The predicted char yield at high temperatures (i.e. at 693 K, 723 K and 733 K) is significantly different from the experimental data, see Figure 4.5-C. However, at a temperature of 623 K, the numerical model only slightly underpredicts the char formation. Taking these into considerations, it is highly possible that the two reactions that lead to char formation (i.e. at lower temperature range and higher temperature range) as proposed by Promdej and Matsumura [131] are governed by two different reaction stoichiometries. This means that the char formation reaction that occurs at low temperature behave in accordance with Eq 4.5 whereas the char formation at high temperature follows an idealized char reaction stoichiometry (e.g. the one that is proposed by Miloslavljjevic et al. [136], which produces solely char and water compounds). This effect, however, is not captured with the current simplified two reactions model.

The results of the numerical model show a very small discrepancy of the conversion level in comparison to the experimental data. Moreover, neglecting the difference in the gas yield at 623 K, the overall results of the gas yield are close to the experimental data. Furthermore, as can be seen from Figure 4.5-C the char yield trend is captured well. It should be also noted that the measurement errors, which are significant – see [131], influence the final degree of model validation. Therefore, it can be concluded that the developed CFD model is a good approximation for glucose gasification in SCW. Moreover, the trend char formation during the process can be predicted accurately using a global char formation kinetics together with an expanded Arrhenius formula.

4.3.3 SENSITIVITY ANALYSIS

In this section the influence of three parameters in glucose gasification in SCW is discussed, namely: a) pre-heated water temperature; b) flow rate ratio between pre-heated water and glucose mixture; c) diameter of the reactor. Since the char formation may affect the SCWG process and could lead to reactor plugging, here the char yield is further studied in detail. Investigated operating conditions and reactor geometry are listed in Table 4.1

Table 4.1 List of investigated cases

Case	Investigated parameter	Pre-heated water temperature	Flow rate ratio of pre-heated water and glucose mixture	Tubular reactor diameter	Operating temperature	Gravity
A	Pre-heated water temperature	323 K	4:1	1 mm	723 K	Non
B		523 K				
C		623 K				
D		673 K				
E		723 K				
F		773 K				
G	Flow rate ratio of pre-heated water and glucose mixture	723 K	4 : 1	1 mm		
H			2 : 1			
I			1 : 1			
J	Tubular reactor diameter	723 K	4:1	1 mm		Yes
K				2 mm		
L				4 mm		
M				8 mm		

4.3.3.1 EFFECT OF PRE-HEATED WATER TEMPERATURE

Several authors [69, 70, 80, 81] suggested that fast heating of biomass by means of injecting it into pre-heated water can minimize char production during SCWG. Therefore, the preheated temperature is investigated in detail in this section. Figure 4.6 shows the char yield when gasifying glucose at 723 K (reactor wall temperature) with pre-heated water temperatures of 323 K, 523 K, 623 K, 673 K, 723 K and 773 K (Case A – F, respectively). The feed mixture temperature equals 300 K in all cases.

Mixing the feed mixture with a relatively cold pre-heated water at 323 K produces the highest char yield. The rate of char formation in the injector tube is presented in Figure 4.7-C top. A wide region with moderate rate of char formation (i.e. larger than $0.5 \text{ mol/m}^3\text{s}$) can be observed from this figure. This occurs because of a large low temperature region (i.e. from 530 K – 660 K) in the injector as displayed in Figure 4.7-A top. As described in Figure 4.2-B, fast char formation kinetics occurs at temperature of 573 K – 673 K. This condition thus leads to a high char yield with the value of 0.0018.

Figure 4.6 Char yield comparison at an operating gasification temperature of 723 K with varying pre-heated water temperatures.

The char yield is only slightly reduced for pre-heated water at temperature of 523 K and at 623 K. As these two cases experience similar heat and mass transfer behavior, only the results at 623 K are displayed in Figure 4.7. In comparison to the case of 323 K displayed in Figure 4.7-A top, a narrower low temperature region (i.e. from 530 K – 600 K) is shown in Figure 4.7-A middle for the case at 623 K. This narrow low temperature region should have led to a lower char yield in the case of 623 K. However, glucose has not diffused throughout the pipe radius when the flow temperature reached 573 K, due to the relatively high viscosity of the pre-heated water at temperature of 623 K. This leads to a highly concentrated glucose in the narrow low temperature region, as is presented in Figure 4.7-B middle. Consequently, this creates an area with an intense rate of char formation (i.e. larger than 3 mol/m³.s) that can be noticed from Figure 4.7-C middle. Eventually, a char yield value of 0.0017 is produced at this condition.

In comparison to the case at 323 K, a major reduction of the char yield at a pre-heated temperature above 673 K is observed: 23%, 27% and 28% are obtained in the case of 673K, 723K and 733 K, respectively. As there is only a minor difference in these three cases, similar mixing and heating behavior may occur at these conditions. Considering this, only results from the case at 723 K is looked further in detail.

Figure 4.7 (A) Temperature, (B) glucose mass fraction, and (C) rate of char formation contour at an operating gasification temperature of 723 K with varying pre-heated water temperature: (top) 323 K, (middle) 623 K, (bottom) 723K.

At a pre-heated water temperature of 723 K, glucose is rapidly heated as can be seen in Figure 4.7-A bottom. In addition, the water density at this

temperature is rather low, and thus a higher flow velocity is achieved, which provides a high mass convective transfer. Additionally, high temperature water (at supercritical conditions or above) significantly enhances the diffusion coefficient of organics by that leads to a high mass diffusivity. Accordingly, fast glucose mixing near the tee junction occurs as displayed in Figure 4.7-A bottom. The combination of a high temperature and a diluted glucose concentration near the tee junction results in a small region with moderate rate char formation as can be seen Figure 4.7-C bottom. This, significantly reduces the char yield to a value of 0.0013.

Based on kinetics described in Figure 4.2, the char formation might even become lower at temperatures higher than 733 K. In addition, in real SCWG system the pre-heated water temperature is highly dependent on the operating temperature and heat recovery configuration, see [27]. Therefore, operating at higher temperatures is suggested to reduce the char yield and to obtain a higher pre-heated water temperature in an energy efficient way.

4.3.3.2 EFFECT OF THE FLOW RATE RATIO OF PRE-HEATED WATER AND GLUCOSE MIXTURE

The flow rate ratio of pre-heated water and feed mixture is an important parameter related to the thermal efficiency on SCWG process and possible feed pumping limitations, see [27] for further information. Calculated char yields for various flow rate ratios are presented in Figure 4.8. It can be seen that a reduction of the flow rate ratio from 4:1 to 2:1 and 1:1 leads to an increase in the char yield by 6% and 25%, respectively.

Figure 4.8 Char yield with varying flow rate ratio.

