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Economic assessment of different biomass hydrolysate applications depending on the operation mode of the fixed-bed pretreatment

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Resumen:

En los últimos años, la gran mayoría de las biorefinerías se han enfocado a la producción de etanol a partir de celulosa, ignorando el potencial de fracciones como la lignina y las hemicelulosas para ser transformadas en productos químicos y combustibles. Las biorefinerías de tercera generación en cambio, apuntan a una utilización eficiente de todas las distintas fracciones. Sin embargo, el pretratamiento de biomasa supone un importante cuello de botella para el proceso, ya que la utilización de bajas relaciones sólido/líquido resulta en elevado consumo energético, gasto de agua y bajas concentraciones de azúcares en los productos. El principal objetivo de este trabajo es investigar la influencia de las condiciones de reacción y de la configuración del reactor durante el pretratamiento con agua caliente presurizada sobre el potencial de la fracción hemicelulósica y sobre la economía general del proceso. Con este objetivo, se ha estudiado la hidrólisis térmica de la paja de trigo en un reactor de lecho fijo de alta presión bajo cuatro modos de operación distintos (batch, flow through, recirculación completa y recirculación parcial). Los distintos modos de operación han sido modelados y simulados en Aspen Custom Modeler (ACM) y las respuestas más importantes del modelo han sido evaluadas mediante Response Surface Methodology (RSM). La influencia de factores como temperatura, tiempo de residencia y acidez del medio durante el pretratamiento ha sido confirmada de manera experimental a escala laboratorio. Por último, las condiciones de reacción y las configuraciones óptimas del reactor han sido integradas en un modelo completo de una instalación de biorefinería. La evaluación económica del proceso integrado evidenció que el consumo de agua es el factor más importante a tener en cuenta si se escogen aplicaciones con bajo valor en el mercado, mientras que si se producen químicos con alto valor añadido, el consumo de agua y la recuperación de los azúcares son igualmente importantes.

Hamburg University of Technology

Institute of Thermal Separation Processes

Master's Thesis

Economic assessment of different biomass hydrolysate applications depending on the operation mode of the fixed-bed pretreatment

by

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Abstract

So far, most biorefinery facilities have focused on the production of bio-ethanol from the cellulosic fraction, disregarding the potential of lignin and hemicellulose fractions for being transformed into a wide range of platform and fine chemicals. Modern biorefineries instead, aim at an efficient utilization of all the different fractions. Unfortunately, pretreatment of the biomass represents a serious bottleneck for the biorefinery process, since the use of low solid-to-liquid ratios results in high energy needs, elevated water consumption and low sugar concentrations of the products. The main objective of this work is to investigate the influence of reaction conditions and reactor operating modes during the Liquid Hot Water (LHW) pretreatment on the potential hemicellulose applications and on the overall economic feasibility of biorefinery facilities. For this purpose, the performance of thermal hydrolysis of wheat straw in a high-pressure fixed-bed reactor under four different reactor configurations (batch, flow through, circulation and partial recirculation) have been studied.

The alternative operating modes for the fixed-bed reactor have been modelled and simulated in Aspen Custom Modeler (ACM).and the most crucial model responses have been studied by means of Response Surface Methodology (RSM). The influence of the pretreatment conditions such as temperature, residence time and acidity of the medium during LHW pretreatment have been successfully confirmed at lab-scale. Particularly, the operation with partial recirculation of hydrolysate presented outstanding results in terms of sugar recovery (60 %) and sugar concentration (40 g/L). Finally, the optimum pretreatment conditions and reactor configurations have been integrated in an existing overall biorefinery model. The economic assessment evidenced that water consumption is the most critical factor for low market value applications whereas the production of finer chemicals is equally dependent on sugar recovery and water utilisation.

Symbols

Latin symbol	Unit	Meaning
a	g/g	Effective acid concentration
cp	J/kg	Specific calorific heat
g	m/s^2	Gravitational acceleration
k_i	var.	Kinetic constant
k_{i0}	var.	Pre-exponential factor
P	bar	Pressure
R_0	-	Severity factor
r_{ij}	Var.	Reaction rate
t	s	Treatment duration
t	s	Time
T	°C	Temperature
U	m/s	Interstitial velocity
y	-	Response variable
Y_{step}	g/g	Filling level variable
Y_{ij}	g/g	Solubilized component concentration
X_H	g/g	Solid hemicellulose concentration
z	-	Axial direction in the fixed bed

Greek symbol	Unit	Meaning
α	-	Relative distance of the star points in a CCD
β	-	Polynomial regression coefficient
ϵ	-	Statistical error
ε	-	Real bed porosity
ε_{act}	-	Actual bed porosity
ε_{eff}	-	Effective bed porosity
ρ	kg / m^3	density

Abbreviations

Abbreviation	**Meaning**
2G	2nd generation (biorefinery)
5-HMF	5-hydroxymethylfurfural
ACM	Aspen Custom Modeler
AGX	Arabinoglucuronoxylan
AP	Aspen Plus
ANOVA	Analysis of variance
App.	Approximately
AX	Arabinoxylan
AS-Lignin	Aquasolve solid lignin
AL-Lignin	Aquasolve liquid lignin
BBD	Box-Behnken Design
C5	Basic sugar unit with five carbon atoms
C5-Sugar	Sugars formed mainly from C5-Monomers
C6	Basic sugar unit with six carbon atoms
C6-Sugar	Sugars formed mainly from C6-Monomers
CCD	Central Composite Desing
CSTR	Continuous stirred tank reactor

DF	Degrees of freedom
DNS	3,5-Dinitrosalicylic acid
Dim.	Dimensionless
DoE	Design of Experiments
FDS	Fraction of design space
HJ	Heating jacket
HPAEC	High-performance anion exchange chromatography
LHW	Liquid hot water (pretreatment)
MESP	Minimum ethanol selling price
MLSP	Minimum lignin selling price
NPV	Net present value
NREL	National Renewable Energy Laboratory
PSE	Process system engineering
RSM	Response surface methodology
TUHH	Technical University Hamburg-Harburg
var	variable
VIF	Variance inflation factor
XOS	Xylo-oligosaccharides
UV	Ultraviolet
VDI	The association of German engineers

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1 Introduction and objectives

1.1 Introduction

During the last decades, the growing environmental concern and the scarcity of fossil fuel resources have attracted attention towards lignocellulosic biomass as a reliable and renewable source of raw materials for the chemical industry. Lignocellulosic biomass is formed from three different kinds of polysaccharides: cellulose, lignin and hemicellulose, which present very differentiated chemical structures, properties and reactivity. Second generation (2G) biorefineries aim at an efficient utilization of all the fractions for the production of bio-originated fuels and chemicals. But still, this technology has to address three major challenges: improve the fractionation of the components avoiding degradation of the sugars, minimize production costs especially derived from water consumption and high energy demand and develop high added-value products from the most underused fractions: lignin and hemicellulose.

The pretreatment of the biomass is a serious bottleneck in the biorefinery process. The use of low solid-to-liquid ratios results in high energy needs, elevated water consumption, and low sugar concentrations. In order to address this issue, an innovative pretreatment technology based on the consecutive hydrothermal and enzymatic hydrolysis in a single high pressure fixed-bed reactor has been developed at the Institute of Thermal Separation Processes. Along with this technology, a model has been proposed by REYNOLDS et al. in [63], which aims at maximizing the sugar recovery, investigating different operating modes and optimizing the conditions for the pretreatment of wheat straw pellets in the fixed-bed reactor system. Recent studies show that high sugar recoveries and low sugar degradation can be achieved with a water flow-through operation, nevertheless, this operation requires high amounts of water. In contrast, experiments with full recirculation of the hydrolysate show high hemicellulose solubilisation with a lower amount of water but with significant sugar degradation.

In addition to the efficient fractionation of the biomass, it is of crucial importance for the biorefinery economic feasibility to expand the product portfolio. So far, biorefinery facilities have focused on the production of bio-ethanol from the cellulosic fraction, disregarding the potential of lignin and hemicellulose as sources of aromatic compounds and rare sugars respectively. The conditions of the pretreatment step have enormous influence on the downstream processes and as a consequence on the potential of the final products. Comprehensive models for the techno-economic assessment of an overall biorefinery facility have been proposed, with especial focus on the market competitiveness of bioethanol. Implementing the pretreatment model and the downstream processes for the desired hemicellulose applications can help to determine which are the water consumption, the energy requirements and the optimum operating conditions and reactor configuration that might ensure the economic feasibility of a future biorefinery.

1.2 Objectives

The main objective of this work is to investigate the influence of operation conditions and reactor configurations over the hemicellulose fraction applications and the overall economic feasibility of biorefinery facilities. For this purpose, the thermal hydrolysis of wheat straw in a high-pressure fixed-bed reactor will be studied under four different reactor operating modes: flow-through, circulation, partial recirculation and batch. The contents of this study are divided in four sections: (i) selection of promising applications of the hemicellulose fraction, (ii) process modelling of the diverse reactor configurations, (iii) experimental characterization of the liquid hydrolysate for different pretreatment conditions and (iv) techno-economic assessment of the investigated processes in an overall biorefinery process.

The selection of an adequate and diversified product portfolio is essential for the viability of 2G biorefineries. Current and future possibilities for hemicellulose transformation will be reviewed, with special focus on applications involving green processing and with potential to compete at a market level against their equivalent petro-based compounds. Influence of varying pretreatment conditions, water consumption and reactor configuration on the hydrolysate characteristics will be studied. The development of accurate mathematical models which emulate the behaviour of biorefinery processes is of especial importance for process optimization and scale-up. The influence of key pretreatment operating conditions such as temperature, reaction time, mass flow and hydrolysate recirculation during hydrothermal hot water pretreatment will be simulated on Aspen Custom Modeler (ACM). In addition, response surface methodology (RSM) will be used for studying parameter interaction and for comparing the performance of different reactor configurations. To give support to the simulation results, model responses for the different reactor configurations and pretreatment conditions will be compared to empirical results from experiments conducted at lab-scale. The adaptability of the fixed-bed reactor set-up to changing reactor configurations will be tested. Finally, the selected operation conditions and the hydrolysate experimental characterization will be integrated in an existing overall biorefinery model including the downstream units for the production of the selected hemicellulose-derived products. Mass and energy balances will be determined in order to present an integrated techno-economic assessment of the different alternatives in terms of product potential, water consumption and energy demand.

2 Fundamentals and state of art

This chapter summarizes the fundamentals and state of art of the modelling and techno-economic assessment of second generation biorefineries for the production of valuable products from lignocellulosic biomass, with special focus on the pretreatment step and the hemicellulose fraction application. In the first place, lignocellulosic biomass characteristics and the possibilities of transformation towards chemicals and fuels are illustrated. Secondly, the operating conditions and important challenges of different alternatives for the pretreatment of lignocellulose materials are discussed Afterwards, current and future promising applications for the hemicellulose fraction are reviewed. Finally, existing models for representing the lignocellulose kinetics, the pretreatment step and for simulating integrated biorefinery processes are described.

2.1 Principles of biorefinery technology

2.1.1 Lignocellulosic biomass composition

Lignocellulosic biomass is the most abundant organic compound on Earth representing, with approximately 150 billion tons, the major portion of the world's annual renewable biomass production [4]. It is composed primarily of the polysaccharides cellulose and hemicellulose and the phenolic polymer, lignin, but elements as proteins, ash and organic acids are also present in minor amounts [82]. Chemical structure of the lignocellulosic biomass can be understood as a natural composite material in which hemicelluloses are covalently bonding cellulose fibres, strong in tension, to a lignin matrix which resists compression and is highly hydrophobic [55]. Composition of lignocellulosic biomass depends principally on the plant species but also remarkable variance is noticed for different geographic location, climate or soil conditions [80]. In particular for wheat straw the composition ranges between 34-40 % for cellulose, 20-25 % for hemicellulose and 15-20% for lignin [84]. Wheat straw is considered one of the most promising raw materials for bioconversion to chemicals and fuels in the so-called second generation biorefineries because of its wide availability, it is the second most abundant residue crop after rice straw, and because of its beneficial effect in the "*Fuel vs Food*" dichotomy [37,43].

Cellulose is the major constituent of lignocellulosic biomass and it is the most important polysaccharide because its fibres are responsible for the structure and shape of the plant. It is a crystalline linear polymer made up of D-glucose units linked with 1-4-β bonds. This structure is a result of multiple intra and intermolecular bonds existing between the different glucose units [66]. Lignin is the major non-carbohydrate component of lignocellulosic biomass and it is considered the second most abundant renewable polymer in the world [35]. Lignin is not just a compound but a variety of them, they are complex, amorphous and three dimensional molecules formed by three different building blocks known as phenyl-propanes, The three-dimensional structure of this compound and the tendency to stablish covalent bonds with cellulose and hemicellulose are responsible for the mechanical structure and resistance against enzymatic degradation and microbial attacks of the plants [74]. Lignin is by far the most common aromatic natural resource on earth and it is the only one available in enough quantity to fulfil the requirements for substitution of current used aromatic compounds in the petrochemical industry [30]. Hemicelluloses are the world's second most abundant renewable polymers after cellulose in lignocellulosic materials [35]. Hemicelluloses are a heterogeneous class of heteropolymers which may contain pentoses (β-D-xylose and α-L-arabinose), hexoses (β-D-glucose and α-D-galactose) and uronic acids [20]. The composition and amount of hemicellulose depends strongly on the plant source, the plant tissue and the geographical location [35]. For the case of wheat straw, as well as for the rest of grass and herbaceous plants, xylans are the most relevant hemicelluloses [21]. Besides the heterogeneity of this fraction, every hemicellulose is formed for a xylose, glucose and/or mannose backbone in which every building block is connected with β-1-4 bonds and with side groups formed mostly by monomers or short oligomers, an example of this structure can be observed in

Figure 2.1. This branched and amorphous structure results in low molecular weights and polymerization degrees, between 50 and 300, compared to cellulose. Consequently, these compounds present attractive properties for conversion in biorefinery such as facility to be hydrolysed and high solubility in water [87]. Current or potential hemicellulose applications as source of monomers or bio-polymers will be discussed in detail in the section 2.3.

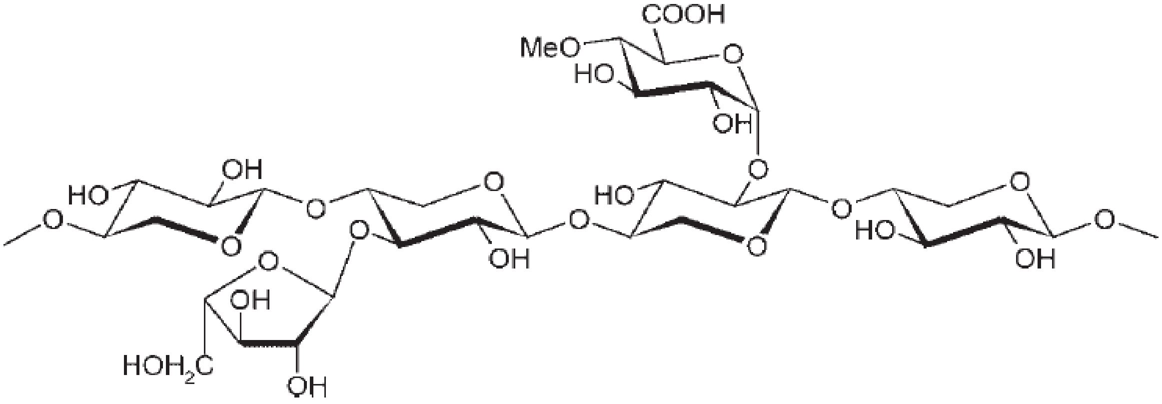

Figure 2.1: Chemical structure of an arabinoglucuronoxylan (AGX), one of the most abundant hemicelluloses in wheat straw [20].

2.1.2 Second generation (2G) biorefineries

Fossil economy is facing serious challenges and alternative production chains are necessary for reducing the dependence on oil and mitigate climate change. In this context, biorefining of lignocellulosic biomass has arisen as a new method for producing energy and chemical products. As defined by CHERUBINI et al. in [14], *"a biorefinery is a facility (or network of facilities) that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass"*. This concept is equivalent to nowadays petroleum refinery which offers a wide product portfolio of refined fuels and chemicals from petroleum. 2G biorefineries aims at an efficient fractionation and transformation of all the biomass fractions.

The main limitation of second generation biorefineries is to overcome the lignocellulose "recalcitrance" or in other words the natural resistance of the plants against degradation [29]. They key factors for the economic feasibility of such facility are: improving the fractionation of the components avoiding their degradation, minimizing production costs especially derived from water consumption and high energy requirements and developing high added-value products from the most underused fractions: lignin and hemicellulose. Hemicelluloses are natural biopolymers with interesting properties for the pharmaceutical and food industries as well as being considered a promising source of rare sugars, namely xylose, arabinose or mannose, which enormous potential as platform chemicals. However, rapid sugar degradation during the pretreatment and the resulting low sugar concentration are still major limitations to its commercialization. Similarly, the lignin fraction is considered the most suitable renewable feedstock to substitute petro-aromatics, acting as a source of different aromatic building blocks. Nevertheless, lignin depolymerisation and valorisation remains a challenge. Despite these outstanding properties, up to now, hemicellulose concentrated solutions and pelletized lignin have been mainly used for co-producing heat and energy helping to close the energetic balance of bioethanol production processes.

2.2 Pretreatment of lignocellulosic biomass

2.2.1 Lignocellulose recalcitrance

Lignocellulosic materials have been widely used in industry and everyday life thanks to its natural resistance against degradation of microbes and surrounding environment conditions [12]. This natural "recalcitrance", defined in 2007 in Science by HIMMEL et al. as "*the natural resistance of plant cell walls to microbial and enzymatic deconstruction*", is nowadays the primary obstacle for an efficient utilisation of all the lignocellulosic biomass fractions. The great complexity of lignocellulose chemistry hinders the development of a low-cost technology for overcoming this recalcitrance, hence the convivence of active and inert compounds and solid, liquid and gas substances cause that the degradation of any of the ingredients is subjected to the constraints of the rest [13]. The set of operations necessary to overcome this resistance are known as pretreatment. The pretreatment is the first step in every biorefinery process and it has a large impact on the economic feasibility of the process because it affects the digestibility of the different sugars and influences downstream costs derived from purification of the products, enzyme loading and water and energy demands. An efficient pretreatment strategy aims at modifying the biomass macroscopic and microscopic structure as well as the chemical composition so that hydrolysis of the carbohydrate fraction to monomeric sugars can be achieved more rapidly and with greater yields. The ideal pretreatment step is capable of extracting hemicelluloses, remove lignin, reduce cellulose crystallinity and increase its surface area (Figure 2.2) [3].

2.2.2 Pretreatment fundamentals

The key features for an ideal pretreatment process are broadly described by ALVIRA et al. in [1] and include: **(1)** flexibility for using multiple crops, **(2)** produce a highly digestible solid, **(3)** avoid degradation of the sugars, **(4)** minimize the amount of toxic compounds released, **(5)** minimize heat and power requirements, **(6)** obtain high sugar concentrations,

(7) increase solid to liquid ratios, **(8)** minimize capital costs and **(9)** limit the amount of solid-waste residues. Each pretreatment process has a specific effect on the cellulose, hemicellulose and lignin fraction; thus, different pretreatment methods and conditions should be chosen according to the process configuration selected for the subsequent hydrolysis and fermentation steps [49]. Therefore, the challenge of any lignocellulose pretreatment strategy is the flexible operation set up that leads to an adequate fractionation of hemicellulose, cellulose and lignin, together with a minor degradation, in order to get maximal fermentation yields and rates [26].

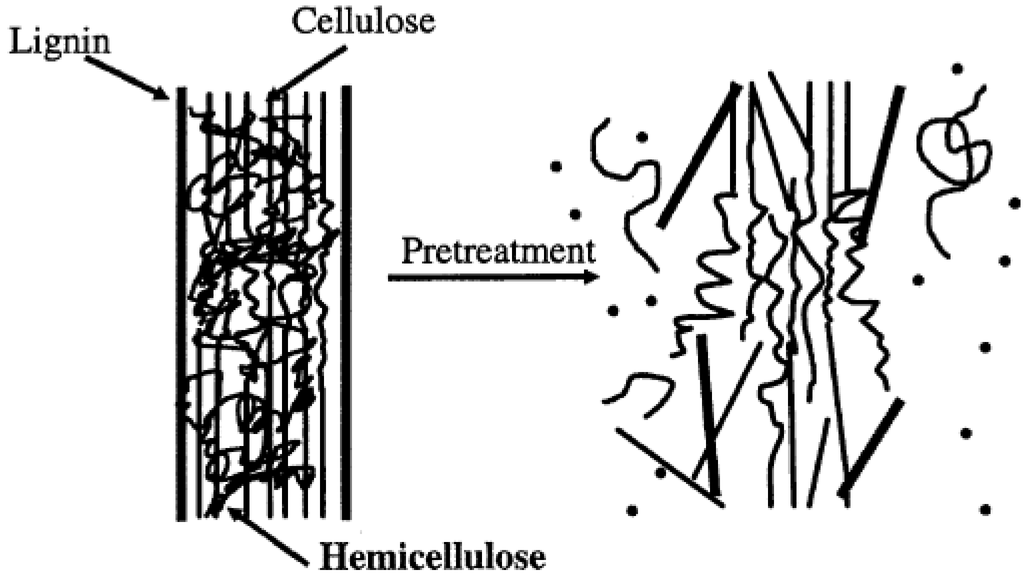

Figure 2.2: Pretreatment effect over the microstructure of lignocellulosic materials. Adapted from [54].

2.2.3 Pretreatment alternatives

Most part of 2G biorefineries have focused their attention in an efficient conversion of lignocellulosic biomass into fuel ethanol. It has been stated that the two main factors affecting the economic feasibility of these facilities are the large flows of water needed for separation and the low profitability of the by-product streams. A variety of technologies have been developed for the pretreatment of all kind of lignocellulosic materials, they are usually classified into physical, chemical, physicochemical and biological treatments. Detailed information concerning the different pretreatment alternatives was presented by MAURYA et al. in [49]. Recent techno-economic studies comparing the different pretreatment technologies using similar feedstocks and analytical methods suggested that there is not an overall winning pretreatment alternative and that the method has to be chosen and optimized accordingly to every available substrate and desired product portfolio [22,35,89,90]. Pretreatment technologies are always a combination of physical and chemical steps and are responsible for more than 40% of the total processing cost [35].

Physical pretreatment

Physical pretreatments are usually applied for reducing the size and disrupting the macroscopic structure of lignocellulosic materials. At first sight, the size reduction by cutting, milling or grinding has major benefits for the easier biomass handling, greater transportability and the homogenisation of the raw materials. Moreover, further studies have shown that the breakdown of the biomass feedstock into smaller particles improves the hydrolysis of the hemicelluloses and the digestibility of the cellulose [7,11]. Physical pretreatment methods act by reducing particle size, cellulose crystallinity and degree of polymerisation, increasing bulk density, porosity and surface area, as well as improving flow properties, providing higher hemicellulose extraction yields and better accessibility of enzymes [35]. In contrast, the main challenge of physical pretreatment methods is the required high energy demand [7].

Thermal hydrolysis

GIRIO et al. in [26] provided detailed information concerning the different pretreatment methods for an efficient removal of hemicellulose, aiming to reduce structural constraints for further enzymatic cellulose hydrolysis. The most studied options for the effective fractionation of hemicelluloses include the use of acids, water, steam, organic solvents and alkaline agents, but the latter two are not selective towards hemicelluloses as they also dissolve the lignin. Lignin phenolic compounds are considered undesired by-products in the liquid fraction, usually known as hydrolysate, because they usually act as microbial growth inhibitors and reduce the potential for bioconversion of hemicelluloses. Thus, acid, water and steam pretreatment are the technologies which provide higher recovery of C5-Sugars, combining high solubilisation from the solid with low degradation of the oligomers, which enhances the further usability of the hemicellulose fraction

Thermal hydrolysis, also known as hydrothermal treatment or liquid hot water extraction (LHW), is considered by many researchers as the best trade-off pretreatment alternative for the valorisation of hemicellulose and lignin [26]. In this step, lignocellulose is treated with water at high temperatures (150 ºC – 230 ºC) during reaction times ranging from a few minutes to an hour and under pressure in order to keep the water in liquid state [35]. At high temperatures, the auto-ionization of the water molecules occurs, leading to the solubilisation of the hemicelluloses and part of the lignin (aquasolv liquid (AL-)Lignin) in the water and the further hydrolysis of the oligosaccharides into monomers [71]. During the hydrolysis of hemicelluloses, acetyl groups are cleaved, especially when arabinose is present, and acetic acid is released, decreasing the pH of the mixture. This operation is usually referred to as autohydrolysis because the presence acetic acid catalyses selectively the reactions of solubilisation and degradation of the hemicelluloses, however, extreme temperatures and acid concentrations will enhance the degradation of the sugars into furfural, 5-HMF and other degradation products. The pretreatment mechanism is based on the selective depolymerisation of the hemicellulose fraction [32,72]. As a result, two product streams are obtained, a liquid phase rich in C5-Sugars and with variable content in AL-Lignin and a solid residue of cellulose and lignin ready for the subsequent enzymatic digestion, leading to a solid residue known as aquasolv solid (AS-)Lignin.

Apart from the remarkably high C5-Sugar extraction yields, LHW pretreatment presents numerous advantages over other methods: it doesn´t require the addition or recovery of any chemicals, the equipment corrosion is reduced and the operation is simple and economical [71]. Besides the high rates of hemicellulose extraction, significant degradation of the sugars is observed when the liquid residence time is high, nevertheless, no significant degradation is observed in the solid phase over time. The different reaction rates of the solid and liquid phase points at the selection of the reactor set-up and configuration as a crucial decision factor regarding this technology. As further discussed in section 2.2.4, the LHW pretreatment of lignocellulosic biomass can be conducted in all kinds of reactors configurations but the operation in a fixed-bed reactor has attracted great attention due to the high sugar recoveries achieved at rather low residence times for the liquid phase. However, this technology is still under investigation at lab-scale and numerous problems regarding the complexity of fixed-bed reactors at large scale have to be overcome. Also, reactor configuration and operating conditions in order to increase the solid-to-liquid ratios and diminish the water and energy demand are yet to be optimized [26,49].

