

# Unlocking the potential of a lignocellulosic biorefinery

Optimizing yields of value-added furanic compounds in aqueous side streams from steam explosion and pellet production

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Dag Helge Hermundsgård

Thesis for the degree of Philosophiae Doctor (PhD)  
University of Bergen, Norway  
2024

UNIVERSITY OF BERGEN



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## **Scientific environment**

This thesis, submitted for the degree of Philosophiae Doctor at the University of Bergen, has been organized into two parts. The first part includes an introduction, scope of the thesis, an experimental section, summary of the results, conclusions, and future outlook. The second part consists of five papers and manuscripts, based on experimental work that was carried out in the period October 2020 – February 2024.

The main part of the work has been performed at the Department of Chemistry, University of Bergen. Part of the work has been carried out in collaboration with RISE PFI AS in Trondheim, the Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), and Arbaflame AS.

The project was funded by Arbaflame AS through the Research Council of Norway under grant No. 321268.

The aim of the work was to investigate the effect of steam explosion pretreatment with different lignocellulosic feedstocks on product yields of value-added furanic compounds and quality of co-produced black pellets. Within this framework, different lignocellulosic feedstocks were steam pretreated at various reaction conditions to find the critical factors for optimal product yields. This approach have resulted in valuable insights into steam explosion pretreatment of lignocellulosic biomass and have contributed to the further development of the steam explosion biorefinery.

## Acknowledgements

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Lastly, but perhaps most importantly, I would like to thank my family and friends for their support during this time as a PhD candidate and throughout my time at the University of Bergen.

## Abstract in English

With an increasing population and a growing demand for energy globally, our reliance on fossil energy sources to cover our energy needs poses a significant challenge given the finite nature of these resources and their harmful effects on the environment. There is an urgent need for development of more sustainable technologies for energy production and the utilization of biomass is a promising candidate. Lignocellulosic biomass represents an extensive and varied renewable resource that is suitable for production of both energy products and organic compounds with industrial applications. Many well-established production processes use lignocellulosic biomass as a feedstock to make bioproducts. The carbohydrates are often used to produce bioethanol and biogas while the lignin fraction is an important source for bio-based aromatics and phenolic compounds.

A biorefinery is an alternative approach to the processing of biomass. The concept of a biorefinery involves the use of different processes to optimally harness the different fractions of the raw material to make a spectrum of bio-products that can add value to the biorefinery operation. To access the constituent biopolymers of the lignocellulose and improve its processability, it is necessary to utilize a pretreatment step that can disrupt the cell structure of the plant and modify the chemical composition of the biomass. Steam explosion pretreatment is a method where high-pressure saturated steam is injected into a reactor containing biomass. The steam rapidly heats the biomass and initiates hydrolysis of the hemicelluloses, causing sugars and organic acids to be released into the liquid steam. Due to the high temperatures and acidic conditions, the sugars are dehydrated to furanic compounds like furfural and 5-HMF, which are both valuable platform chemicals that can be utilized by the chemical industry to synthesis of a wide range of different products, from solvents and resins to fuels and plastics. Furfural is formed from dehydration of pentose sugars and 5-hydroxymethylfurfural can be formed from hexoses.



The main focus of the work presented in this thesis was to investigate the effect of steam explosion pretreatment on different lignocellulosic feedstocks and optimize the process with a focus on the yields of value-added furanic compounds in the aqueous side streams and quality of co-produced black pellets.

Experiments were performed using large pilot-scale reactors at LUBIRC in Sweden using a range of different feedstocks and pretreatment conditions. The first aqueous side stream originates from the condensed vapours that are evacuated from the reactor during the decompression stage. The steam exploded biomass is collected after pretreatment and is washed and filtered to create the second aqueous side stream which contains water soluble compounds that have been released from the biomass during the pretreatment process. The chemical composition of the aqueous side streams is determined using qNMR analysis and yields of value-added compounds in the samples have been determined. Acetic acid, formic acid, furfural, 5-HMF, 2-AF, 5-MF, acetone, methanol, and residual sugars are found to be the most abundant compounds in the aqueous side streams. The properties of the biomass are also evaluated on their suitability for energy pellet production. This is done by pressing the biomass into pellets and analysing properties like calorific value and compression strength.

A diverse range of lignocellulosic raw materials have been assessed throughout this thesis. In addition to high-grade woody biomass raw materials like birch and Norway spruce, low-grade wastes and residues from forestry, agricultural, and industrial crop productions have been examined as possible feedstocks for a steam explosion based biorefinery. The introduction of agricultural and forestry residues in the form of barley straw and BRAT (branches and tops) respectively, as a 10 – 20 % fraction of the feedstock exhibited no negative effects and resulted in high yields of furfural and 5-HMF, in addition to steam exploded biomass with good properties for pellet production. The use of guayule bagasse, and industrial latex production crop, as a feedstock was also investigated. Analysis of side stream composition showed a moderate to high yield of furfural and 5-HMF from guayule bagasse samples where the moisture content of the raw material was increased to 50%. Calorific value in the

steam exploded guayule was found to be comparable to that of woody biomass, but weak binding between biomass fibres due to high extractives content is a challenge for pellet production and requires further research.

The steam explosion pretreatment of lignocellulosic feedstock was found to be significantly influenced by the reaction temperature, as higher temperatures resulted in better hydrolysis of the hemicellulose portion of the raw material and a higher yield of organic compounds in the process side streams. The use of a catalyst in the pretreatment process was also associated with improved reaction yields as catalysed samples in low temperature steam explosion were shown to produce higher yields than their non-catalysed high temperature analogues.

At the ArbaOne biorefinery in Norway, the condensate stream from the full-scale STEX pretreatment of sawdust from softwood is collected and the dissolved furfural and other organic constituents are recovered by distillation. The presence of black insoluble particles in the product stream from condensate upgrading was investigated and found to be furfural polymers, formed in the high temperature environment as furfural formed a separate phase in the by-product stream.

The experiments performed were aimed at improving and evolving the methods and technology necessary to further develop the steam explosion based biorefinery concept. Implementation of biomass washing to recover the non-volatile products like 5-HMF from the steam exploded material is under development and the exploration of alternative feedstock mixes and optimization of the steam explosion process is a continued effort.

## Abstract in Norwegian

Med en økende befolkning og en økende etterspørsel etter energi globalt, er vår avhengighet av fossile energikilder for å dekke våre energibehov blitt en betydelig utfordring på grunn av den begrensede tilgangen på disse ressursene og deres skadelige effekter på miljøet. Det er et behov for utvikling av flere bærekraftige teknologier for energiproduksjon og utnyttelse av biomasse er en lovende kandidat til dette formålet. Lignocellulosisk biomasse representerer en rikelig og variert fornybar ressurs, som egner seg godt til produksjon av både energiprodukter og organiske forbindelser som kan anvendes av industrien. Mange veletablerte produksjonsprosesser bruker lignocellulosisk biomasse som råstoff for å lage bio-baserte produkter ettersom karbohydratene kan brukes til å produsere bioetanol og biogass mens ligninfraksjonen er en viktig kilde for biobaserte aromater og fenolforbindelser.

Et bioraffineri er et moderne alternativ til prosessering av biomasse. Konseptet med et bioraffineri innebærer å bruke ulike teknologier og prosesser for å utnytte de ulike fraksjonene i råstoffet best mulig, for å kunne lage et spekter av ulike bio-produkter som vil øke verdien av bioraffineriets produkt. For å få tilgang til biopolymerne i lignocellulosen og forbedre bearbeidbarheten til råmateriale, er det nødvendig å bruke en forbehandling som kan forstyrre cellestrukturen og modifisere den kjemiske sammensetningen til biomassen. Dampekspløsjonsforbehandling er en metode hvor mettet høytrykksdamp injiseres i en reaktor som inneholder biomasse. Dampen varmer raskt opp biomassen og starter hydrolyse av hemicellulosen, noe som fører til at sukker og organiske syrer frigjøres til den flytende dampen. På grunn av de høye temperaturene og de sure forholdene, dehydreres sukkerne til furanforbindelser som furfural og 5-HMF, som begge er verdifulle plattformkjemikalier som kan brukes av den kjemiske industrien til syntese av et bredt spekter av forskjellige produkter, fra

løsemidler og harpiks til drivstoff og plast. Furfural dannes fra dehydrering av pentosesukker og 5-hydroksymetylfurfural kan dannes fra heksoser.

Hovedfokuset for arbeidet presentert i denne oppgaven var å undersøke effekten av dampekspløsjonsforbehandling på ulike lignocellulosiske råmaterialer og optimalisere prosessen med fokus på utbyttene av verdiøkende furanforbindelser i de vandige sidestrømmene og kvaliteten på samprodusert svarte pellets.

Eksperimenter ble utført med reaktorer i stor pilotskala ved LUBIRC i Sverige ved bruk av en rekke forskjellige råmaterialer og forbehandlingsforhold. Den første vandige sidestrømmen stammer fra de kondenserte dampene som evakueres fra reaktoren under dekompresjonstrinnet. Den dampeksploderte biomassen samles opp etter forbehandling og vaskes og filtreres for å lage den andre vandige sidestrømmen som inneholder vannløselige forbindelser som har blitt frigjort fra biomassen under forbehandlingsprosessen. Den kjemiske sammensetningen av de vandige sidestrømmene bestemmes ved bruk av qNMR-analyse og utbytter av verdiøkende forbindelser i prøvene er bestemt. Eddiksyre, maursyre, furfural, 5-HMF, 2-AF, 5-MF, aceton, metanol og restsukker er funnet å være de vanligste forbindelsene i de vandige sidestrømmene. Biomassens egenskaper vurderes også på deres egnethet for energipelletsproduksjon. Dette gjøres ved å presse biomassen inn i pellets og analysere egenskaper som brennverdi og kompresjonsstyrke.

Et mangfoldig utvalg av lignocellulosiske råstoff har blitt vurdert gjennom denne oppgaven. I tillegg til høyverdige treaktige biomasseråvarer som bjørk og edelgran, har lavverdig avfall og rester fra skogbruk, landbruk og industrielle planteproduksjoner blitt undersøkt som mulige råvarer for et dampekspløsjonsbasert bioraffineri. Innføring av jord- og skogbruksrester i form av henholdsvis bygghalm og BRAT (grener og topper), da en 10 – 20 % fraksjon av råstoffet viste ingen negative effekter og resulterte i høye utbytter av furfural og 5-HMF, i tillegg til dampeksplodert biomasse med gode egenskaper for pellet produksjon. Bruken av guayule bagass og industriell lateksproduksjon som råstoff ble også undersøkt. Analyse av sidestrømsammensetning viste et moderat til høyt utbytte av furfural og 5-

HMF fra guayule bagass prøver hvor fuktighetsinnholdet i råmaterialet ble økt til 50 %. Brennverdien i den dampeksploderte guayule ble funnet å være sammenlignbar med den for treaktig biomasse, men svak binding mellom biomassefibre på grunn av høyt innhold av ekstraktivstoffer er en utfordring for pellet produksjon og krever videre forskning.

Dampekspløsningsforbehandlingen av lignocellulosiske råstoff ble funnet å være betydelig påvirket av reaksjonstemperaturen, da høyere temperaturer resulterte i bedre hydrolyse av hemicellulosedelen av råmaterialet og et høyere utbytte av organiske forbindelser i prosess sidestrømmene. Bruken av en katalysator i forbehandlingsprosessen var også assosiert med forbedret reaksjonsutbytte ettersom katalyserte prøver i lavtemperaturdampekspløsning ble vist å gi høyere utbytter enn deres ikke-katalyserte høytemperaturanaloger.

Ved bioraffineriet ArbaOne i Norge samles kondensatstrømmen fra fullskala STEX-forbehandlingen av sagflis fra bartre og oppløst furfural og andre organiske bestanddeler gjenvinnes ved destillasjon. Tilstedeværelsen av svarte uløselige partikler i produktstrømmen fra kondensatoppgradering ble undersøkt og funnet å være furfural polymerer, dannet i høytemperaturmiljøet da furfural dannet en separat fase i biproduktstrømmen.

Eksperimentene som ble utført var rettet mot å forbedre og utvikle metodene og teknologien som er nødvendig for å videreutvikle det dampekspløsningsbaserte bioraffinerikonseptet. Implementering av biomassevasking for å gjenvinne de ikke-flyktige produktene som 5-HMF fra det dampeksploderte materialet er under utvikling, og utforskning av alternative råstoffblandinger og optimalisering av dampekspløsningsprosessen er en fortsatt innsats.

## List of Publications

- Paper I. Ghoreishi, S.; Løhre, C.; Hermundsgård, D.H.; Molnes, J.L.; Tanase-Opedal, M.; Brusletto, R.; Barth, T. (2022): *Identification and quantification of valuable platform chemicals in aqueous product streams from a preliminary study of a large pilot-scale steam explosion of woody biomass using quantitative nuclear magnetic resonance spectroscopy*. *Biomass Conv Bioref*. <https://doi.org/10.1007/s13399-022-02712-w>
- Paper II. Tanase-Opedal M., Ghoreishi S., Hermundsgård D. H., Barth T., Moe S. T., Brusletto R. (2023): *Steam explosion of lignocellulosic residues for co-production of value-added chemicals and high-quality pellets*. *Biomass and Bioenergy*, Volume 181, 2024, <https://doi.org/10.1016/j.biombioe.2023.107037>.
- Paper III. Hermundsgård D. H., Ghoreishi S., Tanase-Opedal M., Moe S. T., Brusletto R., Barth T. *Maximizing yields of furfural and 5-hydroxymethylfurfural in side streams from steam explosion of lignocellulosic residues*. (Submitted to *Biofuels, Bioproducts and Biorefining*)
- Paper IV. Hermundsgård D. H., Tanase-Opedal M., Brusletto R., Barth T. *Value generation from steam explosion of waste guayule bagasse*. (Submitted to *Industrial Crops and Products*)
- Paper V. Hermundsgård, D.H., Ghoreishi, S., Tanase-Opedal, M., Brusletto, R., Barth, T. Investigating solids present in the aqueous stream during STEX condensate upgrading—a case study. *Biomass Conv. Bioref*. (2022). <https://doi.org/10.1007/s13399-022-03593-9>

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## Abbreviations:

IEA	International Energy Agency
UN	United Nations
U.S. DoE	United States Department of Energy
5-HMF	5-hydroxymethylfurfural
2-AF	2-acetylfuran
2-FMK	2-furyl methyl ketone
5-MF	5-methyl furfural
CCS	Carbon Capture Storage
STEX	Steam Explosion
PET	Polyethylene terephthalate
PEF	Polyethylene Furanoate
NMR	Nuclear Magnetic Resonance
FA	Furfuryl Alcohol
DMSO <sub>2</sub>	Dimethyl Sulfone
MIBK	Methyl isobutyl ketone

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# Part I



# 1.

## Introduction

In the last decades the world has seen rapid growth in population and industrialization. On top of these developments, many countries also continue to see an increase in standard of living which is leading to a significantly higher demand for energy globally. According to the IEA, more than 80% of the current global energy consumption is supplied by non-renewable fossil resources [1] and this overdependence on non-renewables poses a serious challenge as dwindling reserves of fossil resources and the corresponding increase in cost of production as oil fields become older, will ultimately lead to increased energy and fuel costs. Exploiting fossil fuels at this scale also comes with the downside of large greenhouse gas emissions in the form of CO<sub>2</sub>, which release sequestered carbon back into the carbon cycle and contribute heavily to changes in the global climate [2].

The need for alternative solutions to cover the growing energy and fuel demand have led to the development and utilization of renewable resources as an effective way to ease and solve the issues of both growing energy demand and global warming [3, 4, 5].

Currently, fossil fuels are also an important source for raw materials in much of the industrial sector. Industries that produce commodity materials like plastics and polymers, and specialty chemicals for food and medicine production have a strong dependence on compounds derived from fossil resources. When considering alternative carbon-based raw materials for the chemical industry the options are severely limited, as there are only two large-scale sources of renewable carbon on this planet: plants and atmospheric carbon dioxide [6], of which only one is practically exploitable with today's technological development.

Because of these facts, utilization of renewable feedstocks such as lignocellulosic biomass for the sustainable co-production of green fuels, energy, and value-added chemicals is a quickly developing trend in the chemical industry. Two chemicals that have received great interest and attention in later years, as several industries have begun to search for alternative non-fossil building block chemicals to meet the demands from governments and consumers for sustainable and green production, is furfural and 5-hydroxymethylfurfural (5-HMF). Furfural was rated as a good bio-based chemical in the original U.S. department of energy report [7] and have since gained even more interest as Bozell and Peterson found it appropriate to include both furfural and 5-HMF among the top value-added chemicals from biomass, when they revisited the DoE list [8].

The development of bio-based energy carriers and chemical building blocks are important steps toward a sustainable future and makes progress towards goal 7 (affordable and clean energy), 12 (responsible consumption and production), and 13 (climate action) of the UN sustainable development goals [9]. By incorporating lower grade materials and wastes as feedstocks, biorefineries will be able to provide renewable energy from a carbon neutral source at a competitive price. However, to make this a reality research and development of the technologies which facilitate the

conversion of bioresources to bioenergy and biochemicals is necessary. This is still a developing industry and adoption of bio-based products depends in a large part on price, convenience and access to the specific products demanded by the market.

## 1.1 Biomass

The term biomass is defined as organic, non-fossil material of biological origin [10]. Biomass is a renewable resource that can be readily used for energy production. It has fueled the progress of mankind to where we are today and can through development of new sustainable techniques and technologies be just as important in the future. Additionally, biomass is the only renewable and sustainable source of organic compounds [11].

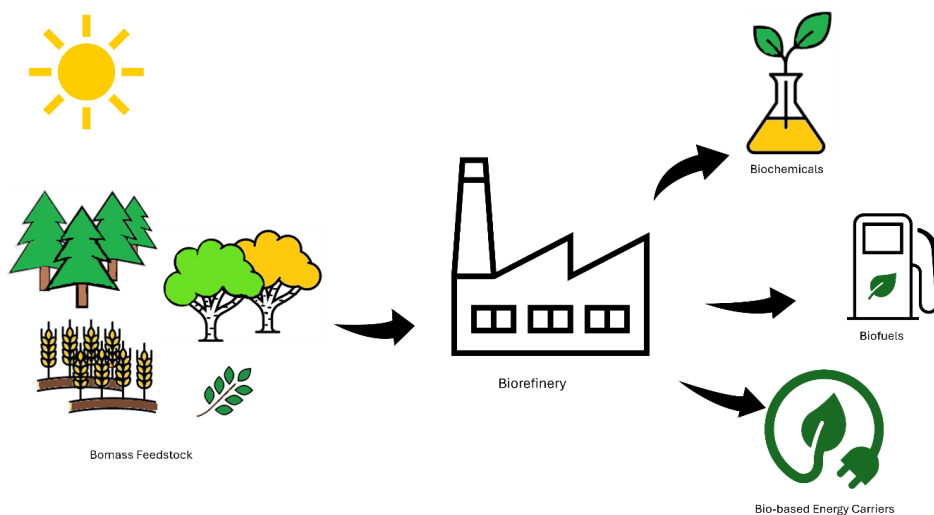


Figure 1: Illustration of the biorefinery concept.

Not all biomass is suitable for use in industrial applications. As an example, the use of edible biomass resources for fuel, chemical, or energy production has long been a complicated ethical dilemma.



Biomass resources can be divided into generations on the basis of the type of material the bioresource is made of [12]. 1<sup>st</sup> generation (Gen 1) bioresources are a category that comprises carbohydrates like sugars and starch, as well as plant and vegetable oils. The main advantage of these carbohydrates in particular is that their structure can easily be broken down to simple sugars which can be extracted from the plant material to be fermented into ethanol, digested for biogas production, or used as substrate in other chemical reactions. The chemical availability of glucose from starch and sugar rich plants also makes them ideal as food for the human species and makes the practical use of Gen 1 biomass as industrial crops ethically complicated.

Gen 1 biomass resources are in essence the only type of biomass that is fit for human consumption and is essential for the survival of people and societies all over the world. The ethical dilemma can be summed up as the fear that Gen 1 crops for industry will outcompete food and feed production, as the energy and fuel industries have more purchasing power than individuals, leading farmers to start selling their crops to industry for a higher price than consumers are able to compete with. As access to food is arguably of higher importance than energy, both governmental and global organizations are working on safeguarding farmland and food crops from being converted to grow industrial crops. Still, balancing this issue is an ongoing process and political policy sometimes struggles with accurately balancing the food versus fuel competition [13].

2<sup>nd</sup> generation (Gen 2) biomass resources, however, comprises non-edible biomass species which are therefore not in direct competition with nutrition for humans. The main type of biomass found in this category is lignocellulosic biomass, which will be discussed more closely in the next chapter, but there are also other non-edible biomass resources such as waste materials and non-edible plant matter. The composition and structure of Gen 1 and Gen 2 biomass can be quite different and because of this difference, new pretreatment methods must be developed in order to utilize Gen 2 biomass for industrial applications.