The increase in char yield is caused by the extension of the low temperature region sensitive to char formation (i.e. from 600K – 665K). A higher feed mixture flow rate requires a higher amount of heat before the feed mixture can reach its supercritical phase. However, the temperature of the pre-heated water is not sufficient to provide rapid heating of the feed. Figure 4.9-B middle and Figure 4.9-B bottom show that at the studied temperature range, a substantial char formation occurs, with a speed varying from 0.005 s⁻¹ up to 0.012 s⁻¹. In addition, the overall glucose concentration, which increases with the flow rate ratio, also effects the total char yield. Both a higher glucose concentration and a faster char formation kinetics lead to an increase of char formation.

It is therefore suggested to increase the pre-heated water temperature when a substantial amount of glucose is fed into the reactor. This will reduce the area with low temperature and prevent excessive char formation. In addition, it is also suggested to have a high flow rate of injected feed. As the feed flow rate is not proportional to the increase of char yield obtained. This can be seen from Figure 4.8. which shows that doubling the injected feed only results in a char yield increase of 6%.

Figure 4.9 (A-C) Temperature and kinetics of char formation contour at an operating gasification temperature of 723 K with varying flowrate ratio. (A) 4:1, (B) 2:1 and (C) 1:1.

4.3.3.3 EFFECT OF REACTOR SCALE-UP

Experimental data [67, 131] used for validation of the developed numerical model is obtained from a 1 mm diameter tube at isothermal working conditions. To achieve an economically feasible throughput in a real SCWG system, larger tube diameters are necessary. As an example, a tube with a diameter of 14 mm is used to deliver 100 kg/h throughput, see [87]. Considering this, the influence of the reactor diameter to char formation is analyzed further. Figure 4.10 presents the char yield for glucose gasification for four different tube diameters with a size of 1 mm, 2 mm, 4 mm and 8 mm (Case J – M, respectively). The flow rate of the pre-heated water and glucose

are modified to keep the velocity, residence time and glucose concentration constant. In addition, gravitational force with the same direction as that of injected feed is imposed for both: case L and M. This is done in order to account for the buoyancy effect which might influence the flow at a reactor diameter of 4 mm and 8 mm.

Figure 4.10 Comparison of char yield at an operating gasification temperature of 723 K for different reactor tube diameters

A significant increase of char production is observed when utilizing large reactor diameters. In comparison to the base case of 1mm, the char yield increases to approximately 9%, 21% and 107%, respectively, when increasing the diameter gradually to 8 mm. There are several reasons for such behavior. One of them is the different flow field that occurs in the large diameter reactor (i.e. 8 mm), as is displayed in Figure 4.11-B Due to the buoyancy, the pre-heated water flow recirculates near the tee junction leading to a gradual heating of the flow inside the injection tube. This behavior results in char formation inside the injection tube since part of the feed is heated up to above 570 K. Furthermore, the pre-heated flow forces the incoming feed to creep on the injection wall toward the bottom of the tube. The slow and dense feed is flowing near the bottom of the tube causing a non-uniform temperature distribution in the pipe, see Figure 4.11-C and D. Implementing several injection inlets at different sides of the tube wall or other configurations might be beneficial to reduce this non-uniform temperature distribution. It should be noted that the recirculation pattern near the tee-junction occurs since the buoyancy overcomes the viscous effect. At this location the Richardson number ranges from 0.97 - 1.25. This might not be a case for a much higher flow rates. Finally, due to the significant increase of tube diameter (i.e. from

1 mm to 8 mm), the isothermal conditions are difficult to obtain instantaneously, as the surface-to-volume ratio is significantly smaller. Thus, the residence time required to achieve an isothermal state is much longer in comparison to e.g. 1 mm tube. This leads to an increase of the low temperature region (i.e. 600 K – 665 K) that is prone to char formation. As a result, a moderate rate of char formation (i.e. above 1 mol/m³.s) can be observed far after the tee-junction for the big reactor diameter, see also Figure 4.11-B.

Figure 4.11 (A-B) Temperature and rate of char formation contour at an operating gasification temperature of 723 K with varying reactor diameter. (A) 1 mm. (B) 8 mm. (C-D) Velocity vector colored with temperature of the 8 mm reactor on the midplane injection location

4.4 CONCLUSIONS

The model developed in this research utilizes two reaction pathways leading to gas and char formation for glucose gasification in supercritical water. Global kinetics mechanisms are derived for both reactions that occur

in this process. The model is validated against several different operating temperatures giving a good match with experimental data. Feed conversion can be predicted accurately with 4% average discrepancy. Related to the gas-containing-carbon yield, the numerical model tends to overestimate this value in average by 15% at temperatures of 693 K – 733K. Furthermore, even though there is a noticeable difference in the predicted char yield in comparison to experimental data at high temperatures, its formation trend is captured well. Thus, it could be concluded that the developed model is a good first step to provide realistic gas and char formation predictions for biomass gasification in supercritical water.

The sensitivity analysis is conducted for three parameters: a) pre-heated water temperatures; b) flowrate ratio between pre-heated water and glucose mixture; c) tubular reactor diameters. The pre-heated water temperature at above 693 K significantly reduces char yield at an operating gasification temperature of 723 K. Reduction of char production by approximately 27% is obtained by increasing the pre-heated water temperature from 323 K to 723 K. Utilizing pre-heated water with a temperature higher than 723 K, however, brings only a minor improvement. This, however, is not tested here for gasification with higher operating temperatures. Additionally, lowering the flowrate ratio of pre-heated water and glucose mixture from 4:1 to 1:1 leads to a 25% increase of char yield. This takes place as there is not enough energy in the water to rapidly heat up the higher flowrate of glucose. Increasing the pre-heated water temperature may reduce this effect. Finally, it is observed that for larger tube diameters, a considerable increase in char production is obtained. Enlarging the tube diameter from 1 to 8 mm increases the resulting char yield by 107%. This is caused by the extended residence time in the low temperature region between 600 and 665 K, partial heating in the injection and a non-uniform temperature distribution inside the tube. Using several smaller injection inlets at different side of tube may increase mixing and fasten the heating process.

CHAPTER 5

DESIGN OF A SUPERCRITICAL WATER REFORMER FOR PILOT SCALE WET BIOMASS GASIFICATION: NUMERICAL STUDY WITH MODEL COMPOUND GLUCOSE

Abstract

Supercritical Water Gasification (SCWG) is a very promising thermochemical process to convert wet biomass (e.g. pig manure and sewage sludge) into syngas. The SCWG technology, however still faces some technical challenges, such as unwanted solid char production resulting in plugging and fouling of the reactor. A fast heat-up of the biomass feedstock is required to minimize the char formation. Most of the experimental set-ups consist of a very small tubular reactor (e.g. 1 mm diameter). To achieve an economically feasible SCWG system, however, larger tube diameters are necessary. A Computational Fluid Dynamics model that utilizes five competing reactions leading to competing gas and char formation, is developed to investigate glucose gasification in SCW. Furthermore, the Euler-Lagrange approach is used in this study, as real biomass behavior can be best simulated by a flow of particles inside a continuous phase. The model validation against an experimental study shows an average discrepancy of 7 % for char yield prediction, and the trend of the gas yield is also simulated well. In addition to this, a sensitivity analysis shows a minor impact of the biomass particle size on the char yield while the effect of the water temperature before biomass injection is much more significant. Finally, three different biomass injector designs for a given pilot-scale reactor diameter are investigated, and it is concluded that the central injection configuration is optimal and generates the least amount of char.