Enzymatic hydrolysis

The solid residue (AS-Lignin) resulting from the thermal hydrolysis, formed mainly from cellulose and the non-dissolved part of the lignin, can be treated enzymatically in order to obtain smaller sugar molecules that will be further transformed into bioethanol or other chemical products. However, significant limitations on the efficiency of the enzymatic action has been observed due to the presence of products of the thermal hydrolysis such as xylose derivatives, furfural, 5-HMF, organic acids and phenolic compounds. These compounds have shown also negatives effects on the further transformation of glucose [38]. The enzymatic degradation of the solid residue is a complex process, it takes places in a heterogeneous system where water has an important role as a reactant but also as transport mechanism for the enzymes. The initial cellulose breakdown takes places when the enzymes are adsorbed onto the solid and then the smaller sugars are cleaved into their monomeric forms. The transformation of hemicelluloses into monomers is more complex and it involves a cocktail of enzymes known as hemicellulases. These enzymes are responsible for the selective cleaving of the different bonds which form the hemicellulose structure. In this case, hemicellulases are only important for removing small residues of hemicelluloses present in the solid residue. LHW pretreatment of lignocellulosic biomass

2.2.4 General reactor configuration

As stated by YU and WU in [92] the reactor configuration has a strong influence in the efficiency of the hydrothermal pretreatment, namely on the C5-Sugar recovery and on the enzymatic digestibility, hence, in the characteristics of the liquid and solid products. Four different reactor configurations have been described in the literature, which provide an effective contact between the lignocellulosic materials and the liquid hot water (Figure 2.3). First, the batch reactor where the biomass particles and the hot water are mixed and stirred together, second, the fixed-bed reactor where the biomass is packed and the water goes through the stationary bed and it is continuously swept out and finally a continuous reactor where both phases are mobile, these phases can move in the same (co-current) or opposite directions (counter-current) [49].

Batch reactor systems have been widely used at lab-scale and results point at an almost complete removal of hemicelluloses if stirring and liquid residence time are long enough [35]. Besides that, studies have shown that the lignin removal while using batch reactors is rather low because the phenolic compounds rapidly reacts with other soluble products forming insoluble species (lingo-humic substances) which are left in the reactor, leading to less digestible solid residues [91]. Also, batch operation in this case faces problems if taken to the industrial scale because the energy demand for an efficient stirring is considerably high. On the other hand, flow through and continuous processes have important potential advantages, including higher hemicellulose recoveries, AL-Lignin removal and thereby enhanced cellulose digestibility [91]. Control of operation in co- and counter-current reactors is more complicated than flow through reactors and they require of higher temperatures and pressures to achieve similar sugar recoveries. Flow through operation is considered a promising alternative for 2G biorefineries, because it allows complete removal of hemicelluloses and AL-Lignin and requires shorter liquid residence times than batch and continuous reactors [71]. Shorter residence times for the liquid avoid the production of degradation products which will inhibit enzymatic and microbial transformation of the sugars. Unfortunately, flow through processes suffer from high water and energy use in addition to a rather more complicated process design and control compared to traditional reactor set-ups [91].

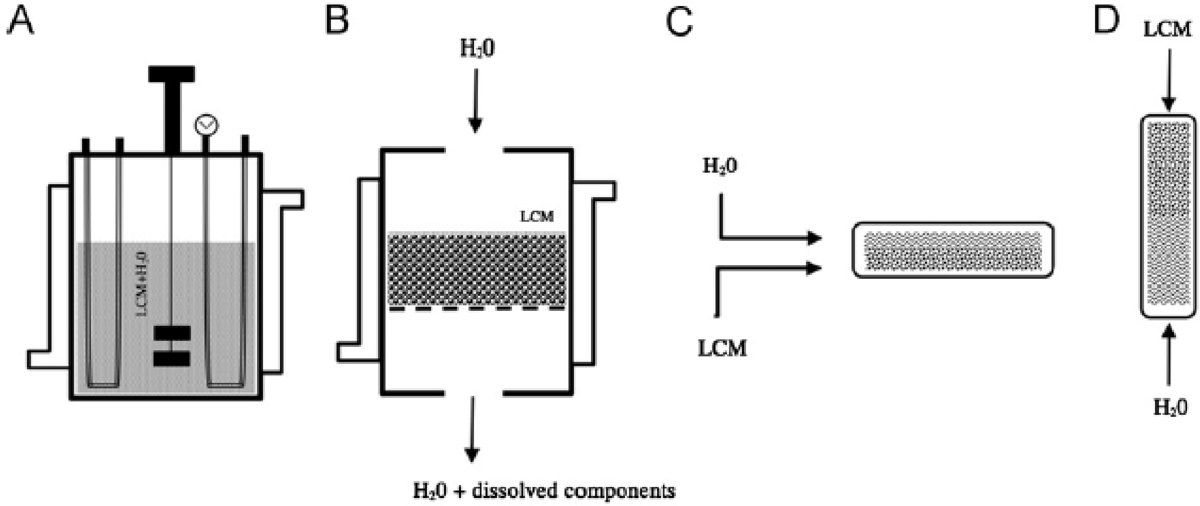

Figure 2.3: Different configuration of reactors for the LHW pretreatment of lignocellulosic materials: (A) batch reactor, (B) semi-continuous reactor (fixed bed), (C) continuous reactor (co-current) and (D) continuous reactor (counter-current).

2.2.5 LHW pretreatment in a fixed-bed reactor

A multistep process for the fractionation of wheat straw developed at the Institute of Thermal Separation Processes, TUHH, has been chosen for the present study. Grinded and pelletized wheat straw is subjected to a hydrothermal treatment for the extraction of hemicelluloses and part of the lignin (AL-lignin). Afterwards, the cellulose rich solid residue from the hydrothermal process is degraded into glucose in continuously stirred batch reactors at ambient pressure by enzymatic hydrolysis. Finally, high purity solid lignin is recovered from the glucose solution. The objectives of the pretreatment focus on a maximal sugar recovery, optimized enzymatic degradation and a high production of valuable by-products derived from cellulose, hemicellulose and lignin as well as a reduced energetic and chemical input. Thermal hydrolysis step and hydrolysate stream, where the hemicelluloses and part of the lignin (AL-lignin) are dissolved are considered the main focus of this research and for that purpose they are highlighted in Figure 2.4.

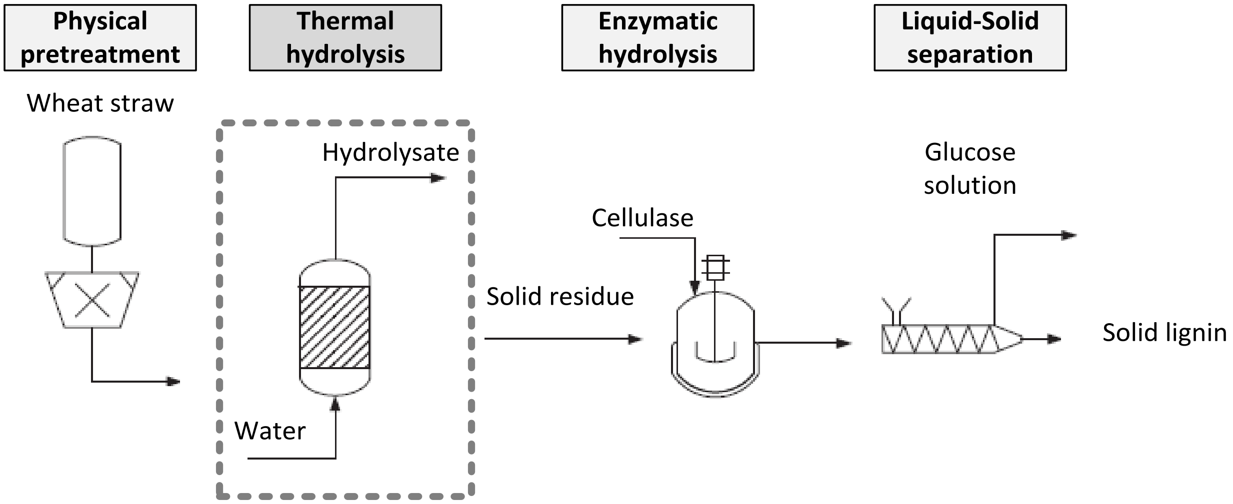

Figure 2.4: Cascade process for the fractionation of wheat straw studied in the Institute of Thermal Process in TUHH [61].

RISSANEN et al. in [68] identified the key parameters influencing the LHW pretreatment of lignocellulosic materials including temperature, pH, biomass morphology, particle size, solid to liquid ratio, heat and mass transfer phenomena and reactor setup. Several studies have been performed studying the influence of these parameters on the hemicellulose extraction. Thereby, previous studies conducted in the Institute of Thermal Separation Processes, in TUHH, have concluded that the optimum conditions for the pretreatment of wheat straw pellets in a pressurized fixed-bed reactor are: temperature of 200 ºC, mass flow of 250 g/min, dry biomass weight of 845.8 g and reaction time of 2100 s [62]. These studies showed that the consecutive thermal and enzymatic hydrolysis of lignocellulosic materials in a single high pressure fixed bed reactor is capable of achieving an outstanding separation of the biomass fractions with low degradation of the sugars, highly digestible solid residue and high purity lignin. However, the studies also pointed out the necessity of reducing the water demand of the process. With this in mind, the partial recirculation of the hydrolysate could constitute a rather simple alternative for reducing water consumption during LHW pretreatment. However, it is well-stablished that the acetic acid catalyses the solubilisation, hydrolysis and further degradation of hemicelluloses. As stated by GRÉNMAN et al. [27], pH in the solution during LHW extraction is directly related to the release of acetyl groups in the mixture. In fact, PEREZ described a comparable influence of pH and temperature during the hydrolysis of hemicelluloses after long residence time [56]. The influence of recirculating low pH hydrolysates to the reactor will be studied in this work, aiming at catalysing the extraction of hemicelluloses while reducing the water needs.

2.2.6 Different fixed-bed reactor operating modes

The main focus of this work is to study the adaptability of the fixed-bed operation to different product requirements by changing the reactor operation mode. For that purpose, the thermal hydrolysis of wheat straw under batch, flow through, full recirculation and partial recirculation will be studied in a 3 L high pressure fixed bed reactor (Figure 2.5). The batch operation consists in filling the fixed bed reactor with hot water and hold at the pretreatment conditions during the whole reaction time (Figure 2.5 a). The advantages of the batch process are that it requires a minimum amount of water and that the operation is very simple. However, mass transfer limitations are expected to influence the hemicellulose solubilisation and the AL-Lignin removal. Also, the acetic acid release is expected to be rather high and in consequence, degradation of the sugars caused by longer residence time for the liquid phase. Nevertheless, it can be a feasible option due to the low energy, water and equipment requirements and the hydrolysate might still be useful for anaerobic digestion. In order to avoid mass transfer problems, the performance of hydrothermal pretreatment under full recirculation of the hydrolysate has been studied (Figure 2.5 b). The liquid product stream is continuously recycled to the reactor until most part of the hemicelluloses is solubilised. The removal of hemicelluloses is expected to be similar to the flow through mode but also degradation of the sugars is enhanced due to the higher acidity of the reaction mixture and the longer reaction time of the liquid. Digestibility of the cellulose is similar to flow through even though the AL-Lignin removal is decreased due to repolymerisation of AL-Lignin caused by the longer liquid residence times. Main advantage of the circulation mode is the minimal consumption of water

In contrast, flow through operation shows high sugar recovery yields and low production of inhibitors, which in addition to the removal of AL-Lignin results in a highly digestible cellulose. Besides that, the sugar concentration of the hydrolysate is rather low and the water and energy demand are extremely high (Figure 2.5 c). Flow through operation in fixed-bed rectors is a recent trend and its applicability at industrial scale is being widely studied currently. The recirculation of part of the hydrolysate is likely to be a compromise between the full recirculation and the flow through modes (Figure 2.5 d). Recycling a percentage of the hydrolysate leads to water and energy savings while the acetic acid recirculated to the reactor catalyses the solubilisation of hemicelluloses. Influence of key parameters such as temperature and pH on the hemicellulose solubilisation and degradation will be monitored for the different operation modes.

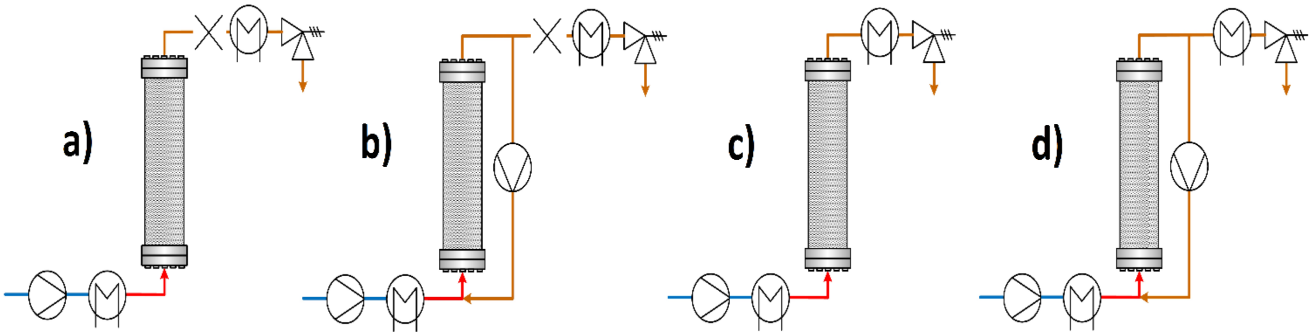

Figure 2.5: Different fixed-bed reactor operating modes. (a) batch mode, (b) full recirculation mode, (c) flow through mode and (d) partial recirculation mode.

2.3 Hemicellulose fraction applications

Besides improving biomass fractionation and minimizing production costs, it is of crucial importance for 2G biorefineries to increase the economic revenue by widening the product portfolio. The potential of lignin and hemicellulose fractions for producing high-added value chemicals are still under investigation. In this regard, liquid hydrolysate characterization and potential applications are the main focus of this work. Hemicellulose's unique structure and composition and its derivatives have shown promising results for many applications. In its oligomeric form, it could be used in pharmaceutical and food industries as a slow drug release compound and as encapsulating agent [10,28,83] In its monomeric form, hemicellulose can be used as a source of platform chemicals and even degradation products as furfural or 5-HMF have interest as bulk chemicals for the industry [68]. LANDUCCI et al. in [40] proposed the following five criteria in order to decide on a suitable product portfolio for 2G biorefineries: **(1)** high theoretical product yields from substrate, **(2)** market interest on the product as an end product or as an industrially important intermediate, **(3)** high production volume (current or potential), **(4)** non-food use of the raw material and **(5)** ability to be biologically synthesized from the common sugars derived from various forms of biomass. According to these criteria, three promising applications of the hemicellulose fraction have been proposed for further analysis in this work: biogas, molasses and furfural.

2.3.1 Biogas

Different studies have shown that the future economic feasibility of 2G bioethanol facilities goes through the transformation of the remaining biomass fractions into other biofuels that will help to close the energetic balance of these facilities [2]. As the use of hemicellulose hydrolysates for ethanol production will require the development of genetically modified microorganisms and further optimization of the process, the anaerobic digestion of hemicelluloses has been proposed as an interesting alternative for harvesting the energy of this fraction [3]. The result of the anaerobic digestion of the hemicellulose fraction is biogas. It is composed mainly of methane and carbon dioxide and it is considered to be clean and renewable form of energy. Different studies have presented biogas as one of the most efficient technologies, showing high energy recovery, environmental benefits and easy implementation [24,95]. In addition, the use of pelletized lignin for energy production could be replaced for hemicellulose-based biogas and the product portfolio could be extended to produce lignin-based phenolic chemicals.

Anaerobic digestion of hemicellulose is a multistep process consisting of hydrolysis, fermentation, acidification and methanation (Figure 2.6) [25]. In conventional anaerobic digestion processes the acidification and methanation steps are conducted in the same reactor and operating conditions but several studies have reported that the degradation products formed during the pretreatment of lignocellulosic biomass, mainly organic acids, furans and phenolic compounds, act as inhibitors of the enzymatic processes resulting in low methane yields [5]. An alternative that can be considered to increase the biomethane production is performing the acidogenic and the methanogenic stages in two separate reactors. In the first stage of the process, the hemicellulose hydrolysate is biodetoxified and hydrogen is recovered, while in the second one, the methanogenic process is carried out under optimal conditions, increasing the biomethane yields. This combined production of biohydrogen and biomethane is very promising because it admits all kind of hydrolysate mixture which allows to use more severe pretreatment conditions [3]. A techno-economic assessment presented by ZECH et al. in [93], confirmed that adding fermentation steps and increasing the complexity of the plant for producing biogas or bioethanol enhances internal energy provision and integration as well as minimizing waste streams, which compensate the increase in capital and equipment cost. JOELSSON in [34] confirmed this point and stated that the profitability of the plant is further improved if yields of conversion are improved and the biogas can be upgraded to biomethane.

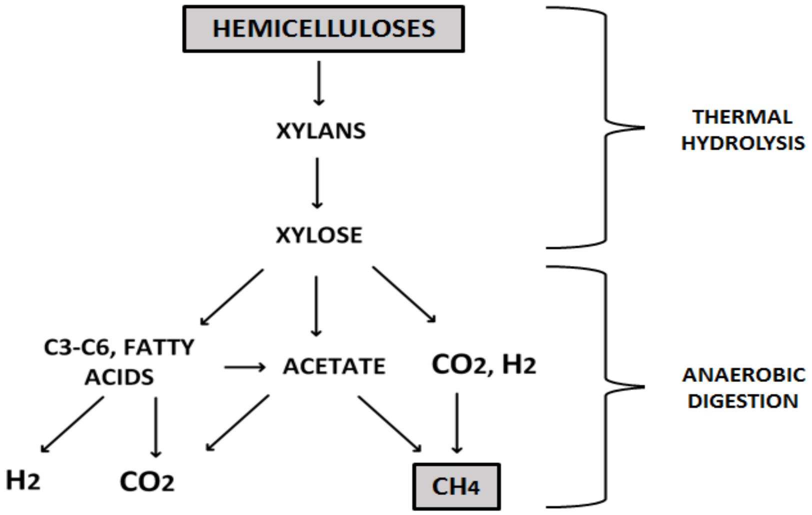

Figure 2.6: Reaction steps in anaerobic digestion of complex polysaccharides. Adapted from [25].

2.3.2 Sugar molasses

C5-Sugar fraction awaits for suitable transformation processes which still sufficient stability, cost effectiveness and high yields. Meanwhile, some applications have been developed which do not require high equipment costs and complex transformation, one example of these applications is molasses. Molasses are concentrated solutions (app. 40 % wt) of xylo-oligosaccharides (XOS) and sugar monomers which have shown interesting properties as food additives for cattle or human consumption [46]. Several studies and organisations support the use of wood sugar molasses as livestock feed resulting in equivalent feeding values to that of cane, beet or corn molasses [41,44,88]. Apart from the equivalent feeding values, MCLAREN et al. published a broad list of studies demonstrating that the acid resistant hemicellulose extracts had a positive effect on the digestibility in the intestine of ruminants, pigs and chickens, stimulating the growth of probiotic strains [23,50]. In addition, phenolic compounds and degradation products derived from the lignin-cellulose complex may stimulate animal growth by 15 % [17].

However, more concentrated and purified solutions of XOS have attracted the attention of the industry because of their demonstrated prebiotic effects. These compounds are not carcinogenic, present low calorific values and as non-digestible carbohydrates, they stimulate the growth of beneficial bacteria in the colon. The need of finding renewable sources for the production of prebiotics has attracted special attention towards the production of XOS for being considered as a promising ingredient in future functional foods [47]. The utilisation of XOS as food additive or cattle feed is growing as long as the interest of the market on prebiotic compounds. SUNTORY in Japan, IBUS in Denmark and the university of Vigo in Spain have developed interesting manufacturing processes for the production and isolation of XOS concentrated solutions. In the short run, the transformation of C5-Sugars into molasses is considered as a good solution but this process still addresses important challenges as avoiding sugar degradation, control the depolymerisation of the xylan compounds and avoid the release of toxic compounds [67].

2.3.3 Furfural

Furfural production is one of the most promising applications for C5-Sugar transformation in modern biorefineries, thus there is no synthetic route available for the production of furfural and it is exclusively produced from renewable biomass resources [70]. Furfural or 2-furaldehyde is a chemical compound of the furan group and is used in oil refineries, as well as in the plastics, food, pharmaceutical and agricultural industries. It was considered as one of the top 12 platform chemicals derived from biomass in a report from the U.S. Department of Energy thank to its potential to replace crude-oil based organics for the production of resins, lubricants, adhesives and plastics as well as a wide range of important chemicals [86]. Furfural presents interesting thermosetting properties, physical strength and corrosion resistance and it is present in 70% of the resins in the market. Due to its unsaturated bonds and aldehyde group, furfural is a highly versatile and key derivative used in the manufacture of a wide spectrum of important chemicals, such as furfuryl alcohol, tetrahydrofuryl alcohol, methyltetrahydrofuran and polyols [18,45]. The current world market for furfural is estimated to range between 200,000-210,000 tpa of which about 60% is used for the production of furfuryl alcohol [9].

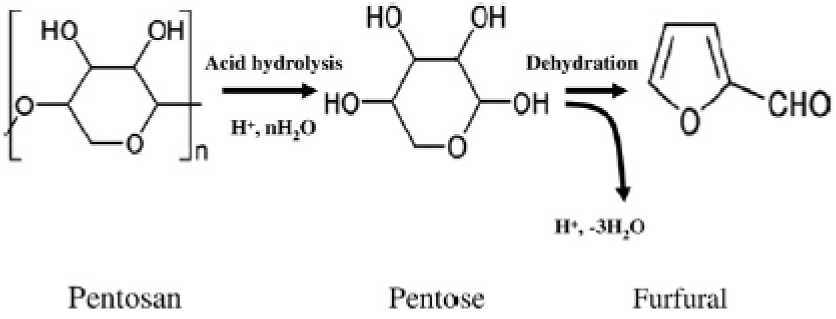

Figure 2.7: Scheme of the two step production of furfural: (1) hydrolysis of the pentose chain catalysed by acids followed by (2) the dehydration of pentose into furfural [65].

Current methods for furfural production are considered old and inefficient, for example the use of mineral acid catalysts results in high equipment corrosion, difficult separation and recovery of the catalyst and pose environmental and health risks [94]. Hence, developing new environmentally friendly processes for the production of furfural is crucial for improving it competitiveness with petroleum-based alternatives in the global market. In this regard, different researches have investigated the use of hemicelluloses as a raw material for furfural production. The transformation of xylan into furfural consists of a two-step process. First, the hydrolysis reaction of the xylans to form xylose monomers and second, a dehydration reaction catalysed by acids in which the xylose is transformed into furfural [70]. In currently existing furfural production processes, the two steps are performed in a single batch reactor which decreases the equipment cost but results in very low yields of furfural. Processes in which the hydrolysis and the dehydration take place in different reactors show higher yields but technology is still under investigation [65,77]. Kinetics of degradation of hemicelluloses are complex with different parallel and series reaction involving macromolecules. As stated by DE LA TORRE et al. in [39], the furfural produced from the degradation of xylose monomers is easily degraded at the same temperature conditions (Figure 3.1). Thus, for improving furfural yields it is necessary a continuous removal of the product from the reaction mixture, technologies for the stripping and the use of biphasic systems have shown promising results [42,69]. The use of LHW pretreatment as a preliminary step for furfural production will be studied in this work.

2.4 State of the art: Modeling of biorefining processes

Although the fundamentals of biorefinery processes are well known, the large number of possible process configurations and products results in a high complex multivariable optimisation problem which cannot be solved using simple heuristics or rules of thumb.

Moreover, experimental work in this field is frequently expensive and time consuming. For these reasons, accurate process models have become essential for the development of profitable biorefinery plants. This chapter gives an insight about the fundamentals and state of art of the mechanistic modelling of LHW pretreatment of lignocellulosic biomass, the RSM analysis of the process dynamics and the existing techno-economic assessment studies of the whole biorefinery process.

2.4.1 Modelling of LHW pretreatment

The development of accurate models predicting the behaviour of the hydrothermal pretreatment of lignocellulosic materials has attracted the attention of several researchers during the last 70 years because of its importance for process optimization and scale-up. Most part of the publications are based on the studies of SAEMAN et al. back in the 40s [73] in which a first order kinetic model for the degradation of cellulose was developed. Afterwards, the model was adapted for explaining the hydrolysis of other polysaccharides, such as hemicellulose and lignin. The generally accepted pathway for the solubilisation and subsequent degradation of hemicellulose consists in the direct release of the xylan from the solid biomass into the liquid phase and its further depolymerisation into shorter oligomers and xylose monomer units, which are transformed into furfural and other pentose degradation products. Moreover, MORINELLY et al. in [53] proposed a first order kinetic model for the rapid degradation of furfural over 200 ºC, which solved significant discrepancies between the original model and experimentally observed furfural consumption rates. For modelling purposes, CONNER et al. in [16] proposed splitting hemicellulose into two fractions: an easily hydrolysed and a resistant portion. In addition, the hydrolysis is catalysed by the acetic acid formed in the solution after the release of acetyl groups present in the side chains of the hemicellulose. As stated by GRÉNMAN et al. in [27], the pH of the hydrolysate is directly influenced by the acetic acid release and it is an essential factor in the hydrolysis kinetics together with temperature. However, pH calculation from the actual acetic acid concentration is not always accurate due to the buffering effect of the hydrolysate and the adsorption of acetic acid [8]. Also, recent studies associate the presence of acetic acid in the liquid with the depolymerisation and condensation reactions affecting lignin [6]. A common approach to the kinetic analysis of different pretreatment methods is to use simplistic predictive models for sugar recovery and hydrolysis yield. The severity factor R_0 has been widely used as a measure of the intensity of the treatment, which includes temperature and residence time in an approximation to the Arrhenius equation. Combined severity factors have been proposed by CHUM et al. in [15] also taking into account the effect of the acetyl groups in order to better fit the experimental values. Nevertheless, these models based on the assumptions of first order homogeneous kinetics reach their limits with the increasing complexity of the reaction systems, especially regarding mass and heat transfer phenomena. [68] identified several parameters influencing the LHW pretreatment of lignocellulosic materials including temperature, pH, biomass morphology, particle size, solid to liquid ratio, heat and mass transfer phenomena and reactor setup, most of them neglected in traditionally used models.

Models describing the performance of LHW pretreatment in fixed-bed reactors are not common so far. Most of them are based on empirical approaches and assume constant and uniform conditions for the solid phase considering only parameter variation in the axial direction which leads to wrong estimations of crucial parameters such as pressure drop or bed porosity which make them unsuitable for scale-up purposes. In many cases, models are fitted to experimental values by using an elevated number of parameters. Often, the nature of these parameters is merely empirical and they lack of interest for describing mass and heat transfer phenomena or non-ideal behaviour. These models cannot be employed for scale-up purposes because its validity is reduced to a unique experimental set-up under determined operation conditions. Mass transfer models are a promising alternative for developing integrated model capable of depicting in a reliable way the behaviour of the different biomass fraction during hydrothermal pretreatment in all kinds of reactor set-ups. This method proposes separate differential mass balances for the bulk liquid and the solid particles and relies on the combination of heterogeneous mass transfer models and first order kinetics as an accurate approximation of the real behaviour of the processes.