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More subdivisions of biomass generations have been created to categorize different types of biomass sources more precisely. 3<sup>rd</sup> generation biomass is a category created to encompass materials derived from microorganisms that are usually not directly consumed by humans, like oils and carbohydrates from algae. A 4<sup>th</sup> generation of biomass has been proposed in different contexts as a genomically prepared super crop which is engineered to incorporate several different properties. The crops need to produce high yields while being able to grow on non-arable land at low nutritional demands and should also have the capabilities of carbon neutral farming, combining crops and carbon capture and storage (CCS) in a farming system as a separate category [14]. As the knowledge of biomass and its application grows, so does the categorization of feedstocks and biomass products.

Established manufacturing processes for a major part of bio-based products are based on first-generation biomass, i.e., edible vegetable oils and sources of carbohydrates, and this is normally in direct competition with food and fodder production. Thus, developing new processes for producing second-generation biofuels and products from non-edible resources such as lignocellulosic biomass can prevent this predicament.

### 1.1.1 Lignocellulosic biomass

Lignocellulosic biomass is a category of more complex biomass which is made up of three main biopolymers: cellulose, a straight polymer chain of glucose comprising about 30–50 wt.% of the biomass; hemicellulose, a heteropolysaccharide polymer of C<sub>5</sub> and C<sub>6</sub> sugars comprising about 20–35 wt.% of the biomass; and lignin, a complex heteropolymer of monolignols which comprises 15–35 wt.% of the biomass [15, 16, 17]. This category includes materials like hardwoods, softwoods, grasses, agricultural and forestry residues, urban wastes, dedicated energy crops, organic municipal solid waste, and industrial wastes, and is a unique, globally available, and renewable carbon-neutral resource and a good feedstock for biorefining [18, 19, 20]. The composition of lignocellulosic materials has considerable variation between species and especially the hemicellulose fraction has a different structure and composition between hardwoods and softwoods [15].

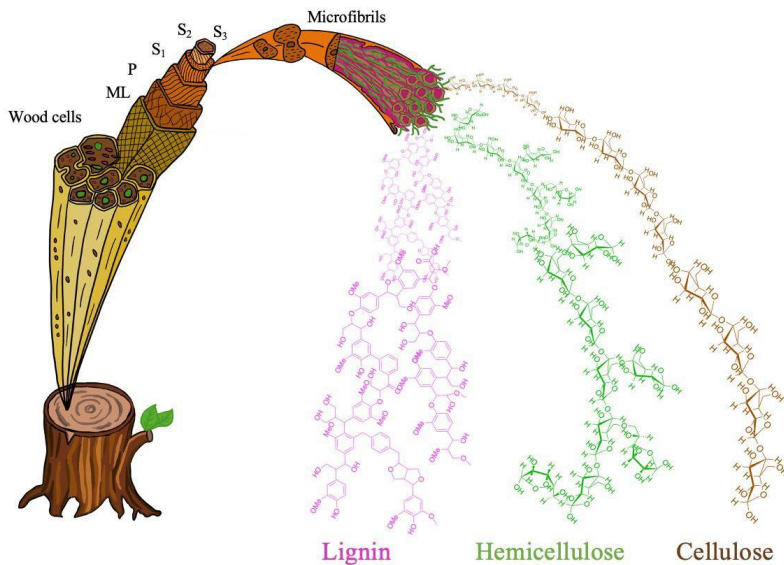


Figure 2: A visual breakdown of woody biomass and its constituent biopolymers (Adapted from Hoffmann P., Jones M. A., 1989 [22] by J. Molnes and used with permission).

The presence of cellulose and hemicellulose in lignocellulosic biomass attracts a lot of attention in terms of potential utilization, while the presence of lignin results in the recalcitrance of lignocellulosic biomass that makes the fractionation of the biomass into its three polymeric constituents a major challenge. This is mainly due to the structural rigidity of the polymeric matrix provided by the strong intermolecular interactions between lignin, cellulose, and hemicellulose [20, 21]. For bio-based products derived from lignocellulosic biomass to be able to replace fuels and chemicals derived from petroleum resources in an economically sustainable way will require high yields of value-added products, low-cost pretreatment techniques, and energetically efficient targeted upgrading processes. Thus, proper fractionation of the feedstock into its constituent polymers is the key for maximizing the economic possibilities of the resource [20, 23, 24].

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### 1.1.2 Waste biomass as feedstock

Lignocellulosic biomass and especially wood has long been an essential part of energy production in the form of firewood and later as wood pellets and briquets. During and after the industrial revolution fossil resources have taken over as the main energy production resource and the demand for energy has risen dramatically and is still increasing [1]. As such, a reliance on wood as the only lignocellulosic feedstock is not a sustainable option and the mobilization and deployment of low-grade materials, such as biomass waste streams as feedstocks for production of energy carriers has a large potential for further exploration [25, 45].

Waste biomass is a large category of biomass materials which comprises everything from non-edible residual materials from agricultural productions and forestry residues to leftovers from industrial processes and solid municipal wastes. What all these biomass materials have in common is that they have a large, underutilized potential, often because they require additional processing to realize their potential as sources for energy and chemicals. In some cases, waste biomass has already been used as an energy source, i.e. as wood pellets made of dried sawdust from forestry and sawmill waste have at times been a popular alternative to firewood [26].

The most readily available of lignocellulosic waste materials is residual straw from grain production [27]. Grains, which are a Gen 1 crop, only constitute around 50 wt% of the crop [28] and the rest is inedible straw which is a lignocellulosic material and can be used as feedstock in a biorefinery. Another example is guayule (*Parthenium argentatum*, pronounced “gwaha-yoo-lee”) which is a small, fast-growing shrub which is central for developing an alternative rubber industry. It produces an allergy friendly latex containing natural rubber compounds [29, 30] and as it thrives in arid environments, it does not compete with farmlands or food production. However, one important aspect to consider with the use of agricultural biomass resources is that they generally have a higher mineral content than woody biomass, leading to an increased ash content in energy carriers made from these materials [31, 32].

## 1.2 Biorefineries

A biorefinery is a facility that deploys processes and technologies for the sustainable processing of biomass into a spectrum of marketable products [33]. This means that similar to an oil refinery, a biorefinery does not produce one single product, but rather incorporate a diverse array of integrated refinery processes that utilizes all the fractions of its raw materials and by-products, either as feedstocks in different processes or as energy resources from which additional value can be recovered [23], maximizing the potential value of the raw material and facilitating production of bioproducts that alone might not be economically feasible to produce, including fuels, power, heat, commodity and fine chemicals, feed products, food additives and many other materials.

The development of economically viable and energy-efficient processes for conversion of low-value lignocellulosic biomass into commercially profitable biofuels and products is a substantial challenge. Most of the existing processes can't compete with petroleum refineries in cost-effectiveness, in part due to incomplete utilization of the biomass feedstock. The biorefinery approach is to improve biomass utilization, become resource efficient through valorization of side streams and the use of waste products from other industries as raw materials, and thus increase the economic outputs of biomass-derived processes, by fully integrating waste streams as potential resources that can be recovered would be a significant economic contribution to the biorefinery. On the other hand, if chemicals from waste streams are not recovered, costly disposal or extensive treatment of the waste is required to not cause damage to the environment. Thus, the use of these waste streams as a resource is strongly recommended.

The first processing step, pretreatment, is preparation of the feedstock to enable further conversion. The main objective of the pretreatment is to disrupt the plant cell structure, overcome the biomass recalcitrance, modify the chemical composition, and improve the processability of the lignocellulosic biomass subjected to different bioenergy conversion processes [3, 24]. Various types of pretreatment methods, including physical (e.g., milling and grinding), chemical (e.g., alkali, dilute acid, oxidizing agents and organic solvents), physicochemical (e.g. steam explosion and wet oxidation), and

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biological methods, have been extensively examined for lignocellulosic biomass [34, 3]. Among these pretreatments, steam explosion, which includes a degree of autohydrolysis, is an efficient and widely used technique. During the steam explosion, the lignocellulosic biomass undergoes a sequence of defibrillation, delignification, and hydrolysis of the hemicelluloses, making the polysaccharides from the hemicellulose available to undergo further reactions.

### 1.2.1 The Arbaflame biorefinery

Arbaflame is a biotech company that uses steam explosion (STEX) as the primary pretreatment method for their biorefinery concept. The primary product of the biorefinery is black pellets that can be used as a coal replacement in energy production or in carbon intensive industrial applications. The steam explosion of lignocellulosic biomass has made it possible to develop a more complete biorefinery around the pellet production process, as the pretreatment also generates side streams, rich in valuable organic compounds, which can be refined to commercial products that will add additional value to the biorefinery production chain and contribute to development of new product streams from the biorefining of lignocellulosic materials.

At the ArbaOne biorefinery in Norway, the steam released from the full-scale STEX pretreatment of is condensed into an aqueous condensate, which contains dissolved furfural and other water-soluble organic constituents. Valuable organic compounds like furfural can be recovered through separation methods such as distillation and the remaining organic acids are digested by anaerobic bacteria, after which the water is clean enough to be released back into nature. Anaerobic digestion also produces methane gas, which adds yet another product to the biorefinery. In addition, further recovery of non-volatile products like 5-HMF by washing of the exploded material is under development. Washing of the biomass have also been correlated with a reduction in ash content of the biomass which is beneficial for production of black pellets for the purpose of coal replacement, especially high-ash raw materials are used as feedstocks [35, 36].

Lignocellulosic biorefineries like the one operated by Arbaflame are at present a developing industry. Optimization and development of the biorefinery process is therefore important for the maturation and growth of the technology. One such development is adapting the biorefinery for use with a wider range of feedstocks, like lower grade forestry and agricultural wastes and rest materials from industrial crops or feedstocks that are native to different parts of the world, adjusting the product streams from the biorefinery to fit the different compositions of these feedstocks and the distinct product demands of those regions.

### 1.3 Valuable compounds and platform chemicals

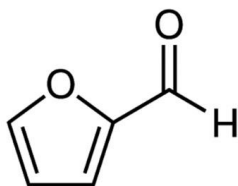
The process of biorefining lignocellulosic material can produce a wide range of chemical products depending on which structures in the biomass are broken down. The main building blocks of lignocellulosic biomass is sugars. Cellulose is made from a strict glucose polymer, while hemicellulose contains both 5- and 6-carbon sugars in a polymeric structure which composition varies between plant families and species [15]. Fermentation of these sugars to produce ethanol is one of the simplest uses of these sugars and one of the oldest biorefining techniques, but sugars derived from lignocellulosic materials can have many different applications, for example as feedstock for production of bioethanol, as a substrate to grow protein rich fish feed [37], or as substrate for conversion into furanic compounds like furfural and 5-Hydroxymethylfurfural, which are highly marketable chemical compounds which can be produced through dehydration of sugars. These molecules are traditionally produced using processes where biomass is pretreated to release C5 and C6 sugars, which then are selectively converted to furfural and 5-HMF respectively, but the same products can also be generated in-situ during more severe pretreatment processes such as steam explosion.

The lignin fraction of lignocellulosic biomass can also be a source for production of fuel and fine chemicals. Conversion of lignin to bio-oil [38, 39] shows it as a potential

oil substitute or a source for aromatic carbon compounds. Many flavor and aroma compounds like vanillin (vanilla) [40] and diacetyl (butter) can also be recovered through treatment of lignin [41].

### 1.3.1 Furfural

Furfural (2-furaldehyde) is an organic compound made up of a furan ring, a five-membered aromatic ring structure with an oxygen in the 1-position, connected with an aldehyde functional group located at the 2-position. In its pure state, furfural is a dense colorless liquid, but through radical reactions initiated by exposure to light, oxygen, and heat, polymerization reactions take place which gives the furfural a brown color with a reddish tint [41]. The intensity of the color corresponds to the amount of polymer residues and will in certain cases turn the furfural dark brown or even black [42].



*Figure 3: Furfural structure (left) and a sample of furfural (right)*

During pretreatment of lignocellulosic material hydrolysis of the glycosidic bonds connecting the polysaccharides in the hemicellulose fraction are cleaved, releasing the sugar monomers from the hemicellulose structure. When a pentose monomer like D-xylose or L-arabinose is hydrolyzed from the hemicellulose chain, a dehydration reaction can occur in which hydrogen and oxygen is eliminated from the pentose in the form of a water molecule leading to an opening of the pentose ring. In the following



step, a second elimination reaction liberates another water molecule. Both steps establish C=C double bonds, and a final elimination of a water molecule leads to closing of the ring and the formation of a furfural molecule [43]

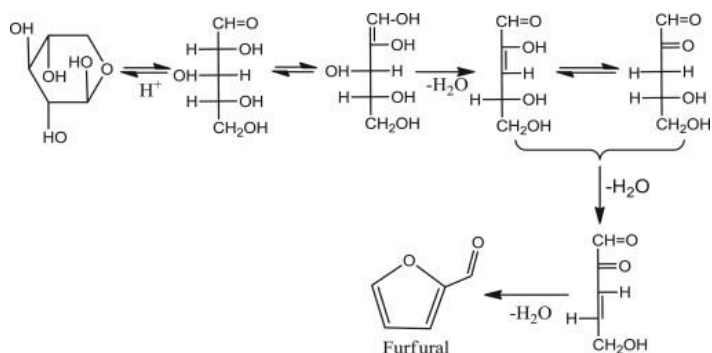


Figure 4: Suggested mechanism for furfural formation from dehydration of C5-sugars. Taken from Yan et al. 2014 [44].

The chemical properties of furfural make it a versatile biobased platform chemical. The aldehyde group supports a wide range of reactions to transform the furfural molecule into a range of products like food additives, solvents, resin and polymer precursor, adhesives, medicine synthesis and many more.

### 1.3.2 5-Hydroxymethylfurfural

5-Hydroxymethylfurfural (5-HMF) is similar to furfural as it is made up of a furan ring with an aldehyde in the 2-position. Additionally, it has a hydroxymethyl group located at the 5-position. Because of its higher melting point, 5-HMF at room temperature is a white powdery solid.

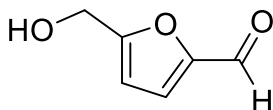


Figure 5: 5-hydroxymethylfurfural structure

When hydrolysis of lignocellulosic biomass releases hexose monomers like glucose a dehydration reaction can transform the glucose monomer into 5-HMF. There are several proposed mechanisms that describe how this conversion takes place. Acid-catalyzed direct dehydration can happen through both cyclic and acyclic pathways, but in both cases an initial reaction transforms the glucose molecule to an intermediate which facilitates two consecutive dehydrations before a final rearrangement which again eliminates a water molecule [23, 45, 46].

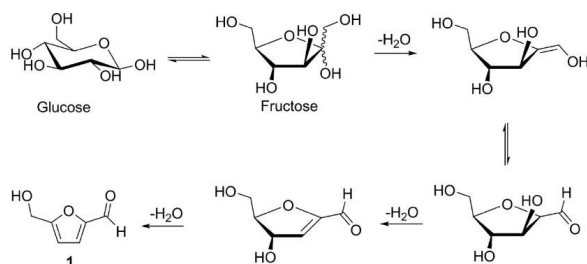
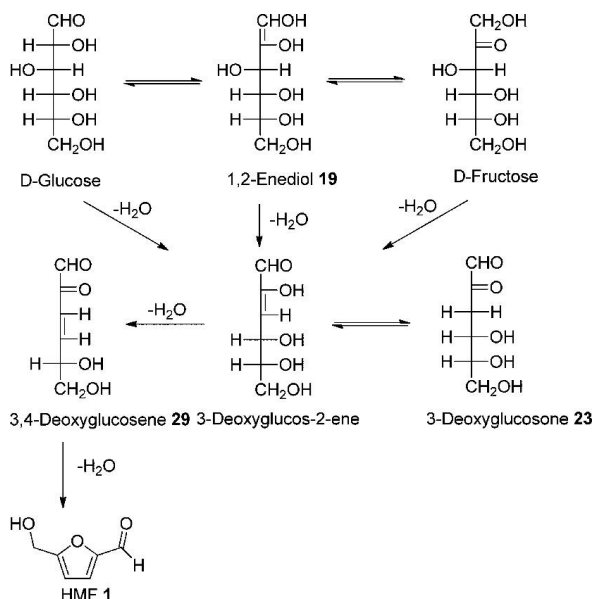


Figure 6: Suggested cyclic reaction mechanism for dehydration of glucose to 5-HMF. Taken from van Putten et al. [46].



*Figure 7: An acyclic reaction pathway for dehydration of hexoses to 5-HMF, proposed by Anet [69]. Taken from van Putten et al. [46].*

Similarly, to furfural, 5-HMF is also a flexible platform chemical for creating different essential chemical structures to be used for a wide variety of purposes. As an example, 5-HMF is used as the precursor synthesis of 2,5-furandicarboxylic acid which is used to produce the PEF bioplastic which is targeted as the successor of fossil-based PET plastic used in most commercial plastic bottles. 5-HMF is also an intermediate in the production of levulinic acid [45]. Levulinic acid and 2,5-furandicarboxylic acid were two of the bio-chemicals classified in the top of U.S. DoE list of important biochemicals [7].

### 1.3.3 Other furanic compounds (5-MF and 2-AF)

During high temperatures and acidic environments some sugar monomers will undergo dehydration reactions that do not result in the production of furfural or 5-HMF. From steam explosion of lignocellulosic biomass, the two most prominent of these furanic compounds are 5-methylfurfural (5-MF) and 2-acetylfuran (2-AF).

S. Moe et al. explains that “The presence of 5-methylfurfural in commercial furfural samples can be explained assuming that 5-methylfurfural is formed from 6-

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deoxyhexoses by the open-chain mechanism proposed for the formation of furfural from aldopentoses and for the formation of 5-HMF from aldohexoses” [47]. S Moe et al. also suggest that 2-acetylfuran can be formed from 6-deoxyaldohexoses through similar, acid-catalyzed dehydration reactions that create the 5-MF molecule [47]

The reason it is important to keep track of other furanic compounds in pretreatment side-streams is that they have similar properties to furfural, such that they can make purification more difficult and interfere with selective reactions in applications of furfural if not removed. An example of this issue is during production of polymer chains from furfuryl alcohol (FA), which is currently one of the largest uses of furfural. The presence of 5-MF as an impurity in furfural creates 5-methylfurfuryl alcohol, which interferes with the polymerization of FA as it attaches to the polymer chain and ends the chain. This results in polymer chains that are too short for their intended use as an impregnation coating.

The boiling point of 2-AF (168 °C) is just a couple degrees higher than that of furfural (162 °C), making them almost impossible to separate by distillation, while 5-MF has a higher boiling point (187 °C) and can therefore be separated from furfural, though not without some difficulty.

Because the yields of these furans are so low, they do not yet have an established market and therefore have not been developed as valuable products. However, because of their chemical properties as furanic compounds they might have an untapped potential as useful precursors.

### 1.3.4 Polymerisation

Both furfural and 5-HMF are quite reactive molecules and while this reactivity can be an advantage as it enables the broad application of these molecules as chemical precursors, it also causes issues as the reactivity of the furans also means susceptible to polymerize under certain conditions. During fractionation of product streams containing furfural and 5-HMF and the purification of these compounds into industrial

grade products, furanic compounds may create solid polymers often referred to as humins.



*Figure 8: Black particles created from polymerization of furfural.*

The formation of humins in industrial processes is a constant challenge as they can clog production lines, reduce the efficiency of the production line, and cause losses in product yields. Understanding what causes the formation of humin polymers, how to best handle their presence in a biorefinery, and ultimately what steps can be taken to minimize the formation of humins during the refining processes is therefore an important aspect in the running of a lignocellulosic biorefinery.

## 1.4 Black pellets as an energy carrier

Energy carriers are substances or systems that contain energy which can be converted into other forms of energy when needed [48]. An energy carrier can be used to store energy or as an indirect way to transmit energy from an energy source to an energy consumer. Firewood is one of the simplest example of an energy carrier as it can be cut and stored for later use as a source of energy. Wood pellets made from dried sawdust are an evolution of this basic concept and by applying pretreatment techniques such as steam explosion, more energy efficient pellets can be made. Degradation reactions that take place during steam pretreatment of the lignocellulosic feedstock cause the release

of oxygen rich compounds from the hemicellulose fraction leading to the steam upgraded black pellets exhibiting both increased calorific values compared with the feedstock [40] and an increase in fixed carbon [49].



*Figure 9: Black pellets produced at the ArbaOne biorefinery.*

In addition to high calorific value, good storage properties are essential for producing a market competitive high-quality energy pellet. During pretreatment the processed biomass particles have developed a coating which provides a strong water resistance, which together with the high physical durability greatly reduces storage related issues [50]. There are a few different properties outside calorific value that are associated with a high-quality pellet. A moisture content between 6 – 10 % is preferred for pellets to have the most effective combustion, and high content of extractives in the biomass will reduce the effective binding strength [51]. Additionally, higher lignin content is associated with good pellet properties like binding ability and thus plays an important role in the creation of high-quality pellets. The high temperature pretreatment causes an increase in lignin plasticity which could contribute to the aforementioned binding and storage properties of the pellets [51].