5.1 INTRODUCTION

Due to the increasing number of the population, the world is currently facing major challenges related to the growing energy demand and overflowing waste streams. For instance, in 2010, the annual production of sewage sludge in EU 27 was 11.5 dry million tons and only 39% of it was recycled [137], while the rest are incinerated or put in a landfill [21, 138]. Another example would be the production of approximately 148 million tons of swine manure per year in Europe [22, 23]. Even though manure can be used for fertilizer, but this might come with a problem of surplus of nutrients in a particular area [139] or health problems due to improper handling [140]. Implementation of the SCWG technology to convert or recycle these biomass wastes is a favorable means to cope with challenges of energy demand and overflowing waste. This technology, however, still faces some challenges, and one of which is char formation that can plug the reactor and also represents a loss of useful carbon [4, 67, 68]. Therefore, it is of major importance to be able to provide insight into char formation during biomass gasification in SCW with a numerical model to better facilitate further process improvement.

In addition to several investigation that have been described in section 3.1 using feedstock such algae, sewage sludge and chicken manure, a number of SCWG for different real biomass compounds (e.g. manure, lignite, olive mill wastewater and wine distillery waste) were also done recently [4, 51-63, 141, 142]. Firstly, investigations related to SCWG of swine and cattle manure in SCW at 873 K and 25 MPa led to approximately 84% and 81%, respectively [52]. In addition to that, other investigations for SCWG of fruit pulp (from waste juice product) and fruit waste conducted at 873 K and 25 MPa, showed a CGE of 49 % for the fruit pulp feed [55] and a CGE ranging from 24 % - 33 % depending on the fruits waste feed [63]. One similarity among these investigations is that these authors noticed that char was produced during the gasification experiments. Through investigations that were conducted using model compounds, Hendry et al. [80] observed no char formation when they implemented an instantaneous feed heating by injecting the feed into pre-heated water right before it enters the reactor. Consequently, Zöhrer et al. [81] then stated that the unwanted char formation can be minimized through a fast heat-up of the feedstock. In relation to results from other investigations using model compounds, this can be seen in section 4.1. On the contrary to the high number of journal papers published on experimental investigation on SCWG

of biomass, there are only few papers related to numerical investigations as has been presented in section 3.1 and 4.1.

Taking these into consideration, it is evident that the amount of literature that addresses SCWG of biomass numerically is quite limited. Furthermore, in the exception of author's work presented in Chapter 4, there is lack of models that account for the chemical reactions that might lead to char formation in the process. In addition to that, the developed models were mostly used to investigate a laboratory scale test-rig. In this research, a Computational Fluid Dynamic (CFD) model that utilizes a five competing reactions leading to competing gas and char formation is developed to investigate glucose gasification in SCW. Furthermore, the Euler-Lagrange approach is used in this study, as real biomass behavior can be best simulated by a flowing particle inside a continuous phase.

In the following section the modelling approach is described and an overview of the fluid properties, the reactions kinetics, and the boundary and operating conditions are discussed. The third section describes the validation of the model against experimental data from the literature that were measured using a small diameter helical coil tubular reactor. In the fourth section, a sensitivity analysis on particle diameters and pre-heated water temperature is presented and finally, the developed model is used to design an optimum injector for a pilot scale SCWG reactor with low char formation.

5.2 MODELLING APPROACH

The numerical investigation is conducted using the Euler-Lagrange approach within a commercial CFD package, ANSYS Fluent 16.0. This approach assumes that the biomass behaves as discrete liquid particles flowing in a continuous phase. The governing conservation equations, the relevant turbulence model and the relation between liquid particles and the continuous phase in the developed model are presented in this section. In addition to that, the reaction kinetics and the method to approximate the relevant fluid properties are described. Finally, the domain of the system and the discretization scheme are presented.

The governing equations and turbulence model that is used in this study are discussed in section 3.2.1 and section 3.2.2, respectively.

5.2.1 DISCRETE PHASE MODEL

This numerical model assumes that the biomass feed (i.e. glucose) is injected in the reactor in the form of droplets. These droplets are initially assumed to have a uniform diameter as there is currently no clear description of the droplet diameter distribution in a SCWG process. Particle trajectories in the continuous phase are predicted by integrating the force balance on the droplets in accordance to Eq 5.1 [110]. The first term on the right hand side of the equation represents the drag force and the particle relaxation time, while the second and third term represent the influence of gravity and additional acceleration, respectively. Interaction between droplets is neglected as they are very much diluted in the continuous phase, and only the interaction between the droplets and continuous phase are considered (i.e. two-way coupling). The dispersion of droplets is predicted using the stochastic tracking (random walk) model.

$$\frac{d\vec{u}_p}{dt} = (\vec{u} - \vec{u}_p) \left(\frac{18\mu}{\rho_p d_p^2} \right) \left(\frac{C_d Re}{24} \right) + \frac{\vec{g}(\rho_p - \rho)}{\rho_p} + \vec{F} \quad \text{Eq 5.1}$$

During the travelling in the continuous phase, the droplets experience heating up and evaporation due to heat transfer from the surrounding fluid. At a relatively low evaporation rate condition and no presence of very fast chemistry, the effect of Stefan flow is minimal [143]. Due to this, the rate of droplet vaporization is assumed to be governed by gradient diffusion, and therefore, the heat and mass transfer in the droplet are calculated using the diffusion-controlled model in ANSYS Fluent. The mass flux at the surface of the droplets is calculated based on the vapor concentration difference at the droplet surface in comparison to the continuous phase, see Eq 5.2. The vapor concentration at the droplet surface can be evaluated assuming that the partial pressure of the vapor at the interphase is equal to the saturated vapor pressure [110], see Eq 5.3. The mass transfer coefficient in Eq 5.2 is obtained using the Sherwood correlation, see Eq 5.4.

$$N_i = k_c (C_{i,s} - C_{i,\infty}) \quad \text{Eq 5.2}$$

$$C_{i,s} = \frac{P_{sat}(T_p)}{RT_p} \quad \text{Eq 5.3}$$

$$Sh_{AB} = \frac{k_c d_p}{D_{i,m}} = 2.0 + 0.6 Re_d^{1/2} Sc^{1/3} \quad \text{Eq 5.4}$$