An integrated model for describing the hydrothermal pretreatment of wheat straw pellets in a pressurized 3 L flow through fixed-bed reactor has been used for simulation and calculation purposes in this work. This model was developed by REYNOLDS et al. at the Institute of Thermal Separation Processes at Hamburg University of Technology and has been validated for temperatures between 185ºC and 215ºC and reaction times from 0 min to 30 min in the fixed-bed reactor. The mathematical model gathers results and conclusions from different studies performed during the last decade in the institute regarding mass transfer, heat transfer and hemicellulose reaction kinetics. REYNOLDS and colleagues studied the degradation pathway of hemicelluloses from wheat straw during LHW treatment and proposed a reaction pathway for hemicellulose solubilisation based on the first model for cellulose degradation described by SAEMAN et al. and including furfural degradation kinetics as proposed by MORINELLY et al. [53,73]. Important parameters regarding mass and heat transfer in the high-pressure fixed bed such as bed porosity, axial dispersion and non-ideal flow properties were analysed in other publications. REYNOLDS coordinated the project and proposed the overall model combining the three separate parts: reaction kinetics, mass transport and heat transfer. Comprehensive description of this model and detailed citation of the different authors who participated in this work can be found in a submitted manuscript [63]. Further details concerning this model along with the implementation in AspenTech Aspen Custom ModelerTM V8.0 (ACM) are described in the following chapter.

2.4.2 Design of Experiments (DoE) for biorefinery process modelling

As previously mentioned, the behaviour of the different lignocellulose fractions during the LHW pretreatment is in occasions too complex to be completely emulated by mechanistic modelling approaches and simple kinetic schemes. Moreover, experimental work in this field is frequently expensive and time consuming. Also, the strategy of single parameter variation from one experiment to another blurs the action of parameter interaction. For this reason, researchers have recently started to consider DoE as a promising alternative for modelling and simulating biorefinery processes [62]. Statistical DoE provides a set of powerful standardized tools for the effective planning and evaluation of experimental designs by minimizing the number of required experiments which avoids the realization of unnecessary experiments and helps to analyse the combined influence of different operation parameters [78]. Additionally, RSM offers a library of statistical and mathematical tools for the modelling and optimization of processes. However, this method is only applicable within a reduced set of parameter boundaries. It does not allow detailed understanding of different transport phenomena which are essential for scale-up purposes. Combining DoE and RSM it is possible to condense the information of the experimental work in the form of a polynomial equation (See equation (3.1)). Even if it is not possible to fully represent the real behaviour of the system with linear or quadratic models, the polynomial represents reliably the local shape of the investigated system responses which facilitates the visual representation of the results and can be used to find the optimal factor setting for a predefined goal. In this work, DoE and RSM are used for minimizing the amount of required simulations and for generating data of the system responses to different pretreatment conditions that can be further transferred to the techno-economic assessment.

2.4.3 Techno-economic assessment of integrated biorefinery processes

For a comprehensive optimization of biorefinery processes, economic, social and environmental issues have to be considered simultaneously. For this purpose, process system engineering (PSE) methods have been introduced for providing a systematic framework capable of combining results generated in simulation studies as well as in experimental works. The PSE methodology starts with the selection of a list of candidate scenarios which are formed for the set of parameters of interest to be evaluated, namely, raw materials, geographical location of the plant, pretreatment process and conditions, selected product portfolio or production volume. Then, data for the different scenarios is generated by simulation or experimental work in order to select the most profitable process design and allocation schemes while considering the environmental impacts. Afterwards, mass and energy integration assessments are performed in order to minimize the consumption of energy and raw materials as well as reducing waste streams. This allows calculating the capital and utility costs, which complete the economic and environmental evaluation of the whole process under the selected conditions. Several works have been published evaluating the single variation with different renewable feedstocks, pretreatment processes and conditions and selected product portfolio on the economic feasibility and the environmental impact of 2G bioethanol biorefineries. However, combined assessment of the influence of reactor configuration, water consumption and selected product portfolio, comparable to the scope of this work, has not been reported.

The net present value (NPV) has been traditionally used as key economic indicator for the evaluation of the different promising scenarios but it has been proven insufficient and invalid for this kind of studies because it tends to underestimate the potential benefits of new technologies and it is based on severe assumptions about the current market behaviour. Recent studies use the minimum ethanol selling price (MESP) as standard for comparing the different scenarios because it gives a reliable idea of the cost-competitiveness and the potential market penetration of the bioethanol in comparison with other petroleum or starch based products. Sensitivity analysis on the bioethanol price can help to evaluate the different alternatives for selecting the pretreatment process conditions and the possibilities of transformation of the by-products. Analogously, other economic indicators such as the minimum lignin selling price (MLSP) have been used for investigating the potential market penetration of determined bio-based products [58,76].

Several techno-economic analysis studies have been performed with the intention of determining the most suitable pretreatment option and conditions for all kinds of biomass feedstocks. FEROZ et al. in [36] investigated four alternative pretreatment processes coupled with three different downstream. The conclusions of this work pointed out that dilute acid and liquid hot water pretreatment are the most promising technologies and that separate fermentation of C5- and C6-Sugars is a great opportunity of reducing ethanol costs. In an exhaustive review, TAO et al. in [85] compared the performance of six different pretreatment options for the fractionation of switchgrass in terms of MESP. The study evidenced that the utilisation of the C5-Sugar fraction for ethanol or monomer sugar production reduces significantly the selling price of ethanol, especially in the case of LHW pretreatment. This study indicated also that LHW pretreatment can just be considered as a competitive option when hemicellulose hydrolysate is transformed into high added-value products. In a study performed based on the INBICON demonstration plant in Denmark, PETERSEN et al. in [59] indicated that high water consumption is the most serious obstacle for LHW pretreatment biorefineries and it evidenced that industrial processes with such high volumes of water are not economically viable due to the high energy required for heating. This point is corroborated by the NREL report in 2011, in which a comprehensive model for the co-fermentation of hemicellulose and cellulose into ethanol is described, including lignin combustion. In fact, this study points at the waste water treatment and the ethanol/water separation units as the most expensive and critical for the economic performance of the whole facility Therefore, further integrated economic and environmental assessments are needed for optimizing the conditions for LHW pretreatment in order to overcome the difficulties of the compromise between high C5-Sugar recovery and low water and energy consumption.

Many researchers have used techno-economic assessment studies for evaluating the transformation alternatives of the bioethanol production side streams. ZECH et al. in [93] studied in 14 different scenarios the performance of the INBICON plant, proposing three valorisation alternatives for the C5-Sugars: animal feed, biogas production and co-fermentation to bioethanol. JOELSSON et al. in [34] corroborated the conclusions of this study and deepened in the assessment of a co-production plant of biogas and bioethanol from lignocellulosic feedstocks. It also stated that upgrading of the biogas to vehicle fuel quality and transformation of xylose to ethanol is necessary for improving the profitability of the plants. MISAILIDIS et al. in [19] investigated the importance of widening the product portfolio of biorefineries and studied the potential commercialization of arabinoxylans (AX) from wheat straw. So far, multiple studies have been published evaluating the performance of different potential applications of the C5-Sugar fraction but there is a need to develop a well-structured methodology that enables decision makers to evaluate the integrated processes and identify the optimal set of products and the best reaction pathways to obtain them. For this purpose, SAMMONS JR. et al. in [75] have developed a systematic method that in his own words will "*assist bioprocessing industries in evaluating the profitability of different possible production routes and product portfolios*". Further elaboration of such assistance tools is crucial for the future development of more flexible biorefinery facilities in which different products can be offered depending on the biomass feedstock composition.

3 Materials and methods

The following chapter summarizes the experimental procedures and analytical methods employed in this work, including required chemicals and laboratory materials. In addition, the modelling of the reactor in ACM, the statistical analysis by means of DoE and the techno-economic assessment in Aspen Plus (AP) are explained in detail.

3.1 Materials

3.1.1 Wheat straw pellets

8 mm wheat straw pellets were obtained from Speers-Hoff, Stelle, Germany. The moisture content of the pellets is 10.03 ± 0.03 wt %. The composition of the dry and pelletized wheat straw is 35.8 wt % of cellulose, 19.6 wt % of xylose, 2.7 wt % of arabinose, 1.6 wt % of others and 23.9 wt % of Klason lignin. The remaining 16.4 wt % is formed for other substances, of which 9.7 wt % is ash. The compositional analysis was carried out at vTI – Institute of Wood Technology and Wood Biology, Germany. For further calculation of yields and recoveries, xylose and arabinose were completely assigned to the hemicellulose fraction while the complete amount of glucose was considered as cellulose.

3.1.2 Chemicals

All commercially available chemicals used in the present work are summarized in Table 3.1. For the reducing sugar analysis, citrate buffer, DNS-reagent and xylose solution had to be prepared.

Table 3.1: Summary of needed reagents and laboratory materials

Chemicals	CAS Number	Supplier
Citric acid monohydrate (≥ 99.5 %)	5949-29-1	Carl Roth
3,5-Dinitrosalicylic acid (DNS) (≥ 98.0 %)	609-99-4	Sigma-Aldrich
D-(+)-Xylose (≥ 98.5 %)	58-86-6	Carl Roth
Sodium hydroxide (NaOH) (≥ 99 %)	6381-59-5	Carl Roth
Potasium sodium tartrate tetrahydrate	1310-73-2	Carl Roth

Citrate buffer

At first, concentrated 1 M buffer is prepared by dissolving 210 g of citric acid monohydrate and approx. 50 g NaOH in 0.7 L of demineralized water. The volume is added up to 1 L and the pH is adjusted to 4.3 with NaOH. Then, the 1 M solution is diluted to the desired concentration of 0.05 M needed for the reducing sugar analysis.

DNS-reagent

5 g of 3,5-dinitrosalicylic acid (DNS) are dissolved in 100 ml 2 M NaOH solution. Afterwards, 150 g of pre-dissolved potassium sodium tartrate tetrathydrate are added. The solution is added up to 500 ml with demineralized water and stirred until all chemicals are dissolved. The bright yellow DNS-reagent is photosensitive and should be stored in a brown glass bottle or shielded by aluminium foil at 4 °C.

3.2 Analytical methods

3.2.1 Analysis of the solid residue

Analysis of solid composition

For sugar analysis, the solid samples are treated in a two-step acid hydrolysis with 72 % (w/w) and 4 % (w/w) H_2SO_4, respectively, according to the protocol developed by NREL[81]. The analysis is conducted using HPAEC with borate puffer as mobile phase. All contained glucose was assigned to the cellulose fraction, whereas all other sugars, mainly xylose as well as smaller amounts of arabinose, galactose, mannose and rhamnose, were summarized as hemicellulose.

Moisture content determination

For accurate determination of the moisture content of the solid residue, a laboratory procedure published by NREL is followed [81]. The wet biomass samples are mixed thoroughly and weighed into pre-dried aluminium pans. The samples are further dried in an oven at 105 ºC for at least four hours. Finally, samples are cooled down in a desiccator, weighed and further dried to constant mass (± 0.1 wt.%).

3.2.2 Analysis of the liquid hydrolysate

Analysis of liquid composition

LHW hydrolysates are analyzed for their sugar monomer and oligomer content in the Central Laboratory of Chemical Analysis, in TUHH. An analytical hydrolysis is executed for 60 min at 121 ºC with 4% (w/w) H_2SO_4. The samples are neutralized with $CaCO_3$, centrifuged and analyzed for their sugar content in an Agilent HPLC with refraction index detection. Pure water as eluent is pumped into a VA 300/7.8 Nucleogel Sugar Na (Machery-Nagel) with a flow rate of 0.3 mL/min. The detection limits are 50 and 100 mg/L before and after analytical hydrolysis, respectively.

AL-Lignin content determination

The AL-lignin content in LHW hydrolysate has been determined gravimetrically. First, two mililiters of the sugar solution are transferred into eppendorf tubes. The liquid samples are centrifuged in pre-dried centrifuge tubes for 20 minutes at 4500 times g. Afterwards, the supernatant liquid is removed with a pipette and the samples are dried to constant mass in an oven at maximal 60 °C.

Density determination

An Anton Paar DMA 4500M density meter was used to determine the density of the LHW hydrolysate samples by means of bending vibration. The density measurements give an insight into the biomass component concentration in the hydrolysates, mainly sugars and AL-Lignin, and of the severity of the pretreatment conditions.

pH determination

The pH of the different samples collected during the experiments was analysed using a WTW pH 340. Previous works have shown that acetic acid is the main organic acid present in the final hydrolysate mixture and that acetic acid release can be easily correlated from the pH value [27]. Nevertheless, only estimated results can be expected given the fact that hemicellulose hydrolysates have shown buffering effects at some extent [8]. pH analysis can be considered a rough estimation of the severity of the pretreatment and has been demonstrated to be a cheaper and faster alternative compared to expensive and time consuming analytical procedures.

Reducing sugar analysis

As described in the NREL lab procedure for the determination of cellulase activity [54], DNS-reagent can be used for the photometric measurement of reducing sugar concentration under alkaline conditions. The functional aldehyde group in reducing sugars like glucose is oxidized to a carboxyl group. In parallel, 3,5-dinitrosalicylic acid is reduced to 3-amino-5-nitrosalicylic acid, which strongly absorbs light at 540 nm [51]. At first, the hydrolysate samples are centrifuged at approximately 2500 times g for 10 minutes. The supernatant is diluted in order to match the valid absorbance range of the applied UV-photometer. Afterwards, 0.167 ml of the diluted sample 0.333 ml 0.05 M citrate buffer and 1 ml DNS-reagent are pipetted into 2 ml centrifuge tubes and mixed thoroughly. The mixture is boiled in a water bath for 5 minutes and cooled in iced water immediately in order to stop the reaction. The colour of the samples should have changed from bright yellow to orange or red, according to the reducing sugar concentration. 0.1 ml of the boiled sample is diluted with 1.25 ml of demineralized water in a polystyrene cuvette and UV-absorbance is measured at 540 nm. A calibration for xylose in a range of 0 – 10 g/l has been conducted prior to the sample analyses.

3.3 Experimental section

3.3.1 Experimental set-up

The fixed-bed biorefinery pilot plant at the Institute of Thermal Separation Processes, TUHH has been constructed and commissioned in 2011 by HOLLENBACH in his Diploma Thesis [31]. The experimental set up has been upgraded and adapted during the following years for admitting different pretreatment configurations and experiments. The plant is designed for performing the consecutive hydrothermal and enzymatic pretreatment of biomass feedstock but in the context of this work, only the hydrothermal equipment will be required. The detailed layout of the pilot plant can be observed in Appendix **¡Error! No se encuentra el origen de la referencia.**.

The core of experimental set-up is a stainless steel high pressure reactor with a volume of 3.9 L. The reactor is equipped with a LAUDA thermal oil bath connected to a heating jacket of 3.6 L for temperature regulation Two different feed lines are connected to the reactor- the fresh feed line F1 and the circulation line F2, both equipped with LEWA diaphragm metering pumps. To compensate the irregular flow caused by the pulsation pump, a cylindric stainless-steel pulsation damper is connected to the fresh feed line F1. Feed line F1 is equipped with an electrical oven and three heating jackets for preheating the inlet water while an additional heating jacket is installed installed in the circulation line for compensating heat losses. The outlet stream can be cooled down in a heat exchanger with cooling water from the local supply network. Biomass is introduced in a stainless-steel cartridge which is sealed by slot screens and inserted into the-high-pressure reactor. Reactor set up can be adjusted in order to set the flow to bypass, flow through or circulation modes. Bottom-up flow direction is set by default in the reactor. In order to avoid the evaporation of the feed, the reactor can be pre-pressurized with nitrogen. Two purge lines equipped with manual valves are connected to the reactor, one on top and one at bottom for decompressing and emptying the reactor when necessary. Pressure in the system is controlled by an overpressure valve which set point can be set manually throughout the experiment. Several thermocouples, pressure gauges and flow-meters are installed in the piping and around the reactor. Data logging is performed using NI LabVIEW on a personal computer at the plant

3.3.2 Experimental procedure

Flow through experiments are considered as the standard and therefore, the following experimental steps are detailed for that particular case. Nevertheless, the special arrangements needed for performing the LHW pretreatment under different operating conditions will be discussed at the end of this section. Note that four different reactor configurations have been studied in this work as previously mentioned in section 2.2.6.

Before starting the LHW experiment, the cooling system for the hydrolysate and the oil bath are switched on. The temperature of the oil bath is set 20 ºC above the desired reaction temperature. For the LHW treatment, demineralized water is pumped from a plastic storage tank. In order to reduce excessive pump pulsation, the pulsation damper, previously compressed with air from the local supply, is connected to the line. The heating system (Oven and heat exchangers HJ1-JH3) are turned on and the flow is set in bypass mode (valve plate S1) until desired temperature is reached. Temperature set point is set 10 ºC above reaction temperature considering the heat loss across the piping. Pressure in the system is regulated manually with the overpressure valve and set to approximately 50 bar. When temperature set-point is reached, the cartridge, previously filled with biomass, is introduced into the reactor and the head of the rector is closed tightly. The reactor is pre-pressurized with nitrogen to a pressure of 30-40 bar in order to avoid feed evaporation. Once pressure and temperature are stable, the flow direction is set to bottom-up (valve plate S2) and the feed is switched to flow through mode (valve plate S1). At the outlet, the LHW hydrolysate is cooled, collected in plastic canisters and weighed. After finishing the experiment, pressure is relieved and the plant is cooled down. Solids and liquid hydrolysate are analyzed as described in section 3.2.

For **batch** and **full circulation** experiments, once the bed is completely wetted and the hydrolysate is flowing out at a constant rate, the feed is switched to bypass (Valve plate S1) and the reactor is isolated closing the inlet and outlet valves (Valve plate S1). When working at **full circulation**, inlet and outlet connections of the circulation line are opened and the circulation pump is switched on and set to the desired flow rate. Intermediate heating in the circulation line is necessary to compensate heat loss across the piping. The set point of the heating jacket is set 25 ºC above the desired reaction temperature. Finally, in both cases, when the desired reaction time is reached, the reactor is carefully decompressed in order to avoid sudden pressure drops that can damage the reactor and piping. Subsequently, the hydrolysate is cooled down and stored in a plastic bottle.

In **partial recirculation** experiments, the hydrolysate is only partially recycled to the bottom of the reactor and fresh water flow is adjusted so the total flow is constant through the fixed bed. The previously described experimental plant equipped with a 3 L high-pressure fixed reactor was unable to conduct the partial recirculation experiments as planned, especially because the circulation pump lacked of sufficient power to overcome the pressure difference between bottom and top of the fixed-bed. In consequence, an analogous plant equipped with a 40 L high-pressure fixed-bed reactor was used for achieving the partial recirculation experiments. This plant was commissioned by SINGER [79] in the Thermal Separations Institute, in TUHH. Detailed explanation of the features of this pilot plant can be found in [61].

3.4 Modelling procedure

3.4.1 LHW simulation in Aspen Custom Modeler (ACM)

For studying the performance of the different operation conditions of a fixed-bed reactor for the hydrothermal treatment of wheat straw, a mathematical model has been implemented and simulated using AspenTech Aspen Custom ModelerTM V8.0 (ACM). The model was developed by REYNOLDS in the TVT, in TUHH, combining the results from previous studies in the same institute, as mentioned in section 2.4.1. The model has been validated for temperatures between 185ºC and 215ºC and reaction times from 0 min to 30 min and the parameters adjusted to fit the experimental behaviour of different experiments performed in the 3 L pilot plant mentioned in the previous subchapter. The single transport phenomena were analysed and modelled independently and later on combined in the general fixed-bed reactor model. The model has been especially elaborated for emulating the solubilisation and degradation of the hemicellulose, therefore, cellulose and lignin fractions are considered inert compounds and are constant throughout the process. Further details regarding the structure of the model are described by REYNOLDS in [63]. All equations named and described in this work are summarized in Table 8.5. The selected reaction pathway was proposed by DE LA TORRE, based on previous studies of SAEMAN and MORINELLY [39,53,73], as discussed in the previous chapter. The reaction pathway implemented in the model can observed in Figure 3.1. The consecutive and parallel reactions describing the hemicellulose degradation are modelled using irreversible pseudo-homogeneous first and second order kinetics with an Arrhenius approach for the temperature dependence including acid-catalyzed effects. Kinetic constants (k_i) are determined from Arrhenius equation. For this calculation, kinetic reaction constants ($k_{i,0}$) were determined previously in a batch reactor.

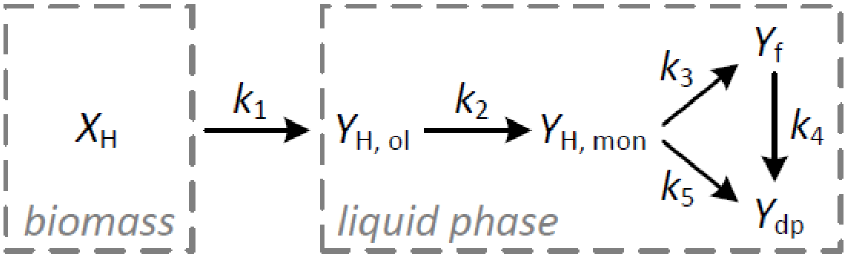

Figure 3.1: Suggested reaction pathway for biphasic hemicellulose degradation during wheat straw autohydrolysis using irreversible pseudo-homogeneous sequential first-order reaction kinetics [63].

Both solid hemicellulose and solubilized oligomers are treated as homogeneous phases, disregarding the chain length. The fast and slow reacting hemicellulose fractions were modelled by means of a second order reaction, accounting for fast degradation at the beginning and a slower reaction rate with advanced reaction progress, in substitution of the α factor by SAEMAN in [73]. Effect of acid concentration is not considered in the solid hemicellulose and its concentration ($X_H(z,t)$) is calculated considering both liquid and solid as homogeneous phases. In contrast, the hydrolytic effect of the acid concentration is considered in the partial mass balance equation for the different hemicellulose components solubilized in the stagnant pore ($Y_{i,pore}(z,t)$) and in the bulk liquid ($Y_i(z,t)$). The effective acid concentration in the pore ($a_{,pore}(z,t)$ and in the bulk liquid

$a(z,t)$ is calculated in the same way as the solubilised sugar components. The reaction rates of the individual species are calculated separately for the stagnant $r_{i,pore}(z,t)$ and the free liquid $r_i(z,t)$. Water density changes have been taken in account when calculation interstitial fluid velocity $u(z,t)$ and continuity equation $m(z,t)$. The suggested reaction mechanism starts with the solubilisation of the solid hemicelluloses into the swelling pores, followed by the consecutive hydrolysis of the compounds towards monomers and degradation products in parallel to the mass transfer from the pores to the bulk liquid. The oligomers, monomers and degradation products can be independently released into the flowing liquid with different values for transfer resistances (k_{Ai}). A scheme of the reaction mechanism can be observed in Figure 3.2.

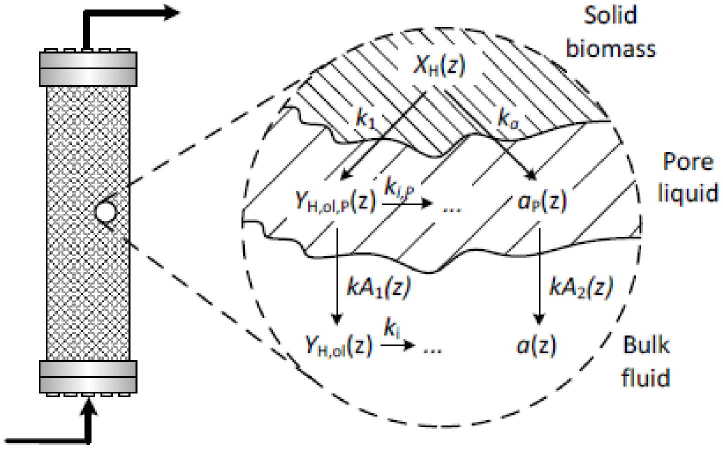

Figure 3.2: Modelling approach from hemicellulose hydrolysis and mass transfer from solid to liquid phase in the swollen biomass pores and the free moving liquid [63].

The biomass fixed-bed reactor is modelled using a one-dimensional model in which the solid and liquid phases are treated as continuous phases, assuming ideal mixing in radial direction. Reactor system is discretized using a backward difference method with the origin of coordinate z at the inlet of the reactor, hence, at the bottom in this case. Empty spaces were identified inside the reactor, below and above the biomass bed. These spaces are modelled as continuously stirred tank reactors (CSTR) with respect to mass and energy balances. Note that reaction of the solubilised compounds is also considered in the CSTR spaces. The overall fixed bed pretreatment is modelled according to a sequence of **(1)** filling of the bottom CSTR, **(2)** hot water percolating the biomass bed and **(3)** hydrolysate compounds fill the upper CSTR and leave the reactor system. The complete CSTR- fixed bed- CSTR can be observed in Figure 3.3.