The properties acquired by the biomass fibers during the steam explosion pretreatment makes black pellets a great contender as a substitute for coal as a solid fuel source. The similarities between the pellets and coal also means that much of the same equipment

can be used, making the transition between coal fired and pellet fired power plant both cost and time efficient.

## 1.5 Economic aspects

An important factor in every biorefinery is the economic viability of new technologies and methods for biomass conversion and product generation. Before deciding to integrate chemical compounds as product streams from the biorefinery, it is important to conduct comprehensive quantification and evaluation of their economic potential. This include assessing the market value, industry demand, cost of product integration, and potential revenue from the product. Furthermore, valorisation of the various product and by-product streams deriving from the steam explosion process is essential for the continued development of the biorefinery concept. By identifying and extracting the compounds that add value to the biorefinery and optimizing the biorefinery process to yield the most desirable product mix, the profitability and sustainability of the production can be improved. The concept of a biorefinery also has the ability to foster innovation in the biomass industry as innovative solutions are needed to solve the problems of upgrading valuable by-products from process streams.

A full-scale biorefinery with the capacity to process upwards of 100,000 tons of raw material yearly, could achieve a production of up to 70,000 tons of pellets a year in addition to hundreds of tons of furfural and 5-HMF worth approximately 1.4 million dollar [16]. These numbers are estimated assuming a stable market price for furfural and 5-HMF which in reality may vary depending on demand and supply around the globe. However, recovery of these valuable compounds from the steam explosion side streams adds significant value to this biorefinery concept and as the technologies develop and more industries choose bio-based precursors over fossil ones, the size of the market for furfural, 5-HMF, and many other bio-based platform chemicals is expected to grow, and prices should stabilize as they are less exposed to large swings in the demand and supply.

# 2.

## Scope

This thesis aims to investigate five aspects of the STEX-based biorefinery:

- How the different side streams in a steam explosion based biorefinery are affected by the variation in feedstock and pretreatment variables by focusing on how the yields of some valuable compounds, especially furfural and 5-hydroxymethylfurfural, can be optimized through modifications to the steam explosion parameters for the distinct input feedstock.
- How the inclusion of catalysts affects the release of sugars from the lignocellulosic structure and dehydration of these sugar monomers to furanic compounds in the steam explosion process.
- A study on a polymerization issue that developed in the furfural distillation column was also performed. While this case study does not fall within the immediate aim of this thesis it is connected to the larger prospect of identifying



and recovering valuable compounds from the side streams of the steam explosion biorefinery.

The optimization studies are done through 3 different experimental series, all performed in large pilot-scale steam explosion reactors at the Lund University Biobased Industry Research Centre (LUBRIC). Extraction and analytical quantification of side streams from these experimental trails are then performed by project partners at PFI RISE and NTNU in Trondheim, Norway, and UiB in Bergen, Norway, according to their fields of expertise.

Additionally, a separate study on a polymerization issue that developed in the furfural distillation column was done.

# 3.

## **Experimental Methods and Procedures**

This chapter will introduce the experimental methods and the analytical procedures that have been used throughout this thesis. The experimental procedures will cover the function of the steam explosion pretreatment method, which has been the main experimental method used in this thesis, and a general overview of the variables that have been employed in the different papers, including which raw materials that have been used as feedstocks. In addition, the analytical procedures used to characterize the products resulting from the steam explosion of various lignocellulosic biomasses is described, including a description of proton NMR and a brief overview of methods used to determine pellet qualities.

## 3.1 Experimental methods

### 3.1.1 Steam explosion pretreatment

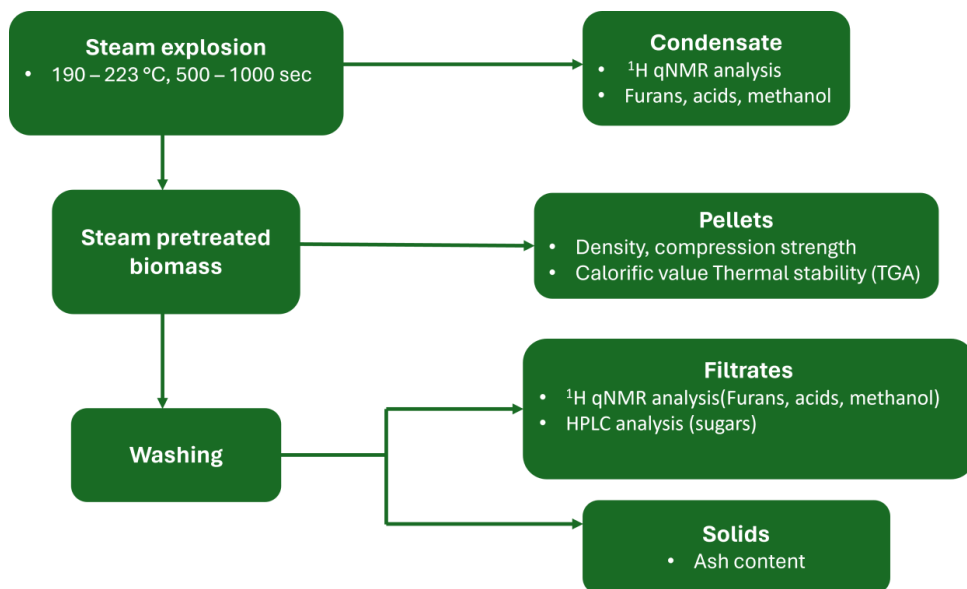
Steam explosion is a physiochemical pretreatment technique that injects high-pressure saturated steam into a closed reactor containing lignocellulosic biomass. Here the steam rapidly heats up the biomass to moderately high temperatures of 160-260 °C, which initiates hydrolysis of the hemicellulose and other chemical and physical changes. The high-pressure steam is held in the reaction vessel for a short amount of time before the vessel is rapidly depressurized in an explosive decompression. This decompression ruptures the wood fibres, depolymerizes lignin by cleaving  $\beta$ -O-4 linkages [52] and further degrades the hemicellulose constituents while the cellulose fraction largely remains intact [10, 53].

Steam explosion is an energy efficient and environmentally friendly pretreatment method because it does not require the use of solvents or chemical additives. The process mainly relies on high-pressure saturated steam, which is steam that is in equilibrium with the water it is evaporated from. This has the advantage of not containing any droplets, making it pure “dry” steam. The use of acid catalysts may be used to improve the hydrolysis of the lignocellulosic material [54, 55, 56, 57] and can also contribute to catalysis of the dehydration of sugar monomers released from the hydrolyzed hemicellulose [16, 58, 59, 43, 46]. As a result, steam explosion pretreatment has been described as a promising method for pretreatment of lignocellulosic biomass [60, 61, 62].

### 3.1.2 Experimental setup for the steam explosion experiments

Steam explosion has been the main experimental focus in this thesis and thus, four of the papers use it as the main experimental procedure. In paper 1 and 3 only the aqueous samples are of relevance, but in paper 2 and 4 solid product streams are also analysed.

Below is an illustration that presents the different product streams, including which analyses were performed.



*Figure 10: Schematic showing the steps in the steam explosion experiments and the different analysis performed on the product streams.*

The steam explosion experiments were all conducted at the Lund University Biobased Industry Research Centre (LUBIRC) in Sweden, with their 4 L and 10 L steam explosion reactors. The majority of experiments were conducted using the 4 L reactor. The system is set up, so it monitors the temperature within the reactor and adjusts the steam pressure to provide the target reaction temperature. The temperature ranges used in the steam explosion experiments differ depending on the biomass type used. 190 °C – 200 °C was used for hardwoods and 210 °C – 223 °C for softwoods. The exception was guayule which was treated at temperatures between 190 °C – 215 °C. Residence time of biomass in the reactor before depressurization was set to 8 minutes for experiments performed for papers I-III, but in paper IV the residence times of 500 seconds and 1000 seconds were chosen for the guayule bagasse.

The methods used in the experimental work for paper I-IV utilize a range of different raw materials as feedstocks for steam explosion pretreatment. Paper I use a hardwood species, represented by birch, and one softwood species, represented by Norway spruce. Paper II and III use the same wood species as experiments in paper I but also utilize barley straw, both by itself and as 10% – 20% of the raw material in mixed feedstock samples with birch making up the remaining fraction. Similarly, BRAT (an abbreviation of Branches and tops) was utilized in a feedstock mix consisting of 10% – 20% BRAT, with Norwegian spruce making up the remaining raw material of the feedstock mix. It is important to note that the BRAT used in the experiments was synthetic BRAT, meaning that instead of branches and tops from Norway spruce, a blend of 70% Norway spruce and 30% bark was made to simulate the properties of BRAT. The raw material used as feedstock for steam explosion in paper IV was guayule bagasse from a producer of natural latex. Guayule is a small shrub that can grow in arid climates and produce extractives containing isoprene which can be extracted for rubber production. The received feedstock had a very low moisture content and was steam exploded both as received and rehydrated to 50% moisture content.

Aside from pressure and temperature experiments performed for paper I and paper II-III examined the effect of other variables such as catalyst use by the addition of SO<sub>2</sub> gas in low temperature steam explosion for paper I and impregnation of the biomass with acetic acid prior to pretreatment for papers II and III. Paper I also investigated the effect of preheating the flash tank and the size of the steam explosion reactor.

When the steam explosion was completed, the condensate was collected in a bottle before being weighed and frozen. Each individual batch of steam exploded biomass was collected, weighed, and placed in cold storage.

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### 3.1.3 Experimental procedures for investigation of black particles

The final paper investigates solid particles found during upgrading of the target compounds from the condensate stream of a full-scale steam explosion biorefinery in eastern Norway. The particles were first collected and exposed to a series of analyses. A solubility trial was conducted, where the ability of different solvents to dissolve the black particles were examined. A small amount of black particles were weighed in and placed in a glass vessel with a stirring magnet and solvent was added to the glass before the lid was placed on the glass vessel and the vessel was placed on a magnetic stirrer where it would stir for 24 hours. At the end of the process the contents of the glass vessel were filtered through a glass fibre filter and the undissolved particles were weighed.

To replicate the formation of the black particles in a laboratory environment, several experiments were conducted using benchtop distillation setup with total reflux. This was done in an attempt to simulate the conditions that were present in the full-scale unit when the black particles were originally formed. In the round flask condensate was added and heated to temperatures of 96 °C – 104 °C to resemble conditions found in the heat exchanger where black particles were found. Several variables were altered during the experimental series. Seeding particles were introduced to the system, the pH of the liquid mixture was altered, and additional furfural was added to the liquid in order to induce formation of more black particles.

## 3.2 Characterization of liquid products

Identification and quantification of products in the aqueous product streams from the steam explosion of biomass were performed using two methods. Proton qNMR was mainly employed to quantify organic compounds in the condensate and filtrate samples, while HPLC was employed to quantify the content of different sugar monomers in the filtrate samples.

### 3.2.1 Nuclear Magnetic Resonance spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is an analytical method that uses the inherent magnetic properties of atomic nuclei to enable the quantification of certain organic molecules together with the ability to elucidate the molecular structure of compounds being analysed. Spin is a property of nuclei with odd atomic number and, or odd mass, meaning that these nuclei with a quantized spin angular momentum creates a magnetic field with a magnetic moment. It is this magnetic moment that makes NMR analysis possible [63, 64].

Proton NMR, or  $^1\text{H}$  NMR, is commonly used for analysis of organic compounds and have been used in the characterization of condensates and filtrates throughout this PhD thesis, as proton NMR is well suited for quantification of compounds with a high abundance of H-nuclei as it gives strong signals and has reasonably short relaxation times. Since the aqueous samples contain a large quantity of water, which has NMR-active protons, the water signal is suppressed using presaturation pulses during the relaxation delay [65].

Nuclei with the spin property have a quantized number of allowed spin states which is determined by a physical constant. Proton NMR uses the  $^1\text{H}$  nuclei which has two allowed spin states called  $+1/2$  and  $-1/2$ . Normally these fields have a random orientation, but when a sufficiently strong external magnetic field is applied, the nuclei will align with the field in relation to one of its allowed spin states. For the  $^1\text{H}$  nuclei, this means either aligning with the field or against it. There is however a difference in the energy states of the two alignments, as aligning with the field requires less energy, and this energy difference is a function of the strength of the external magnetic field and a constant  $\gamma$  that is unique for each isotope [63, 64].

By supplying radiofrequency (RF) waves with the Lamor frequency, which is the spin frequency of a nuclei in a magnetic field, the nuclei can absorb the energy of the RF waves and change its spin state from the  $+1/2$  aligned state to the  $-1/2$  opposite aligned state. When this happens, the nuclei are in resonance with the magnetic field. When the

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nuclei switch back to the  $+1/2$  spin state it releases energy that is detected by the NMR apparatus and transforms that energy into a signal [63, 64].

Because of small differences in local electromagnetic environments, different protons will have slightly different resonance frequencies. This is because valence electrons will rotate under the effect of a magnetic field and this electron circulation induces an opposing magnetic field. This diamagnetism results in an effect called shielding, where protons in the same local environment as valence electrons will be shielded by the circulating electrons and effectively experience a smaller magnetic field. On the other hand, protons positioned close to electronegative atoms will be deshielded as these nuclei pull the electrons towards themselves and away from the proton and will effectively experience more of the external magnetic field [63].

Since a shielded proton experiences a reduced magnetic field, it also requires a lower frequency RF wave to create resonance and a lower frequency will be absorbed by the NMR apparatus. An NMR spectra is usually represented as a 2D plot where the x axis represents the absorbed frequency, and the y-axis represents the intensity of the signal. Difference in absorbed frequency is commonly referred to as chemical shift and a universal calibration standard tetramethyl silane (TMS) is used as reference for the 0-value of the axis because of the strong shielding of its protons. [63, 64]

Because the shielding of a proton depends on the surrounding molecular structure, the chemical shifts of unique chemical structures will generate almost unique NMR spectra. Spin-spin splitting is another phenomena that helps differentiate between similar structures. In addition to the effect of shielding, the spin of protons on adjacent carbon atoms can interfere with one another as a proton with  $+1/2$  spin state can slightly deshield a proton on adjacent carbon and a  $-1/2$  spin state will slightly increase shielding of the same proton. This results in a marginal differences in the absorbed frequency and splits the signal from the proton into two peaks, which is called a doublet [63, 64]. In more complex molecules this coupling phenomenon may create different kinds of multiplet signals that enhances the effectiveness of NMR as an analytical tool, as it can function as a fingerprint during structural elucidation. Signals in the NMR



spectra can then be identified by either comparing with online spectra databases, or with NMR spectra prepared with standard compounds.

NMR is not only useful for structural elucidation but also for quantification of compounds in a sample. The strength of the RF signal that is detected by the NMR apparatus is proportional with the number of magnetically distinct atoms of the type being investigated, that exist in a sample. By using an internal standard (IS) with a known concentration as a basis from which the concentration of identified compounds can be quantified. The signals of identified compounds can be compared to the integral of the IS resonance peak with its known concentration. This is because the intensity of the  $^1\text{H}$  NMR signals are proportional with the number of hydrogen atoms that make up the signal.

Below are two spectra illustrating the look of NMR spectra from condensate and wash filtrates from steam explosion of lignocellulosic biomass. The figures do not identify 5-MF and 2-AF as their peaks are too small to be properly identified at the scale of the figure.

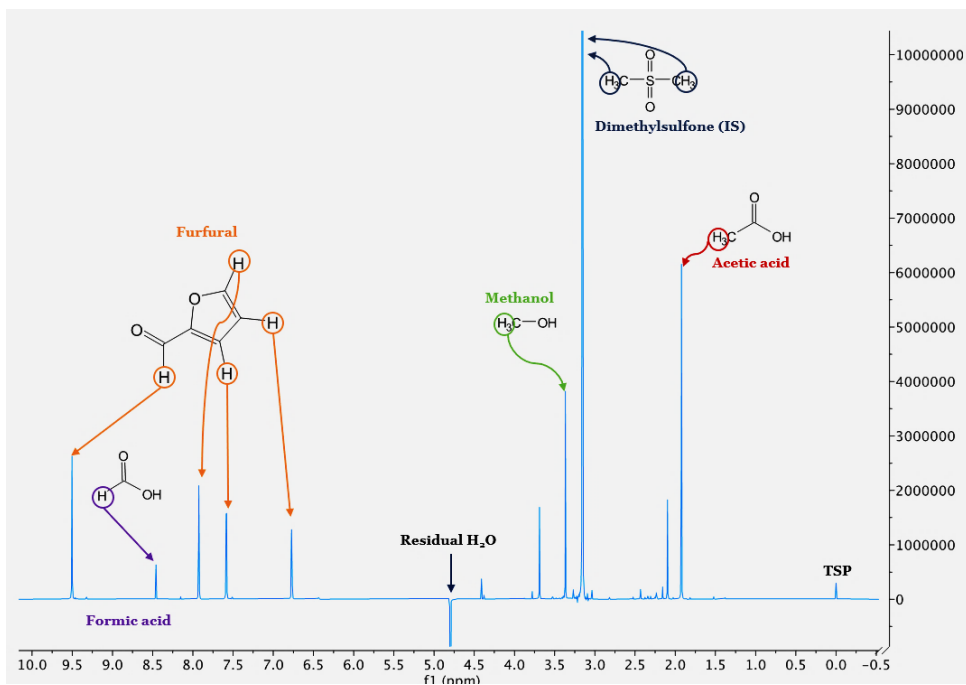


Figure 11: NMR spectra of a condensate sample, outlining the identified compounds from their peaks. Appropriated from Ghoreishi et al. [16]

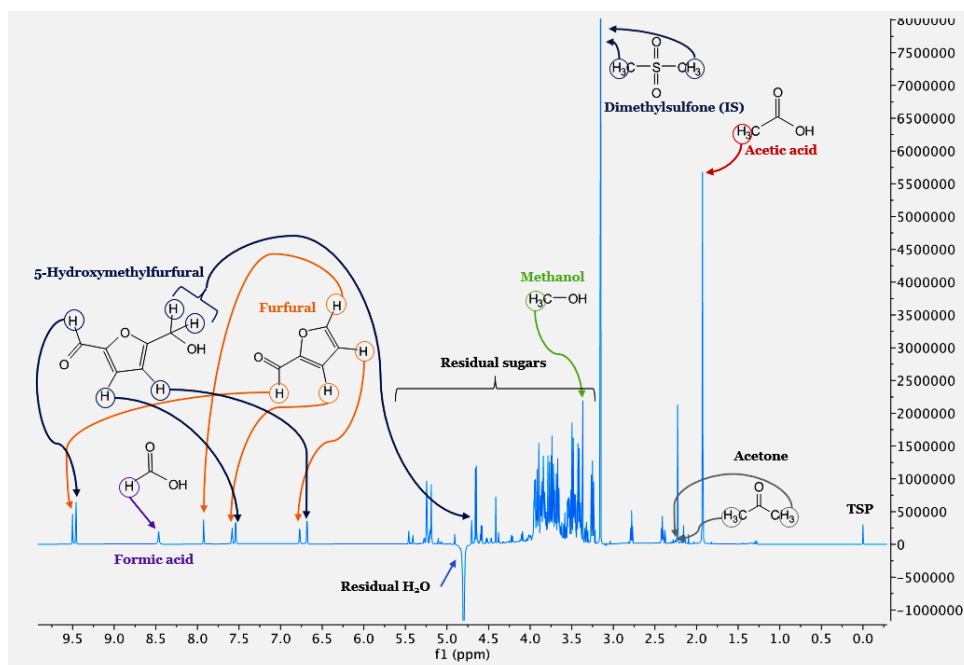


Figure 12: NMR spectra of a filtrate sample, outlining the identified compounds from their peaks. The composition of sugars in the sample has not been elucidated. Appropriated from Ghoreishi et al. [16]

### 3.2.2 NMR sample prep

Preparation of the aqueous condensate and filtrate samples for q-NMR analysis is done according to the protocol reported by Løhre et al. [65]. First, 8 mL of each sample is placed in a vessel and an internal standard (IS) is added, in the form of dimethyl sulfone (DMSO<sub>2</sub>) in distilled water. The amount of IS added to the sample can be adjusted to ensure optimal quantification, but 200 μL to 400 μL of internal standard is generally used.

Following this a stock solution with 20 % deuterium oxide (D<sub>2</sub>O) containing TSP was added to the sample in a 1:1 volume ratio, such that the samples have a 10% volume of D<sub>2</sub>O. Finally, the analyte solution is filtered and 600 μL of each prepared sample is transferred to an NMR tube.