The change of the droplet temperature in time is calculated in accordance to the heat balance shown in Eq 5.5 [110]. The first term on the right side of the equation represents the convective heat transfer from the droplet to the continuous phase, while the second term represents the sensible heat change in the droplet.

$$m_p c_p \frac{dT_p}{dt} = h A_p (T_\infty - T_p) + \frac{dm_p}{dt} h_{fg} \quad \text{Eq 5.5}$$

5.2.2 FLUID PROPERTIES AND REACTION KINETICS

Part of the explanation in this section are discussed in section 3.2.3 and section 4.2.1

As glucose is dissolved in the presence of excess water, its decomposition behavior is assumed to be in accordance to a pseudo first-order kinetic [4, 71]. In the current investigation, a CFD model that considers 5 competitive decomposition reactions is developed and the reaction schematic is shown in Figure 5.1. These reactions are based on the glucose decomposition pathway that was proposed by Promdej and Matsumura [131].

Figure 5.1 Glucose decomposition pathway that is used in the CFD model

The gas formation reaction is represented as reaction 3 in Figure 5.1, and its empirical stoichiometry (Eq 4.4) is derived from the experimental results of Lee et al. [71]. Reaction 1 (Eq 5.6) and reaction 2 (Eq 5.7) in Figure 5.1 represent the forming of intermediates during the gasification (i.e. 5-HMF and Total-Organic-Compound, TOC), and for simplification, it is assumed that these intermediates have similar properties as glucose. Assuming that the

char formation solely produces pure carbon and water, an idealized reaction stoichiometry (Eq 4.5 and Eq 5.10), similar to what is obtained by Milosavljevic et al. [144] is used. All reaction stoichiometries mentioned above, which determine the gaseous and char product compositions, are assumed to be independent of the feed concentration.

Kinetics of the reactions is described using the Arrhenius equation, see Eq 5.11.

$$k_r = A \exp^{-\frac{E_a}{RT}} \quad \text{Eq 5.11}$$

The Pre-exponential factor (A) and Activation Energy (Ea) for the different rate constants are summarized in given in Table 5.1. These values are obtained are obtained from the work of Promdej and Matsumura [131].

Table 5.1 List of A and Ea values for the 5 decomposition reactions

	Unit	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5
Rate constant	s ⁻¹	k1	k2	k3	k4	k5
A	s ⁻¹	314.2	2.52×10^8	36.25	3.07×10^8	4.48×10^{-04}
Ea	kJ/mol	42.34	103.6	47.24	123.8	-4.705

The negative value for the activation energy of reaction 5 is not a physical value but a mathematical expression to account for deactivation of reaction at high temperature (i.e. no char is formed at high temperature). This type of formulations is commonly used in the literature [132-134]. In accordance to the experimental results of Promdej and Matsumura [131], reaction 1 and 4 are assumed not to occur at temperatures above 750 K and 650 K, respectively. Kinetics of reaction 1 to 5 are shown in Figure 5.2A to 2E, respectively.

Figure 5.2-E shows a significant deviation between the predicted and the experimental kinetics for reaction 5. To account for this, an expanded Arrhenius formula as is given in Eq 5.12 is used, see [18]. The 2nd order

polynomial formula that is used to correct the kinetics at the temperature range of 570 – 750 K is given in Eq 5.13. The results of this correction are presented in Figure 5.2-F

$$k_{r,expanded} = A T^{\beta} \exp^{-\frac{Ea}{RT}} \quad \text{Eq 5.12}$$

$$\beta = -(1.617283 \times 10^{-5}) T^2 + (2.11213 \times 10^{-2}) T - 6.83927 \quad \text{Eq 5.13}$$

5.2.3 EXPERIMENTAL DATA, GEOMETRY AND BOUNDARY

Experimental results on SCWG of glucose published by Promdej and Matsumura [131] are used to validate the developed CFD model. Their experiment was performed in a helical tubular reactor that is equipped with an injector inlet, which contains two inlets and resembles a tee junction, see Figure 5.3-B. The tube has a 1 mm inner diameter and a 20 m axial length. The pre-heated water that provides an instantaneous heating comes from the main inlet. The feed solution, which contains 7.5 wt-% glucose, is introduced from the injection inlet. The volume ratio of the main inlet flow to the injection inlet flow is maintained at 4:1. The experiment was done at 25 MPa for varying operating temperature between 573 – 733 K. The influence of the residence time was investigated by varying the total mass flow rate during the experiments.

Figure 5.2 (A-E) Kinetics of reaction 1 – 5, from Promdej and Matsumura [131]. (F) Corrected kinetics of reaction 5 with the 2nd order polynomial for the temperature exponent.

The numerical domain that is used in the current CFD investigation is a shortened version of the experimental setup, with an approximate length of 5 m instead of 20 m. This modification is done due to the impractical computational power required to simulate the whole reactor. Additionally, it is expected that the main processes will occur in the first part of the reactor. To compensate for this shorter length, the flow velocity is varied such that the

residence time of the feed in the simulation matches the residence time in the experiments of Promdej and Matsumura [131]. The change of the flow velocity has only a slight effect on the overall heat transfer that takes place in the simulation in comparison to the experimental situation. This is confirmed by the fact that for both simulation and experiment, the Nusselt number is much higher than 1. This represents a very high heat transfer coefficient for both cases, which is due to the small reactor diameter (1 mm) and the high wall temperature. Furthermore, a low Richardson number (i.e 0.087) is found in the simulation, which means that the natural convection in the system can be ignored as it is much lower than the forced convection. Taking all these into account, it is assumed that the final amount of produced char is dominated by the residence time. The residence time is therefore kept at the same value as that of the experiments for a fair comparison of the simulation results with experimental data. Figure 5.3-B presents the schematic overview of the whole reactor together with the injector tube.

Figure 5.3 (A) Schematic of the helical reactor (B) Schematic of the injector tube

Experimental data [131] showed that an isothermal condition is achieved right after the feed injection. Therefore, the value for both pre-heated water and operating temperature are assumed to be equal, and varies between 573 – 733 K. The wall temperature is assumed to be constant and equal to the investigated operating temperature. Mass flow boundary conditions are imposed for both inlets. The flow rate of the preheated water ranges is varied 2.6×10^{-4} kg/s to 4.31×10^{-5} kg/s, for operating temperatures of 623 – 723 K. The injected feed mixture temperature is kept constant at 300 K, whereas the total feed mixture flow is varied from 6.54×10^{-4} kg/s to 1.08×10^{-5} kg/s for operating temperature of 623 K to 723 K. The feed mixture is made up of water as a continuous phase and pure glucose with a 7.5 wt-% that is injected as a discrete phase in the form of droplets. These droplets enter with a uniform

diameter of 50 μm and are subjected to evaporation. Both inlets assume a turbulence intensity ratio of 5 %, which is necessary to determine the k and ω for the relevant turbulence model. The used mass flow rates correspond to a residence time of approximately 7 seconds for the relevant operating temperature. The pressure outlet boundary condition is used to impose an operating pressure of 25 MPa.