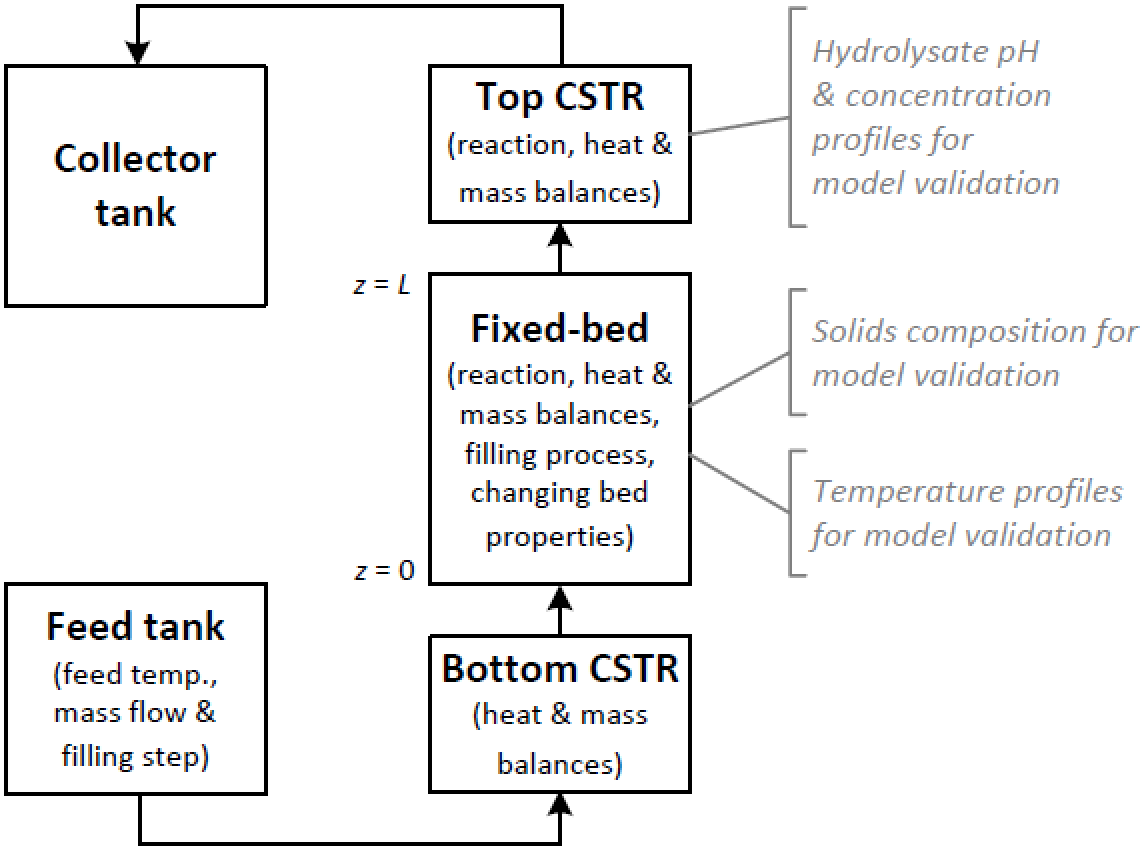

Figure 3.3: General fixed-bed model scheme used in the model [63].

The solid phase is considered to have a constant bulk volume with variable porosity and density. Two sorts of porosities are defined for the biomass fixed-bed: the actual bed porosity $\varepsilon_{act}(z,t)$, describing the pure solid volume fraction, and the effective flow porosity ε_{eff}, representing the available volume for volume flow, including stagnant liquid on the particle surface, biomass swelling and dead-zones. Previous studies have shown that the effective porosity reaches a constant value of 0,41 almost instantly after the biomass is wetted [64]. The real porosity $\varepsilon(z)$ included in the mass balances is determined as an average of the actual and the effective porosity depending on the filling level of the reactor. Heat balances have been calculated having in account that hemicellulose degradation kinetics depend mainly on the local reaction temperature $T(z,t)$, hence heat losses, mixing effects, water during the filling process and dispersional effects have to be considered at every position of the fixed bed. For solving the heat balance, an overall heat capacity of the whole system $(\rho \cdot cp)$ (z,t) is calculated including the biomass, the moisture, the applied fluid and the stainless-steel reactor. Full description of the equations, balances and boundary and initial conditions constituting the model are detailed in [63].

Simulation considerations

The mathematical model is implemented in ACM. This software allows to structure the mathematical model in independent building blocks or scripts that can be interconnected via ports. The mathematical model is implemented in seven different blocks: **(1)** feed tank, **(2)** mixer, **(3)** bottom CSTR, **(4)** fixed bed reactor, **(5)** top CSTR, **(6)** splitter and **(7)** collector tank. In the feed tank, the desired conditions for the LHW treatment are selected (temperature, mass flow, pressure and reaction time), also, $Ystep$ is initialized. The simulation plan with detailed description of reactor configurations and reaction conditions used is summarized in Table 8.1 and Table 8.2. Accumulative mass balances for the hydrolysate are calculated in the collector tank. In this work, the model has been extended to emulate four different under four different reactor configurations, namely batch, flow through, partial recirculation and full recirculation. Two variables $Fbatch$ and $Fcirc$, emulating inlet and outlet valves respectively, have been introduced for regulating the water and hydrolysate flows in the system. Mass and energy balances have been re-written in the mixer and splitter blocks for simulating the different operating modes. The filling process is equivalent for all the operating conditions, then, when the reactor is filled, the simulation is stopped and the operating configuration is selected. The simulation ends when the desired reaction time is reached. An implicit Euler method is used as integrator for solving the equations. Finally, the calculated hydrolysate properties are summarized in a table and transferred to an excel file in order to adapt the simulated values to the model responses evaluated by means of RSM. The different model responses evaluated by means of RSM can be observed in Table 4.2.

3.4.2 Design of Experiments (DoE) and Response Surface Methodology (RSM)

Stat-Ease Design-Expert® 8.0.7.1 has been used for experimental design and analysis. Set-up and analysis of the designs were conducted according to the standard procedure implemented in the software. In addition, polynomial expressions for modelling and assessment of the most important model responses have been obtained by means of Response Surface Methodology (RSM).

Central Composite Design (CCD) for LHW pretreatment

For the planning of the simulations and evaluation of the different operating conditions for the LHW pretreatment of wheat straw in a fixed bed reactor, a Central Composite Design (CCD) has been used. CCD was chosen over Box-Behnken Design (BBD) due to its higher stability, even though the external values ($\pm\alpha$) cannot be used for estimation purposes (

Figure 3.4). A complete simulation plan has been proposed by means of DoE in order to observe the local shape of the most interesting model responses under the four different operating conditions. Repetition of the central points is not required, given the accurate replicability of the simulations.

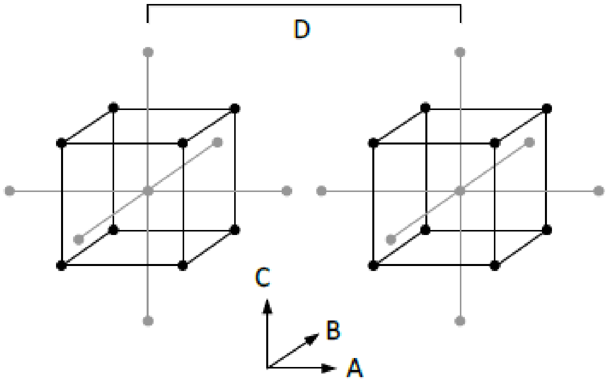

Figure 3.4: 4-factor, 5-level Central Composite Design (CCD). The external points are merely used for providing stability to the design and cannot be reliably used for parameter estimation [60].

For examining the batch, flow through and full recirculation operating modes a 3-factorial rotatable ($\alpha = 2$) has been used. The three factors to be optimized are temperature (A), reaction time (B) and mass flow (C). The factor ranges have been chosen in agreement with the validity of the model: temperature 170-230 ºC, reaction time 0-30 min. and mass flow 160-320 g/min. Temperature factor A refers to the temperature set-point in the reactor which might differ from actual reaction temperature due to heat transfer to the biomass and to the stainless-steel reactor. Reaction time starts at the beginning of the simulation, comprehending both filling time and reaction time. The wheat straw mass is 1 kg in all the experiments. Examined values of the factors at the different levels can be observed in Table 3.2.

Table 3.2: CCD (3 factors, 5 levels) design for the LHW pretreatment valid for: batch, flow through and full recirculation experiments.

Factor	**Coding**	**Units**	**Levels**				
			- α	**-1**	**0**	**+1**	**+α**
Temperature	A	ºC	170	182.16	200	217.838	230
Time	B	s	1200	1443.24	1800	2156.76	2400
Mass flow	C	g/min	160	192.43	240	287.568	320

For partial recirculation simulations, the recirculation rate (D) has been taken in account as a fourth factor, ranging between 0.1 and 0.9, because operations with values 0 and 1 are equivalent to flow through and full circulation operation respectively. The values conforming the 4-factorial CCD can be observed in Table 3.3.

Table 3.3: CCD (4 factors, 5 levels) design for the LHW pretreatment valid for: partial recirculation experiments.

Factor	**Coding**	**Units**	**Levels**				
			- α	**-1**	**0**	**+1**	**+α**
Temperature	A	ºC	170	185	200	215	230
Time	B	s	1200	1500	1800	2100	2400
Mass flow	C	g/min	160	200	240	280	320
Recirculation rate	D	dim.	0.1	0.3	0.5	0.7	0.9

Statistical analysis and evaluation (RSM)

The most important model responses have been evaluated with the Response Surface Methodology (RSM). This tool allows to fit experimental data to a quadratic polynomial, showed in (3.1). Y stands for the model response, x_i are the different factors selected for the DoE, β_i are the constant polynomial regression coefficient and ϵ is the statistical error of the expression. The regression coefficients are determined by the method of least squares.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j} \sum \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \epsilon \qquad (3.1)$$

Model responses regarding hemicellulose solubilisation, C5-Sugars recovery, furfural production and C5-Sugars degradation are evaluated by this method. The polynomial expressions have been used to study the changing liquid hydrolysate characteristics under different operating conditions. A summary of the different model responses evaluated for fully characterizing the hydrolysates can be observed in Table 4.2. Also, Stat-Ease Design-Expert® 8.0.7.1 is equipped with powerful optimization tools for determining the optimal parameters which maximize the desired responses. Moreover, graphical assistance tools have been used for representing the local shape of the model responses. Statistical interpretability of the results can be assessed before the simulation execution by means of the variance inflation factor (VIF), leverage and the FDS graph (fraction of design space) [52]. In addition, an analysis of variance (ANOVA) for the generation of a significant prediction model for the investigated design space was carried out. The ANOVA analysis is summarized in a table which contains indicators such as sums of squares, mean squares and degrees of freedom for the entire model, all model terms and the residuals. Finally, several visual diagnostic tools for the evaluation of the model quality are provided by the software. Thereby, the accuracy and prediction performance of the model can be checked. All the tests regarding evaluation and assessment of the model variance and predictability will be discussed in detail in section 4.

3.4.3 Techno-economic assessment in Aspen Plus (AP)

Techno-economic assessments allow to integrate results from multidisciplinary investigations such as reaction rates and yields, mass and energy integration, selection of the best available technologies and economic assessment of the fixed and operational costs of the facility. For a complete understanding of the influence of the pretreatment configuration and conditions on both the economic viability of the process and the potential of the offered product portfolio, a techno-economic assessment has been developed by the Institute of Environmental Technology and Energy Economics in TUHH. Comprehensive description of the modelling in AP, the necessary technological and economic assumptions and the methodology followed is detailed by SCHMIDT in [76].

The economic assessment is performed in the context of an overall biorefinery based on process modelling with Aspen Plus. This biorefinery model describes the fractionation, transformation and downstream separation of wheat straw from the raw material to the final products (Figure 3.5). The pretreatment process integrated in the overall model is based on the cascade process described in 2.2.5 and shown in Figure 2.4. Reactor configuration and conditions of the thermal hydrolysis step are main focus of this study (orange in Figure 3.5). Most part of the input data regarding reaction rates and yields have been extracted from the ACM model and from previous experimental work in the Institute of Thermal Processes, in TUHH. The necessary data for the transformation and downstream separation steps have been extracted from literature. The model implements numerous possible applications for the different fractions conforming the lignocellulosic materials. In the context of this work, the transformation of the liquid hydrolysate towards molasses, biogas, fertilizers and furfural will be investigated (green in Figure 3.5) while glucose is transformed into bioethanol and lignin is dried and milled for being directly sold in the market. Detailed layout of the process can be observed in Figure 8.6.

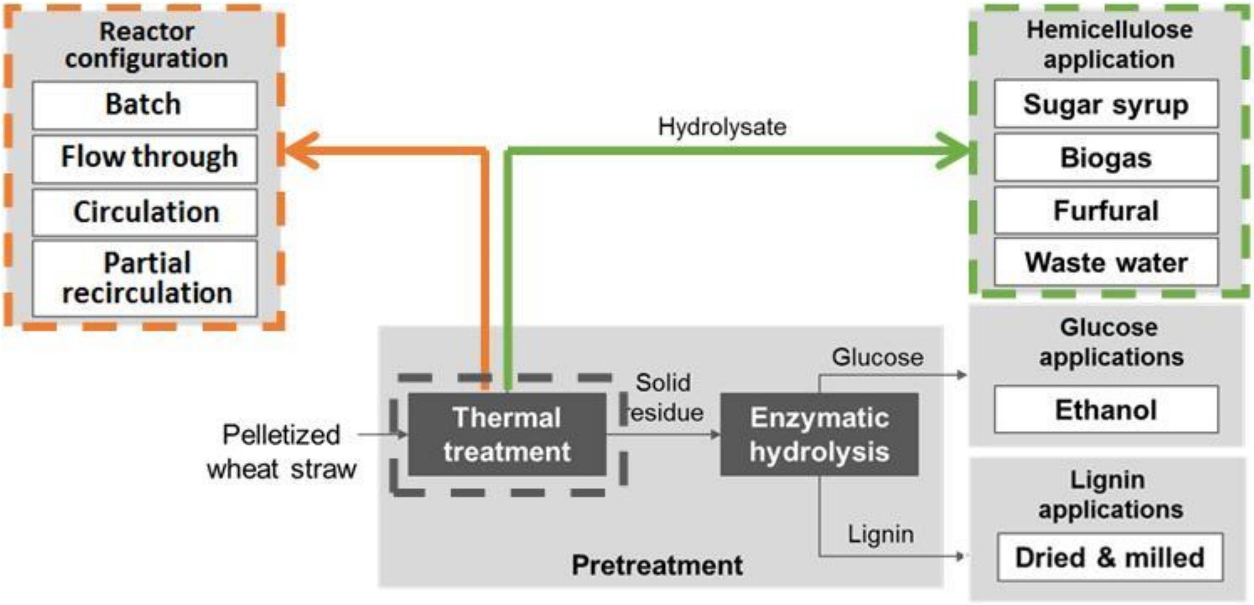

Figure 3.5: Overall block diagram of the 2G biorefinery model implemented in AP for studying the influence of the reactor configuration and product portfolio on the economics of a bioethanol facility. Adapted from [76].

A set of pretreatment configurations and conditions have been selected for studying the influence of the pretreatment step on the overall economic assessment of the process. Four different reactor configurations have been studied. Base case scenarios were selected for flow through and circulation operating modes based on the standard experiments performed at lab-scale **(b)**. Two other reaction scenarios have been selected according to the conditions which maximize sugar recovery **(m)** and minimize water consumption **(w)**. Batch and partial recirculation operating mode have not been implemented in the overall model but their economic performances have been evaluated by comparison with the flow through and circulation scenarios. Summary of the selected pretreatment configurations and conditions is shown in Table 3.4.

Table 3.4: Summary of the selected pretreatment configuration and conditions for the techno-economic study.

Reactor configuration	Scenario	Temperature (ºC)	Time (min)	Liquid/Solid
Batch (not implemented)	-	185	25	3.2
Flow through	b	200	30	9.1
	m	217.8	24	12.1
	w	200	30	5.9
Circulation	b	185	30	3.2
	m	200	30	3.3
	w	230	30	3.0
Partial recirculation (0.5) (not implemented)	-	200	33	5.2

In order to study the combined economic impact on the overall 2G biorefinery of the different pretreatment options and the selected product portfolio, a set of scenarios have been selected. The feasibility of using flow through and full circulation pretreatment options for the production of biogas, solid and liquid fertilizers, C5-Sugar molasses and furfural have been studied. The performance of batch and partial recirculation operating modes have been studied qualitatively. Disposal of the remaining liquid hydrolysate streams as waste water is also contemplated in the economic assessment. Table 3.5 summarizes the investigated scenarios.

Table 3.5: List of selected scenarios for studying the influence of pretreatment conditions on the available product portfolio.

Scenario	Pretreatment step	Hydrolysate application
A	Flow-through (b, m, w)	Molasses
B	Flow-through (b, m, w)	Biomethane, solid and liquid fertilizer
C-1	Flow-through (b, m, w)	Furfural, solid fuel and waste water
C-2	Flow-through (b, m, w)	Furfural, solid fuel and biomethane
D	Flow-through (b, m, w)	Waste water
E	Circulation (b, m, w)	Molasses
F	Circulation (b, m, w)	Biomethane, solid and liquid fertilizer
G-1	Circulation (b, m, w)	Furfural, solid fuel and waste water
G-2	Circulation (b, m, w)	Furfural, solid fuel and biomethane
H	Circulation (b, m, w)	Waste water
I	Batch	(n/a)
J	Partial recirculation	(n/a)

The economic assessment of the described facility is carried out by means of lignin production costs because there are not reliable data available on lignin market prices. The production costs are estimated using the minimum lignin selling price (MLSP) as reference, according to the methodology of equivalent annual costs described in VDI-6025, VDI-2067 and in [58] by PETERS. This methodology includes capital-, consumption- and operation-linked costs as well as the revenues from the by-products. The calculations are based on the mass and energy balances of the process simulations in Aspen Plus® and the Aspen Energy Analyzer®. Further details regarding the cost calculation methodology, the pricing of the equipment and raw materials and the market value of the products is described by SCHMIDT in [76].

4 Results and discussion

The influence of changing reactor configuration during LHW treatment on the potential of the liquid hydrolysate and on the economic viability of a 2G biorefinery, has been studied in three separate sections. First, four different reactor configurations for a high-pressure fixed bed reactor were modelled and optimized by means of DoE and RSM in ACM. Then, lab-scale experimentation at optimal conditions and laboratory analysis of liquid and solid product streams were conducted for corroborating the modelling results. Finally, the influence of reactor configuration and water consumption on the economic feasibility of a 2G biorefinery was studied by integrating the modelling results in an overall bioethanol facility model in AP. This chapter is structured according to the three differentiated research blocks.

4.1 Modelling of different reactor configurations

This subchapter summarizes the results of the modelling of four different reactor configurations for the hydrothermal pretreatment of wheat straw in a fixed bed reactor. First, a simulation plan for a comprehensive study of the behaviour of the model was performed by means of DoE. Afterwards, different model responses were evaluated by means of RSM for characterizing the liquid and solid product streams. Finally, the conditions for the LHW were optimized for each of the reactor configurations. These modelling results are veryfied experimentally in chapter 4.2.

4.1.1 Simulation plan (DoE)

Two different DoE designs have been used for simulation purposes in this work. The first design is based on a rotatable CCD with 3 factors and 5 levels and it has been used for the simulation and planning of batch, flow through and full circulation experiments. The second design is based on a rotatable CCD with 4 factors and 5 levels, which has been used for simulating and planning the partial recirculation experiments.

It is possible to assess the statistical predictability of the designs prior to the execution of the experiments. In Table 4.1, important parameters for the assessment of the designs are summarized. The models are fitted to a quadratic polynomial and present 19 and 30 design points respectively. The simulation plan detailing the conditions of these design points are listed in Table 8.1 and Table 8.2. For fitting this polynomial, 18 and 29 degrees of freedom (DF) are necessary, of which 9 and 14 belong purely to the model while the rest are assigned to the residuals. The DesignExpert software recommends that at least 3 df are assigned to the lack of fit while 4 DF should be assigned to pure error. The polynomials are formed from 3 and 4 linear terms, 3 and 6 interaction terms and 3 and 4 quadratic terms respectively. If model terms are insignificant and can be eliminated, more degrees of freedom are left for residuals. In this case, the generated CCD provided an adequate number of degrees of freedom and no model terms need to be aliased. Variance inflation factor (VIF) indicates how much the variance of a model coefficient increases due to lack of orthogonality in the design and it is of especial importance for measuring multicollinearity. In the design, VIF values are very close to one which implies that multicollinearity is not affecting the calculation of the coefficients. Leverage is used to measure the potential for a design point to influence the model coefficients. Leverage values close to one are undesired, in this case, the maximum leverage values are 0.6698 and 0.5833, respectively.

Table 4.1: Summary of parameters for assessing statistical predictability in a CCD design.

Design Parameter	1	2
Operating mode	Batch Flow through Full circulation	Partial recirculation
Design type	CCD	CCD
Factors	3	4
Levels	5	5
Design points	19	30
Total DF	18	29
Model DF	9	14
Residuals	9	15
Lack of fit	5	10
Pure error	4	5
Linear terms	3	4
Interaction terms	3	6
Quadratic terms	3	4
Maximum leverage	0.6698	0.5833
Mean leverage	0.5263	0.5
VIF Range	1-1.04	1-1.05

After reviewing all the statistical outputs for design evaluation, it is recommended to observe the fraction of design space (FDS) plot of the standard error over the design of space (Figure 4.1). FDS plots offer a simple way to compare the prediction performance of different experimental designs. A flat FDS means that the overall prediction error will be constant while a lower curve indicates that the prediction error will be smaller. It can be observed that in this case the FDS plots are flat across all the design space and that the accuracy and predictability of the results decreases on the borders of the design ranges.

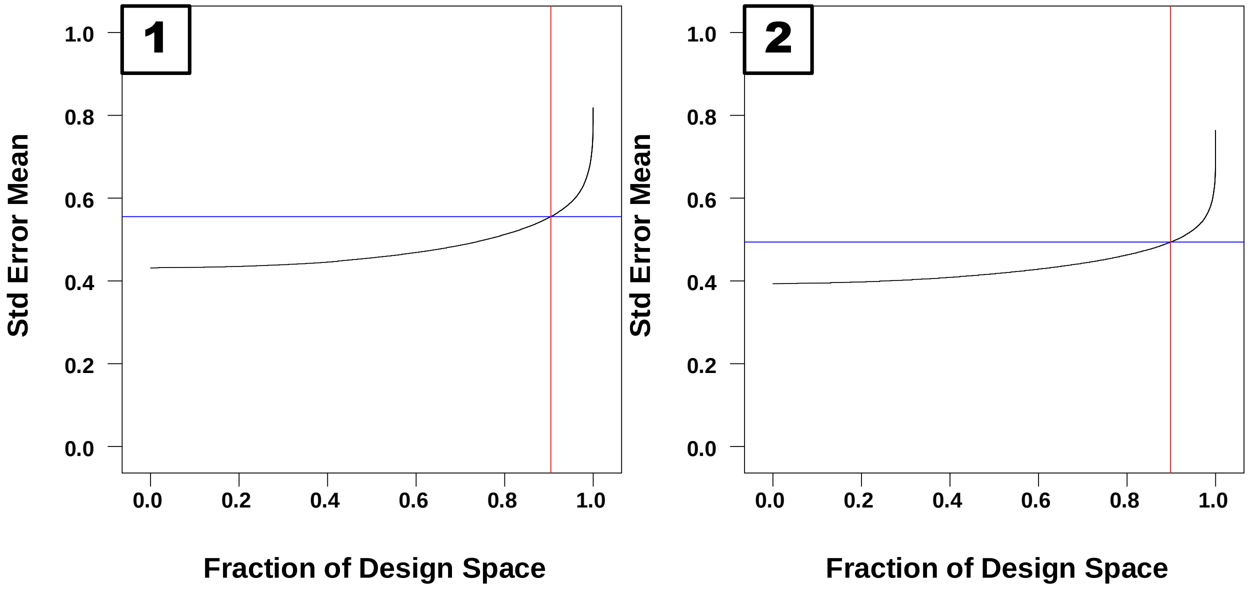

Figure 4.1: FDS plot for the CCD 3 factorial design used for the simulation of batch, flow through and full circulation models (1) and the CCD-4 factorial design used for the simulation of partial recirculation model (2).

4.1.2 Model responses (RSM)

The results from the simulations have been evaluated by means of Response Surface Methodology (RSM). The responses have been selected for evaluating the fractionation performance, characterizing the liquid hydrolysate and monitoring the degradation of the sugars. Polynomial expressions for estimating the value of the different responses at determined conditions of temperature, reaction time, mass flow and recirculation rate have been obtained. The regression factors of these polynomials give an insight to the most influencing factors and provide important information regarding parameter interaction. The quadratic polynomial expressions have been graphically represented for a better understanding of the different pretreatment behaviours. The responses evaluated for the four different operating conditions are summarized in Table 4.2.

Table 4.2: List of model responses evaluated by means of RSM for the different operating conditions.

Response	Coding	Units
Total hemicellulose solubilisation	THS	%
C5-Sugar recovery	SR	%
C5-Sugar concentration	SC	g/L
C5-Oligomer recovery	OR	%
C5-Oligomer concentration	OC	g/L
C5-Monomer recovery	MR	%
C5-Monomer concentration	MC	g/L
Monomer to oligomer ratio	MOR	%
Furfural yield	FY	%
Furfural concentration	FC	mg/L
Degradation product formation	DPF	%
Degradation product concentration	DPC	mg/L
pH	pH	-

Total hemicellulose solubilisation

The total hemicellulose solubilisation is a key parameter for achieving an efficient separation of the different biomass fractions. It can be considered as a rough approximation to the enzymatic digestibility of the solid residue because the removal of hemicelluloses and AL-Lignin increases porosity and surface area of the remaining biomass fractions, enhancing the accessibility of the enzymes to the cellulose matrix. The total hemicellulose solubilisation is calculated as the fraction of the hemicelluloses present in the solid that are transferred to the liquid phase during the hydrothermal pretreatment.

Hemicellulose solubilisation is extremely dependent on temperature and reaction time. The catalytic effect of the acid concentration on the hydrolysis of hemicelluloses have been widely studied, nevertheless, the mechanism of the acid hydrolysis of hemicelluloses in the solid phase has not been clearly stated yet. Mass transfer has also a significant influence on the hemicellulose solubilisation given the fact that the hemicellulose will solubilise first in the biomass pore and then it will be transported to the bulk liquid. The total hemicellulose solubilisation for the four different operating set-ups studied is depicted in Figure 4.2.