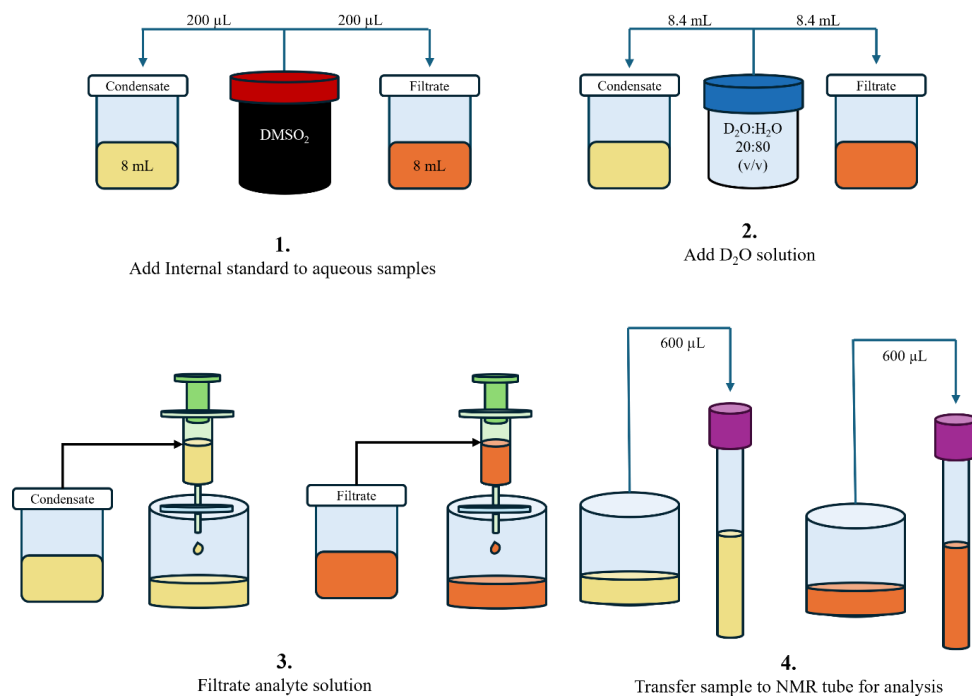


Figure 13: An illustration of the work-up protocol used for preparing aqueous samples for NMR analysis. Adapted from Ghoreishi et al. [16]

Acquisition of NMR spectra was performed with Topspin 4.0 and IconNMR on a 600 MHz Bruker AVANCE NEO NMR-spectrometer equipped with a QCI CryoProbe with four RF channels.

### 3.2.3 Characterization of sugars with HPLC

During steam explosion of lignocellulosic biomass, the hemicellulose fraction undergoes heavy degradation through hydrolysis of its polysaccharides and dehydration of the resulting sugar monomers. However, not all sugars are converted to furanic compounds. Because of the short reaction time of the steam explosion, a major part of the sugars won't be dehydrated into furans and will therefore remain in the steam exploded biomass. Sugars are water soluble and can therefore be extracted from

the steam exploded biomass during the washing step. While NMR is a tool well suited for the analysis of even complex solutions of organic compounds, the identification and quantification of solutions containing multiple different sugar monomers has so far been a to work intensive task for this project.

High performance liquid chromatography using a refractive index detector (RID) is a common method for analysis of sugar compounds. Filtrates produced from washing of steam exploded biomass were analyzed by HPLC with a SPD-M20A photodiode array and an RID-20A refractive index detector, using a mobile phase based on deionized water [47].

### 3.3 Characterization of solid products

The second product stream from steam explosion of lignocellulosic biomass is the steam exploded biomass itself. Analysis of the changes in biomass properties before and after STEX pretreatment determines if the feedstock is a suitable candidate for production of black pellets.

#### 3.3.1 Elemental analysis

Elemental analysis was employed in paper 2 to evaluate the change in elemental composition of the lignocellulosic biomass before and after pretreatment. The method of elemental analysis works by combusting a prepared sample at high temperatures in the presence of excess oxygen. When the sample is exposed to this environment its constituent elements are oxidized into gasses such as CO<sub>2</sub>, H<sub>2</sub>O, and NO<sub>2</sub> which is separated and analysed by a thermal conductivity detector (TCD). The results from this process can be used to calculate the mass contribution of carbon, hydrogen, nitrogen, and by difference oxygen in the sample [66].

### 3.3.2 Evaluation of pellet qualities

To evaluate the quality of pellets from steam exploded biomass the three main aspects to consider are compression strength, thermal qualities, and ash content.

### 3.3.3 TGA-FTIR

Thermogravimetric analysis (TGA) is used to characterize and evaluate the thermal degradation behavior of the pellet samples and weight loss in a temperature program heating the sample from 35-900 °C at a constant heating rate of 10 °C/min in an inert N<sub>2</sub> atmosphere. The decomposition of the sample occurs at higher temperatures and the gases released during decomposition are collected and analyzed using an FT-IR instrument [40].

### 3.3.4 Compression strength

The durability of a pellet is crucial for its capabilities as an energy carrier. A strong and structurally sound pellet has the benefit of minimizing issues related to storage and transport and is therefore a more competitive product. However, there is also such a thing as a pellet that is too hard. The ideal pellet is firm, but ultimately breaks down into evenly sized particles when ground or crushed in a power plant. The compression strength of a pellet is therefore measured to make sure it satisfies structural requirements. The compression strength is defined as the force at breakage when a pellet is placed between two metal plates and compressed at a fixed strain rate while force and distance are recorded [40].

After drying to a target moisture content of 8-10%, a pellet can be made using a Zwick Roell pelletizer, while controlling the temperature (80°C), maximum applied force (9 kN), and using a pellet compression speed of 5 or 10 mm/min. The pellets are

compressed until there is a 10% drop in maximum force. Measurements like size and density is usually collected during this process.

### 3.3.5 Ash content

The ash content is an important factor during combustion of energy carriers. Certain impurities in the biomass can lower the melting point of ash, which causes slagging if used in industrial furnaces and power plants. Slagging causes issues with furnace performance and efficiency and increases maintenance costs [67].

Ash content is analyzed in both raw material and steam exploded biomass. The ash content is quantified at 525 °C and 900 °C according to ISO 1762 and ISO 2144 standards. Ash composition can also be further characterized using pyrolysis GC–MS (pyrolysis gas chromatography mass spectroscopy), by pyrolyzing ash samples at 600 °C in a reactor to see which organic materials remain after being exposed to 900 °C in a muffle oven.

### 3.3.6 Calorific value

To measure the energy content of biomass it is normal to use a bomb calorimeter. This is an instrument that induces a complete combustion of a material sample, which is placed in a closed chamber surrounded by water. This container with water is also isolated and the temperature of the water monitored closely. When the combustion of the pellet happens, the combustion chamber becomes hot, and this heat energy is transferred to the water surrounding the chamber. The calorific value of the combusted sample is calculated from the change in temperature of the water surrounding the combustion chamber.

# 4.

## Main Results

This chapter summarizes the main results achieved within this PhD project. The experimental and analytical work that has been done is presented as five individual papers in part II of this thesis. The order of the papers represents the order in which the experimental work was done, and results were obtained. The exception to this is the fifth paper which is placed at the end because it addresses a challenge with the downstream upgrading of the by-products, which falls outside of the themes of papers 1-4. Each paper is presented with a summary that describes the focus and the main findings.



#### 4.1 **Paper 1** – Identification and quantification of valuable platform chemicals in aqueous product streams from a preliminary study of a large pilot-scale steam explosion of woody biomass using quantitative nuclear magnetic resonance spectroscopy.

One of the main objectives of this PhD project have been to explore how steam explosion pretreatment of various lignocellulosic feedstocks influence the composition of the aqueous side stream originating from the pretreatment process and especially how the yield of value-added furanic compounds in these side stream can be optimized by changing the input variables of the pretreatment. Paper 1 investigates a larger range of these pretreatment variables and reports their effect on the aqueous product streams.

Multiple variables considered for these experiments. Steam explosion was performed using different reactor scales (4 L and 10 L scale), Norwegian spruce was steam exploded at temperatures of 210 °C (low) and 223 °C (reference), while Birch were steam pretreated at 190 °C (low) and 200 °C (reference). A catalyst in the form of gaseous SO<sub>2</sub> was introduced to one experiment for each feedstock at low temperature steam explosion. In addition, a preheated flash tank for collection of steam exploded material was used for one high temperature steam explosion using the 4L reactor for each of the feedstocks.

Figure 4.1 and 4.2 presents the concentration of identified compounds in the condensate and wash filtrate samples from different reaction conditions.

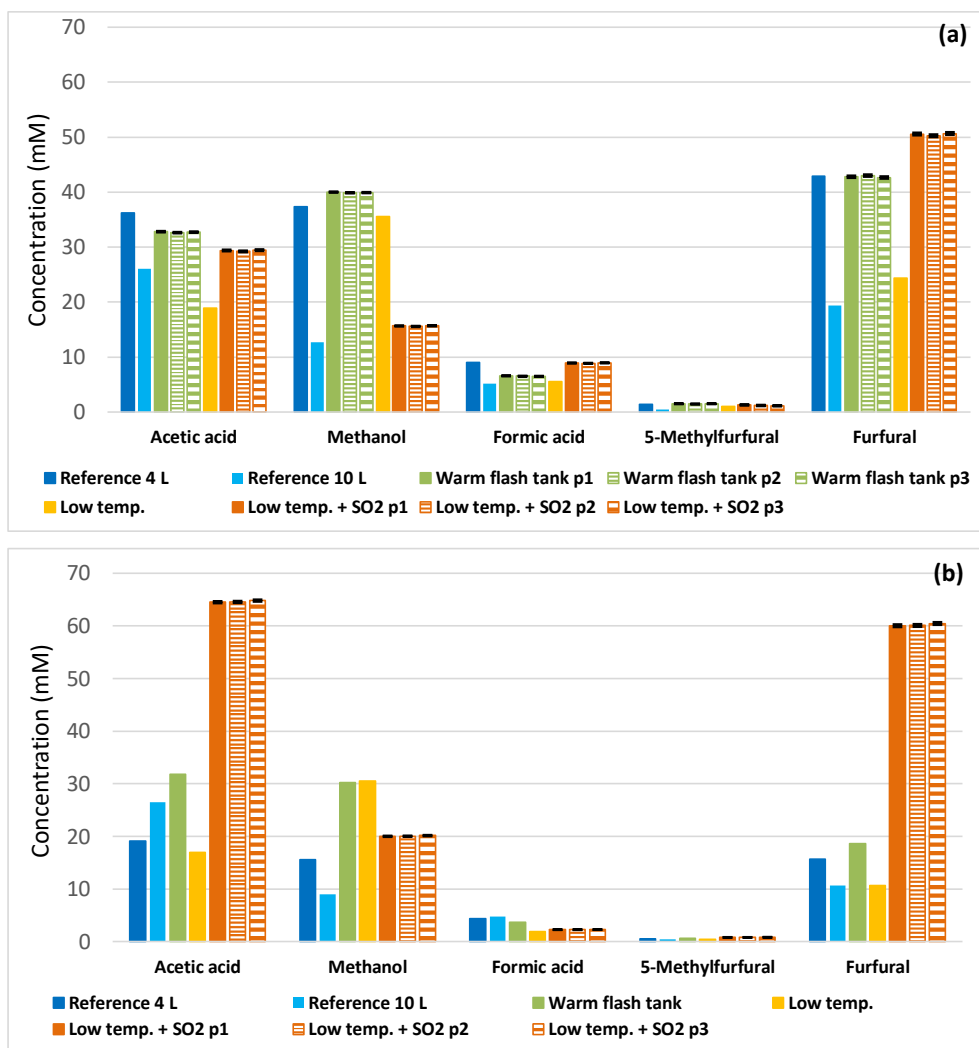


Figure 4.1: Concentration of identified compounds in condensate from steam explosion of Norway spruce (a) and birch (b). Figure is taken from Ghoreishi et al. [16]

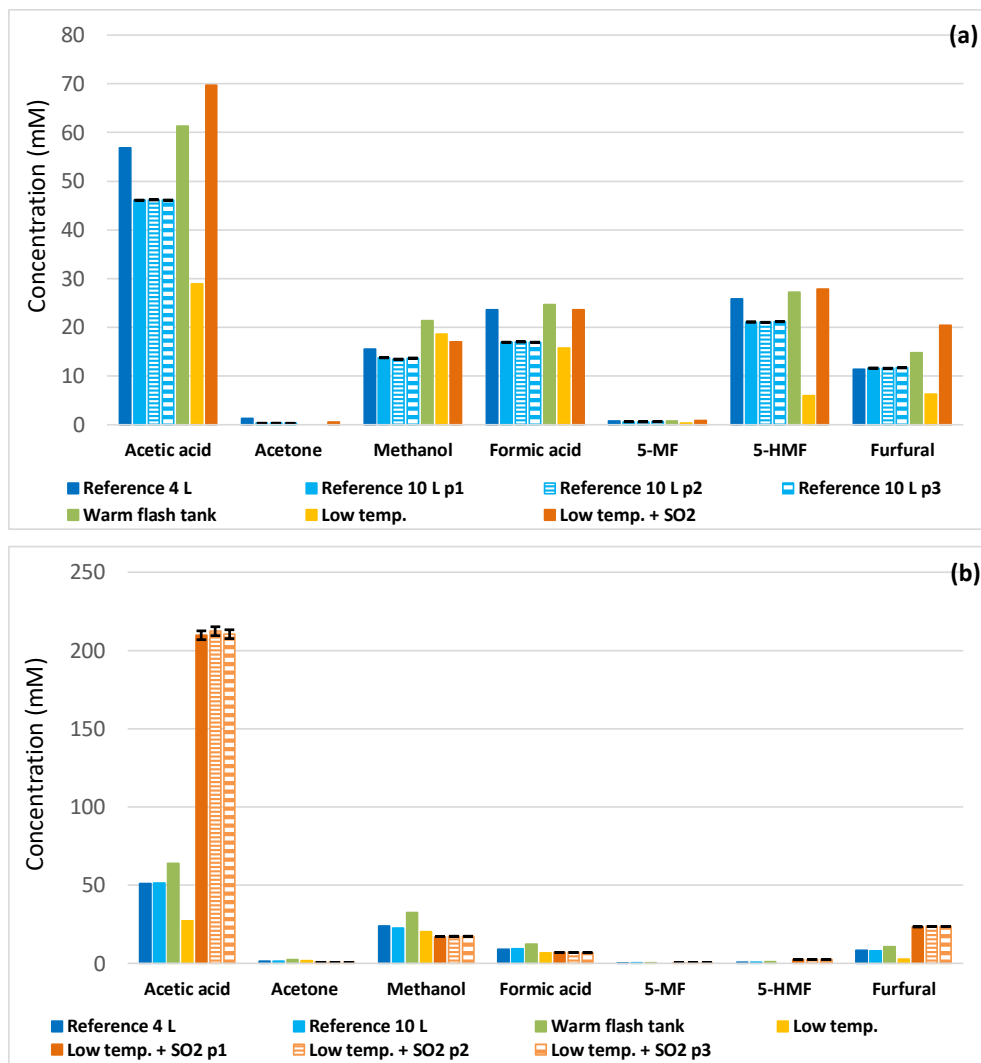


Figure 4.2: Concentration of the identified compounds in the wash filtrates from steam explosion of Norway spruce (a) and birch (b). Figure is taken from Ghoreishi et al. 2022 [16]

What is immediately clear is that the use of SO<sub>2</sub> catalyst in low temperature pretreatment of birch corresponds with a significant increase in yield of furfural. The release of acetic acid, which is associated with increased hydrolysis of hemicellulose also sees a manyfold increase from the addition of the SO<sub>2</sub> catalyst.

In Norway spruce the yield of furfural also increases with catalysed steam explosion pretreatment, but not to the same extent as with birch. Additionally, the results from steam explosion with a 4L reactor using a pre-warmed flash tank at high temperatures results in slightly lower but comparable yields to the catalysed steam explosion pretreatment.

By calculating the yields of the value-added products furfural and 5-HMF an estimation of the additional value generated by the biorefinery can be found. Assuming production numbers from the ArbaOne biorefinery, a stable market value for furfural and 5-HMF and using the highest yielding conditions of low temperature SO<sub>2</sub> catalysed steam explosion, 89.4 tons of furfural worth approx. 735k \$ and 152.5 tons of 5-HMF worth approx. 702k \$ a year from processing Norway spruce. Using the same condition on steam explosion of birch the biorefinery can produce 103.1 tons of furfural worth approx. 866k \$ and 13.9 tons of 5-HMF worth approx. 64k \$ yearly. Recovering these valuable compounds from the steam explosion side streams adds significant value to this biorefinery concept.

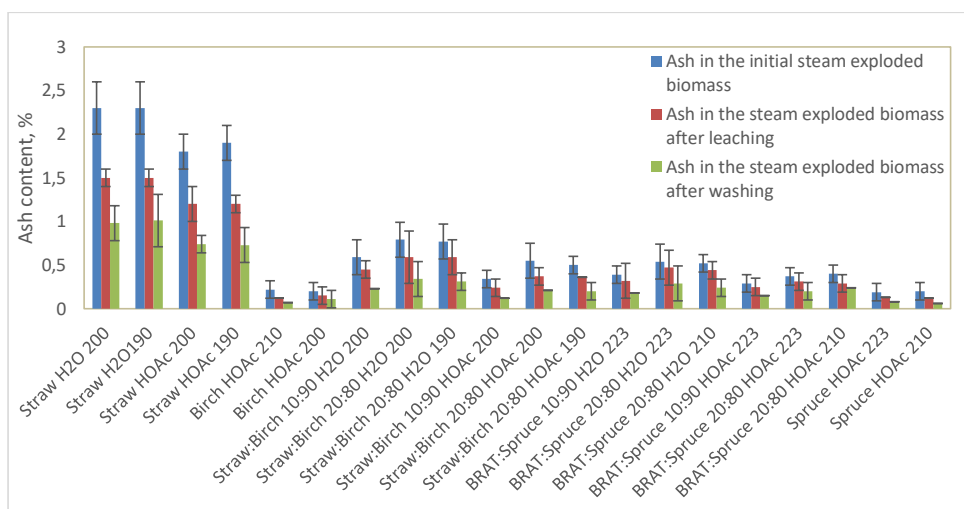
## 4.2 Paper II – Steam explosion of lignocellulosic residues for co-production of value-added chemicals and high-quality pellets

The steam explosion pretreatment connected with this PhD project focuses on production of black pellets that can be used as energy carriers and coal substitutes. Paper II investigates the properties of steam exploded biomass where a portion of the raw material consists of low-grade feedstock from agricultural or forestry waste. The raw materials were also impregnated with acetic acid/water prior to the pretreatment process. Mixed feedstock consisted of birch (hardwood) or Norway spruce (softwood) mixed with a waste material of a comparable biomass type, straw for hardwood and BRAT for softwood. BRAT is an abbreviation for branches and tops and represents forestry residues. The waste residue material was mixed with the woody biomass in a fraction of either 10% or 20% of the total mass. Table 4.1 displays an overview of the steam explosion experiments that were performed.

*Table 4.1: Overview of experiments showing feedstocks, impregnation medium, reaction temperature, and pressure.*

Sample	Material mix	Impregnation liquid	Residence temperature [°C]	Residence pressure [bar]
Straw	100	H <sub>2</sub> O	190	13
Straw	100	H <sub>2</sub> O	200	16
Straw	100	HOAc	190	13
Straw	100	HOAc	200	16
Birch	100	HOAc	200	16
Birch	100	HOAc	210	25
Straw: Birch	20:80	H <sub>2</sub> O	190	13
Straw: Birch	20:80	H <sub>2</sub> O	200	16
Straw: Birch	10:90	H <sub>2</sub> O	200	16
Straw: Birch	20:80	HOAc	190	13
Straw: Birch	20:80	HOAc	200	16
Straw: Birch	10:90	HOAc	200	16
Spruce	100	HOAc	210	20
Spruce	100	HOAc	223	24
BRAT: Spruce	20:80	H <sub>2</sub> O	210	20
BRAT: Spruce	20:80	H <sub>2</sub> O	223	24
BRAT: Spruce	10:90	H <sub>2</sub> O	223	24
BRAT: Spruce	20:80	HOAc	210	20
BRAT: Spruce	20:80	HOAc	223	24
BRAT: Spruce	10:90	HOAc	223	24

An important insight from these experiments with low-grade feedstocks was that the inclusion of a washing step before pelletization resulted in a significantly reduced ash content in the steam exploded biomass, especially for the experiments using only straw as these saw a reduction in ash of up to 80%. This reduction in ash content is important for the application of black pellets as solid fuels as high content of mineral compounds, which often is present in agricultural materials and low-grade feedstocks, can create issues when combusted in industrial furnaces.



*Figure 4.3: Ash content of steam exploded biomass samples before and after washing step and before pelletization. Figure is adapted from Tanase-Opedal et al. 2024 [40]*

The analysis of the elemental composition of the biomass feedstock supports the fact that that the pretreatment has caused a high degree of hydrolysis in the hemicellulose fraction, and the recovery of furanic compounds and other organic compounds from side streams have increased the H/C ratio, as well as decreased the O/C content in the biomass. The steam explosion conditions that have been applied has a strong effect on the degree of hemicellulose degradation and yield of compounds extracted with MIBK such as vanillin, further suggesting that the depolymerization of lignin also related to

the severity of the pretreatment. Both increased temperature and acetic acid impregnation correspond with a greater removal of hemicellulose.