5.2.4 NUMERICAL METHODS AND DATA ANALYSIS

Numerical results presented in this article are obtained by assuming a two way turbulence interaction between the discrete phase and the continuous phase. In addition, a uniform droplet diameter is applied for the glucose feed. The unstructured mesh method is used to discretize the geometry into tetrahedral elements in the core and hexahedral prisms on the wall boundary. The pressure based solver taking into account the gravitational force is utilized, and a coupled computational scheme is applied to calculate the velocity and pressure relation. The volumetric reaction approach is used assuming laminar-finite rate reactions based on the reactions kinetics and stoichiometries that are described in section 5.2.2. All of the relevant conservation equations are solved with a second order upwind scheme. The convergence criteria are the residual values that have to be below 10^{-4} for continuity equation and 10^{-6} for the other equations. To avoid the hysteresis effect due to initial simulation conditions, all of the simulations are conducted for several hundreds more iterations after the convergence criteria are reached. The model employs the pseudo-transient technique together with the BCG stabilization method to maintain the stability of the solver during the calculation process.

The methods to validate the model are discussed in section 4.2.5.

5.3 RESULTS AND DISCUSSION

This section presents the numerical results obtained with the CFD model. These results are validated against experimental data and any discrepancies are discussed in detail. Subsequently, a sensitivity analysis on the influence of the droplet diameter of the glucose feed and the pre-heated water temperature is conducted.

5.3.1 MODEL VALIDATION

All numerical calculations are done in a discretized mesh that has been selected from a mesh independency study. This mesh independency study is conducted to ensure that the selected mesh contains a sufficient resolution to resolve the governing equations and that the results are no longer dependent on the grid size. The mesh refinement is implemented only for the injector tube that is shown in Figure 5.3-B, which is acceptable as the isothermal condition is achieved very rapidly. Mesh refinement is done by doubling the number of the elements at this location. The three meshes that are considered consist of: 1) 2.7 million elements; 2) 3.8 million elements; 3) 6.2 million elements. These numbers represent the amount of elements only on the injection part. Mesh 1 with 2.7 million elements provides satisfactory results and is selected for the rest of the investigations.

The developed model is validated for three different operating temperatures, which are: 623 K; 698 K; and 733 K. Figure 5.4-A and B show the comparison of the carbon yield contained in the produced gaseous compounds and char. As it can be observed from these figures, the model can predict the gas yield accurately, with an average difference of 30%. The highest disparity that occurs at 733 K is due to the continuous high rate production of 5-HMF. As can be seen in Figure 5.2-A, the decomposition of glucose toward 5-HMF tends to be deactivated at high temperature. This behavior is not captured in the implemented pseudo first-order kinetic model and this leads to an even higher production of 5-HMF at this temperature. This brings about the reduction of the produced TOC as there are two competing glucose decomposition reactions. The smaller available amounts of TOC ultimately contribute to less production of gaseous compounds. In addition to that, Figure 5.2-C displays that TOC gasification behavior goes further away from the Arrhenius description with an increase of temperature. This also contributes to the difference in the predicted carbon-containing gas yield. Implementing the expanded Arrhenius equation would be advantageous to improve the accuracy of the model.

Figure 5.4-B shows a minor discrepancy between the calculated and measured char yield of approximately 7 %. At lower temperature the model tends to underestimate the char production and it tends to slightly overestimate it at high temperature. This phenomenon is due to the fact that the dominant char production mechanisms are different at these two temperatures. Char formation from 5-HMF described with reaction 4 is more dominant at lower temperature, where else at higher temperature the char

production mainly comes from TOC as is determined by reaction 5. These processes are captured quite nicely with the current five reactions model.

Considering the obtained results, it can be concluded that the general trend of the gas formation is captured properly, and the inaccuracies in the char formation predications are relatively minor. Therefore, the model is used for further investigation.

Figure 5.4 Comparison of numerical and experimental results of carbon contained in char and gaseous compound at 623 K, 698 K and 733 K

5.3.2 SENSITIVITY ANALYSIS

The influences of two parameters on the char yield prediction from the model are discussed here. The two parameters are: a) glucose droplet diameter; b) pre-heated water temperature when operating at a high reactor temperature. Further information related to the parameter values and operating conditions are listed in Table 5.2

Table 5.2 List of investigated parameters in the sensitivity analysis

Case	Investigated parameter	Droplet diameters	Pre-heated water temperature	Operating temperature	Reactor diameter
A	Droplet diameter	50 μm	623 K	623 K	1 mm
B		100 μm			
C		150 μm			
D		50 μm	733 K	733 K	
E		100 μm			
F		150 μm			
G	Pre-heated water temperature	50 μm	300 K	823 K	
H			400 K		
I			500 K		
J			600 K		

Case	Investigated parameter	Droplet diameters	Pre-heated water temperature	Operating temperature	Reactor diameter
K			700 K		
L			800 K		

5.3.2.1 EFFECT OF PARTICLE DIAMETER

The influence of the injected droplet diameter on the char formation in SCWG process is studied using three different diameters of 50 μm , 100 μm and 150 μm . This investigation is done for two different operating temperatures, namely 623 K and 733 K. The size of the glucose droplets is expected to affect the evaporation period of the feed and this will determine the availability of glucose feed to react with water in the continuous phase (e.g. in the mixing and locally colder zone or in the more uniform hot zone).

Figure 5.5-A and B show that the varying droplet diameters show a relatively minor effect on the produced char. This behavior is due to the fact that the residence time of the glucose droplets in the heat up zone (e.g. region with non-isothermal temperature distribution) is significantly smaller than the time required for complete evaporation of the droplets (see Figure 5.6). This means that for all of the droplet diameters, the surrounding fluid temperature is comparable for most of the time span during the evaporation process. Therefore, all three cases (i.e 50, 100 and 150 μm) show a similar glucose flow field and experience a similar char reaction process and thus a similar char yield during gasification. On the other hand, Figure 5.5A and B show that reactor temperature has a major influence to the char yield.

Figure 5.5 Char yield comparison with varying particle diameters at different operating temperatures of 623 K and 733 K

In addition to this, it was also observed that the char formation process is relatively slow compared to the evaporation rate. This can be shown by using a timescale ratio (τ_r), which can be defined as follows:

$$\tau_r = \frac{\tau_{reaction (R5)}}{\tau_{evaporation}} \quad \text{Eq 5.14}$$

Where $\tau_{evaporation}$ is the required time for the droplets to evaporate completely, and $\tau_{reaction (r5)}$, represents the required time for reaction five at the investigated operating temperature (i.e. 623 K and 733 K). Reaction 5 is used in this ratio as this represents the kinetics of char formation at high temperature. For all operating conditions and this reactor size, it is calculated that the value of $\tau_r \gg 1$. This means that evaporation is quite fast in comparison to the kinetics of char formation.