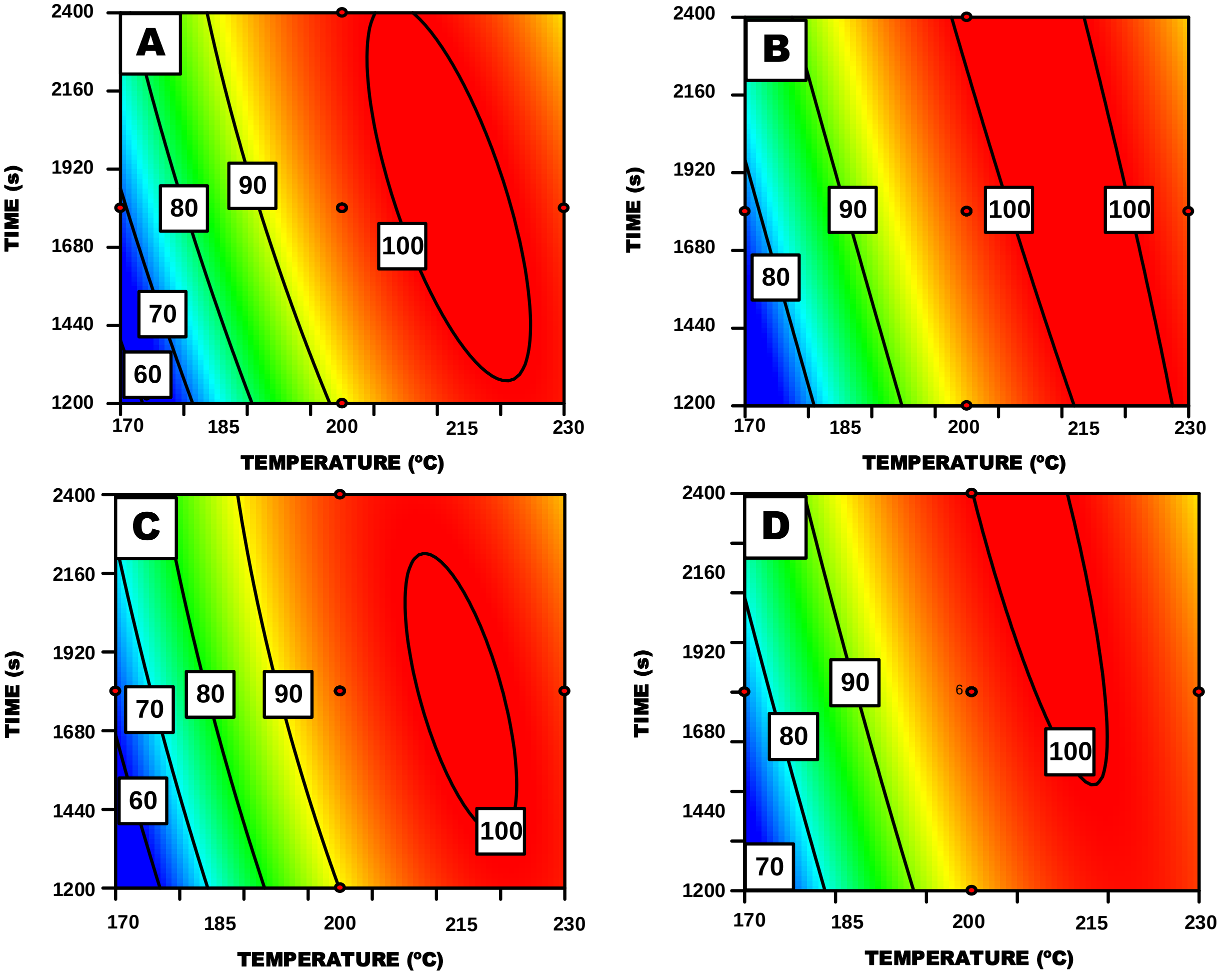

Figure 4.2: Contour plot of total hemicellulose solubilisation (%) as a function of temperature and reaction time (240 g/min) for the different reactor configurations: (A) batch, (B) flow through, (C) full recirculation and (D) partial recirculation.

As shown in Figure 4.2, complete removal of hemicelluloses can be achieved with the four different operating modes at temperatures over 215 ºC. High yields of around 90% are obtained at 200 ºC and reaction times of 1900 s. The interaction of temperature and time can be recognized by the diagonal shift of the curves. Note that the temperature factor used for the DoE and therefore depicted in the graphs, is the set point temperature and not the actual temperature in the reactor. Thereby, narrower regions in plots C and D indicate that the temperature set points are not reached because of the heat losses in the circulation line. Simulations for the different reactor configurations at 200 ºC, 250 g/min and 2000 s were performed in order to observe the mean temperature inside the reactor, as given in Figure 4.3.

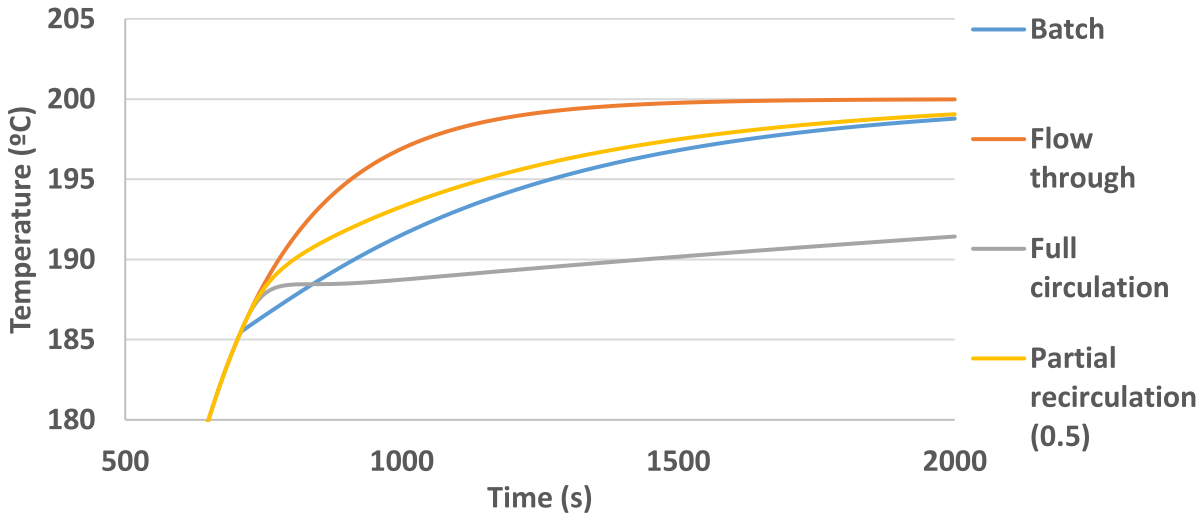

Figure 4.3: Plot for the time evolution of the mean temperature (ºC) inside the reactor during LHW treatment for different reactor configurations.

The plot shows that the main heating of the system is due to the fresh feed of water to the reactor and that increasing the circulation rate leads to a decrease on the mean temperature. The complete removal of hemicelluloses improves the enzymatic digestion of the solid residue, nevertheless, other factors such as the lignin removal or the repolymerization of the sugars may affect the digestibility. Unfortunately, the lignin removal is not represented in the model but these effects will be further discussed in the next subchapter with the help of lab-scale experimentation.

C5-Sugar recovery

C5-Sugar recovery can be considered as a measurement of the quality of hemicellulos extraction. It measures the number of hemicelluloses that can be recovered from the liquid hydrolysate, having in account the losses in the solubilisation step and the further degradation of the sugars. Therefore, it is calculated as the fraction of hemicelluloses present originally in the solid biomass which are solubilised in the liquid hydrolysate at the end of the pretreatment, calculated in weight basis. The C5-Sugar recovery accounts for C5-Oligomer recovery and C5-Monomer recovery, nevertheless, the observed amount of monomeric sugars in all the experiments is rather low. Thus, C5-Sugar recoveries are mostly due to the contribution of oligomeric chains. Sugar recovery is strongly dependent on temperature and residence time. Provided that the hemicellulose solubilisation from the solid to the liquid is almost total under all the different operating conditions, lower sugar recovery values are caused by acid catalysed degradation of the sugars. Contour plots for the C5-Sugar recovery model responses are shown in Figure 4.4

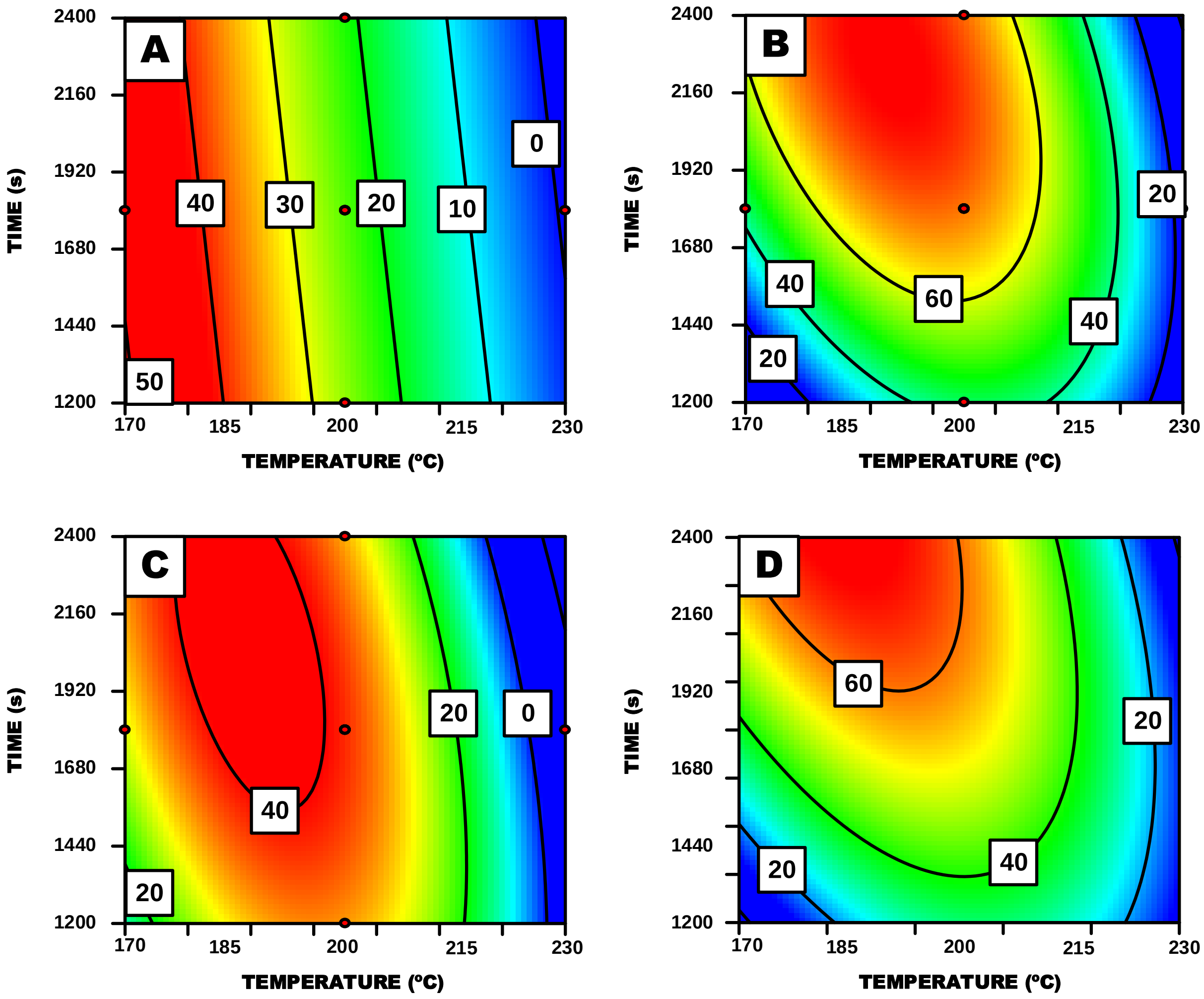

Figure 4.4: Contour plot of C5-Sugar recovery (%) as a function of temperature and reaction time (240 g/min) for the different reactor configurations: (A) batch, (B) flow through, (C) full recirculation and (D) partial recirculation.

For all reactor configurations excepting batch, temperature, reaction time and mass flow are significant parameters. A closer look to the ANOVA analysis shows that these parameters are present in its linear and quadratic forms in the model as well as a significant interaction parameter between temperature and time. The presence of quadratic terms allows to find a maximum within the limits of the design space, as it can be noticed from the figures B, C and D. Maximum sugar recoveries are reached at intermediate temperatures of 200 ºC, which is indeed absolutely consistent with the previous optimization of the LHW pretreatment in this reactor [60]. Below that temperature, the solubilisation of hemicelluloses is rather low (see Figure 4.2) and above 200 ºC the degradation of the sugars is already severe. Degradation effects are remarkable in batch and full circulation modes due to the higher liquid residence times. For batch operation, the sugar recovery is merely dependent on temperature and degradation of the sugars is significant even at mild reaction conditions.

Contour plots of flow through and partial recirculation modes are very similar but slightly longer reaction times are needed for achieving higher sugar recoveries in the case of partial recirculation. It is noticeable also that the maximum of sugar recovery is achieved at similar temperatures, this is of especial important because as recently described, the temperature depicted in the plots is not the actual temperature in the reactor but the temperature set point. An assessment of the temperature profile (see Figure 4.3) showed that the real temperature in the partial recirculation mode is lower than expected, especially due to the heat losses in the recirculation and the lower amount of fresh hot water entering the reactor. The observed effect of achieving similar sugar recovery at a lower temperature could be explained by a higher concentration of organic acids due to the recirculation of the hydrolysate. The higher acid concentration might lead to a faster hydrolysation of the sugars into the liquid by combining the effect of temperature and pH.

C5-Sugar concentration

Obtaining hydrolysates with high sugar concentration is one of the biggest challenges of 2G biorefineries. Higher concentration hydrolysates lead to a reduction of size and complexity of downstream processing and separation equipment. There are two main factors affecting the sugar concentration: First, the amount of water used for the separation and second, the degradation of the sugars. Up to now, there is a technological compromise between these two factors. On one hand, degradation can be minimized when using significant amounts of water. But on the other hand, this results in low concentrated hydrolysates and vice versa. In this context, the suggested partial recirculation operating mode shows interesting features as a compromise between flow through and circulation reactor configurations. C5-Sugars concentration comprises both monomers and oligomers, nevertheless, no significant concentration of monomers was obtained during the LHW treatment, which points at a rapid degradation of the monomers towards furfural and other degradation products. Sugar concentration contour plots for the different operating conditions are shown in Figure 4.5.

The sugar concentration shows very different behaviours depending on the pretreatment operating modes. For the batch reactor, there is a linear dependence with temperature whereas mass flow and reaction time are not significant parameters. Really high sugar concentrations are obtained at low temperatures and reaction times, nevertheless, at these same conditions, the removal of hemicelluloses (see Figure 4.2) is too low to be considered as an efficient pretreatment option. For flow through operation, the model response is dependent linearly on temperature, mass flow and reaction time, in addition, it shows a quadratic term for temperature which allows to find a maximum within the limits of the design space of app. 40 g/L. In turn, the full circulation model response shows linear and quadratic terms for temperature as only significant terms and the slight shift of the curves points to a parameter interaction of temperature with time. In this case, the maximum in sugar concentration is above 60 g/L. Sugar concentration during partial recirculation operation is influenced by all the factors linearly, the interaction factor between temperature and time and also by the temperature quadratically. The maximum in this case is above 40 g/L. Summarizing, batch and full circulation modes show the highest sugar concentrations due to the lower amount of water used. However, as discussed earlier, a higher degradation of the sugars is expected under these pretreatment conditions for these configurations.

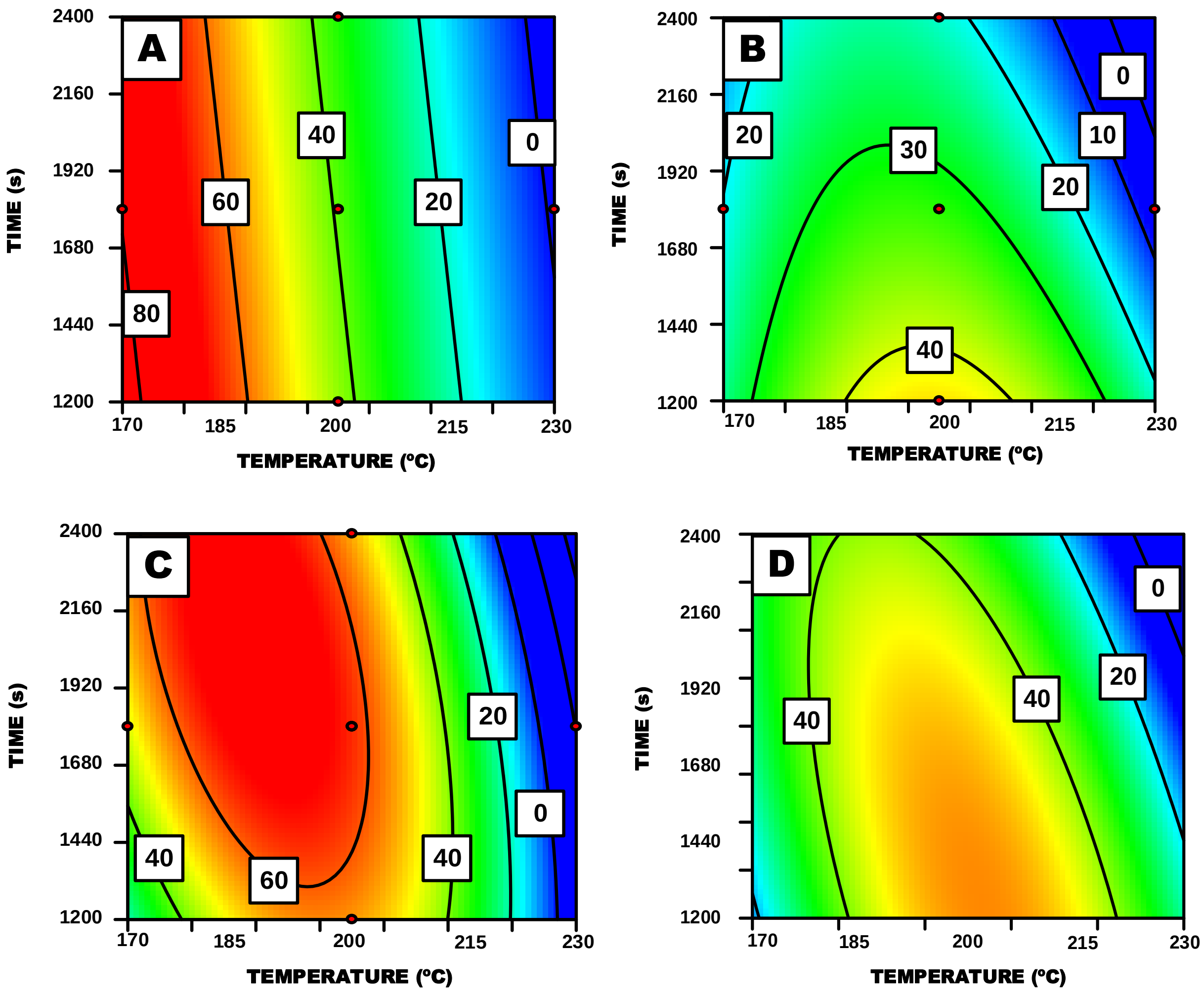

Figure 4.5: Contour plot of C5-Sugar concentration (g/L) as a function of temperature and reaction time (240 g/min) for the different reactor configurations: (A) batch, (B) flow through, (C) full recirculation and (D) partial recirculation.

Additionally, it can be noticed that higher sugar concentrations can be achieved under partial recirculation compared to the flow through mode. Two confronted effects are influencing the sugar concentration during partial recirculation experiments: The reduction of water consumption and the higher liquid residence time. The relative weight on the sugar concentration of these two differentiated effects is assessed on Figure 4.6.

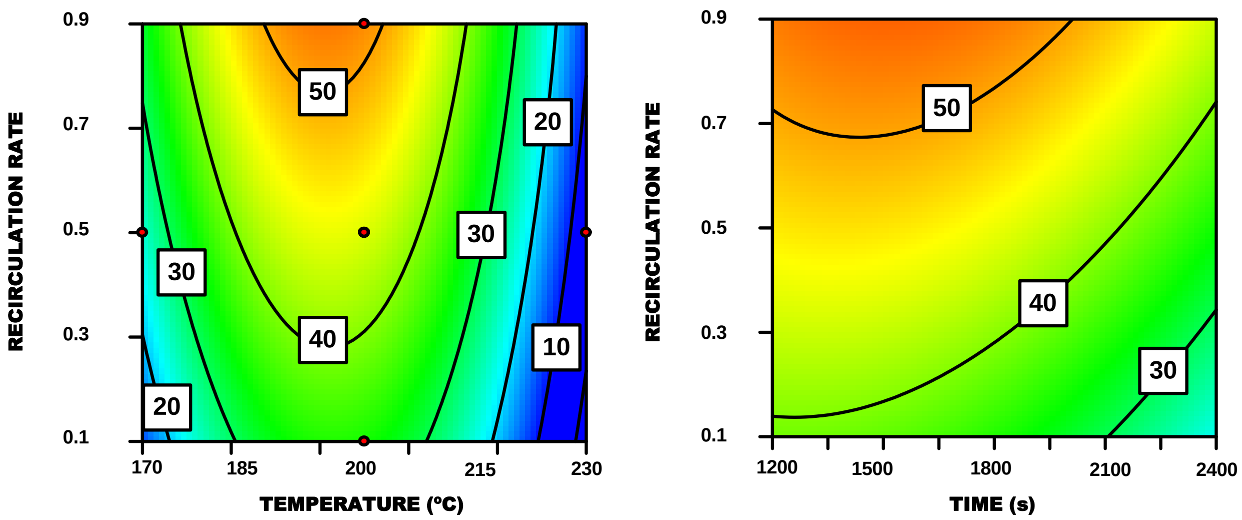

Figure 4.6: Contour plot of sugar concentration (g/L) as a function of temperature and recirculation rate (240 g/min, 1800 s) (left) and as a function of time and recirculation rate (240 g/min, 195 ºC) (right).

From these plots, it can be deduced that temperature has a dominant influence for obtaining high concentrated sugar solutions. The effect of temperature is prominent over the remaining factors, namely recirculation rate, acidity of the medium and liquid residence time. In the first graph, it can be observed that changes in temperature are stronger than changes in the recirculation rate. Again, temperatures over 200 ºC lead to excessive sugar degradation. As will be apparent, increasing recirculation rate is enhancing sugar concentration due to the reduction of water amount whereas no significant degradation is observed due to the longer liquid residence time. In the right plot, it can be corroborated that increasing reaction time has milder effect on sugar degradation than the effect of reducing water consumption. Given these results, it is reasonable to believe that the partial recirculation of hydrolysate to the reactor will not enhance sugar degradation severely and that the effects of increasing acid concentration and liquid residence time will be compensated in terms of sugar concentration and sugar recovery for the reduction of water utilisation.

Furfural and degradation products formation

Furfural is one of the main degradation products of C5-Sugar monomers as well as 5-HMF is for C6-Sugar monomers. The yields and concentration of furfural and other degradation products have been modelled in order to assess the sugar degradation behaviour and the severity of the pretreatment for the different suggested configurations. Furfural and degradation products formation are calculated as the fraction of compound present in the liquid hydrolysate compared to the original hemicellulose concentration in the solid. Contour plots depicting the model responses for furfural production are given in Figure 4.7.

As it can be deduced from these contour plots, furfural production is strongly dependent on temperature and the similar trends between the different configurations point to fast kinetics of formation and degradation. For every configuration, the amount of furfural produced below 200 ºC is almost negligible. Anyhow, the maximum yields observed at 230 ºC do not exceed values of 10 %. Slight parameter interaction between temperature and reaction time can be observed, which indicate a combined effect on the degradation of the sugars. Nonetheless, furfural is a product of interest for 2G biorefineries as discussed in previous chapters and for that purpose it has been included in the techno-economic assessment study. A preliminary idea in this research was to study if LHW pretreatment could constitute a first step for the production of furfural. At first sight, furfural yields are far too low to be considered an efficient alternative. In addition, it has been observed that the conditions that enhance furfural production are also promoting its fast degradation. Maximum furfural yields together with corresponding degradation products for the different reactor configurations are summarized in Table 4.3.

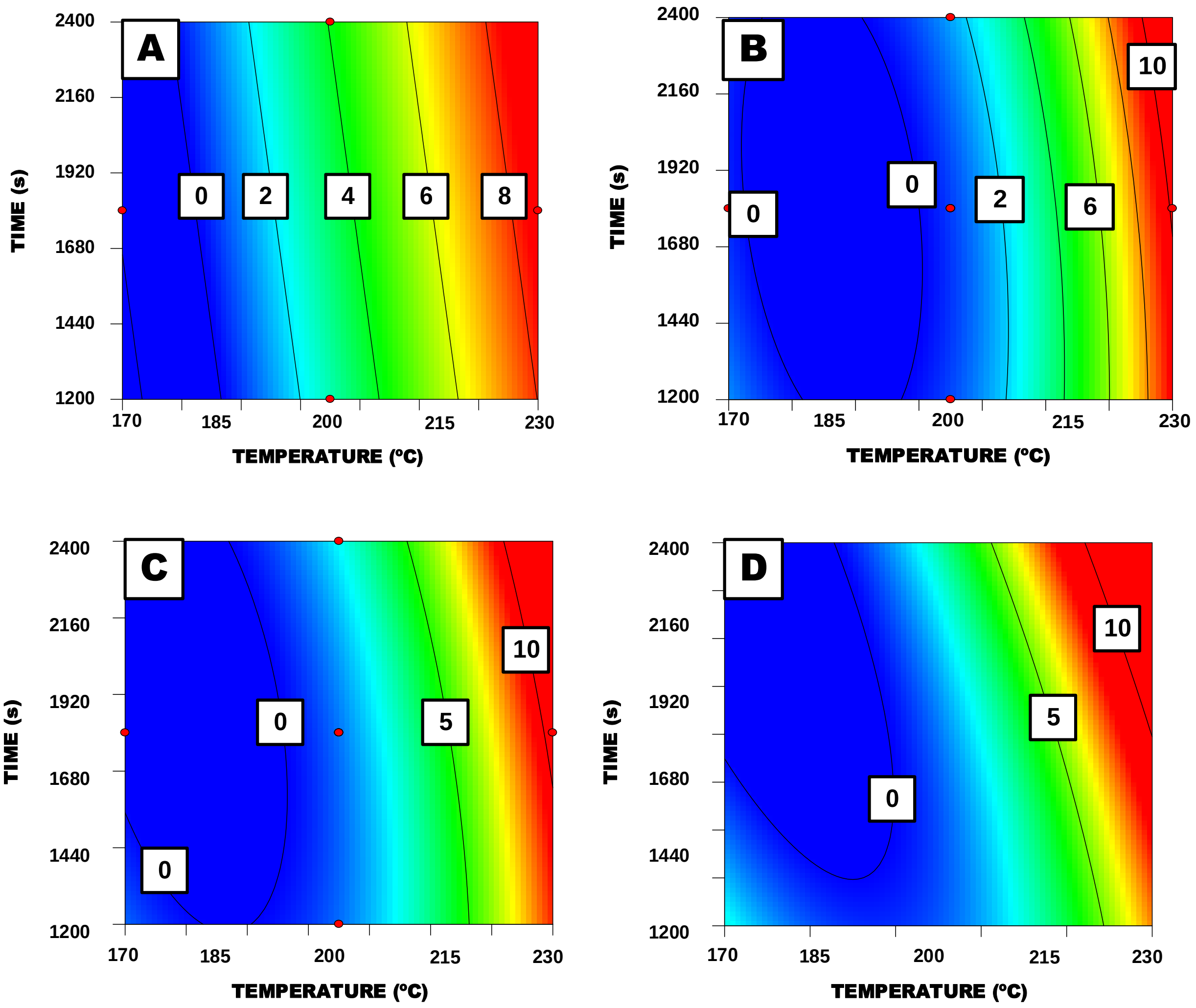

Figure 4.7: Contour plot of furfural formation yield (%) as a function of temperature and reaction time (240 g/min) for the different reactor configurations: (A) batch, (B) flow through, (C) full recirculation and (D) partial recirculation.