The pellets produced from the different steam exploded feedstocks were of high quality, possessing high densities, calorific values, and compression strength. Pellets were compressed at 9 kN to give the highest possible pellet density and compression strength and this resulted in pellet densities between 1226 kg/m<sup>3</sup> (birch) and 1314 kg/m<sup>3</sup> (spruce and BRAT mix). Generally, the lowest pellet densities and lowest compression strength pellets belonged to straw and birch, including the mixed feedstocks, while spruce/BRAT mixtures produced the strongest and most dense pellets. Figure 4.4 Shows the density and compression strength of the pellets pressed from steam exploded biomass.

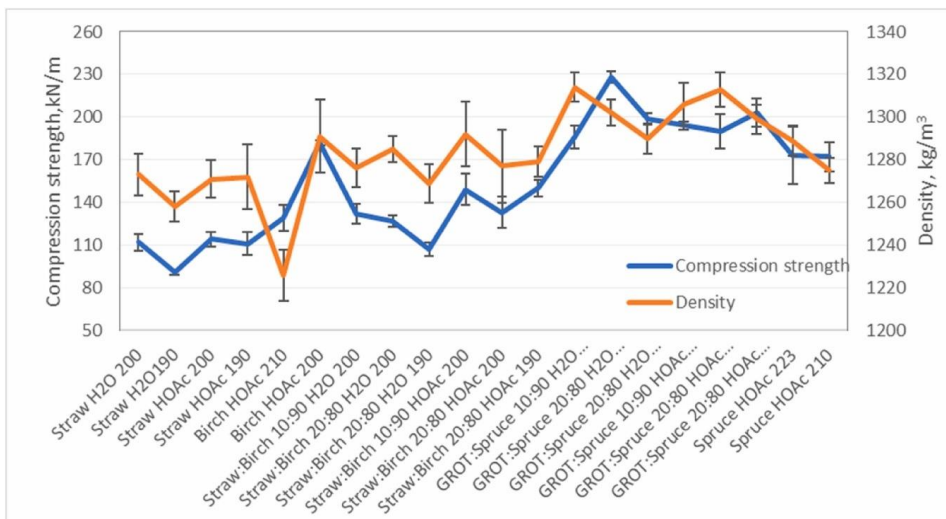


Figure 4.414: Compression strength and density of pellets made from samples of steam exploded biomass (GROT = BRAT). Figure is taken from Tanase-Opedal et al. 2024 [40]

The steam explosion pretreatment also increased the calorific value of the feedstocks as calorific values of straw and birch samples were measured to 18-19 MJ/kg, while spruce and BRAT samples possessed higher calorific values of 20 MJ/kg. The calorific

value of different steam exploded biomass samples plotted against their pellet density can be seen in figure 4.5.

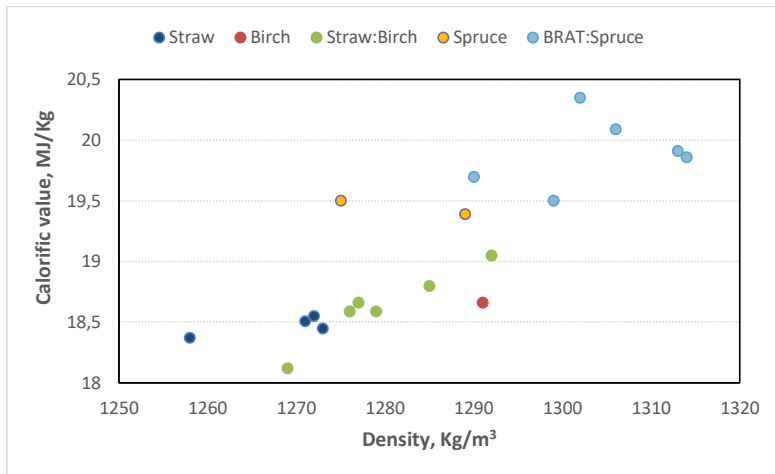


Figure 4.5: Calorific value of steam exploded biomass samples plotted against pellet density. Figure is adapted from Tanase-Opedal et al. 2024 [40]

These results support that using feedstocks including low-grade and low-value raw materials can produce sufficiently high-quality pellets for the use as a coal substitute for the purposes of energy production.



### 4.3 Paper III – Maximizing yields of furfural and 5-hydroxymethylfurfural in side streams from steam explosion of lignocellulosic residues

Paper II and paper III are companion pieces as they describe results from the same steam explosion experiments. Steam explosion pretreatment of single and mixed feedstocks of various origin, with or without acetic acid impregnation, and with high and low temperatures fitted to the biomass type (softwood or hardwood). An overview of the experiments with feedstocks and steam explosion parameters can be found in table 4.1.

Paper III analyses the composition and calculates the yields of organic compounds in the two aqueous side streams originating from the steam explosion process, the condensate and the wash filtrate, to investigate the effect of using low-grade waste residues in feedstocks has on the composition of these side streams. The yield of these recoverable compounds from steam explosion of feedstocks containing low grade raw materials can then be compared to literature values to assess whether this feedstock will result in a competitive yield of value-added products compared to conventional feedstocks.

The water-soluble compounds identified in the aqueous samples by NMR were acetic acid, formic acid, methanol, acetone, furfural, 5-HMF, 5-MF, and 2-AF. The total quantified yields of these compounds from both condensate and wash filtrate streams are displayed in figures 4.6 and 4.7.



Figure 4.615: The total yields of identified organic compounds found in side streams from steam explosion of hardwoods and agricultural waste materials. Figure is taken from Hermundsgård et al. (manuscript)



Figure 4.716: Total yields of identified organic compounds found in side streams from steam explosion of softwoods and forestry residues. Figure is taken from Hermundsgård et al. (manuscript)

The results from the NMR analysis show that the steam explosion process effectively hydrolyses the hemicellulose fraction of the biomass and converts the hydrolyzed sugars into furanic compounds. The results also demonstrate that pretreatment conditions have a large impact on the composition of the by-product streams, as higher temperature pretreatment correlates with increased yields of furfural and 5-HMF. The use of acetic acid impregnation before the pretreatment process can further increase the effective hydrolysis of hemicellulose and act as a catalyst in the conversion of sugars into furans. The effect of catalyzing the reaction with acetic acid is significantly larger in the birch and straw samples compared to the spruce and BRAT ones. Since acetic acid is a green and relatively cheap catalyst its use in steam explosion pretreatment is highly encouraged.

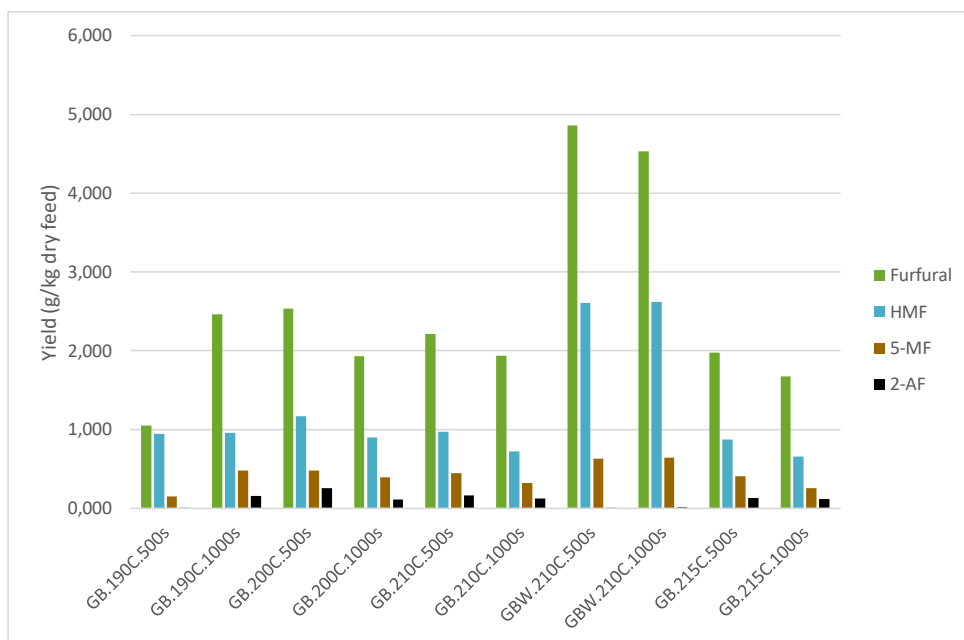
The achieved yields from steam explosion of mixed grade feedstocks compare well to literature values, suggesting that the inclusion of agricultural and forestry residues to the feedstocks can be an economically efficient way of producing furfural and 5-HMF from a steam explosion biorefinery.

#### 4.4 Paper IV – Value generation from steam explosion of waste guayule bagasse

Paper 4 presents an explorative STEX pretreatment of guayule bagasse, a waste material from a production method for natural rubber that is under development. The aim of this research was to investigate co-production of black pellets and value-added chemicals, like furfural and 5-HMF, to examine the effect of using a low-grade waste from an industrial crop as the raw material and look to optimize the process for the Arbaflame steam explosion biorefinery.

The received guayule bagasse was very dry with only a 7.3% moisture content and so steam pretreatment with a temperature range of 190 – 215 °C was chosen. Two batches of guayule bagasse were also soaked in water to increase moisture content to 50%, to investigate whether the change in moisture content of the feedstock would increase yield of valuable compounds.

The composition of the side streams was similar to those reported in paper I and III, containing acetic acid, formic acid, methanol, and the furanic compounds furfural, 5-HMF, 5-MF and 2-AF. The collective yield of furanic compounds from the condensate and filtrate streams is presented in figure 4.8.



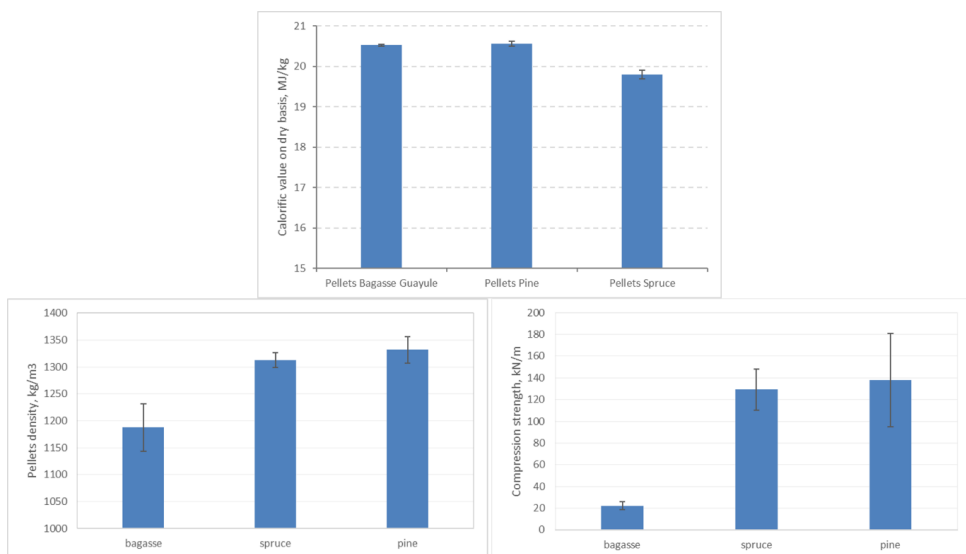
*Figure 4.817: The collective yield of furanic compounds from the condensate and wash filtrates from steam explosion of guayule bagasse. Figure is taken from Hermundsgård et al. (manuscript).*

Steam explosion of guayule bagasse showed efficient hydrolysis of the hemicellulose structures and conversion of sugars into furanic compounds.

The yield of furanic compounds benefit significantly from the rehydration up to 50% moisture content, yielding up to 2.5 times as much product while also resulting in the highest yields of dissolved sugars in the wash filtrates. The general reduction in yield when reaction time is increased also points to an increase in loss reactions happening to the furanic compounds. However, levulinic acid which is a common reaction product of 5-HMF was not identified in any of the side streams. The yield of valuable compounds in side streams from steam explosion of guayule bagasse is lower than what is generated from traditional lignocellulosic feedstocks, but the yields from rehydrated guayule bagasse still represents a significant value proposition for a biorefinery.

A separate batch of pretreated guayule bagasse was made for producing pellets and investigate the pelletizing properties of the steam exploded material. The ash content of the guayule bagasse was found to be much higher than that of wood, but the use of a washing step after the steam explosion process reduced this to the low level needed for the pellets to comply with coal replacements standards. The remaining ash compounds were found to contain some organics including isoprene which is likely to be residues remaining after the latex extraction process.

In comparison with wood pellets the pellets made from guayule bagasse had good calorific value of 20.5 MJ/kg, but pellet density and compression strength were significantly lower than expected. Figure 4.9 illustrates the comparison between guayule pellets and pellets made from spruce and pine wood.



*Figure 4.9: Comparison of calorific value (top), density (bottom left), and compression strength (bottom right) between guayule pellets, spruce pellets and pine pellets. Figure is taken from Hermundsgård et al. (manuscript).*

The structural integrity of a pellet is dependent on the bonding strength between the fibers in the biomass which is correlated with its chemical composition. Lignin content contributes positively to stronger pellets while the presence of extractives usually has

a negative effect on the bonding of biomass fibers. It is therefore likely that compounds like isoprene, found among the ash compounds, negatively impact the pelletization properties of the guayule.

The use of guayule as a feedstock in a steam explosion biorefinery focusing on production of energy carriers like pellets shows great potential. The high calorific value of the pellets produced and the high yields of value-added compounds recoverable from side streams presents an opportunity for an economically effective use of the waste guayule bagasse from the production of natural latex. However, the process still needs further development to be able to meet the criteria for pellet density and compression strength.



## 4.5 Paper V – Investigating solids present in the aqueous stream during STEX condensate upgrading – a case study

Working with a complex system of organic compounds such as the condensate stream from a steam explosion process, may introduce new complications the biorefinery processes. Steam explosion of biomass and valorization of chemical by-products is a challenging process where formation of unwanted solids is almost impossible to avoid and is therefore necessary to understand the conditions that lead to their formation to be able to handle these undesirable by-products and maintain a functional biorefinery. Paper V examines the source of such unwanted solid by-products formed during fractionation of the STEX condensate into marketable compounds, mainly furfural.

During separation of the light fraction containing methanol, acetone, and other minor volatile compounds, from the furfural, acids, and water an insoluble black solid compound was created. Its accumulation in the distillation equipment clogged pipes and drastically reduced the flow and therefore efficiency of the separation process.

Samples of the black particles were collected and exposed to a series of analyses. The first test was a solubility trial, where the ability of different solvents to dissolve the black particles was examined. The solvents were selected based on literature, industrial standards, and availability and the solvents and their effectiveness in a 24-hour solubility test can be found in Table 4.2. A Soxhlet extraction using THF that was used to examine the soluble components is also included in the list.

Table 4.2: Solvents tested in solubility trial with results.

Solvent extraction (24 h)	Dissolved mass [wt%]
Ethyl acetate	33,4
Acetone	33,7
Tetra Hydro Furan (THF)	28,0
THF – Soxhlet extraction (20 h)*	23,0
Pyridine	24,3
Ethylenediamine	25,5
Dimethylformamide	15,7
Ethoxyethanol	26,3
Furfural	17,3
Methyl tert butyl ketone (MIBK)	26,2
Dichloromethane	32,5
NaOH 50%	12,4
Methanol	29,1
Ammonium solution 9% (detergent)	20,6
Nitric acid 10% (48 h) *	88,1
Nitric acid 20% *	Fully dissolved

As the results of the solubility test show, most solvents failed to have any significant effect on the black particles. Only nitric acid showed any real effect in breaking up the black polymer. The particles were then examined for ash content, mineral composition (ICP-MS), chemical composition (Py-GC-MS and elemental analysis) and chemical structure (FT-IR). The dissolved compounds from the Soxhlet extraction were analysed on GC-MS and showed that the dissolved compounds mostly consisted of various terpenoids. This was further supported by results from Pyr-GC-MS.

Further investigation into the composition of the black particles mainly supported a theory of humin formation, as inorganics were not present to a noticeable degree. The observation of a heavy black liquid in a drainage pipe from the distillation column, was discovered to be furfural. This made it clear that furfural was the likely cause of the particles.

A benchtop distillation setup was prepared to reproduce the conditions that caused particle formation during the full-scale condensate upgrading. The experiments involved heating condensates to distillation temperatures at different conditions to induce the formation of black particles. Heating a 2-phase solution of water and furfural

made it possible to recreate a similar black solid polymer shown in figure 4.10. Later testing at Sulzer Chemtec's laboratory have also managed to reproduce a similar product.



*Figure 4.1018: Pictures of the recreation of black particles at laboratory scale. Figure is taken from Hermundsgård et al. 2022 [42].*

The analyses combined with the reproduction of particle formation in a laboratory setting strongly indicate that the particles are created from a polymerization reaction between furfural molecules and that wood extractives such as terpenoids which may be present in the aqueous streams is adsorbed onto the particles. The heating of the condensate stream to higher temperatures likely allows furfural to separate from the water phase and form a separate furfural phase where it can react with itself following reaction mechanisms described by Zeitsch [39].

# 5.

## Conclusions and Outlook

### 5.1 Summary and main conclusions

The case for integration of a biorefinery concept around a steam explosion pretreatment for energy pellet production, focusing on high quality woody biomass and recovery of valuable platform chemical from side streams was presented in Paper I. The steam explosion generated high yields of value-added compounds like furfural, 5-HMF, and 5-MF which can be isolated from the side streams and sold for commercial use, creating additional value for the biorefinery. The inclusion of a washing step to extract the all the furanic compounds created during the steam explosion process was also presented here. The use of a catalyst exemplified by SO<sub>2</sub>-gas in the pretreatment process provided a more efficient hydrolysis of the hemicellulose fraction of the feedstocks, enabling the recovery of higher by-product yields from the side streams at lower reaction temperatures and improving the energy efficiency of the pretreatment process. The improvements observed with the use of a catalyst are promising, but SO<sub>2</sub> may not be a

suitable catalyst for use in a full-scale biorefinery process as its use is associated with adverse risks to human health and the ecosystem. The search for a greener catalyst with similar effectiveness should therefore be prioritized. In order to optimize the conditions for this biorefinery concept the optimization of furfural and 5-HMF yields will have to be balanced against the properties of the pellets produced from the steam exploded feedstock.

Expanding the range of usable feedstocks for the steam explosion biorefinery was the focus of paper II and III. Paper II examined the effect of steam explosion on the biomass feedstock as well as how incorporating a fraction of low-grade, low-value residues from agriculture and forestry operations impacts pellet qualities like ash content, calorific value, and pellet structure. The steam explosion had a considerable effect on the composition of the biomass, reducing oxygen content of the material through release of organic compounds converted from the hydrolysed hemicellulose. Through the steam explosion and the following washing step, ash content was significantly reduced, and non-converted sugar monomers and oligomers could be recovered from the steam exploded biomass. The inclusion of low-grade biomass residues did not negatively impact the quality of the energy pellets and thus indicates that incorporation of low-grade materials into the feedstock presents a cost-efficient way of producing high-quality energy pellets.

Investigating the use of low-grade residues in the feedstocks and the effects of impregnating the biomass with acetic acid prior to steam explosion was the aim of paper III. The incorporation of a fraction of low-grade raw materials in the feedstock does not seem to present any issues regarding the yield of furfural and 5-HMF from the steam explosion pretreatment. Conversely, higher yields of 5-HMF were observed in samples including BRAT than in samples only containing spruce. The addition of acetic acid in the biomass had a strong catalytic effect on hydrolysis of the hemicellulose and conversion of hydrolysed sugars to furfural and 5-HMF. Especially in the samples using hardwood feedstocks, the acetic acid significantly increased the yield of furfural at both low and high temperature steam explosion. While not as

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effective as SO<sub>2</sub>, acetic acid was demonstrated to be a strong alternative for a green catalyst in steam explosion pretreatment of lignocellulosic biomass.

The expansion of usable feedstocks for the steam explosion biorefinery into wastes from industrial crop productions, particularly from unconventional raw materials, led paper IV to explore waste guayule bagasse as possible candidate for co-production of energy pellets and valuable platform chemicals using steam explosion. The steam explosion pretreatment resulted in an efficient hydrolysis of the hemicellulose and produced high yields of furfural and 5-HMF. However, the moisture content of the received guayule bagasse was remarkably low, and the highest yields were reported when the raw material was rehydrated to 50% moisture. The correlation between moisture content and compound yields should be examined further to optimize the steam explosion process. The quality of the pellets made from steam exploded guayule bagasse was promising as the pellet displayed high calorific values, but pellet density and compression strength were inferior to pellets made from wood. The weak binding between biomass fibres in the pellets was found to be an effect of extractives being present in the biomass after steam explosion. Isoprene, which is the natural latex compound present in guayule, was found to also be present in the steam exploded guayule bagasse and will need to be removed to improve the pelletization properties of the material. Guayule bagasse displays promising qualities as a feedstock for a steam explosion biorefinery, but optimization of the process is needed to maximize the yield of value-added compounds in side streams and issues with residual extractives like isoprene need to be solved to improve the quality of the pellets produced.