Figure 5.6 (A-B) Results obtained for investigation at 623 K and 733 K for three different particle diameter. (line, —●—) required time for evaporation, (line, —■—) residence time of particle in the heating up zone

5.3.2.2 INFLUENCE OF PREHEATING TEMPERATURE

From literature [69, 70, 80] it is known that rapid heating of the feed can minimize char formation. This was also numerically investigated at an intermediate reactor temperature (i.e. 723 K) in our previous study, see [145]. In the present study, the injected feed with a droplet diameter of 50 μm at a reactor temperature of 823 K is subjected to six different pre-heated water temperature.

Results in Figure 5.7 show that injecting the feed into lowest pre-heated water temperature (i.e. 300 K) at a reactor temperature of 823 K leads to an exceptionally small char yield of approximately 0.00039. This value is approximately ten times lower than the char yield found when implementing a pre-heated water and reactor temperature of 723 K, see Figure 5.4-B.

The use of small diameter size reactor tube (for cases that are shown in Figure 5.4 and Figure 5.7) creates a highly enhanced heat transfer due, which ensures that the operating temperature (i.e. reactor temperature of 823 K) is achieved rapidly. This reduces the zone that has a non-isothermal temperature distribution near the tee junction. Additionally, it has been shown in, Figure 5.2-F that the kinetics of reaction 5 is significantly higher at the temperature of 723 K compared to at the temperature of 823 K. This means that the production of char throughout the whole gasification process is higher for the case at temperature of 723 K, in comparison to case at 823 K. These two

factors lead to a significant decrease in char yield when utilizing a reactor temperature of 823 K.

Figure 5.7 Char yield comparison for varying pre-heated water temperatures at an operating temperature of 823 K with a particle size of 50 μm

Figure 5.7 shows that there is no change in the char yield found by applying a hotter pre-heated water from 400 K up to the temperature of 600 K. A char yield decrease of approximately 8 % and 9 % is observed when using a pre-heated water temperature of 700 and 800 K respectively. This decrease in char yield is due to the difference in heating process and evaporation behavior.

Figure 5.8-A shows that the use of relatively colder water flow (i.e. 300 K) leads to a slower heating up of overall fluid flow. This subsequently leads to the evaporation of the glucose droplets in the region with fluid temperature of 530 K – 670 K. This behavior can lead to a high char formation as both of the char formation kinetics are quite fast at that temperature range. On the contrary, implementing a pre-heated water flow of 800 K significantly changes the temperature distribution in the flow. Glucose droplet trajectories shown in Figure 5.8-B suggest that these droplets are completely evaporated in a high temperature region (i.e. higher than 750 K). This difference in evaporation behavior is the main reason for the reduction of the char yield.

Figure 5.8 Temperature contour and diameter of tracked glucose droplets. Reactor wall condition at 823 K with a pre-heat water temperature of: (A) 300 K; (B) 800 K.

5.4 EFFECT OF INJECTOR DESIGN FOR A PILOT SCALE REFORMER

In this section, the developed model is used to evaluate three different injector designs. The geometries of the designs are explained briefly and the corresponding boundary conditions for the simulations are given. Finally, the results in relation to the char yield are discussed.

5.4.1 GEOMETRY AND BOUNDARY CONDITIONS

The three numerical domains that are investigated in this section are shown in Figure 5.9: I) straight pipe with a 90 ° degree injection tube; II) straight pipe with a 45 ° degree injection tube; III) straight pipe with a central injection tube. The inner diameter of the pipe is set to 13.8 mm and the total mass flowrate in the system is set to 150 kg/h, and these values are in accordance

with the reactor developed by our project partner, SPARQLE International b.v. The total heated length of the pipe is approximately 2.9 m. This length is acceptable as an isothermal condition (and therefore no further heat up occurs) is reached after approximately 1.5 m from the pre-heated water inlet. The inner tube for the feed injection is set to 6 mm for all of the injector designs.

For the numerical calculations, a mass flow boundary condition is imposed on the main inlet and injector tube with a value of 0.033 kg/s and 0.00833 kg/s, respectively. The temperature of the flow from the main pipe and injector tube are set to 823 K and 300 K, respectively. For all the investigated cases, the overall glucose concentration in the system is set to be 5 wt-%. This glucose is injected as droplets particles with a uniform diameter of 150 μm . In addition, a constant temperature boundary condition equal to 823 K is set on the pipe wall. Finally, a pressure outlet boundary condition is used to provide an operating pressure of 25 MPa.

Figure 5.9 (A-C) Schematic of injector configuration I, II and III

5.4.2 INFLUENCE OF INJECTION DESIGN AND FEED TEMPERATURE

Numerical results show that using different injector designs may lead to a noticeable reduction in the char yield. Implementation of the injector design I, while injecting the feed at 300 K, leads to a char yield of approximately 0.0005. In comparison to this value, using injector design II and III reduces the char yield to 6% and 25%, respectively. These results can be seen in Figure 5.10-A.

Figure 5.10 Char yield comparison at two different pre-heated water temperatures for all designs. (A) 300 K; (B) 473 K. For both cases the reactor temperature is 823 K

It can be seen from the temperature contour in Figure 5.11-A that there is only a minor difference for injector design I and II. The cold water that comes from the injection inlet is heated up gradually along the pipe length. On the contrary, the heating up process of the cold water with injector design III is considerably faster. This is due to the creation of a flow vortex by the central injection tube that enhances the mixing process.

Figure 5.11-B presents the rate of char formation for all three injector designs. This figure clearly demonstrates that the char formation process occurs in a location further from the injection point. This is due to the fact that there is no evaporated glucose available for any reaction process near the injection point. The evaporation of glucose droplets occurs slowly and it is completed only after the droplets move further downstream. After the evaporation of the droplets, the gasification and char formation reactions start to take place.

Figure 5.11-B shows that the area in which char is intensely produced is similar for design I and II, but a more noticeable difference (i.e. narrower region) can be seen for design III. Different recirculation patterns throughout the pipe length are the major reason of this behavior. Injector design I produces a twin swirls pattern as can be seen in Figure 5.11-C. This swirl carries the relatively hot water near the wall (as well as the char-producing-compounds) and mixes it with the colder fluid in the core flow. The char-producing-compounds are exposed to a colder surrounding temperature and this leads to a higher char yield. In contrast to this, only one whole swirl pattern is observed when using injector design III, see Figure 5.11-E. Within this one-swirl pattern, the mixing of hot and cold water does not take place. The char-producing-compounds are always carried near the wall and are surrounded by the relatively hot fluid. This greatly reduces the char yield to a 25 % difference in comparison to design I. Figure 5.11-D shows that injector design II produces a swirl pattern that is in between the other two patterns, and it slightly reduces the char yield.