Therefore, the selectivity towards furfural at these conditions is very low and it is not possible to produce significant amount of this compound without degrading the sugars to another inhibition products. Hence, even if furfural can be easily separated from the reaction mixture due to its high volatility, the degradation of the remaining sugars in the hydrolysate will be almost complete and other technologies for production of furfural from the extracted monomeric or oligomeric sugars should be considered.

Table 4.3: Maximum model responses for furfural production and degradation products formation for the different reactor configurations.

Model response	**Reactor configuration**			
	Batch	**Flow through**	**Full circulation**	**Partial recirculation**
Furfural (g/L)	11.96	4.09	7.15	13.10
Degradation products (g/L)	52.21	18.30	31.64	56.28
Furfural yield (%)	7.31	9.12	8.00	8.01
Degradation products yield (%)	31.92	40.81	35.42	34.41

4.1.3 Optimisation of different operating conditions

In order to investigate the different reactor configurations at lab-scale, an optimization of the model responses has been performed with the help of DesignExpert. This software has implemented several optimization tools which allow to maixmize the desired model responses according to different criteria. Sugar recovery and sugar concentration have been maximized for each of the LHW pretreatment configurations. Given the lower influence of reaction time and mass flow on the model responses, both parameters have been condensed into a water consumption parameter which is more valuable for the scope of this study, especially regarding the techno-economic assessment. The results of the optimization are summarized in Table 4.4.

Table 4.4: Optimum conditions for C5-Sugar recovery and C5-Sugar concentration of the different reactor configurations.

Operation	Temperature (ºC)	Water consumption (kg)	Sugar recovery (%)	Sugar conc. (g/L)
Batch	182.16	3.00	30.47	49.84
Flow through	193.75	6.34	63.77	37.96
Full circulation	190.01	3.00	40.43	66.13
Partial recirculation	192.54	5.13	58.45	39.90

From the results, it can be observed that optimum temperatures are ranging between 180-190 ºC, avoiding excessive sugar degradation. The low sugar recovery and sugar concentration obtained during the batch process, compared to full circulation process, is triggered by the lower hemicellulose solubilisation. Mass transfer limitations and poor AL-Lignin removal might be responsible of the low efficiency of the separation. As for the temperature difference between these two configurations, it confirms the assumptions of a lower mean temperature in the reactor when circulation of the hydrolysate is used at some extent. Of all the pretreatment options, full circulation yields the maximum sugar recoveries with a liquid to solid ratio of 3:1. Comparing flow through with partial recirculation mode, it can be observed that similar sugar concentrations, 37.96 g/L and 39.90 g/L, and sugar recoveries, 63.77 % and 58.45 %, can be achieved respectively. However, this similar performance comes with a lower reaction temperature (app. 10ºC) and lower water consumption (10 % less). Apparently, the recirculation of part of the hydrolysate might constitute an improvement of the economic feasibility of the process as a result of reducing energy and water consumption. This statement will be further investigated in the section 4.3 within the techno-economic assessment.

However, partial recirculation should not be considered as a single operation because the behaviour of the system varies dramatically with changing recirculation rate. The performance of this operation ranges from flow through operation to full circulation. Therefore, selecting just one maximum point is not a trivial choice. For this purpose, simulations have been performed at different recirculation rates in order to identify the compromise set of parameters that will maximize the effect of the partial recirculation mode. As given in Figure 4.8, sugar recovery decrease significantly with recirculation rates above 0.5 while sugar concentrations do not increase significantly throughout the whole recirculation rate range. Therefore, the longer liquid residence times caused by the recirculation of the hydrolysate are not influencing the sugar degradation as severely as expected. The relatively constant sugar concentration can be explained due to the fact that the higher sugar concentration values are compensated by the lower amounts of water. It can also be noticed that the water reduction can reach up to 50% compared to the standard flow through mode. The simulations which show more promising performance are those with the recirculation of 50 and 66 % of the hydrolysate because they present higher sugar concentrations with no significant decrease of sugar recovery.

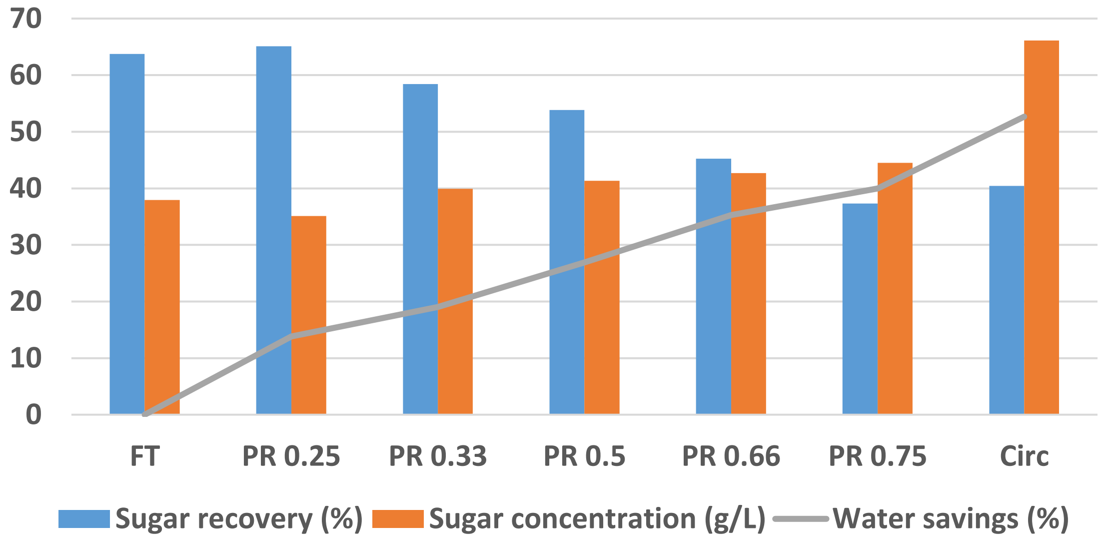

Figure 4.8: Comparative performance of partial recirculation operation from flow through mode to full circulation in terms of sugar recovery (%), sugar concentration (g/L) and water reduction (%).

4.2 Lab-scale experimentation on different reactor configurations

This subchapter summarizes the results of the lab-scale experiments and the subsequent laboratory analysis performed for each of the suggested operating conditions of the fixed bed reactor. First, an experimental plan is presented, according to the optimal conditions extracted from the simulation work. Then, the solid and liquid product streams are analysed in order to corroborate some of the results from the modelling section.

4.2.1 Experimental plan

Four experiments have been conducted at lab-scale for veryfing the results from the mathematical model discussed in the previous subchapter. The conditions for these experiments have been selected for maximizing sugar recovery and sugar concentration in the hydrolysate, according to the simulation results (Table 4.5). Samples were taken from the hydrolysate and the solid residue in order to perform subsequent analysis. For ensuring statistical reliability, experiments were replicated twice and analysis three times.

Table 4.5: Experimental plan for the tests conducted at lab-scale

Operating mode	**Experimental plant**	**Parameter**			
		Temperature (ºC)	**Reaction time (min)**	**Mass flow (g/min)**	**Recirculation rate (dim.)**
Batch	3L	185	25	250	-
Flow through	3L	200	30	250	0
Full recirculation	3L	200	30	250	1
Partial recirculation	40L	200	33	250	0.5

The laboratory procedures followed for the analysis are described in section 3.2. The analytical results for the liquid and the solid samples are summarized in Table 4.6 along with the standard deviation of the measurements. Plots depicting the influence of the reactor configuration on the measured properties are given in the Appendix (Figure 8.1-8.5).

Table 4.6: Analytical results for the liquid and solid samples from the lab-scale experiments.

Parameter (Units)	Reactor configuration			
	Batch	Flow through	Full circulation	Partial recirculation
Moisture content (%)	51.78 ± 2.12	69.91 ± 5.38	54.32 ± 5.11	74.04 ± 0.34
pH	5.9 ± 0.1	4,7 ± 0.5	4.5 ± 0.6	4.42 ± 0.06
Density (g/cm^3)	1.026 ± 0.004	1.0174 ± 0.0001	1.024 ± 0.009	1.021 ± 0.001
D-xylose DNS equivalent (g/L)	6.13 ± 1.24	13.59 ± 4.36	20.89 ± 4.90	19.02 ± 4.68
AL-Lignin (g/L)	10.25 ± 5.07	16.8 ± 0.8	11.92 ± 3.42	15.3 ± 0.4
AL-Lignin recovery (%)	11.81 ± 5.84	48.27 ± 2.38	13.74 ± 3.94	36.6 ± 0.9

4.2.2 Solid Product characterization

Solid samples were extracted from the treated biomass in order to analyse the chemical composition and to determine the moisture content. Unfortunately, the solid composition analysis performed by the Thünen Institute for Wood Research was not on time for being included in this work, nevertheless, results will be further assessed and included in the electronic version.

Moisture content analysis of the solid residue is accepted as a good estimation of the changing porosity of the solid. This change is caused by the solubilisation of the different fractions, mainly hemicelluloses but also AL-Lignin. When the wheat straw pellets are introduced into the reactor they present a moisture content of app. 10% which increases to values ranging from 50 % in the batch and circulation process to 70 and 75 % in flow through and partial recirculation respectively, as it can be observed in Figure 8.1. These values correspond to a higher solubilisation of hemicelluloses but also, of other fractions such as AL-Lignin, as depicted in Figure 8.5. Acid-soluble lignin recoveries are very low for batch and circulation experiments, barely over 10 % of the original acid-soluble lignin is present in the final hydrolysate. In contrast, flow through operation and partial recirculation show rather high acid-soluble lignin removal rates, with 48.27 and 36.62 % respectively.

These results indicate that during batch and circulation processes there is an accumulation of lignin and degradation products in the reactor due to the longer residence times employed for the liquid phase. As previously discussed in section 2.2.6, these compounds tend to form aggregates (lingo-humic substances) and repolymerise, precipitating onto the surface of the solid. The precipitation of these substances is the cause of the lower removal of AL-Lignin and it might result in less enzymatically digestible AS-Lignin residue [91]. However, previous studies in the institute have shown that highly digestible solids can be produced in circulation experiments, showing that the enzymatic degradability is not severely affected by this phenomenon. The lower recovery rates encountered in the batch process might be caused by significant mass transfer limitations due to the lack of mixing in the reactor which leads to a bad wetting of the biomass. YANG et al. demonstrated that pumping effects have strong influence on AL-Lignin removal [91]. Therefore, it can be deduced that during the circulation experiment the removal of AL-Lignin occurs at higher rates than in the batch process but due to the longer reaction times, most part of the lignin is precipitated. These statements will help to confirm the hemicellulose solubilisation results provided by the simulations in ACM.

In contrast, good removal of AL-Lignin is achieved with flow through and partial recirculation experiments, given the fact that the hydrolysate containing lignin fragments and degradation products is continuously flushed out of the reactor. The lower AL-Lignin recovery in partial recirculation experiments compared to flow through can be explained by the higher liquid residence time resulting from the recirculation of the hydrolysate. In that case, repolymerisation of lignin compounds is expected at some extent. Further studies should be performed regarding the enzymatic digestibility of the different solid residues presented in this section. Nevertheless, previous studies have shown a 90% of enzymatic digestibility for the flow through and the full recirculation under similar conditions. Therefore, it can be stated that partial recirculation will not just provide high concentrated sugar solutions but also a highly digestible solid residue.

4.2.3 Liquid hydrolysate characterization

Liquid samples were taken from the hydrolysate in order to analyse the chemical composition and to determine interesting properties such as the pH, the density and the AL-Lignin that can help to estimate the efficiency and the severity of the process. The results of the sugar composition analysis performed by the Central Laboratory of Chemical Analysis, are shown in Figure 4.9. HPLC is used for identifying separately the presence of monomeric sugars, oligomeric sugars, degradation products and organic acids.

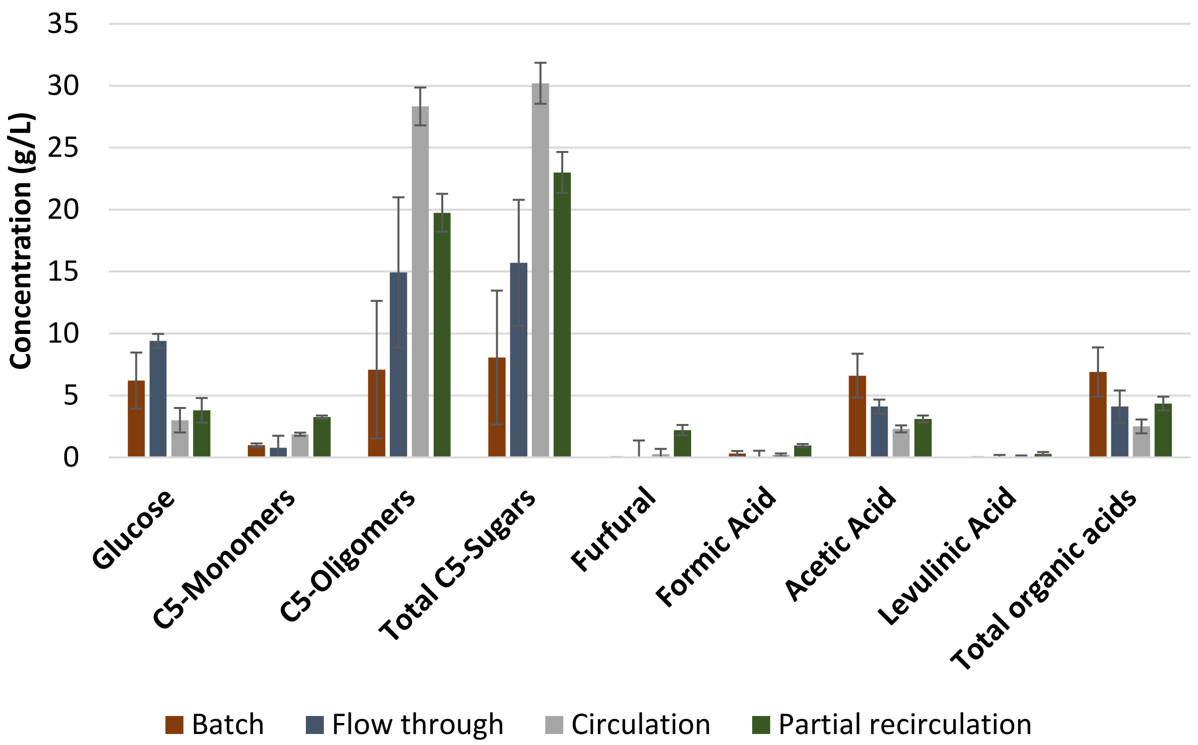

Figure 4.9: Liquid composition analysis (g/L) depicting C5-monomers, C5-oligomers, degradation products and organic acids present in the liquid hydrolysate.

Glucose present in the hydrolysate is considered to have origin on the amorphous fraction of cellulose, therefore it would not be included in the hemicellulose calculations. In the first place, it can be observed that the fraction of C5-Sugars corresponding to C5-monomers is as low as expected and deduced from the model. Most part of the sugars present in the liquid mixture are formed from oligomeric chains. No significant difference in this regard can be noticed between the different reactor configurations. The major difference in behaviour between these categories is present in the C5-Sugar concentration. As discussed previously, the batch process present serious solubilisation and degradation problems and the presence of sugars in the hydrolysate is very low. In this case, the model is overestimating the concentration of sugars obtained by the batch simulation given the fact that not all the mass transfer limitations occurring during this process are implemented in the model. As the model predicted, the highest sugar concentrations can be achieved when operating with circulation strategies. However, the partial recirculation experiments showed outstanding results in this field, with C5-Sugar concentrations over 35 g/L. This difference cannot be fully explained by the better performance of the 40 L plant where these experiments were conducted. But it also leads to the conclusion that no severe sugar degradation occurs because of the longer residence times and the recirculation of the organic acids. In fact, it can be observed from this analysis, that no severe sugar degradation, mainly to furfural, happened. These results are in good agreement with previous optimization studies performed for the flow through [64] and circulation [57] operating modes of the reactor at the Institute of Thermal Separation Processes in TUHH.

The DNS sugar analysis underlined the assumptions from the liquid composition analysis and from the model responses. In view of these results, it can be stated that hemicellulose solubilisation is lower in batch mode and the sugar degradation is very high. And that the sugar concentrations achieved with the partial recirculation mode is higher than in the flow through mode and significantly similar to the full circulation. The same trends are confirmed from the results of the density determination.

pH determination has been performed to the liquid samples in order to assess the acidity of the reaction mixture. pH has been widely used as an estimation of the severity of the pretreatment due to the release of acetyl groups observed during the solubilisation and the hydrolysis of hemicelluloses. The main acid in the liquid hydrolysate is acetic acid but also lower amounts of formic acid and levulinic acid are present. Lower pH values were expected for the hydrolysates of more severe pretreatments due to higher temperature, reaction time or residence time. pH is rather high in the batch pretreatment compared to the other configurations. This can be explained for the lower solubilisation of hemicelluloses, in consequence, a lower amount of acetyl groups is released into the liquid. It can also be caused due to the reaction of these acetic groups with other substances present in the reaction mixture which leads to the precipitation or adsorption of the acetic acid. This explanation can also be extended to full recirculation and partial recirculation experiments which pH was expected to be lower due to a higher solubilisation and hydrolysis of the hemicelluloses. Many researchers have pointed at an unexpected increase of the final pH during the hydrothermal pretreatment and the mechanisms behind the buffering effect of hemicelluloses has not been clearly stated yet [8,63]. Different studies point at the adsorption of acetic groups or the back polymerisation of the lignin substances [48,56]. pH should be monitored in the future during the partial recirculation in order to observe the behaviour and in order to understand if the acetic acid and the acids in general are influencing and catalysing the reaction.

As stated throughout this section, the implemented model in ACM emulated reliably the behaviour of the different reactor configurations in the studied ranges of temperature (170-230 ºC), mass flow (160-320 g/min) and reaction time (1200-2400 s). Not enough laboratory experiments were carried out in this work in order to extend the outstanding accuracy of the model during flow through operation [63,64] to other reactor configurations such as circulation or partial recirculation. Nevertheless, the trends when comparing the different reactor configurations in terms of sugar recovery, sugar concentration and sugar degradation were reliably represented. The bigger problems were encountered for modelling the batch reactor given the fact that the macroscopic mass transfer limitations caused by phenomena such as channelling, poor wetting or biomass compacting due to sudden decompression of the reactor are not fully represented in the model. However, these phenomena are not significant for the rest of the suggested reactor configurations, therefore, including these effects in the model is not crucial for a reliable representation of LHW pretreatment.

4.3 Techno-economic assessment of a 2G biorefinery

In this section, the results of the techno-economic study performed in the Institute of Environmental Technology and Energy Economics, in TUHH are assessed and discussed in order to determine the influence of reactor configuration, pretreatment conditions and product portfolio selection on the overall economics of the process.

4.3.1 Preliminary considerations

Exemplary work has been performed by SCHMIDT in [76] for calculating production costs and product revenues for all the scenarios listed in Table 3.5. A process flow diagram of the overall design, including the sequential pretreatment process and the different fraction applications and separation processes is given in Figure 8.6. The economic evaluation is calculated from five budget items. Detailed description of the budget allocations included in each of the items can be found in Table 8.3 The capital, consumption and operational costs and the revenues from the proceeds items are balanced with the lignin price, calculated for this purpose with the annuity method [96]. The pretreatment conditions for each of the studied reactor configurations as well as the different scenarios depending on the selected product portfolio have been previously discussed in 3.4.3. The necessary input data regarding sugar recovery and pretreatment conditions have been extracted from both the simulation work in ACM and laboratory experimental work. All the input data needed for the techno-economic assessment have been correlated to the same design basis in order to minimize the discrepancies between the modelling and the experimental work (See Table 8.4). The economic performance of flow through and circulation reactor configurations for the different pretreatment scenarios, calculated in terms of minimum lignin selling price (MLSP) is presented in Figure 4.10.

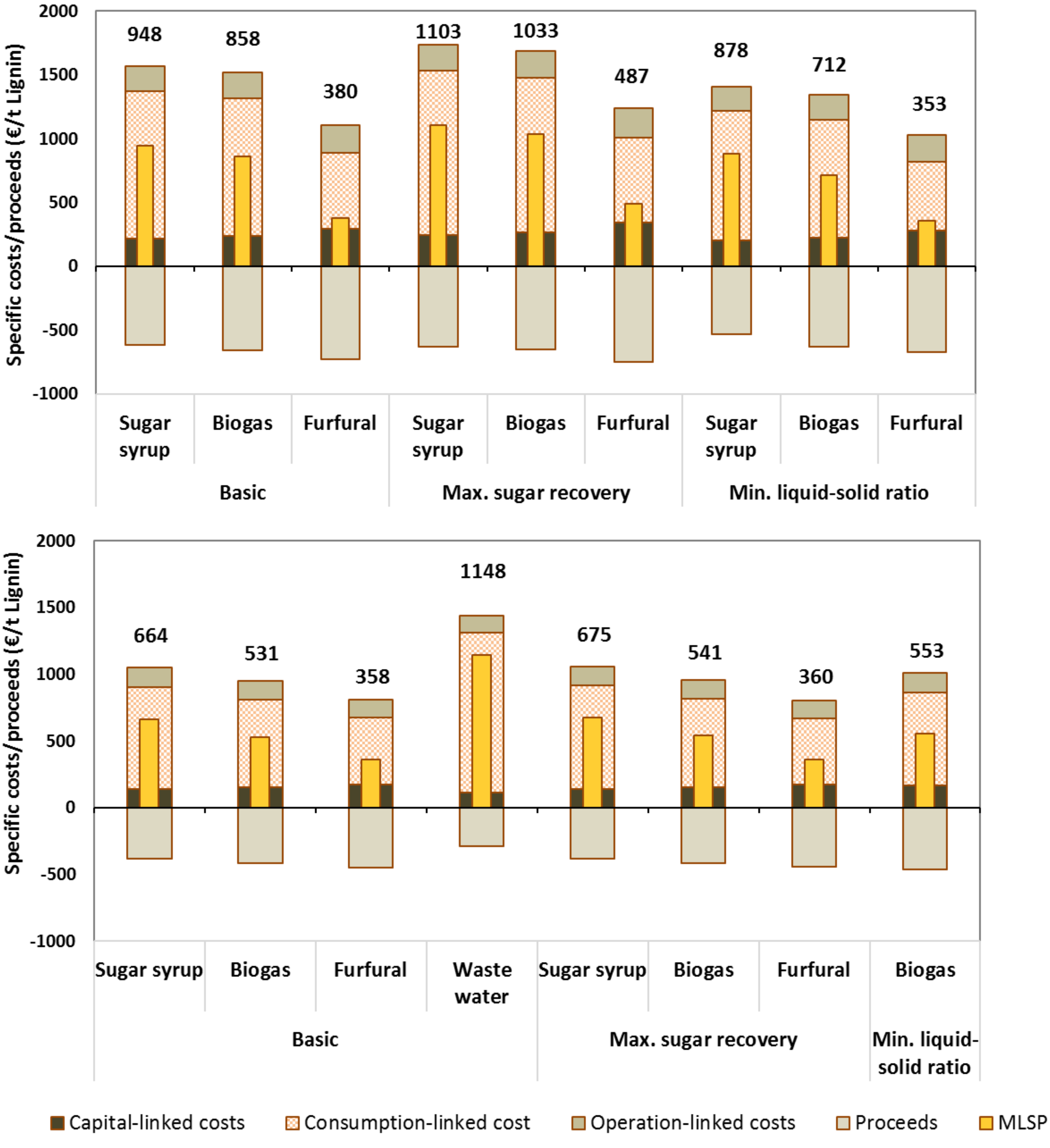

Figure 4.10: Techno-economic assessment of the different scenarios for (up) flow through and (bottom) circulation pretreatment. Economic performance is evaluated in terms of MLSP (€/t Lignin)

In the figure the different costs and revenues for two of the studied scenarios can be observed. The different scenarios are listed on the **ab**scissae. As depicted in Table 3.5, a candidate scenario is formed by a pretreatment option- determined by the reactor configuration and LHW conditions- and by the final desired product. The accumulated costs of each candidate scenario are formed from the capital-linked, consumption-linked and operational-linked costs and are represented on the positive side of the ordinate axis. On the negative side, the revenues from all the final products excepting lignin are depicted. The yellow columns represent the MLSP of each scenario. The results will be evaluated in three differentiated sections according to the influence of pretreatment conditions, reactor configurations and product portfolio.

4.3.2 Influence of pretreatment conditions

From this perspective, it can be noticed that the three scenarios (base case, maximum sugar recovery and minimum liquid/solid ratio) for a determined product do not show a high influence on the final MLSP. This effect is remarkable in each of the studied products and applicable for both pretreatment processes. As an example for the reader, it is possible to observe that the MLSP for sugar syrup production in the flow through mode present values of: 948, 1103 and 878 €/t respectively. The low variability on the lignin selling price is explained by the fact that an increase of the consumption-linked cost is counterbalanced by an increase of the proceeds revenues, and vice versa. Whereas, the capital and operation-linked costs are rather stable within a determined product option. In order to confirm this statement, a sensitivity analysis was performed for temperature, which was determined to be the most influencing factor during the pretreatment. Varying pretreatment temperature in the studied range, from 170 to 230 ºC, had a minor impact on the overall economics of the process, with barely a ± 5 % of the total cost. Hence, the studied conditions of the LHW pretreatment: temperature, mass flow and reaction time do not have a direct impact on the overall economics of the whole process. In contrast, as studied in the previous section, these conditions affect largely the recovery of the sugars and the concentration of the products which explains the changes on consumption-linked costs and on the income obtained from selling the products.