Unlike papers I-IV, paper V is a case study investigating an issue observed during upgrading of the condensate stream in Arbaflames full-scale biorefinery. Formation of insoluble black particles in a distillation unit was determined to be the result of a polymerization reaction between furfural molecules that separate from the condensate to form a separate phase and react due to high temperature conditions in the heat exchanger and distillation unit. Additionally, other compounds present in the condensate such as extractives contribute to the particle formation by adsorbing to the surface of the furfural particle. The particles have characteristics like humins formed

from reactions between 5-HMF and sugars, but the reaction mechanisms must be more closely researched to better understand the conditions that initiates these reactions. Later experiments using vacuum distillation have been able to limit the issue, suggesting that high temperature plays an important role in the formation of the particles.

## 5.2 Outlook

The results presented in papers I-IV in this thesis presents a positive outlook for the future and strongly support the case for a biorefinery based on steam explosion pretreatment of lignocellulosic biomass that can utilize a wide range of lignocellulosic feedstocks including low-grade residues from industrial crops or forestry and agricultural processes. However, paper V demonstrates that research and development will be necessary to solve possible downstream issues from the upgrading of the valuable compounds in the aqueous side streams.

The market for furfural and 5-HMF is still developing and will likely be object to price fluctuations caused by global variations in supply and demand. Prices will likely stabilize as more commercial applications of furfural and 5-HMF become economically viable as a substitute to fossil-based chemicals and a sufficient global demand might see values increase as markets and technologies continue to mature.

Continued expansion of the steam explosion biorefinery through further optimization of the pretreatment methods and development of new techniques for extracting valuable chemicals and materials from the pretreated biomass will also increase the value proposition of the biorefinery. Introduction of catalysts like acetic acid to the pretreatment process have shown to increase the effectiveness of pretreatment and inclusion of a catalyst in a full-scale biorefinery process will further improve the concept.

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### 5.2.1 Recovery of furans from the STEX side streams

The focus of the research presented in this thesis has been on examining possible lignocellulosic feedstocks for their yields of chemical by-products that can be sold to add value to the biorefinery. However, the development of methods and techniques for isolation of these valuable product, so they can be sold to industrial manufacturers, is just as important and is going to have a greater focus moving forward.

The results presented in this thesis have demonstrated that a large fraction of the valuable chemical products remain in the steam exploded biomass. Thus, the recovery of furfural and non-volatile products like 5-HMF from this side stream through implementation of a process for washing the steam exploded biomass is of great importance. Using water to wash the biomass is also a cheap and effective way of extracting these water-soluble compounds. However, automation of a large-scale washing step can be challenging, as wet biomass fibers are difficult to work with. A method for mixing and dissolving the target compounds from the steam exploded biomass in water before separation of the solids from the liquid needs to be developed and equipment suitable for a full-scale washing process needs to be acquired.

For environmental and economic efficiency, the amount of water used in such a washing process should be limited. High consumption of freshwater for extraction purposes increases demand for water resources, which may not be a problem in Norway but could be an issue in other parts of the world. High water usage also increases the amount of extractant that needs to be processed, which again increases the operational costs for the biorefinery.

### 5.2.2 Product discovery and development

Furfural and 5-HMF are not the only valuable compounds that can be recovered from biorefining of pretreated lignocellulosic biomass. The fraction of hydrolysed sugars that are not converted furanic compounds have great potential value. Sugars are water soluble and will be extracted from the steam exploded biomass through washing with



water and is present in the wash filtrates. The separation of such a complex mixture as the wash filtrates, without loss of product is challenging. Technologies like membrane filtration, use of selective extractions, or even reactive extraction are compelling options for this purpose, but development of a customized solution for optimal product recovery relative to economic feasibility is the important factor.

There are many possible pathways for utilizing the sugars extracted from the steam exploded biomass. Fermentation to bioethanol is a popular conversion method, biogas production through anaerobic digestion is another possibility as biogas is a product of high demand for its versatile uses and can simultaneously be used as fuel in the biorefinery itself. One of the more interesting possibilities is using the sugars as a substrate to grow single cell proteins [37] which can replace soy as a protein source in feed used in industrial animal farming. In Norway, fish farming is highly dependent on soy and roughly 70% of Norwegian soy imports are consumed by the fish farming industry. As soy production is often associated with deforestation of rainforests and other negative environmental effects, it can be challenging to find sustainably grown soy and so alternative feed from single cell protein grown on sugars from sustainable wood industries, or even agricultural wastes could be a great choice [68]. Localizing the production of fish feed will also reduce reliance on imports and contribute to a reduction in the transportation emissions and costs associated with soy imports.

Other chemical compounds of high value may also be recoverable from steam explosion of lignocellulosic biomass. The depolymerization of the lignin fraction is a source of many commonly used flavour compounds like guaiacol (smoky flavour used in many barbeque products) and vanillin (main flavour compound in vanilla). Vanillin has already shown to be present in the steam exploded biomass and was extracted with MIBK with yields up to 1300 mg/kg dry input biomass from softwoods [40]. The molecular structure of vanillin is shown in figure 5.1.

Another compound that can be formed during steam explosion of lignocellulosic biomass is 2,3-butanedione, also known as diacetyl, whose structure can be found in figure 5.1. Diacetyl is the dominant flavour compound in butter and is used as an

additive in margarine, baked goods, beer and alcoholic beverages, and other products that feature a buttery taste or smell. During pretreatment of lignocellulose acetaldehyde molecules can be formed as degradation products from the propenyl group of a coniferyl aldehyde derived from the lignin fraction of biomass. Acetaldehyde readily reacts with oxygen to form acetyl radicals which react with each other to form diacetyl. However, in the presence of an excess of oxygen the acetyl radicals will react with the oxygen to form acetic acid [41]. The low boiling point of diacetyl suggest that it could be recovered from the condensate steam of the steam explosion process, but analyses of condensate samples and chemical standards using NMR have revealed the challenges of identifying and quantifying diacetyl using this method. Its presence in the condensate steam has however been noticed as samples of the lights fraction from the condensate upgrading have an intense smell of butter. Recent analyses using HPLC in connection with an UV-vis detector have also been able to identify diacetyl in condensate samples from steam exploded biomass. Diacetyl is an established product with a high market price and thus upgrading this compound to market quality would greatly increase the value of the biorefinery.

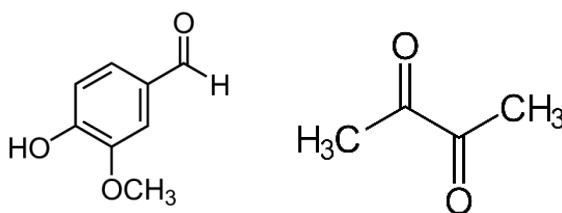


Figure 5.119: Chemical structures of vanillin (left) and 2,3-butanedione (right)

### 5.2.3 Continued work on the Arbaflame steam explosion biorefinery

Along with the development and adoption of a method for full scale washing of steam exploded biomass to recover 5-HMF and furfural, progress is being made in the effort to upgrade side streams and purify by-products to meet market standards. A method has been established to separate furfural from the condensate stream and removal of impurities from the furfural to create a marketable product is well under way.

Trials and experiments reported in this thesis have all been performed in pilot-scale reactors. Efforts to optimize the full-scale steam explosion process at ArbaOne have been made and plenty of samples have been collected and analyzed to find ways to improve the yield of furfural in the condensate stream. Initiatives are also planned to apply the knowledge acquired from the experimental series to the full-scale biorefinery. Experimental results have encouraged the introduction of a catalyst to the steam explosion pretreatment, in order to more effectively hydrolyze the feedstock and increase the dehydration of sugars to furanic compounds and possible options are being reviewed. Similarly, considerations are being made to utilize lower-grade raw materials as part of the feedstock as a possible measure to further increase the cost effectiveness of the biorefinery. These are promising developments towards unlocking the potential of the lignocellulosic biorefinery.

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# Part II









# Paper I

Identification and quantification of valuable platform chemicals in aqueous product streams from a preliminary study of a large pilot-scale steam explosion of woody biomass using quantitative nuclear magnetic resonance spectroscopy

**Authors:**

Solmaz Ghoreishi, Camilla Løhre, Dag H. Hermundsgård, Joakim L. Molnes, Mihaela Tanase-Opedal, Rune Brusletto and Tanja Barth

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# Identification and quantification of valuable platform chemicals in aqueous product streams from a preliminary study of a large pilot-scale steam explosion of woody biomass using quantitative nuclear magnetic resonance spectroscopy

Solmaz Ghoreishi<sup>1</sup> · Camilla Løhre<sup>1</sup> · Dag Helge Hermundsgård<sup>1,2</sup> · Joakim Lindgaard Molnes<sup>1</sup> · Mihaela Tanase-Opedal<sup>3</sup> · Rune Brusletto<sup>2</sup> · Tanja Barth<sup>1</sup>

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## Abstract

Steam explosion breaks down the polymeric matrix and enables the recovery of valuable compounds from lignocellulosic feedstock. In the steam explosion process, biomass is treated with high-pressure steam which subsequently generates large quantities of a condensed aqueous liquid (process effluent) and a filtered aqueous liquid (filtrate) that contain furfural, 5-hydroxymethylfurfural, 5-methylfurfural, methanol, and acetic acid as major constituents. This study addresses the identification and quantification of value-added chemicals in the aqueous product streams using quantitative analytical nuclear magnetic resonance spectroscopy with water suppression. This work reports a screening study for two different types of sawdust (Norway spruce and birch) at two different scales (4 L and 10 L reactors) using different reaction temperatures (190–223 °C) and corresponding pressures (13–24 bar), with and without the addition of SO<sub>2</sub> gas. The duration of all experiments was 8 min. The process effluents contained acetic acid, methanol, formic acid, 5-methylfurfural, and furfural. Acetic acid (0.5 g/kg dry input biomass) and furfural (1.0 g/kg dry input biomass) were more abundant than methanol, formic acid, and 5-methylfurfural for both feedstocks. The addition of SO<sub>2</sub> increased the furfural yields, indicating more efficient hydrolysis of hemicelluloses under acidic conditions. Filtrate samples also contained 5-hydroxymethylfurfural, with the highest concentrations (5.7–6.0 g/kg dry input biomass) in the filtrates from spruce. The different feedstocks and steam explosion temperatures strongly influenced the overall yields of the target compounds, in some cases tripling the concentrations. The results can be used to improve the profit margins in a pellets and chemicals biorefinery, as demonstrated in the ArbaOne pellets plant.

**Keywords** Lignocellulosic biomass · Steam explosion · Biorefinery · Aqueous product streams · Furfural · 5-Hydroxymethylfurfural

## 1 Introduction

Modern society is overdependent on petroleum-based resources and is thus seriously challenged by dwindling fossil fuel reserves and growing environmental concerns [1–3]. As a result of this, the production of biofuels and chemical

building blocks from renewable feedstocks is a developing trend in the chemical industry for replacing fossil resources while simultaneously mitigating climate change [3–5]. When considering alternative carbon-based raw materials for the petrochemical industry, options are limited, as there are only two large-scale sources of renewable carbon on this planet: plants and atmospheric carbon dioxide [6]. Established manufacturing processes for bio-based chemicals are mainly based on first-generation biomass, i.e., edible vegetable oils and sources of carbohydrates, and this is normally in direct competition with food and fodder production. Thus, developing new processes for producing second-generation biofuels and products from non-edible resources such as lignocellulosic biomass can prevent this predicament [5, 7].

✉ Solmaz Ghoreishi  
Solmaz.Ghoreishi@uib.no

<sup>1</sup> Department of Chemistry, University of Bergen, Norway, Allégaten 41, N-5007 Bergen, Norway

<sup>2</sup> Arbaflame As, Henrik Ibsens gate 90, N-0230 Oslo, Norway

<sup>3</sup> RISE PFI, Høgskoleringern 6B, NO-7491 Trondheim, Norway

However, the development of economically viable and energy-efficient processes for converting low-value lignocellulosic biomass into commercially useful biofuels and products is a considerable challenge. At present, most of the proposed processes are unable to compete economically with petroleum refineries in part due to incomplete utilization of the biomass feedstock. The biorefinery approach, to improve biomass utilization, and thus, the economic outputs of biomass-derived processes encompass an integrated and diversified processing plant where the incoming biomass feedstock is completely converted into a wide range of valuable products, including fuels, power, heat, chemicals, and materials [5, 8–10].

Lignocellulosic biomass comprising residues from forestry, agriculture, municipal sources, and industry is considered a sustainable feedstock for this purpose since it is renewable, readily available, and has a wide spatial distribution in nature. Lignocellulosic biomass is heterogeneous and composed of three principal constituents with different structural compositions: approximately 30–50% cellulose, a polymer of glucose; 20–35% hemicellulose, a heteropolymer containing mostly xylose; and 15–35% lignin, a complex heteropolymer of monolignols. The structural rigidity of the polymeric matrix provided by the strong intermolecular interactions has proven problematic for the efficient utilization of lignocellulosic biomass [1, 5, 6, 11]. Successfully replacing fuels and chemicals derived from petroleum with bio-based products derived from lignocellulosic biomass will therefore require high-yield, low-cost, and energetically efficient targeted upgrading processes. Hence, new industrial technologies must strive to minimize the consumption of energy and chemicals, while limiting the generation of downstream pollutants such as waste gas, wastewater, and solid waste materials [1, 6, 11].

For lignocellulosic biomass, a pretreatment step can be used to disrupt the plant cell structure and overcome its recalcitrance, making polysaccharides easily available for reactions like enzymatic hydrolysis, and increasing the surface area [4, 12, 13]. The most widely investigated pretreatment techniques for woody biomass include dilute acid hydrolysis, steam explosion, organosolv, and sulfite pretreatment [5, 14]. Among these pretreatments, steam explosion, which includes a degree of autohydrolysis, is an efficient and widely used technique. During the steam explosion, the lignocellulosic biomass undergoes a sequence of defibrillation, delignification, and hydrolysis of the hemicelluloses. However, the crystallinity of cellulose tends to increase due to the crystallization of amorphous portions, which can be a disadvantage of the technology since the hydrolysis processes will generally be more difficult with high crystallinity [13, 15–17]. Advantages of steam explosion pretreatment include low capital investment, moderate energy requirements, and low environmental impacts as no acids, bases, or solvents are

normally required, which simplifies the subsequent biorefinery stages and reduces their cost. Additionally, uncatalyzed steam explosion pretreatment avoids the additional chemical costs and associated problems derived from equipment corrosion [4, 15, 18]. Steam explosion pretreatment has proven effective for a wide range of different biomasses [8, 19–22].

The steam explosion process involves exposing the lignocellulosic material to high-pressure saturated steam for a specified period and then reducing pressure swiftly, thus making the materials undergo an explosive decompression which results in the deconstruction of the lignocellulosic matrix [8, 13, 15]. During this treatment, the high-temperature steam causes the release of organic acids such as formic acid and acetic acid from a formyl and acetyl functional groups in biomass. These compounds can catalyze hydrolytic degradation of the chemical bonds connecting the woody polymers. The autohydrolysis reactions result in the loss of hemicellulose, which is dissolved in the hot condensed water and can be recovered in the liquid fraction to be further converted into value-added products [8, 23–25]. Acetic acid hydrolyzes xylan polymers into monomeric xylose units and xylose oligomers, and the acidic conditions can lead to further dehydration of the monomeric sugars. This pretreatment can also cause the melting of lignin and its partial depolymerization through the cleavage of the predominant  $\beta$ -O-4 ether and other acid-labile linkages producing a series of lignin monomer derived alcohols and condensation byproducts [8, 15, 26]. The main factors that affect the steam explosion process are temperature, residence time, particle size, and moisture content. Typically, the steam explosion process operates at temperatures ranging from 160 to 260 °C for 1 to 30 min, depending on the feedstock. Optimal hemicellulose solubilization and hydrolysis can be achieved either by high temperature and short residence time or lower temperature and longer residence time. Furthermore, sugar degradation products such as furfural and 5-hydroxymethylfurfural, and soluble phenolic compounds such as catechol and vanillin can be generated in the process with increasing yields at high temperature and long residence time [8, 16, 27].

The optimal solubilization and hydrolysis conditions are also highly dependent on the structural composition of the feedstock. Therefore, a distinction must be made between hardwoods and softwoods [5, 15, 18]. Softwoods have a higher cellulose content (40–45%), higher lignin (26–34%), and lower pentosan (7–14%) content compared to hardwoods (cellulose 38–49%, lignin 23–30%, and pentosans 19–26%) [28]. Acetylated xylans are the predominant hemicellulosic species found in hardwoods, whereas softwoods are mainly composed of glucomannans. Hardwood xylans mainly consist of xylose and glucuronic acid and are relatively labile and will therefore undergo autohydrolysis under milder conditions compared to softwood xylans due to the high content

of acetyl groups. In contrast, softwoods have a higher proportion of partly acetylated glucomannans and galactoglucomannans, and xylans correspond to only a small fraction of their total hemicellulosic content. Hence, the steam explosion is found to be less effective for softwoods due to the low content of acetyl groups in the hemicellulose portion and high lignin content [5, 18, 29].

According to a review on pretreatment techniques, acid-catalyzed steam treatment using  $H_2SO_4$  or gaseous  $SO_2$  is the most suitable pretreatment technique for softwoods [30]. In general, 1–5% w/w of  $SO_2$  is used to treat the biomass at temperatures of 190–210 °C for hardwoods and 200–220 °C for softwoods. The  $SO_2$  gas penetrates the biomass and by explosive decompression, hemicellulose will be hydrolyzed to soluble sugars as a result of glycosidic bonds cleavage [22, 31, 32]. Carrasco et al. reported in 2010 that between 50 and 60% of the xylan could be recovered as soluble xylose from the steam treatment of sugarcane bagasse at 190 °C for 5 min using 2% w/w of  $SO_2$  as a catalyst [33]. In a study from 2005, Öhgren et al. reported that a high overall yield of xylose (78%) can be achieved with one-step steam explosion pretreatment of corn stover using 2% w/w  $SO_2$  as catalyst [34]. However, issues such as equipment corrosion, high purchase costs of  $SO_2$ , and additional costs for neutralization as well as recycling must be taken to account when considering the application of  $SO_2$ -catalysis in a full-scale steam explosion process [18, 31].

A plethora of valuable products can be synthesized from bio-based platform chemicals, where a special group of furan derivatives is identified as among the top 10 value-added molecular platforms by the US Department of Energy (DOE) due to their widespread application as feedstocks for bulk chemicals and fuels. The most important furans are furfural, 5-hydroxymethylfurfural (5-HMF), and 2,5-furandicarboxylic acid (FDCA). Additionally, furans are highly carbon efficient during their synthesis as they retain all five carbon atoms initially present in the pentoses and 5-HMF retains all six carbon atoms initially present in the hexoses [5, 35]. Several recent studies have shown that furfural and 5-HMF can be produced from biomass at high yields and at low costs (1000–5000 USD/ton) if produced at scales above 10 kton/year [10, 36]. According to Trivedi et al., the global bio-based platform chemicals market accounted for 13.83 billion USD in 2017 and is expected to reach 31.56 billion USD by 2026 growing at a compound annual growth rate (CAGR) of 9.6% during the forecast period [37].

Furfural is a key platform chemical produced from acid-catalyzed dehydration of biomass-derived C5 sugars, mainly xylose (from xylan), with a global market of around 400 kilotons per year. Furfural can further be transformed into fuels and value-added chemicals which are widely used in oil refining, plastics, pharmaceutical, and agrochemical industries [1, 35, 36]. Currently, 90% of furfural is produced

by China, South Africa, and the Dominican Republic. From 2006 to 2016, the cost of furfural has been between 800 and 1600 USD/ton. The furfural price increased to 2700 USD/ton at the end of 2017 due to environmental regulations enforced on China's furfural production industry. Thus, in 2017, the furfural market was valued at around 400 million USD. However, the furfural market is expected to undergo a considerable expansion in the coming years due to a rapidly growing demand for furfuryl alcohol. Indeed, the largest amount of furfural (around 60% of the global furfural market) is converted to furfuryl alcohol which is primarily used to produce foundry resins [5, 36, 38, 39]. In addition, furfural can undergo successive hydrogenation and/or hydrogenolysis reactions to produce polymer precursors such as furfuryl alcohol, tetrahydrofurfuryl alcohol, and 1,5-pentanediol, as well as renewable solvents including 2-methyltetrahydrofuran and cyclopentanone. Succinic acid which is a versatile building block with a wide range of applications can be derived from furfural through oxygenation [36, 40].