As is displayed in Figure 5.10-B, the difference in char formation between the three injector designs for a slightly warmer feed seems to be not noticeable. A char yield of about 0.00028 is obtained with injector design I and a feed temperature of 473 K. In comparison to this, utilizing injector design II and III lead to a slight reduction of the char yield with 10% and 25% reduction, respectively. Nevertheless, when using injector designs II and III, the trend of the char formation reduction remains relatively similar to the case with the feed at temperature of 300 K. In comparison to the use of a cold feed (i.e. 300 K), pre-heating the feed to 473 K leads to a 44% reduction of char formation. The relatively warmer fluid environment due to the pre-heating of the feed can significantly minimize char formation in the reactor. Looking at the char yield, design III is considered as optimal for the pilot scale test.

Figure 5.11 (A-B) Temperature and rate of char formation contour of three different injector designs. (C-E) front view streamline colored with temperature of design I, II and III, respectively.

5.5 CONCLUSION

A CFD model including five competing reactions for gas and char formation has been developed. Validation against experimental results shows only a small discrepancy of 7% for the char yield prediction. For the validation against the gas yield, the general trend is simulated properly with an average inaccuracy of 30%. These discrepancies might be due to the excess production of 5-HMF at high temperatures. This does not occur in reality, as experimental data show that the reaction that produces 5-HMF is deactivated at high temperature. To mitigate this effect, a similar behavior could therefore be imposed in the CFD model. Another reason for these discrepancies can be due to the inaccurate reaction kinetics. This effect can be minimized with the use of the extended Arrhenius equation. Taking these into consideration, it can be concluded that the model can provide an acceptable simulation for the SCWG of glucose.

Two parameters have been investigated for the sensitivity analysis, which are: a) glucose droplet diameter; b) pre-heated water temperature. It is found that the droplet diameter plays a minor role related to the char yield in the investigated configuration. This is due to the fact that the evaporation time for all particle sizes is longer than the time required for the heating of the feed. This means that all droplet sizes face a same surrounding temperature profile resulting in a comparable char yield. However, for a larger reactor diameter the behavior can be different because of more non-uniform temperature regions. In addition, it was found that for pre-heated water a temperature of 700 K and above is beneficial in reducing char formation. This is mainly due to the fast droplet evaporation and fast heating up of the surrounding fluid temperature.

An investigation on three different injector designs on a reactor with a pilot scale diameter is also conducted. It is shown that a central injection design can provide 25 % reduction of char formation in comparison to the standard 90 ° degree injection tube. This behavior is due to the creation of a single swirl pattern in the central injector design, as in contrast with the two swirls pattern of the other injector design. The single swirl pattern carries the char-producing-compounds near the wall and increases its exposure toward a relatively hot surrounding fluid. This ultimately minimizes the production of char. In addition, it is also found that pre-heating the feed is highly beneficial in reducing the char formation. Pre-heating the feed from 300 K to 473 K leads to a beneficial reduction of 44% of the char yield.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The direct injection of relatively cold biomass into pre-heated supercritical water has been investigated. The main purpose of this novel design is to reduce the char formation during the fast heating up of the biomass. An energy efficiency analysis has shown that the direct injection system has in general a lower thermal efficiency compared to the conventional premixed system. This is due to the fact that the biomass is only partially preheated in the direct injection system, and consequently the amount of residual heat in the product gas is increased. In addition to that, non-isothermal mixing of biomass with supercritical water also plays a role in decreasing the system performance. In general, a thermal efficiency reduction of 8% – 23% can be expected when using this novel approach.

In the present study a system model of the SCWG process has been developed to analyze the performance of the novel direct injection system. The operating parameters that have a significant influence to the system's performance are: a) ratio of hot supercritical water to the total feed; b) the reactor temperature. To achieve an optimum thermal efficiency, it is recommended to have a ratio of the hot bypass supercritical water to the total feed, in the range of 0.4 – 0.5. Operating with a lower value than 0.4 will significantly reduce the thermal efficiency because of less heat recovery within the system, while a higher value does not result in a significant increase of the thermal efficiency because of the fact that the heat exchanger is less efficient due to the high energy requirement for the water phase change. Additionally, a higher value will result in a highly concentrated biomass that is difficult to pump. With respect to the reactor temperature, it is suggested to operate at a temperature between 570 °C – 600 °C. Operating at a temperature that is higher than 600 °C will lead to an unnecessary loss of thermal efficiency and a reduction in the heat exchanger effectiveness. Lower temperatures than 570 °C may lead to a longer residence time in which the biomass stays in the near-critical condition, which might favor the char formation process. The optimizing method for the thermal efficiency of the system was based on a pinch point analysis. For a reactor temperature of 575 °C, a cold biomass stream with 12 wt-% dry matter content (translated into 8 wt-% biomass of the total feedstream) and a 0.4 ratio of hot supercritical water

to the total feed, the direct injection system achieved an overall thermal efficiency of 50%. This value is still lower than the efficiency of the conventional premixed SCWG system having a thermal efficiency in the range of 33% – 72%.

The direct injection of wet biomass into hot supercritical water will have an influence on the mixing, heat transfer and chemical reactions (gas and char formation) after the injection point and in the reactor. To provide insight into flow and reaction behavior in the biomass SCWG system, numerical modelling has been applied. Three different CFD models have been developed, which are: a) single-phase model for glycerol gasification; b) single-phase model for glucose gasification; c) multi-phase model for glucose gasification.

The single-phase model for glycerol gasification has been developed as glycerol does not produce char when gasified. So with this model the mixing, heat transfer and gas formation can be investigated without char formation processes. The validation of the model against experimental data from literature shows only a slight difference of 6% for the temperature at the reactor outlet, and 16% discrepancies for the carbon gasification efficiency. In this model for glycerol gasification the Arrhenius formula is replaced by the expanded Arrhenius formula to describe the reaction kinetics and this turned out to be beneficial in the performance of the model compared to the experimental data. Detailed numerical results show that the injection of cold biomass into hot supercritical water leads to the occurrences of flow recirculation in the injection tube, which may result in a gradual partial heating of the wet biomass favoring extra char formation for other feed than glycerol. The recirculation may be reduced by using a smaller injection tube or by increasing the injection flow rate. In addition to that, the gravitation force causes a swirling motion of the fluid as it flows in the reactor creating a non-uniform concentration and temperature distribution. This will have a significant effect on the reaction progress.