Besides that, it can be observed in the circulation plot that the total cost is rather constant for all of the depicted scenarios, which can be explained by the fact that the water consumption is nearly the same for scenarios b, m and w. In addition, it can be observed that increased sugar recovery between candidates (b) and (m) is not affecting the MLSP and the overall economics. The increase in sugar recovery is compensated with the increase of energy consumption for raising the temperature 25 ºC. In contrast, flow through operation show higher variability for the different pretreatment conditions when comparing the same product. The higher variability is caused by the large difference on water amount among the different flow through options. In view of the results it can be concluded that MLSP is reduced when using less amount of water, even though the recovery of sugars is decreased and the degradation enhanced.

Consequently, it can be stated that downstream processing for the transformation and separation of the liquid hydrolysate on the final products is the dominant step in the process and that the energy demand of the pretreatment is almost negligible compared to the overall process costs. This conclusion is in good agreement with the techno-economic studies performed by PETERSEN in the INBICON demonstration plant in Denmark, which concluded that high rates of water consumption are the most serious limitation of LHW pretreatment [59]. To this point, it can be concluded that pretreatment temperature should be chosen for maximizing the sugar recoveries whereas water consumption should be minimized, disregarding the loss of sugar due to degradation.

4.3.3 Influence of reactor configuration

In this regard, the techno-economic assessment has been performed for two reactor configurations: flow through and circulation. The conclusions have been extended qualitatively for batch and partial recirculation set-ups. It can be deduced from the figure that in general, the LHW in circulation mode is more economically profitable than flow through operation even though the income from the products is much lower. This is explained by the increase of associated costs of the water intensive options. This statement is especially obvious when comparing low added value-products, namely sugar molasses and biogas, provided that the MLSP for these applications in each of the scenarios for circulation mode is lower than in flow through mode. As an example, the MLSP for the syrup cost for the circulation are 664 €/t and 675 €/t whereas in the flow through mode the values are ranging between 878 – 1103 €/t. Therefore, it can be concluded that water consumption is the main factor affecting the overall economics of biorefineries and that the increase of sugar recovery of flow through processes do not compensate the amount of water needed. Nevertheless, this trend is not confirmed when producing furfural. As seen in the figure, MLSP for furfural are very similar in the cases of circulation and flow through, given the fact that the production volume is much higher in the latter case. The increase of product incomes compensates the amount of water used. This result points out that efforts on obtaining large volumes of high concentrated hydrolysates are economically worth it only if high value products are manufactured.

Batch operation results were not integrated in the model but they can be qualitatively related to the case of circulation at high temperatures due to the similar operation costs, water consumption and sugar yields. It has been observed that during the batch process, very poor hemicellulose and lignin removal is achieved, therefore, enzymatic digestibility limitations affecting the production of bioethanol and lignin might appear. Moreover, the reaction conditions lead to a total degradation of the sugars which point at biogas production as the only technologically feasible option. The water amount needed for the batch process is the same as in the circulation and the reduction of reaction temperature observed in the previous section is not sufficient to be an economic advantage. For these reasons, batch process in a fix bed reactor is not considered as a promising option for biorefineries.

Given the fact that the main drawback and lack of competitiveness of the flow through operation is the amount of water needed, the partial flow through operation could be considered rather interesting. Moreover, as observed when producing high added value products, the increase of water consumption costs is balanced by the higher amount of product obtained. This statement is true for circulation and flow through, therefore, it should be extended to partial recirculation Thus, the performance of this reactor configuration is an intermediate between both in terms of water consumption and sugar recoveries (see Figure 4.8). Partial recirculation operation has the advantage of being able to work in a compromise between flow through operation and circulation which can be useful for the future of biorefineries. This flexibility would allow to select different products according to varying raw materials and it would be possible to adapt the manufacturing process to market fluctuations.

4.3.4 Selection of product portfolio

Four applications for the C5-Sugar hydrolysate were considered in the techno-economic assessment. At first sight, it can be observed that the profitability trends of the products are the same and that reactor configuration or pretreatment conditions do not have a direct impact on the profitability of a determined product. Nevertheless, it can be noticed from the minimum liquid to solid ratio in the circulation operating mode that if reaction conditions are too severe, the potential portfolio of products to be offered is reduced due to the high rates of sugar degradation. In general, waste water treatment is the less profitable option, followed by the production of sugar molasses, biogas and furfural.

The possibility of sending the C5-sugar hydrolysate to an out of battery limits waste water treatment unit was contemplated as an option. However, it can be observed that the treatment costs are extremely high even for circulation experiments due to the high carbon content of the hydrolysate. It is in indeed the most expensive option in the whole panorama of scenarios reviewed and any valorisation of the sugars would improve the overall economics of the process. Same conclusion was achieved by TAO et al. after investigating different performance of six pretreatment processes with additional valorisation of hemicelluloses [85].

As shown in the figure, the production of a sugar syrup from the sugar hydrolysate is the less profitable product in every case. The market price of the product is not sufficient to overcome the excessive costs of separation and processing. This result is especially obvious in the flow through operating mode, where the energy demand is exaggerated due to the high utilisation of water. In good agreement with these results MISAiLIDIS et al. studied the need of developing refining processes of sugar molasses for improving the benefit of modern biorefineries and the market penetration of arabinoxylans [19]. In spite of the limitations of this product, it is confirmed that the valorisation of the hydrolysate even for producing low added value products, improve the economic feasibility of the biorefinery.

From the results, it can be observed that the economic performance of a biorefinery based on biogas production is extremely dependent on water consumption. However, it constitutes a profitable option for both processes. In the case of flow through it will allow to minimize the amount of water taken to waste water treatment and will help to close the energetic balance of the facility. Nevertheless, biogas production is more profitable for the circulation mode given the fact that rather good yields of transformation can be obtained from the degradation products (50 %) whereas the conversion rates for hemicelluloses reach 90 %. Recent studies by JOELSSON et al. confirmed the coproduction of bioethanol and biogas as a promising option for improving the economics of biorefineries and also demonstrated that further improvements can be achieved with the upgrading of biogas towards biomethane [33,34].

Furfural performance is of especial interest within the scope of this work because it depicts the necessity of developing new applications for transformation of C5-Sugars.

From the figures, it can be observed that the MLSP of furfural is the lowest in every case and that the values are very similar regarding the reactor configuration, ranging from 353-487 €/t for flow through and 358-360 €/t for circulation. These lower prices are possible thank to the high added value of furfural in the market. Flow through operation in this case is as profitable as circulation, in spite of the high water consumption and the low conversions of sugars into furfural (app. 50%). These results confirm that developing high added value products is especially important if flow through operation wants to be successful at industrial scale. The sugar recovery is only worth it when coupled to the production of high added value products, just as stated by TAO et al. in [85]. Intensifing the process adding new units for the production of high added value applications increase the actual performance of the 2G biorefineries. Nevertheless, there are strong restraining to these technologies given the fact that even if furfural is relatively easy to produce due to the easy separation through distillation and the direct degradation kinetics, it is difficult to find applications that yields higher conversions due to the high amount of cell growth inhibitors present in the mixture and the low concentrations of the hydrolysates.

5 Conclusions

This research aimed at studying the adaptability of the high-pressure fixed bed reactor for the LHW pretreatment to different operating conditions. Four different reactor configurations (batch, flow through, circulation and partial recirculation) were suggested and modelled in ACM. Two DoEs were successfully performed for studying the performance of the model with each of the studied reactor configurations. Critical model responses for the characterization of the liquid hydrolysate were studied by means of RSM, such as total hemicellulose solubilisation, sugar recovery, sugar concentration or sugar degradation. In general, the responses pointed at a good removal of hemicelluloses from the solid for all the reactor configurations, excepting the batch, where most probably mass transfer problems limited the solubilisation. The results from the modelling section depicted different behaviours for each of the configurations, especially regarding the sugar recovery and the sugar concentration. From the model results it was concluded that the fixed bed reactor system is highly adaptable to multiple configurations and that the reactor configuration has a large influence on the hydrolysate and solid residue characteristics.

In order to corroborate the simulation results, lab-scale experiments were conducted at the optimal conditions for each of the reactor configurations. The experiments were conducted in a 3 L and a 40 L plant for the LHW extraction of wheat straw pellets and samples were taken from the solid residue and the liquid hydrolysate in order to perform different analytical determinations. Important parameters such as liquid sugar composition, pH, AL-Lignin content and moisture content were measured. The trends observed during the assessment of the simulation results were in good agreement with the analytical results from the experimental work. Especially promising results were obtained from the partial recirculation operation. Both simulation and experimental work confirmed that the recirculation of a fraction of the hydrolysate provides higher concentrated sugar solutions than flow through at slightly lower sugar recoveries. The increase of C5-Sugar concentration is explained by the decrease of water consumption, which ranges between 10-50 % compared to flow through operation. Besides that, no severe sugar degradation was observed due to the higher liquid residence times and the recirculation of organic acids. Moreover, the acidity of the solution was not as significantly increased as expected, probably due to the pH buffering effect of hemicellulose solutions.

The other main objective of this work was to link the ACM model for the pretreatment with an existing overall biorefinery model in AP. Integrating simulation results allow to study the influence of changing reactor configurations and reaction conditions of the pretreatment on the overall economics of the process. Changing pretreatment conditions such as temperature, mass flow and residence time did not have a significant influence on the economics of the process (barely a ±5 %). The techno economic study showed that when producing low-value products such as biogas or sugar molasses, the water consumption is the dominant parameter influencing the economic feasibility of the process. This scenario promoted the minimization of water; therefore, circulation operation was the most profitable option in this case. In contrast, when producing higher added value products, namely furfural, the water consumption had not such a big impact on the economics and the higher sugar recoveries from flow through and partial recirculation modes, balanced the cost of increasing the amount of water. Finally, it was concluded that the development of high added value products from the hemicellulose fraction is critical for increasing the revenues of these technologies.

6 Future prospects

In this work, the influence of changing conditions and reactor configurations during LHW pretreatment was studied. In view of the simulation results, it was concluded that the fixed bed reactors are very versatile and that the configuration of the reactor influences strongly the characteristics of the hydrolysate. In addition, from the techno economic assessment it was observed that the economic feasibility of the process is highly dependent on the water consumption and on the revenues obtained from the side streams. In brief, future 2G biorefineries might use fixed bed reactors flexible to different operating modes in order to offer a wider product portfolio adjustable to seasonal raw materials or variable market demand. Nevertheless, as it was depicted from the economic assessment, up to now there exists just a few applications available for C5-Sugar transformation. Most part of current applications present low added-value products which have to be coupled with low water consumption alternatives. In contrast, the development of new products, namely furfural, succinic acid or levulinic acid, with high conversion yields and high added-value might increase the economic profitability of water-intensive alternatives.

From the results of the simulation and experimental work, it was observed that partial recirculation operation could constitute an interesting alternative for the pretreatment of lignocellulosic materials, given the increase on sugar concentration and water reduction along with mild degradation of the sugars. In this regard, better understanding of the reaction mechanisms during the recirculation of hydrolysate would be needed for optimizing the process. The pH buffering effect of hemicelluloses, formation of lingo-humic substances and repolymerisation of lignin onto the solid have to be completely understood in order to guarantee a high quality solid residue, too. In this investigation, it was assumed that the enzymatic digestibility of the solid residue obtained from partial recirculation was not compromised. Nevertheless, further investigation on this topic need to be conducted.

According to the results of this research, it can be stated that integrating modelling results for the pretreatment in an overall biorefinery model allow to study both processes with a different perspective. Further implementation of new product applications for the techno-economic assessment and more detailed information about the pretreatment kinetics will open new ways for 2G biorefineries to develop. Deeper research in this holistic approach might allow decision makers to select the adequate pretreatment operation and conditions for obtaining a desired product from the currently available biomass feedstock

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7 References

[1] P. Alvira, E. Tomas-Pejo, M. Ballesteros, M.J. Negro, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review, Bioresour. Technol. 101 (2010) 4851–4861.

[2] B.E.L. Baeta, D.R.S. Lima, O.F.H. Adarme, L.V.A. Gurgel, S.F. de Aquino, Optimization of sugarcane bagasse autohydrolysis for methane production from hemicellulose hydrolyzates in a biorefinery concept, Bioresour. Technol. 200 (2016) 137–146.

[3] B.E.L. Baeta, D.R.S. Lima, J.G.B. Filho, O.F.H. Adarme, L.V.A. Gurgel, S.F. de Aquino, Evaluation of hydrogen and methane production from sugarcane bagasse hemicellulose hydrolysates by two-stage anaerobic digestion process, Bioresour. Technol. 218 (2016) 436–446.

[4] M. Balat, G. Ayar, Biomass Energy in the World, Use of Biomass and Potential Trends, Energy Sources. 27 (2005) 931–940.

[5] S. Bolado-Rodriguez, C. Toquero, J. Martin-Juarez, R. Travaini, P.A. Garcia-Encina, Effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the biochemical methane potential and kinetics of the anaerobic digestion of wheat straw and sugarcane bagasse, Bioresour. Technol. 201 (2016) 182–190.

[6] M. Borrega, K. Nieminen, H. Sixta, Effects of hot water extraction in a batch reactor

on the delignification of birch wood, BioResources. 6 (2011) 1890–1903.

[7] G. Brodeur, E. Yau, K. Badal, J. Collier, K.B. Ramachandran, S. Ramakrishnan, Chemical and physicochemical pretreatment of lignocellulosic biomass: a review, Enzyme Res. 2011 (2011) 787532.

[8] A. Cabeza, C.M. Piqueras, F. Sobrón, J. García-Serna, Modeling of biomass fractionation in a lab-scale biorefinery: Solubilization of hemicellulose and cellulose from holm oak wood using subcritical water, Bioresour. Technol. 200 (2016) 90–102.

[9] C.M. Cai, N. Nagane, R. Kumar, C.E. Wyman, Coupling metal halides with a co-solvent to produce furfural and 5-HMF at high yields directly from lignocellulosic biomass as an integrated biofuels strategy, Green Chem. 16 (2014) 3819.

[10] A.F.A. Carvalho, P. de O. Neto, D.F. da Silva, G.M. Pastore, Xylo-oligosaccharides from lignocellulosic materials: Chemical structure, health benefits and production by chemical and enzymatic hydrolysis, Food Res. Int. 51 (2013) 75–85.

[11] R.P. Chandra, R. Bura, W.E. Mabee, A. Berlin, X. Pan, J.N. Saddler, Substrate pretreatment: the key to effective enzymatic hydrolysis of lignocellulosics?, Adv. Biochem. Eng. Biotechnol. 108 (2007) 67–93.

[12] H. Chen, Theoretical basis of lignocellulose biorefining, in: Lignocellul. Biorefinery Eng., Elsevier, 2015: pp. 19–36.

[13] H. Chen, Lignocellulose biorefinery process engineering, in: Lignocellul. Biorefinery Eng., Elsevier, 2015: pp. 167–217.

[14] F. Cherubini, The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Convers. Manag. 51 (2010) 1412–1421.

[15] H.L. Chum, D.K. Johnson, S.K. Black, Organosolv Pretreatment for Enzymatic-

Hydrolysis of Poplars .2. Catalyst Effects and the Combined Severity Parameter, Ind. Eng. Chem. Res. 29 (1990) 156–162.

[16] a. H. Conner, L.F. Lorenz, Kinetic modeling of hardwood prehydrolysis. Part III. Water and dilute acetic acid prehydrolysis of southern red oak, Wood Fiber Sci. 18 (1986) 248–263.

[17] D.F. Crawford, W.B. Anthony, R.R. Harris, Evaluation of Concentrated Hemicellulose Extract as Cattle Feed, J. Anim. Sci. 46 (1978) 32.

[18] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Acidic cesium salts of 12-tungstophosphoric acid as catalysts for the dehydration of xylose into furfural, Carbohydr. Res. 341 (2006) 2946–2953.

[19] C. Du, G.M. Campbell, N. Misailidis, F. Mateos-Salvador, J. Sadhukhan, M. Mustafa, R.M. Weightman, Evaluating the feasibility of commercial arabinoxylan production in the context of a wheat biorefinery principally producing ethanol. Part 1. Experimental studies of arabinoxylan extraction from wheat bran, Chem. Eng. Res. Des. 87 (2009) 1232–1238.

[20] A. Ebringerová, Structural Diversity and Application Potential of Hemicelluloses, Macromol. Symp. 232 (2005) 1–12.

[21] A. Ebringerová, Z. Hromádková, T. Heinze, Hemicellulose, in: T. Heinze (Ed.), Polysaccharides I, Springer-Verlag, Berlin/Heidelberg, 2005: pp. 1–67.

[22] T. Eggeman, R.T. Elander, Process and economic analysis of pretreatment technologies, Bioresour. Technol. 96 (2005) 2019–2025.

[23] G.C. Fahey, J.E. Williams, G.A. McLaren, Influence of molasses lignin-hemicellulose fractions in rat nutrition, J. Nutr. 106 (1976) 1447–1451.

[24] L.C. Ferreira, P.J. Nilsen, F. Fdz-Polanco, S.I. Pérez-Elvira, Biomethane potential of wheat straw: Influence of particle size, water impregnation and thermal hydrolysis, Chem. Eng. J. 242 (2014) 254–259.

[25] S. Ghosh, M.P. Henry, R.W. Christopher, Hemicellulose conversion by anaerobic digestion, Biomass. 6 (1985) 257–269.

[26] F.M. Gírio, C. Fonseca, F. Carvalheiro, L.C. Duarte, S. Marques, R. Bogel-Łukasik, Hemicelluloses for fuel ethanol: A review, Bioresour. Technol. 101 (2010) 4775–4800.

[27] H. Grenman, K. Eranen, J. Krogell, S. Willfor, T. Salmi, D.Y. Murzin, Kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system, Ind. Eng. Chem. Res. 50 (2011) 3818–3828.

[28] Y. Guan, X.M. Qi, G.G. Chen, F. Peng, R.C. Sun, Facile approach to prepare drug-loading film from hemicelluloses and chitosan, Carbohydr. Polym. 153 (2016) 542–548.

[29] M.E. Himmel, S.-Y. Ding, D.K. Johnson, W.S. Adney, M.R. Nimlos, J.W. Brady, T.D. Foust, Biomass recalcitrance: engineering plants and enzymes for biofuels production, Science. 315 (2007) 804–807.

[30] J.E. Holladay, J.F. White, J.J. Bozell, D. Johnson, Top Value-Added Chemicals from Biomass - Volume II?Results of Screening for Potential Candidates from Biorefinery Lignin, 2007.

[31] D. Hollenbach, Scale-up einer Laboranlage zur Thermischen Hydrolyse von Biomasse, TUHH, 2011.

[32] T. Ingram, T. Rogalinski, V. Bockemühl, G. Antranikian, G. Brunner, Semi-continuous liquid hot water pretreatment of rye straw, J. Supercrit. Fluids. 48 (2009) 238–246.

[33] E. Joelsson, D. Dienes, K. Kovacs, M. Galbe, O. Wallberg, Combined production of biogas and ethanol at high solids loading from wheat straw impregnated with acetic acid: Experimental study and techno-economic evaluation, Sustain. Chem. Process. 4 (2016) 22.

[34] E. Joelsson, B. Erdei, M. Galbe, O. Wallberg, Techno-economic evaluation of integrated first- and second-generation ethanol production from grain and straw, Biotechnol. Biofuels. 9 (2016) 1.

[35] E. de Jong, R.J.A. Gosselink, Lignocellulose-Based Chemical Products, in: Bioenergy Res. Adv. Appl., Elsevier, 2014: pp. 277–313.

[36] F.K. Kazi, J.A. Fortman, R.P. Anex, D.D. Hsu, A. Aden, A. Dutta, G. Kothandaraman, Techno-economic comparison of process technologies for biochemical ethanol production from corn stover, Fuel. 89 (2010) S20–S28.

[37] S. Kim, B.E. Dale, Global potential bioethanol production from wasted crops and crop residues, Biomass and Bioenergy. 26 (2004) 361–375.

[38] Y. Kim, E. Ximenes, N.S. Mosier, M.R. Ladisch, Soluble inhibitors/deactivators of cellulase enzymes from lignocellulosic biomass, Enzyme Microb. Technol. 48 (2011) 408–415.

[39] A.M. de la Torre Sánchez, Modeling liquid hot water hydrolysis of wheat straw in a batch reactor, (2014).

[40] R. Landucci, B. Goodman, C. Wyman, Methodology for evaluating the economics of biologically producing chemicals and materials from alternative feedstocks, Appl. Biochem. Biotechnol. 45–46 (1994) 677–696.

[41] J. Larsen, M. Østergaard Petersen, L. Thirup, H. Wen Li, F. Krogh Iversen, The IBUS Process -- Lignocellulosic Bioethanol Close to a Commercial Reality, Chem. Eng. {&}

Technol. 31 (2008) 765–772.

[42] H. Li, X. Chen, J. Ren, H. Deng, F. Peng, R. Sun, Functional relationship of furfural yields and the hemicellulose-derived sugars in the hydrolysates from corncob by microwave-assisted hydrothermal pretreatment, Biotechnol. Biofuels. 8 (2015) 127.

[43] J.S. Lim, Z. Abdul Manan, S.R. Wan Alwi, H. Hashim, A review on utilisation of biomass from rice industry as a source of renewable energy, Renew. Sustain. Energy Rev. 16 (2012) 3084–3094.

[44] G.P. Lofgreen, K.K. Otagaki, The Net Energy of Blackstrap Molasses for Fattening Steers as Determined by a Comparative Slaughter Technique, J. Anim. Sci. 19 (1960) 392.

[45] F. López, M.T. García, M.J. Feria, J.C. García, C.M. de Diego, M.A.M. Zamudio, M.J. Díaz, Optimization of furfural production by acid hydrolysis of Eucalyptus globulus in two stages, Chem. Eng. J. 240 (2014) 195–201.

[46] H. Mäkeläinen, M. Juntunen, O. Hasselwander, Prebiotic Potential of Xylo-Oligosaccharides, in: Prebiotics Probiotics Sci. Technol., 2009.

[47] H. Mäkeläinen, M. Juntunen, O. Hasselwander, Prebiotic Potential of Xylo-Oligosaccharides, in: Prebiotics Probiotics Sci. Technol., 2009.

[48] C.M. Martínez, D.A. Cantero, M.D. Bermejo, M.J. Cocero, Hydrolysis of cellulose in supercritical water: reagent concentration as a selectivity factor, Cellulose. 22 (2015) 2231–2243.

[49] D.P. Maurya, A. Singla, S. Negi, An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol, 3 Biotech. 5 (2015) 597–609.

[50] G.A. McLaren, J.E. Williams, G.C. Fahey, T.R. Smith, J.E. Smith, H.A. Woolf, Influence of Acid-Resistant Hemicelluloses on Urea Nitrogen Utilization by Lambs, J. Anim. Sci. 43 (1976) 1072.

[51] G.L. Miller, Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar, Anal. Chem. 31 (1959) 426–428.

[52] D.C. Montgomery, Design and Analysis of Experiments, 7th Edition, 2009.

[53] J.E. Morinelly, J.R. Jensen, M. Browne, T.B. Co, D.R. Shonnard, Kinetic characterization of xylose monomer and oligomer concentrations during dilute acid pretreatment of lignocellulosic biomass from forests and switchgrass, Ind. Eng. Chem. Res. 48 (2009) 9877–9884.

[54] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, M. Ladisch, Features of promising technologies for pretreatment of lignocellulosic biomass, Bioresour. Technol. 96 (2005) 673–686.

[55] B. of C.& E. NIIR, The complete technology book on wood and its derivatives, National Institute of Industrial Research, Kamla Nagar, Delhi, 2009.

[56] V. Pérez Martínez, Acid Hydrolysis of Hemicelluloses From Hardwood and Softwood With Homogeneous and Heterogeneous Catalysts, (2015) 163.

[57] F. Perz, Kreislauffahrweise der Heißwasserhydrolyse im Weizenstroh-Festbett, 2014.

[58] M.S. Peters, K.D. Timmerhaus, Plant Design and Economics for Chemical Engineers, 1991.

[59] M.Ø. Petersen, J. Larsen, M.H. Thomsen, Optimization of hydrothermal pretreatment of wheat straw for production of bioethanol at low water

consumption without addition of chemicals, Biomass and Bioenergy. 33 (2009) 834–840.

[60] W. Reynolds, Master Thesis: Modeling and Optimizing Thermal-Enzymatic Hydrolysis of Wheat Straw in a High-Pressure Fixed-Bed using Response Surface Methodology, (2013).

[61] W. Reynolds, V. Baudron, C. Kirsch, L.M. Schmidt, H. Singer, L. Zenker, C. Zetzl, I. Smirnova, Odor-Free Lignin from Lignocellulose by Means of High Pressure Unit Operations: Process Design, Assessment and Validation, Chemie Ing. Tech. 88 (2016) 1513–1517.

[62] W. Reynolds, C. Kirsch, I. Smirnova, Thermal-Enzymatic Hydrolysis of Wheat Straw in a Single High Pressure Fixed Bed, Chemie Ing. Tech. 87 (2015) 1305–1312.

[63] W. Reynolds, A.M. de la Torre Sanchez, I. Smirnova, Document not published yet: Modeling hydrothermal flow-through pretreatment of wheat straw in a high-pressure fixed-bed reactor, (2017).

[64] W. Reynolds, H. Singer, S. Schug, I. Smirnova, Hydrothermal flow-through treatment of wheat-straw: Detailed characterization of fixed-bed properties and axial dispersion, Chem. Eng. J. 281 (2015) 696–703.

[65] W. Riansa-Ngawong, P. Prasertsan, Optimization of furfural production from hemicellulose extracted from delignified palm pressed fiber using a two-stage process, Carbohydr. Res. 346 (2011) 103–110.

[66] P. Rice, Energy, the biomass options By Henry R. Bungay Published by Wiley Interscience, New York, 1981, viii + 347 pp., price {£}19.05, Chem. Eng. J. 25 (1982) 121.

[67] G.L. Riley, ed., Food waste: Practices, management and challenges, Nova Science

Publishers Inc, Hauppauge New York, 2016.

[68] J. V. Rissanen, D.Y. Murzin, T. Salmi, H. Grénman, Aqueous extraction of hemicelluloses from spruce - From hot to warm, Bioresour. Technol. 199 (2016) 279–282.

[69] S. Rivas, C. Vila, V. Santos, J.C. Parajó, Furfural production from birch hemicelluloses by two-step processing: A potential technology for biorefineries, Holzforschung. 70 (2016).

[70] C. Rong, X. Ding, Y. Zhu, Y. Li, L. Wang, Y. Qu, X. Ma, Z. Wang, Production of furfural from xylose at atmospheric pressure by dilute sulfuric acid and inorganic salts, Carbohydr. Res. 350 (2012) 77–80.

[71] H.A. Ruiz, R.M. Rodríguez-Jasso, B.D. Fernandes, A.A. Vicente, J.A. Teixeira, Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: A review, Renew. Sustain. Energy Rev. 21 (2013) 35–51.