5-Hydroxymethylfurfural (5-HMF) is also considered one of the top 10 value-added bio-based chemicals by the US DOE. 5-HMF and its derivatives are versatile precursors to produce medicines and pharmaceuticals, bioplastics, biopolymers, and biofuels [41–43]. 5-HMF contains two different functional groups, a hydroxyl group, and an aldehyde group, making it an attractive starting material for transformation into a wide range of chemicals with important industrial applications. 5-HMF is a product of acid-catalyzed dehydration of cellulose and all types of C6 sugars, including monomeric and polymeric carbohydrates such as fructose, glucose, mannose, galactose (from glucomannan), and starch [36, 41, 42]. 5-HMF can undergo successive oxidation, rehydration, and hydrogenation reactions to produce platform chemicals and liquid fuels such as 2,5-furandicarboxylic acid (FDCA), adipic acid, levulinic acid, 2,5-dimethylfuran, and gamma-valerolactone (GVL) [40, 41]. FDCA is one of the most extensively investigated products from 5-HMF and is another key bio-derived platform chemical, which can be converted to succinic acid and adipic acid, both of which have a wide range of applications [41, 44]. The global 5-HMF market was valued at around 55,900 K USD in 2018 and is expected to reach 62,700 K USD by the end of 2025 [45]. Unfortunately, the industrial production of 5-HMF remains an economic challenge for large-scale applications. The main reasons impeding the rapid expansion of 5-HMF production are the low reactivity of glucose, the relatively high price of the starting material (fructose), and the low yields of 5-HMF obtained from simple processes in aqueous reaction media [5].

The work presented here was performed as a preliminary study in the development of a full-scale commercial biorefinery in Eastern Norway, producing black wood

pellets and platform chemicals. Steam explosion is considered a sustainable and promising technology for improving the pelletizing properties for co-firing biomass pellets and coal. The pellets from steam-exploded biomass have increased calorific value, higher density, and are more impact and abrasion resistant and water-repellent, making them superior to conventional pellets in terms of storage and handling. They thus have the potential to become a valuable part of the future sustainable energy supply chain [46, 47]. During the full-scale steam explosion process, large quantities of a condensed aqueous liquid (process effluent) and a filtered aqueous liquid (filtrate) are generated. These fractions contain considerable amounts of furfural and 5-hydroxymethylfurfural (5-HMF), and also methanol, acetic acid, acetone, and formic acid. Filtrates have also been shown to contain various amounts of dissolved sugar monomers and oligomers. However, these components were not considered in this study.

Currently, only a few studies have analyzed organic compounds in the aqueous phase streams from hydrothermal treatment of lignocellulosic biomass [48, 49]. Analysis of small organic molecules in aqueous product streams can be challenging due to limitations in the application of chromatographic methods, such as signal overlap due to similar chromatographic properties especially in HPLC (high-pressure liquid chromatography) and solvent delay in GC-based (gas chromatography) analysis that can exclude a wide range of components. To provide improved analytical data, quantitative NMR spectroscopy has recently developed into a well-established technique and has been widely used for the analysis of organic compounds at low concentrations in metabolomics, pharmaceuticals, natural products, and food and beverage. In 2017, Elliot et al. reported a quantitative  $^{13}\text{C}$  NMR procedure for the detection and accurate quantification of  $\alpha$ -hydroxy acids, esters, and lactones from Sn-beta-catalyzed conversion of xylose, without using reference standard compounds [50]. In 2020, Halleraker and Barth published a quantitative NMR study of aqueous phase products from the hydrothermal conversion of lignin. Acetic acid, acetone, methanol, formic acid, dimethyl ether, phenol, and catechol were reported to be compounded with the highest concentrations [51]. In 2018, Yue et al. reported a study where various qualitative and quantitative NMR techniques were applied in the analysis of process waters from hydrothermal carbonization (HTC) of furfural residues. Without separation and purification, 5-hydroxymethylfurfural, glycerol, formic acid, methanol, acetic acid, levulinic acid, hydroxyacetone, and acetaldehyde were identified and quantified to be the main detectable compounds [52]. In a recent study, Løhre et al. reported a preparative laboratory procedure combined with subsequent  $^1\text{H}$  NMR spectroscopy for the identification and quantification of biorefinery products in aqueous product streams [53]. The procedure gives highly

accurate results with excellent reproducibility for quantitative analytical purposes.

In this study, we aim to identify and quantify the molecular platform compounds generated in the aqueous product streams from the steam explosion of woody biomass at the pilot scale. The concentration of furfural, 5-HMF, and the other major organic components (acetic acid, acetone, methanol, and formic acid) in the process effluents and filtrates from the steam explosion of two different types of woody biomass (Norway spruce and birch) are compared. The study also aims to find the optimal steam explosion parameters for maximizing furfural and 5-HMF in the product streams. This is done by evaluating the composition of organic compounds in the aqueous phases as a function of reactor scale and experimental pretreatment conditions. The effect of adding  $\text{SO}_2$  as an acid catalyst during steam treatment is also evaluated. The quantification of the aqueous organic components was performed by using quantitative nuclear magnetic resonance spectroscopy (qNMR).

## 2 Materials and methods

### 2.1 Chemicals

All reagents and solvents were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification. All standard components are commercially available.

### 2.2 Large pilot-scale steam explosion

The steam explosion processing was performed on a large pilot scale at Lund University Biobased Industry Research Center (LUBIRC) in Sweden. Two different types of woody biomass, Norway spruce (softwood), and birch (hardwood) were investigated as feedstocks, and experiments were conducted at two different scales (4 L and 10 L reactors) using different reaction temperatures (190–223 °C) and pressures (13–24 bar). The duration of the pressurized step was 8 min in all experiments. At the decompression, a gas phase product is formed. This gas, which is mainly steam and some small organic compounds, is condensed and collected through an outlet connected to the decompression valve of the reactor. This product is referred to as effluent/condensate in this work. Samples produced at LUBIRC, i.e., the wet steam-exploded biomasses and process effluents, were sent to RISE PFI for further distribution. The wet steam-exploded biomass was vacuum filtered at RISE PFI to give the filtrate samples.

In total, 10 effluent samples and 10 filtrate samples are included in this study. An extended overview over investigated steam explosion parameters and sample information is given in Table 1. As shown in Table 1, experiments using

**Table 1** Extended overview of experimental large pilot-scale steam explosion conditions

Experiment name	Biomass type	Amount of dry biomass (g)	Reactor scale (L)	Residence temp. (°C)	Residence time (s)	Residence pressure (bar)	SO <sub>2</sub> injection
Reference 4 L	Norway spruce	800	4	223	480	24	
Reference 10 L		700	10	223		24	
Warm flash tank		800	4	223		24	
Low temp		800	4	210		20	
Low temp. + SO <sub>2</sub>		800	4	210		20	3% w/w
Reference 4 L	Birch	800	4	200		16	
Reference 10 L		700	10	200		16	
Warm flash tank		800	4	200		16	
Low temp		800	4	190		13	
Low temp. + SO <sub>2</sub>		800	4	190		13	1.5% w/w

birch as feedstock have been conducted at milder severity to maintain the quality of the produced pellets. According to previous investigations performed at LUBIRC and unpublished internal results birch requires temperatures below 200 °C to provide high-quality pellets while simultaneously generating high furfural and 5-HMF yields in the aqueous product streams.

The parameters investigated in this experimental sequence include two temperatures, the effect of keeping the exploded mass uncooled for the duration of the two batches of 400 g biomass when using the 4 L reactor (termed “Warm flash tank”) and the effect of changing the scale to a 10 L reactor with one run using 700 g biomass. The loading capacity of the 10 L reactor is 700 g dry material, while the 4 L reactor can be loaded with 400 g dry material. In addition, in two of the experiments conducted in the 4 L reactor, SO<sub>2</sub>-gas was used as an acid catalyst to improve hemicellulose hydrolysis. The amount of steam added to the reactor depended on the degree of filling. The optimal filling level used in LUBIRC is 70%, as a higher degree of filling leads to uneven heat transfer and variable conversion of the material. The most abundant organic species present in the effluent and filtrate samples were quantified using the procedure described in Sections 2.3, 2.4, and 2.5.

### 2.3 Preparation of samples for qNMR analysis

Samples for q-NMR analysis were prepared by using 8 mL of each aqueous sample and adding 400 µL (for the effluent samples) and 200 µL (for the filtrate samples) of a 2.1 M solution of dimethyl sulfone in distilled water (TraceCERT® DMSO<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>SO<sub>2</sub>) as internal standard (IS). The target concentration of IS in the effluent and filtrate samples at this stage was approx. 0.100 M and 0.052 M, respectively, ensuring analysis within its optimal range of quantification. A stock solution containing 0.010 M sodium phosphate dibasic dihydrate buffer (≥ 99.0% Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O) and 20%

deuterium oxide (99.9 atom % D D<sub>2</sub>O containing 0.05 wt. % TSP (3-(trimethylsilyl)-propionic-2,2,3,3-d<sub>4</sub> acid), sodium salt) was prepared and added to the sample in a volume ratio of 1:1, giving the analyzed sample a 10% volume of deuterium oxide. The NMR samples were prepared according to the protocol reported by Løhre et al. [53]. The stepwise preparation of the NMR samples is illustrated in Figs. 1 and 2.

### 2.4 NMR spectral acquisition

NMR acquisition was engaged by Topspin 4.0 and IconNMR on a 600 MHz Bruker AVANCE NEO NMR-spectrometer equipped with a QCI CryoProbe with four RF channels. NMR acquisition parameters in this study, using pre-saturated water suppression, are described elsewhere [53].

### 2.5 Identification and quantification

Compound identity was determined by using online databases and NMR spectra of standard compounds. The most abundant compounds in the effluent samples were selected for quantification. They comprised acetic acid (1.93 ppm), acetone (2.24 ppm), methanol (3.37 ppm), formic acid (8.47 ppm), 5-methylfurfural (2.43, 6.44, 7.51, and 9.33 ppm), 5-hydroxymethylfurfural (4.70, 6.68, 7.54, and 9.46 ppm), and furfural (6.77, 7.58, 7.93, and 9.50 ppm). The final 5-methylfurfural, 5-hydroxymethylfurfural, and furfural concentrations were calculated based on the average value of their corresponding signals. To ensure stable values for the NMR chemical shifts from one spectrum to another, the pH should be held constant. In this context, the buffer concentration can be increased (≤ 200 mM). However, the spectra acquired in this study did not display shift variations because of pH variations.

Integration regions for quantification were selected as the region around each signal out to but not including <sup>13</sup>C



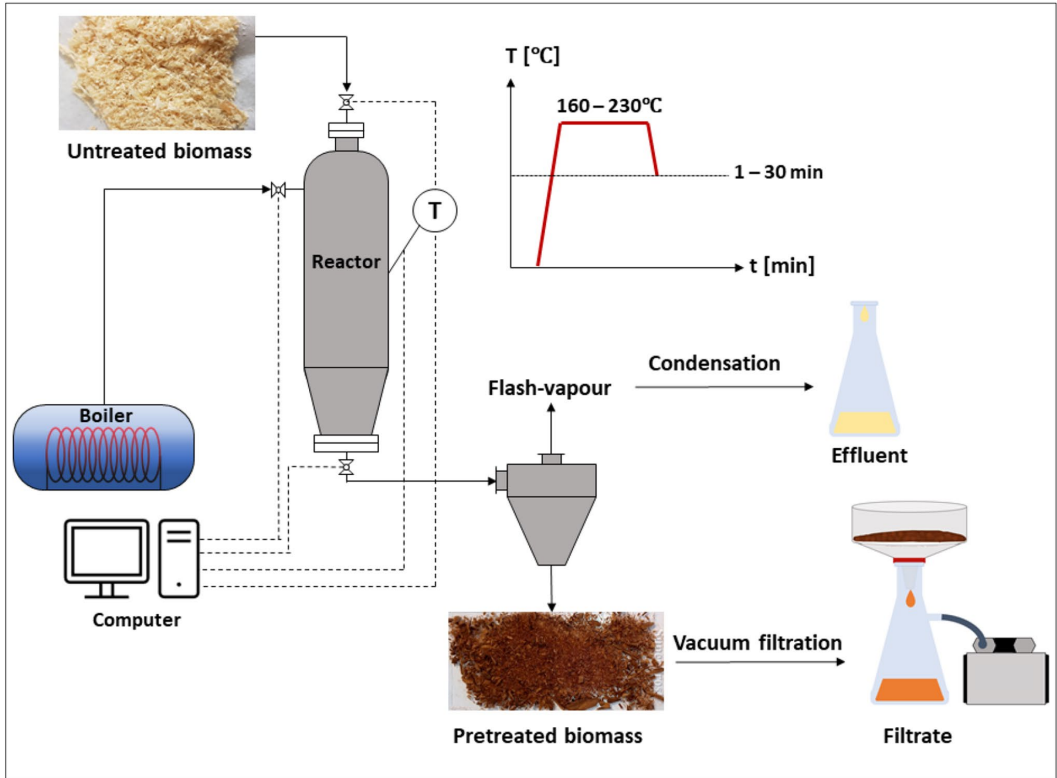


Fig. 1 Flow chart illustrating steam explosion unit at LUBIRC and the origin of the aqueous samples

satellite signals. All components were quantified relative to the internal standard ( $\text{DMSO}_2$ ) concentration. Quantification of components was performed by direct calculation from the resonance peak integrals, together with internal standard concentration, initial volumes of samples, molecular masses, and a normalization of the number of protons giving rise to the respective signals. NMR data were processed using a line broadening of 0.30 Hz, and signals were integrated (10–0 ppm) using TopSpin 4.0.7 software. Signals from labile protons, such as –OH and – $\text{NH}_2$ , were not considered in this study [53]. The concentration of each component [A], given as millimolar (mM), was calculated according to Eq. (1), where  $I_A$  is an integral of the component and  $NP_A$  is the number of protons giving rise to the signal.  $I_{\text{DMSO}_2}$  is the integral of the  $\text{DMSO}_2$  signal,  $NP_{\text{DMSO}_2}$  is the number of  $\text{DMSO}_2$  protons giving rise to the signal (6 protons), and  $[\text{DMSO}_2]$  is the concentration of  $\text{DMSO}_2$  in the NMR sample.

$$[A] = \frac{I_A \times NP_{\text{DMSO}_2} \times [\text{DMSO}_2]}{NP_A \times I_{\text{DMSO}_2}} \quad (1)$$

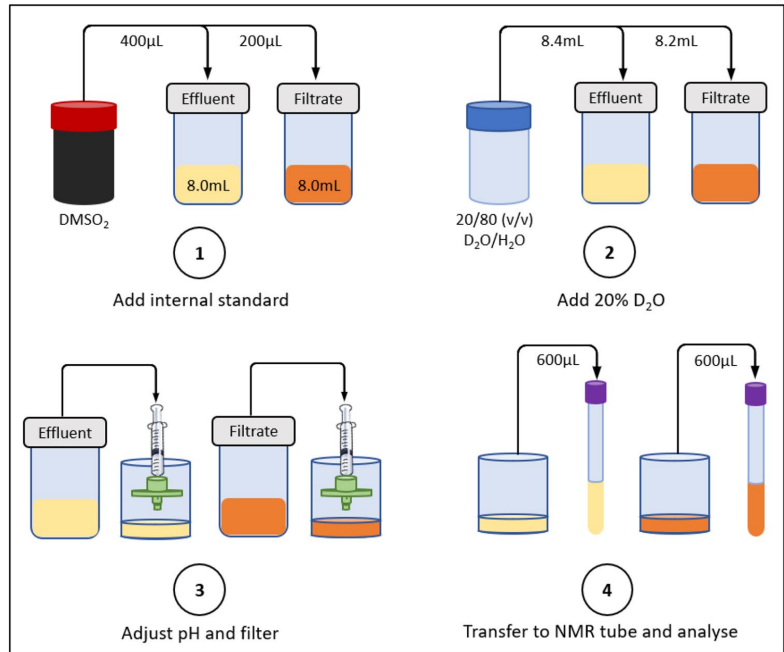
The yield of each component ( $m_A$ ), given as g of component/kg of dry input material, was calculated according to Eq. (2), where [A] is the concentration of each component measured according to Eq. (1) and  $M_A$  is the molar mass of each component.

$$m_A = \frac{[A] \times \text{total amount of aqueous sample} \times M_A}{\text{amount dry input material} \times 1000} \quad (2)$$

The recovery of biomass after the steam explosion process, given as (%), was calculated according to Eq. (3).

$$\text{Recovery of biomass (\%)} = \frac{\text{Amount of dry pretreated biomass (g)}}{\text{Amount of dry input biomass (g)}} \times 100 \quad (3)$$

**Fig. 2** Stepwise preparation of the qNMR samples including the addition of the internal standard to the effluent and filtrate samples



## 2.6 Reproducibility

In order to evaluate the precision related to the reproducibility of the sample workup and subsequent NMR quantification procedure, three repeated workups using three different effluent samples (*Warm flash tank* and *Low temp. + SO<sub>2</sub>* from Norway spruce and *Low temp. + SO<sub>2</sub>* from birch) and two different filtrate samples (*Reference 10 L* from Norway spruce and *Low temp. + SO<sub>2</sub>* from birch) were prepared. The parallel quantifications are noted as *p1*, *p2*, and *p3*.

## 3 Results and discussion

### 3.1 Samples

The quantitative results from 10 steam explosion processes are shown in Table 2. It was unfortunately not possible to measure the exact volume of produced process effluents during steam explosion due to sampling issues. Thus, the amounts of the effluent samples in Table 2 are

**Table 2** Quantitative results showing product output from the steam explosion experiments

Experiment name	Biomass type	Amount of wet steam-exploded biomass (g)	Dry matter (%)	Amount of dry steam-exploded biomass (g)	Recovery of biomass (%)	Estimated amount of effluent (mL)	Amount of filtrate (mL)
Reference 4 L	Norway spruce	3176	23.9	760	95.1	182	1220
Reference 10 L		3306	19.2	636	90.9	194	1575
Warm flash tank		3350	23.8	796	99.5	191	1110
Low temp		3209	23.7	762	95.2	47	710
Low temp. + SO <sub>2</sub>		3363	19.8	667	83.8	41	1300
Reference 4 L	Birch	3317	22.9	758	94.7	58	750
Reference 10 L		2691	23.5	631	90.1	64	1050
Warm flash tank		2635	29.7	782	97.8	60	635
Low temp		2925	27.3	799	99.8	46	370
Low temp. + SO <sub>2</sub>		3142	22.5	705	88.1	41	1150

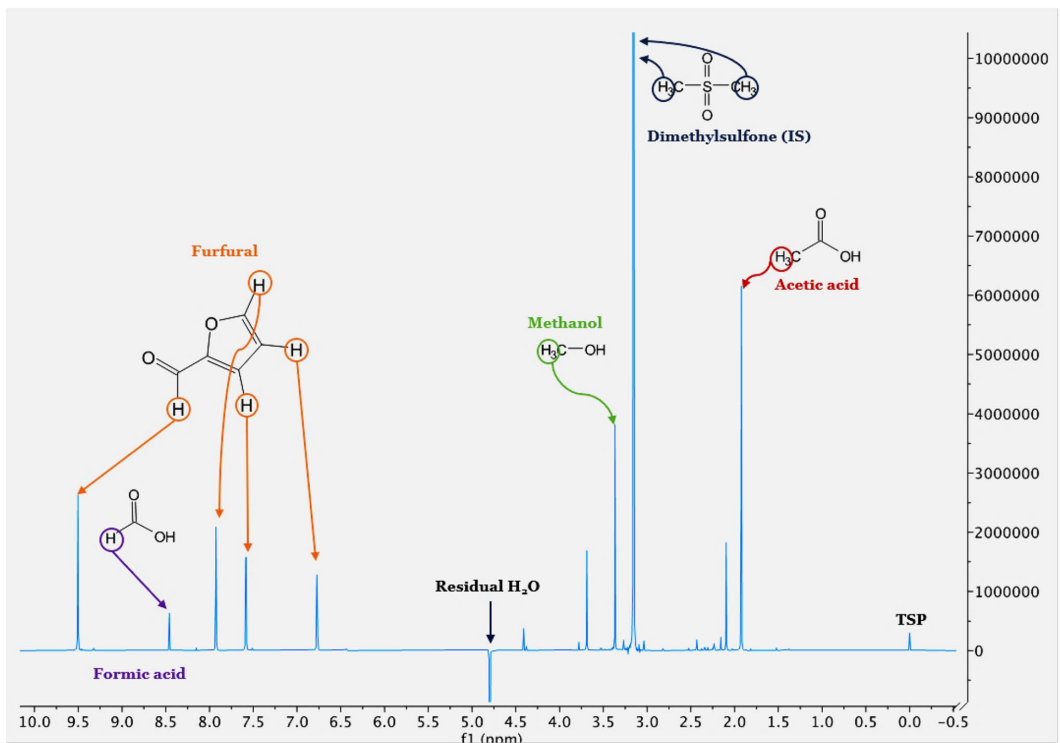
estimated volumes based on internal results obtained from comparable steam explosion processes. As shown in Table 2, for both feedstocks, a higher amount of process effluent is measured for experiment *Reference 10 L* compared to experiment *Reference 4 L*, which can be due to a higher volume of injected steam during the heating stage in experiment *Reference 10 L*. As expected, the lowest amounts of effluents are recovered from the experiments conducted at low residence temperatures and pressures. Furthermore, the lowest filtrate yields are recovered in the experiment *Low temp.* when using both feedstocks. The lowest yields of the exploded biomasses were obtained in the experiments performed using  $\text{SO}_2$  as an acid catalyst, which can be due to the more efficient hydrolysis of hemicelluloses under acidic conditions.