The CFD model for glucose gasification has been developed to reveal the key parameters for char formation in SCWG. The single-phase model assumes that glucose can only be converted to either gas or char via two different reaction paths. This simplified approach is used as a first step towards the utilization of CFD modelling for this research. The model results show that the glucose conversion can be simulated with only 4% average difference compared to experimental data from literature. Furthermore, a slightly larger discrepancy of 15% for the gas yield (for carbon containing components) has been seen when analyzing the process at operating

temperatures of 420 - 460 °C. At low temperatures (e.g. 350 °C), the char formation is predicted well, while at higher temperatures than 350 °C the char formation is underpredicted. For further improvement, an Euler-Lagrange multi-phase CFD model with five competing reactions for gas and char formation prediction has been developed. The application of a discrete phase approach (Euler-Lagrange) has been applied to better mimic the biomass particle behavior (evaporation and devolatilization) during SCWG. This more complex model proves to be very accurate with only 7% average difference for the char yield calculation at operating temperatures of 350-420 °C compared to experimental data. In addition to this, the general trend of the gas yield is also captured well. Remaining inaccuracies can be minimized by applying the expanded Arrhenius method in future studies. Additionally, experimental data show that reaction that decomposes glucose into 5_HMF is deactivated at high temperatures. Therefore, similar behavior should also be included in the reaction scheme of the CFD model. An important finding from the numerical results is that the injection of glucose into supercritical water at a temperature of 450 °C decreases the char yield with 27% in comparison to heating both compounds (i.e. glucose and water) slowly from room temperature (premixed conventional situation). Injection in hotter supercritical water does not bring a major reduction of the char formation. It is also found that reducing the flow rate ratio of hot supercritical water and cold biomass from 4:1 to 1:1 does influence the char formation and leads to an increase in the char yield by 25%. This can be explained by the insufficient energy in the water to rapidly heat up the higher flowrate of cold biomass.

The complex model for glucose gasification has also been tested for a larger reactor diameter to consider upscaling effects. An important finding is that enlarging the reactor diameter from 1 to 8 mm significantly increases the char formation in the process. An increase by approximately 107% was observed when the gasification takes place in a 8 mm diameter tube reactor at a temperature of 450 °C. This increase is due to: 1) the extended residence time in which the biomass stays in the low temperature region between and 330–390 °C; 2) a non-uniform temperature distribution inside the reactor tube; 3) partial heating in the glucose injection tube. Finally, the effect of the configuration of the biomass injector on the char formation has been investigated. The results revealed that the so called central injection design can reduce the char yield with 25 % in comparison to the standard 90 degree injection tube. This can be explained by the different swirl patterns that occur inside the reactor affecting the overall heat transfer. Furthermore, pre-heating the feed from 25 °C to 200 °C is highly beneficial for char reduction as

calculations a reduction of char formation with 44%. It is noted that the discrete phase approach also provides a new insight into the char formation during the gasification process. It is observed that the position with intensive char formation is not located near the injection point, but more downstream. This is due to the fact that particles evaporate and release glucose occurs rigorously at this location. The released glucose is surrounded by water at a temperature of 670 – 740 K, which is critical for char formation process. This situation ultimately leads to an intensive char formation.

6.2 RECOMMENDATIONS

It has been mentioned that the application of a pinch analysis to the flow process can achieve a sufficiently high thermal efficiency of 50%. The overall thermal efficiency can further be improved by utilizing the remaining residual heat of the system for other potential applications, such as district heating or for heat input of an organic Rankine cycle system. The influence of combining any of these options with supercritical water gasification on the overall energy efficiency should be investigated.

The economic feasibility of a SCW plant with direct injection system of the biomass feed should also be further studied. An interesting option that can be considered is to replace the preheated water stream by another biomass or waste stream such as organic waste water that has less tendency to char formation during heating up. The biomass slurry (sewage sludge) can then be injected into this preheated organic waste stream. In this way two different biomass feeds can be used which will certainly improve the energy efficiency and the economic feasibility of the system.

The CFD modelling can be further improved by considering the char (that is produced during the gasification process) as a discrete phase material. In this way, it is possible to observe the location in which the char particles may hit the wall of the reactor. Also, salt precipitation can be included in the CFD model as a discrete phase particle, as this is another major challenge for the SCWG. Additionally, it is recommended to investigate the full pilot-scale reactor with the CFD model with a further experimental validation of the model. For this purpose a pilot-plant with direct biomass injection should be developed. First tests could be done with glucose to test the model.

The developed CFD model can be used to design a pilot-scale reactor that operates with real biomass. For this purpose, a laboratory set-up that can provide the decomposition kinetics of this real biomass is essential. It is recommended to use a continuous experimental set-up, as it is shown by

literature that kinetics obtained from a batch set-up (autoclaves) is noticeably lower. This set-up, should also be able to provide a complete carbon balance, as several literature show a significant inaccuracies when closing the carbon balance.

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NOMENCLATURE

A	Pre-exponential factor	[1/s]
C_f	Mass flow of carbon in the biomass feed	[kg/s]
CGE	Carbon gasification efficiency	[%]
D, D_h	Diameter and hydraulic diameter	[m]
Ea	Activation energy	[kJ/mol]
Fr	Froude number	Dimensionless
F_2	Blending function	[-]
g	Gravity	[m/s ²]
Gr	Grashof number	Dimensionless
G_k, Y_k	Generation and dissipation of k	[m ² /s ²]
G_ω, Y_ω	Generation and dissipation of ω	[1/s]
h	Specific enthalpy	[J/kg]
J_i	Diffusion flux	[kg/m ² s]
J_q	Heat flux density	[J/m ² s]
k	Turbulence kinetic energy	[m ² /s ²]
k_r	Rate constant of the reaction	[1/s]
M	Molar mass	[kg/kmol]
p	Pressure	[Pa]
q_r	Heat generation or consumption	[J/m ³ s]
R	Universal gas constant	[kJ/mol K]
S	Strain rate magnitude	[-]
S_k, S_ω	User-defined source term of k and ω	[-]
t	Time	[s]
T	Temperature	[K]
u	Velocity	[m/s]
ν	Kinematic viscosity	[m ² /s]
x	Cartesian coordinate	[m]

Greek symbols

α^*, α_1	Damping coefficient	[-]
β	Temperature exponent	Dimensionless
β_b	Thermal expansion of the bulk fluid	[1/K]
δ_{ij}	Kronecker delta	[-]
μ	Dynamic viscosity	[Pa s]
μ_t	Eddy viscosity	[Pa s]

ρ	Density	[kg/m ³]
τ_{ij}	Viscous stress tensor	[-]
ψ	Molar rate formation	[kmol/m ³ s]
ω	Specific dissipation rate	[1/s]

Subscripts

b	Bulk
e	End
s	Start
w	Wall

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PUBLICATIONS

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