[72] H.A. Ruiz, A.A. Vicente, J.A. Teixeira, Kinetic modeling of enzymatic saccharification using wheat straw pretreated under autohydrolysis and organosolv process, Ind. Crops Prod. 36 (2012) 100–107.

[73] J.F. Saeman, Kinetics of wood saccharification : hydrolysis of cellulose and desomposition of sugars in dilute acid at high temperature, Ind. Eng. Chem. 37 (1945) 43–52.

[74] J.K. Saini, A.K. Patel, M. Adsul, R.R. Singhania, Cellulase adsorption on lignin: A roadblock for economic hydrolysis of biomass, Renew. Energy. (2016) 29–42.

[75] N.E. Sammons, W. Yuan, M.R. Eden, B. Aksoy, H.T. Cullinan, Optimal biorefinery product allocation by combining process and economic modeling, Chem. Eng. Res.

Des. 86 (2008) 800–808.

[76] L.M. Schmidt, M. Kaltschmitt, Document not published yet: Economic Assessment for the Production of Solvent-free Lignin by Thermal-Enzymatic Treatment Using Fixed-Bed Reactor Technology, Not yet Publ. (2017).

[77] B. Shen, Y.X.Y.X. Liu, Y.X.Y.X. Liu, J.H. Peng, Study on Furfural Production from Hemicelluloses, Adv. Mater. Res. 690–693 (2013) 1382–1385.

[78] K. Siebertz, D. Van Bebber, T. Hochkirchen, Statistische Versuchsplanung: Design of Experiments (DoE), Chem. Biodivers. 1 (2010) 336.

[79] H. Singer, Hamburg University of Technology Scale-up of the Hydrothermal and Enzymatic Hydrolysis of Wheat Straw in a by, (2015).

[80] E. Sjöström, Wood chemistry: Fundamentals and applications, Academic Press, Inc, San Diego, California and London, England, 1993.

[81] A.N. Sluiter, Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples: Laboratory Analytical Procedure (LAP): Issue Date, 3/31/2008, National Renewable Energy Laboratory, 2008.

[82] J.B. Sluiter, R.O. Ruiz, C.J. Scarlata, A.D. Sluiter, D.W. Templeton, Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods, J. Agric. Food Chem. 58 (2010) 9043–9053.

[83] X.F. Sun, H.H. Wang, Z.X. Jing, R. Mohanathas, Hemicellulose-based pH-sensitive and biodegradable hydrogel for controlled drug delivery, Carbohydr. Polym. 92 (2013) 1357–1366.

[84] F. Talebnia, D. Karakashev, I. Angelidaki, Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation, Bioresour.

Technol. 101 (2010) 4744–4753.

[85] L. Tao, A. Aden, R.T. Elander, V.R. Pallapolu, Y.Y. Lee, R.J. Garlock, V. Balan, B.E. Dale, Y. Kim, N.S. Mosier, M.R. Ladisch, M. Falls, M.T. Holtzapple, R. Sierra, J. Shi, M.A. Ebrik, T. Redmond, B. Yang, C.E. Wyman, B. Hames, S. Thomas, R.E. Warner, Process and technoeconomic analysis of leading pretreatment technologies for lignocellulosic ethanol production using switchgrass, Bioresour. Technol. 102 (2011) 11105–11114.

[86] T. Werpy, G. Petersen, Top value added chemicals from biomass, NREL, Colorado, 2004.

[87] O. Wienhaus, M. Lewin, J.S. Goldstein, Wood structure and composition. 512 S., 164 Abb., 32 Tab., Marcel Dekker Inc., New York 1991. (International Fiber Science and Technology). Hardcover, J. F{ü}r Prakt. Chemie/Chemiker-Zeitung. 334 (1992) (1992) 729.

[88] D.L. Williams, J.D. Moore, L.C. Martin, A.D. Tillman, Studies on Liquid Hemicellulose and Cane Molasses as Carbohydrate Sources in Urea-Containing Diets of Sheep, J. Anim. Sci. 28 (1969) 667.

[89] C.E. Wyman, V. Balan, B.E. Dale, R.T. Elander, M. Falls, B. Hames, M.T. Holtzapple, M.R. Ladisch, Y.Y. Lee, N. Mosier, V.R. Pallapolu, J. Shi, S.R. Thomas, R.E. Warner, Comparative data on effects of leading pretreatments and enzyme loadings and formulations on sugar yields from different switchgrass sources, Bioresour. Technol. 102 (2011) 11052–11062.

[90] C.E. Wyman, B.E. Dale, R.T. Elander, M. Holtzapple, M.R. Ladisch, Y.Y. Lee, Coordinated development of leading biomass pretreatment technologies, Bioresour. Technol. 96 (2005) 1959–1966.

[91] B. Yang, C.E. Wyman, Effect of Xylan and Lignin Removal by Batch and Flowthrough Pretreatment on the Enzymatic Digestibility of Corn Stover Cellulose, Biotechnol. Bioeng. 86 (2004) 88–95.

[92] Y. Yu, H. Wu, Understanding the primary liquid products of cellulose hydrolysis in hot-compressed water at various reaction temperatures, Energy and Fuels. 24 (2010) 1963–1971.

[93] K.M. Zech, K. Meisel, A. Brosowski, L.V. Toft, F. Müller-Langer, Environmental and economic assessment of the Inbicon lignocellulosic ethanol technology, Appl. Energy. 171 (2016) 347–356.

[94] K.J. Zeitsch, The chemistry and technology of furfural and its many by-products, Elsevier, Amsterdam and New York, 2000.

[95] H. Zilouei, M. Taherdanak, Biohydrogen from Lignocellulosic Wastes, in: Lignocellul. Bioprod., n.d.

[96] A Dictionary of Accounting, Oxford University Press, 2010.

8 Appendix

Table 8.1: Experimental plan for flow through, batch and full recirculation simulations according to the DoE assessment with a 3 factor-5 level CCD.

Experiment	**Temperature [ºC] (A)**	**Time [s] (B)**	**Flow [g/min] (C)**
1	170	1800	240
2	182.16	1443.24	192.43
3	182.16	2156.76	192.43
4	182.16	1443.24	287.57
5	182.16	2156.76	287.57
6	200	1800	160
7	200	1200	240
8	200	1800	240
9	200	2400	240
10	200	1800	320
11	217.84	1443.24	192.43
12	217.84	2156.76	192.43
13	217.84	1443.24	287.57
14	217.84	2156.76	287.57
15	230	1800	240

Table 8.2: Experimental plan for partial recirculation simulations according to the DoE assessment with a 4 factor-5 level CCD.

Experiment	Temperature [ºC] (A)	Time [s] (B)	Flow [g/min] (C)	Recirculation rate [dim.] (D)
1	170	1800	240	0.5
2	185	1500	200	0.3
3	185	1500	200	0.7
4	185	2100	200	0.3
5	185	2100	200	0.7
6	185	1500	280	0.3
7	185	1500	280	0.7
8	185	2100	280	0.3
9	185	2100	280	0.7
10	200	1800	160	0.5
11	200	1200	240	0.5
12	200	1800	240	0.1
13	200	1800	240	0.5
14	200	1800	240	0.9
15	200	2400	240	0.5
16	200	1800	320	0.5
17	215	1500	200	0.3
18	215	1500	200	0.7
19	215	2100	200	0.3
20	215	2100	200	0.7
21	215	1500	280	0.3
22	215	1500	280	0.7
23	215	2100	280	0.3
24	215	2100	280	0.7
25	230	1800	240	0.5

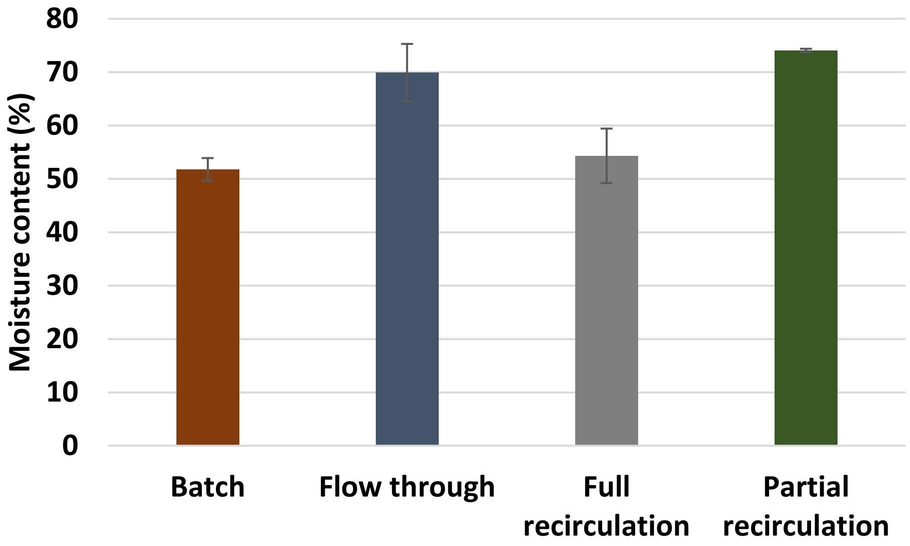

Figure 8.1: Moisture content (%) analysis of the solid biomass residue under different operating conditions.

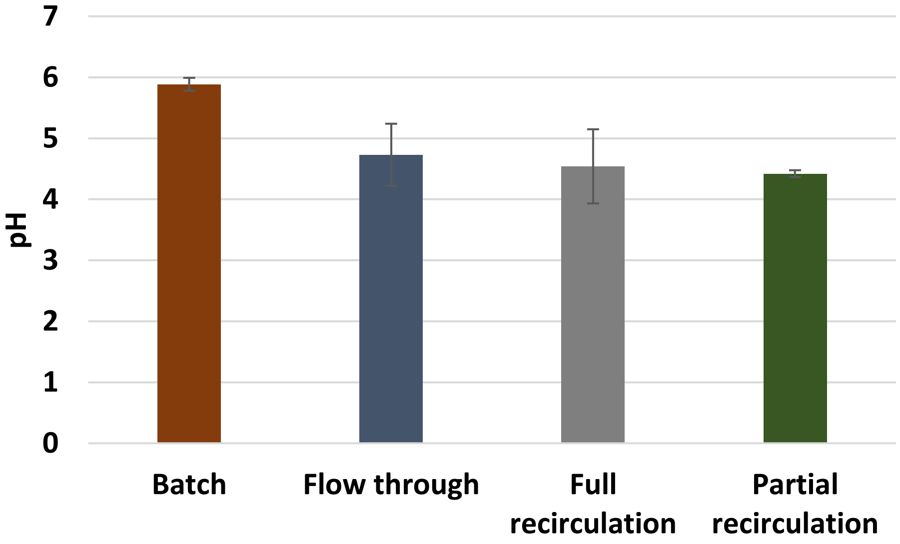

Figure 8.2: pH determination of the liquid hydrolysate under different operating conditions.

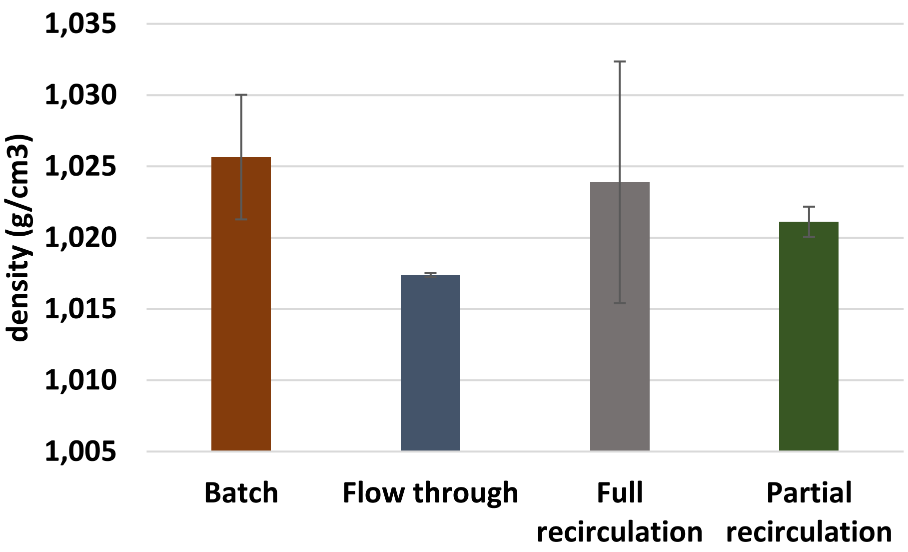

Figure 8.3: Density determination (g/cm³) of the liquid hydrolysate under different operating conditions.

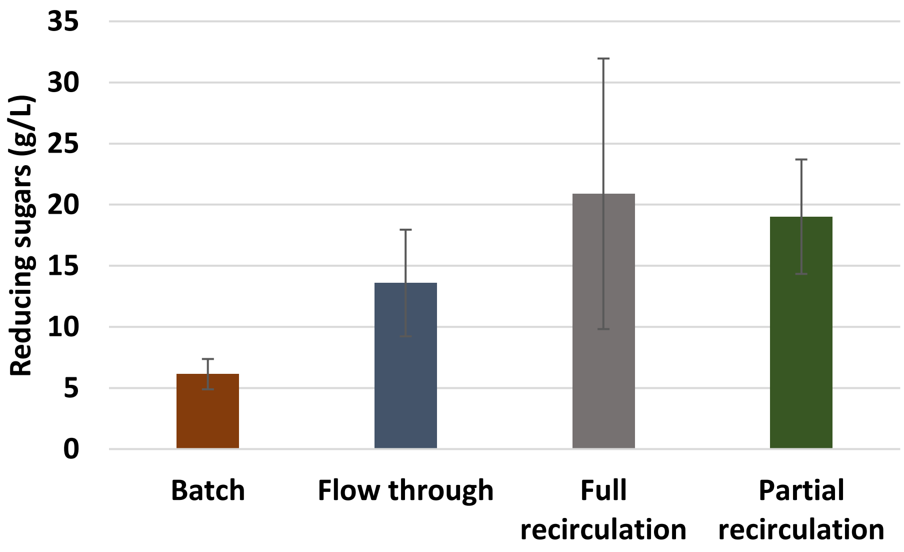

Figure 8.4: DNS-Reducing sugar (g/L) analysis of the liquid hydrolysate under different operating conditions.

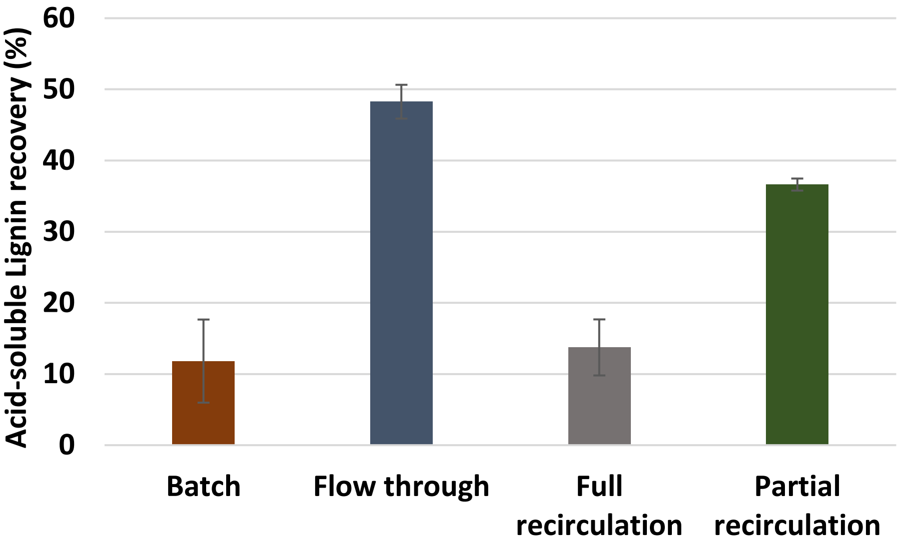

Figure 8.5: AL-Lignin recovery determination of the liquid hydrolysate under different operating conditions.

Table 8.3: Summary of budget items used for the economic evaluation [76].

№	Budget item	Meaning
1	Capital-linked cost	Fixed costs of building the facility and cost equipment
2	Consumption linked cost	Operational costs such as water consumption, energy provision, raw materials and utilities
3	Operational-linked cost	Labour, licences, patents and other administrative costs
4	Proceeds	Revenues from the product sell (except lignin)
5	Minimum lignin selling price	Revenues from the dried and milled lignin

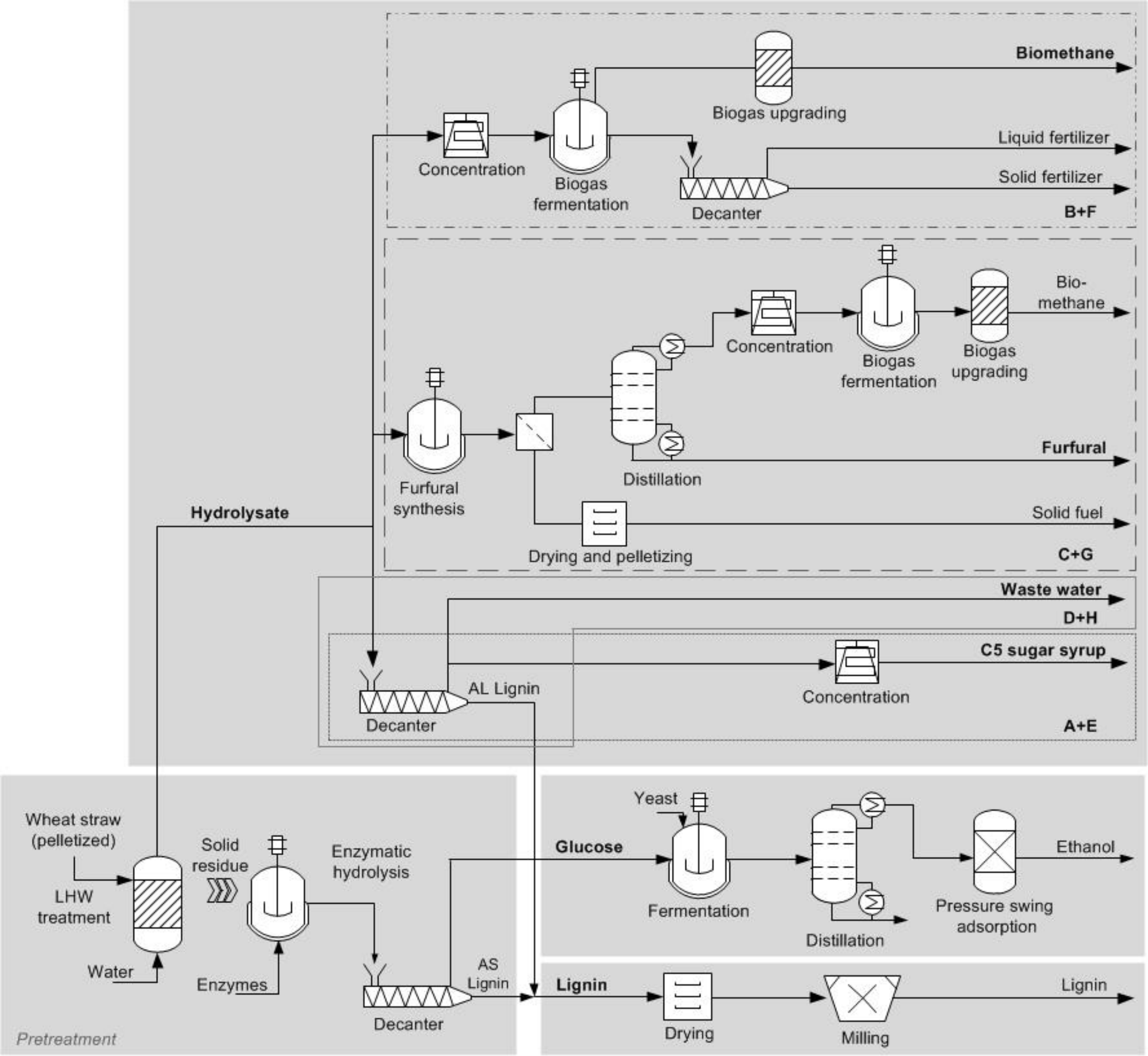

Figure 8.6: Process flow diagram of the 2G biorefinery implemented in AP for the techno-economic assessment [76].

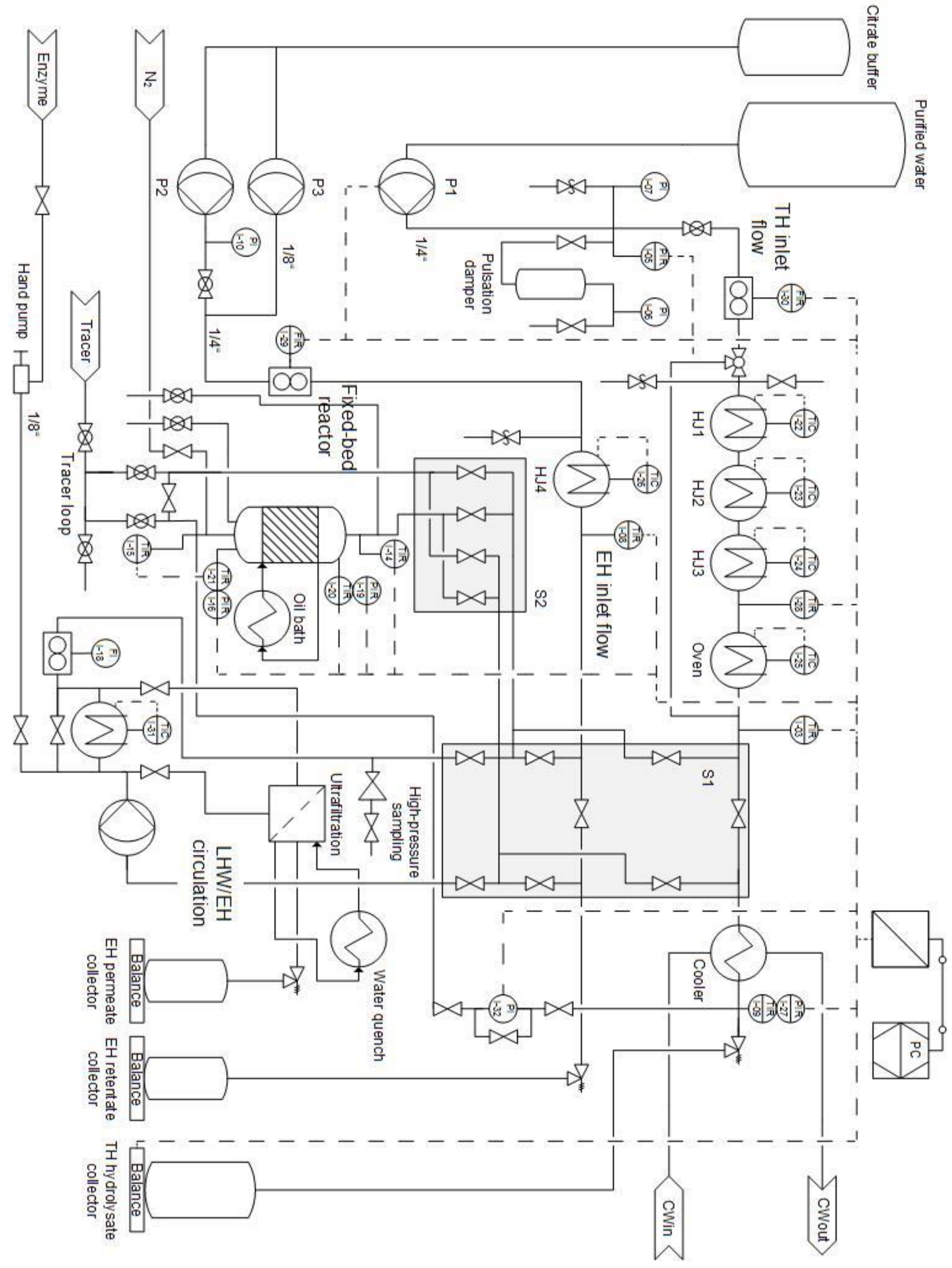

Figure 8.7: Pipes and instrumentation diagram of the complete experimental set up for the combined thermal and enzymatic pretreatment of lignocellulosic biomass in a 3L high pressure fixed-bed reactor. TVT, TUHH.

Table 8.4: Summary of pretreatment conditions and (correlated) sugar yields used for the techno-economic assessment [76].

			Flow-trough			Circulation	
Parameters	**Unit**	**(b)**	**(m)**	**(w)**	**(b)**	**(m)**	**(w)**
Parameter							
Temperature	°C	200	200	217.8	185	200	230
Duration	min	30	30	24	30	30	30
Liquid/solid	—	9.1	12.1	5.9	3.2	3.3	3.0
Conversion							
Hem. → C5-Olig.	%	55.2	60.4	24.4	15.5	20.7	-
Hem. → C5-Mono.	%	6.9	7.6	3.0	2.4	3.2	-
Hem. → Furfural	%	3.2	3.2	3.2	-	-	-
Hem. → Degr.	%	34.7	28.8	69.4	69.0	62.0	100
Cel. → C6-Olig.	%	3.9	3.9	3.9	2.6	2.6	2.6
Cel. → C6-Mono.	%	0.5	0.5	0.5	-	-	-
Cel. → HMF	%	0.1	0.1	0.1	-	-	-
Lig. →AL-Lig.	%	63.8	63.8	63.8	99	99	99

Table 8.5: List of model equations and balances described in the text.

Equation	Parameter	Abbreviation	Equation
(8.1)	Filling step	$Y_{step}(z)$	Differential mass balance
(8.2)	Reaction constant	$k_i(z,t)$	Arrhenius equation
(8.3)	Actual bed porosity	$\varepsilon_{act}(z,t)$	Fixed bed mass balance
(8.4)	Real porosity	$\varepsilon(z)$	Actual and effective porosity correlation
(8.5)	Solid hemicellulose concentration	$X_H(z,t)$	Simplified mass balance equation
(8.6)	Water mass balance	$m(z,t)$	Continuity equation
(8.7)	Interstitial fluid velocity	$u(z,t)$	Interstitial velocity definition
(8.8)	Local temperature	$T(z,t)$	General heat balance
(8.9)	Overall system heat capacity	$(\rho \cdot cp)(z,t)$	Linear combination of system heat capacities
(8.10)	Individual reaction rate	$r_{i,j}(z,t)$	Reaction rate expression for individual species
(8.11)	Effective acid concentration	$a_{i,j}(z,t)$	Partial differential mass balance
(8.12)	Solubilized component	$Y_{i,pore}(z,t)$,	Partial differential mass balances