## 3.2 Effluent/condensate composition

### 3.2.1 Identification and quantification of organic components in the process effluents

A  $^1\text{H}$  spectrum for the effluent sample from experiment *Low temp.* +  $\text{SO}_2$  using Norway spruce as feedstock is depicted in Fig. 3, including proton signal identification. The peak at 4.7 ppm is a residual water signal from the pre-saturated water suppression acquisition. The most abundant compounds identified in the effluent samples are acetic acid, methanol, formic acid, 5-methylfurfural (5-MF), and furfural.  $^1\text{H}$  signals from 5-MF are very small and are therefore not marked in Fig. 3. The proton signals at 2.1 ppm and 3.7 ppm have not yet been identified, despite analysis of standards of relevant compounds such as 2-acetylfuran and diacetyl.

Signal integrals of the components and calculated concentrations, given as mM, are presented in Table S1 in the supplementary material. Concentration calculations are performed according to Eq. (1) given in Section 2.5



**Fig. 3** Proton spectrum for the process effluent recovered from experiment *Low temp.* +  $\text{SO}_2$  using Norway spruce as feedstock. Dimethyl sulfone ( $\text{DMSO}_2$ ) is used as an internal standard (IS)

and the internal standard (DMSO<sub>2</sub>) integral was standardized to 6.000 (corresponding to the number of protons in DMSO<sub>2</sub>).

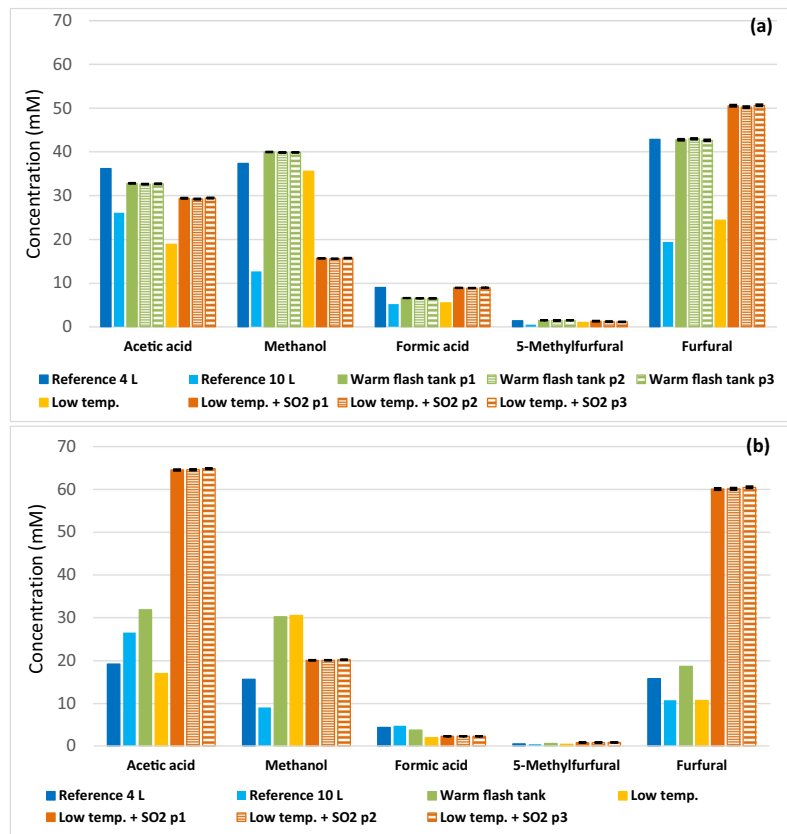
As shown in Fig. 4, acetic acid, methanol, and furfural are found in considerably higher concentrations than formic acid and 5-methylfurfural in the process effluents from both feedstocks. The concentration of all identified components, except methanol, was lowest in the process effluents from the experiment *Low temp.* A comparison of experiment *Reference 10 L* with experiment *Reference 4 L*, shown in Fig. 4a, which are performed at the same pretreatment temperature, indicates an increase in the concentration of the components with increased amounts of raw material. The highest concentrations of furfural were achieved in experiment *Low temp. + SO<sub>2</sub>* where SO<sub>2</sub>-gas has been used as an acid catalyst to improve the hydrolysis of the hemicelluloses. In order to quantify the relationship between the pretreatment parameters and the formation of the identified compounds, more experiments are required.

### 3.2.2 Yields on a feedstock basis

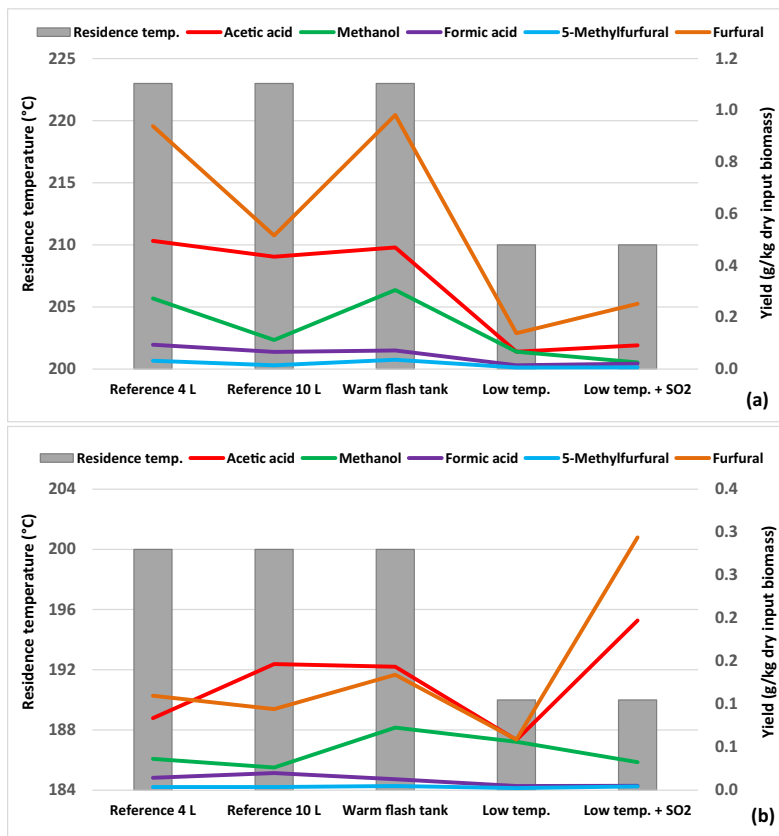
The relationship between the estimated yields of the major compounds in the process effluents on an input weight basis and the residence temperature of the steam explosion processes is shown in Fig. 5. Since the volumes of the effluents reported in this study are estimated values, the reported yields (given as g compound/kg dry input material) have a larger uncertainty than the measured concentrations. The results can still be used to compare the effect of different processing conditions. For the replicated samples, the average yield of each component is shown in Fig. 5.

As shown in Fig. 5, the yields of acetic acid and furfural decreased significantly as a function of decreased pretreatment temperature when the reactor scale and amount of input material were kept constant. The higher yields of acetic acid and furfural in the effluent samples performed at higher temperatures and pressures can be attributed to the more efficient release of acetic acid from acetyl groups in the biomass structure. Acetic acid catalyzes hydrolytic reactions

**Fig. 4** Concentration of the identified components in the process effluents from the steam explosion of Norway spruce (a) and birch (b)



**Fig. 5** Schematic overview of the relationship between the yield (g/kg dry input biomass) of the components in the effluent samples from the steam explosion of Norway spruce (a) and birch (b) and the residence temperature (°C)



in the wood polymers by more efficient conversion of the dissolved hemicelluloses in the aqueous fractions to furan derivatives, including furfural (autohydrolysis). A maximum in the approximate yield of acetic acid has been found to be 0.5 g/kg dry input biomass in the effluent samples produced from the experiments *Reference 4 L* and *Warm flash tank* using Norway spruce as feedstock. The higher amount of acetic acid found in the effluent samples from Norway spruce does not reflect the fact that softwoods have a lower content of acetyl groups in the hemicellulose part, making softwoods generally less susceptible to pretreatment using steam explosion than hardwoods.

As previously described and shown in Fig. 5a, the yield of all components is considerably higher in the effluent sample from experiment *Reference 4 L* compared to the effluent sample from experiment *Reference 10 L*. This was expected due to higher substrate loading in the experiment *Reference 4 L*. In addition, the injected steam volume used in the heating stage was also higher in the experiment *Reference 10 L*, thereby diluting the final product stream.

Since no experiments in this work give a direct comparison between the composition of an effluent sample from a 4 L scale and an effluent sample from a 10 L scale, the role of the reactor scale on the concentration/yield of the components remains unresolved. However, the yield of all the components in the effluent samples from the experiments *Warm flash tank* and *Reference 4 L* that are conducted at the same scale under the same reaction conditions have shown to be quite similar (see Fig. 5a).

As shown in Fig. 5b, the effluent sample obtained from experiment *Reference 4 L* contains higher amounts of furfural, 5-MF, and methanol in comparison with experiment *Reference 10 L*. In addition, the yield of all components is considerably lower in the effluent sample from experiment *Reference 4 L* using birch as feedstock compared to the effluent sample from experiment *Reference 4 L* using Norway spruce as feedstock. Moreover, the yield of acetic acid and furfural is highest in the effluent sample from the experiment *Low temp. + SO<sub>2</sub>* when using birch as feedstock.

The higher yield of furfural in the process effluents produced from the steam explosion of Norway spruce compared to the effluent samples from the steam explosion of birch was expected due to more severe steam explosion conditions. Moreover, a comparison of experiment *Low temp.* with experiment *Low temp. + SO<sub>2</sub>* shows that the addition of SO<sub>2</sub> gas has significantly increased the yields of furfural, indicating, as expected, more efficient hydrolysis and subsequent dehydration of hemicelluloses under acidic conditions. The lowest furfural yields were found in the *Low temp.* experiments. A possible explanation for this could be that these experiments were conducted using lower temperatures and pressures, thus resulting in a less efficient hydrolysis of the hemicellulose and ultimately leading to poor furfural yields. However, the noticeably high furfural yield in the effluent samples from the experiments *Reference 4 L* and *Warm flash tank*, between 0.9 and 1.0 g/kg dry input biomass, makes the recovery of furfural from the effluent samples very relevant and is considered to have a good economic potential.

The optimal utilization of hemicellulose in lignocellulosic biomass for furfural production should include selective dissolution of hemicellulose from raw biomass and selective formation of furfural from dissolved hemicellulose derivatives. Based on the results obtained in this work, the production of furfural with high yields and selectivity from the hemicellulose fraction of woody biomass is challenging but should be achievable. As mentioned in Section 1, this study is in the preliminary stage

for implementation in a full-scale commercial biorefinery in Eastern Norway. In preliminary investigations of distillation for the recovery of furfural from the process effluents (unpublished results), furfural fractions with quite high purity containing only trace amounts of impurities, mainly consisting of furanic compounds and water, have been recovered.

### 3.2.3 Analytical precision and accuracy for process effluents

Furfural and 5-MF contain 4 <sup>1</sup>H signals each (see Table S1). The proton signal at 7.51 ppm was excluded from the calculation of the 5-MF concentration average in the effluent samples due to a significantly higher peak integral compared to the integrals from the other three 5-MF signals. The measured concentration averages of furfural and 5-MF based on 4 and 3 <sup>1</sup>H signals, respectively, resulted in standard deviations of <4% and <9%, giving a  $\sigma < 2.1$  mM of furfural and  $\sigma < 0.1$  mM of 5-MF concentrations.

As shown in Table 3, the preparative laboratory procedure combined with qNMR spectroscopy provides excellent reproducibility for three repeated sample workups with standard deviations of <0.5% of each compound average, except 5-MF with a standard deviation of <7%, which can be due to uncertainties associated with the integration of the weak 5-MF proton signals.

**Table 3** Quantification data from three workup replicates of effluent samples from experiments *Warm flash tank* and *Low temp. + SO<sub>2</sub>* from Norway spruce, and *Low temp. + SO<sub>2</sub>* from birch

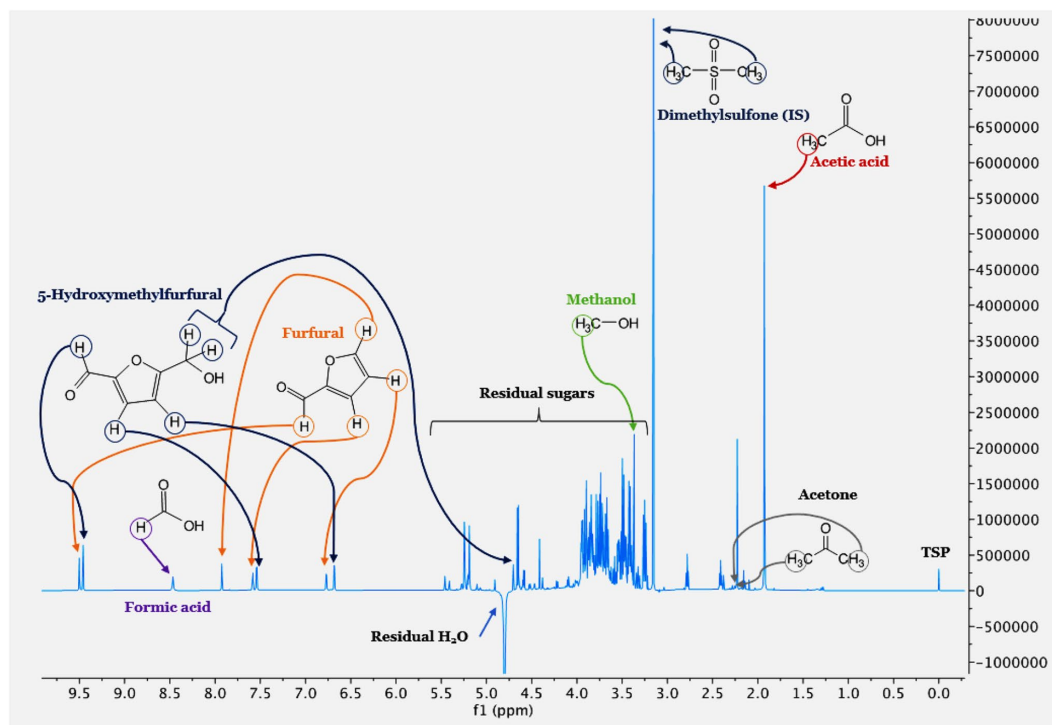
Biomass type	Experiment name	Concentration (mM)				
		Acetic acid	Methanol	Formic acid	5-MF	Furfural
Norway spruce	<b>Warm flash tank p1</b>	32.81	40.01	6.58	1.38	42.80
	<b>Warm flash tank p2</b>	32.63	39.88	6.53	1.37	43.01
	<b>Warm flash tank p3</b>	32.73	39.92	6.51	1.38	42.66
	<b>Average</b>	32.72	39.94	6.54	1.38	42.83
	<b><math>\sigma</math></b>	0.09	0.07	0.03	0.01	0.18
	<b>Standard deviation (%)</b>	0.28	0.18	0.46	0.72	0.42
	<b>Low temp. + SO<sub>2</sub> p1</b>	29.39	15.66	8.92	1.16	50.58
	<b>Low temp. + SO<sub>2</sub> p2</b>	29.22	15.57	8.87	1.02	50.26
	<b>Low temp. + SO<sub>2</sub> p3</b>	29.45	15.70	8.94	1.07	50.67
	<b>Average</b>	29.35	15.64	8.91	1.08	50.50
	<b><math>\sigma</math></b>	0.12	0.07	0.04	0.07	0.21
	<b>Standard deviation (%)</b>	0.41	0.45	0.45	6.48	0.42
Birch	<b>Low temp. + SO<sub>2</sub> p1</b>	64.50	20.00	2.24	0.78	60.03
	<b>Low temp. + SO<sub>2</sub> p2</b>	64.55	20.01	2.25	0.79	60.08
	<b>Low temp. + SO<sub>2</sub> p3</b>	64.80	20.14	2.26	0.81	60.45
	<b>Average</b>	64.62	20.05	2.25	0.79	60.19
	<b><math>\sigma</math></b>	0.16	0.08	0.01	0.02	0.23
	<b>Standard deviation (%)</b>	0.25	0.40	0.44	2.53	0.38

### 3.3 Filtrate composition

#### 3.3.1 Identification and quantification of organic components in the process filtrates

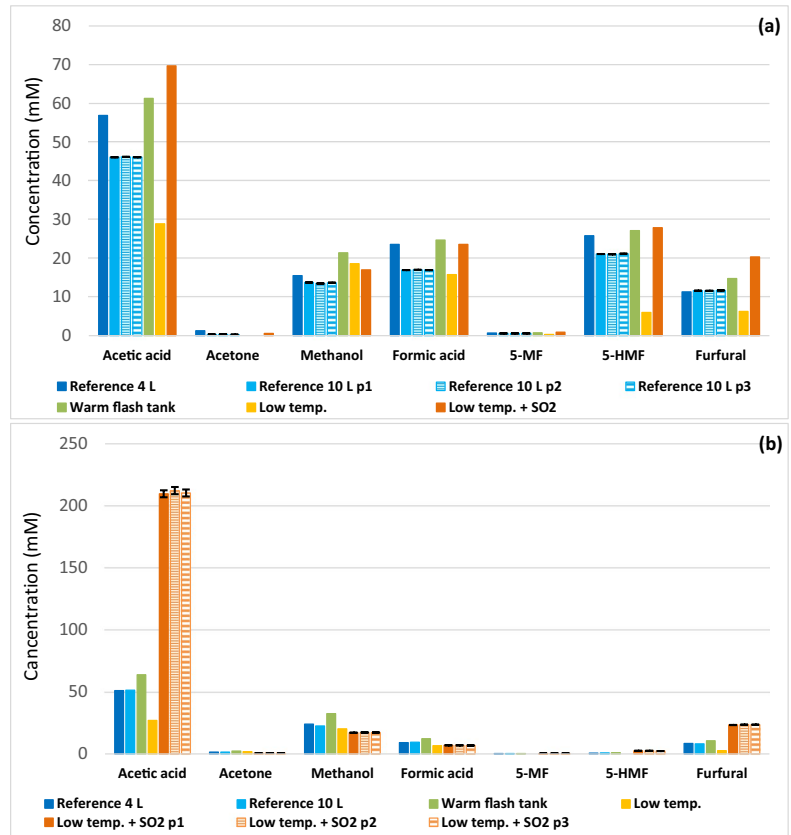
The chemical composition of the dissolved organic compounds in the filtrate samples is different from the effluent samples as the less volatile components adsorbed to the solid residue are collected in addition to the remaining volatiles. A  $^1\text{H}$  spectrum for the filtrate sample from experiment *Low temp. + SO<sub>2</sub>* using Norway spruce as feedstock is depicted in Fig. 6, including proton signal identification. The most abundant compounds identified in the filtrate samples are acetic acid, acetone, methanol, formic acid, 5-methylfurfural (5-MF), 5-hydroxymethylfurfural (5-HMF), and furfural. 5-HMF and acetone are examples of the additional components relative to the effluent. Signals from sugar residues and other minor peaks were not considered in this study. Integrals of each component and calculated concentrations (mM) are presented in Table S2 in the supplementary material.

As depicted in Fig. 7a, the concentration of all the components in the filtrate samples from the experiments performed using Norway spruce as feedstock was lowest in the experiment conducted at a low temperature, except for the concentration of methanol. In general, the concentration of all components increased with increasing pretreatment severity. Additionally, a comparison of experiment *Low temp.* with experiment *Low temp. + SO<sub>2</sub>*, which were carried out at the same temperature (210 °C), indicates a significantly higher concentration of all components (except methanol) in the filtrate samples from the experiment conducted using SO<sub>2</sub>-gas as an acid catalyst in the process, which concur with previously discussed results. Moreover, the concentration of all the components has shown to be lower in the filtrate sample from experiment *Reference 10 L* compared to the filtrate sample from experiment *Reference 4 L*, which was expected due to higher substrate loading in the experiment *Reference 4 L*, as well as higher volume of the produced filtrate in the experiment *Reference 10 L* which dilutes the final product stream.



**Fig. 6** Proton spectrum for the process filtrate from experiment *Low temp. + SO<sub>2</sub>* using Norway spruce as feedstock. Dimethyl sulfone (DMSO<sub>2</sub>) is used as an internal standard (IS)

**Fig. 7** Concentration of the identified components in the process filtrates from steam explosion of Norway spruce (a) and birch (b)



Based on the results shown in Fig. 7b, variations in the concentration of the organic components in the filtrate samples from experiments using birch as feedstock have shown to be proportional to variations in the residence temperature, except for the results obtained from experiment *Low temp. + SO<sub>2</sub>*. Thus, the concentration of the components has decreased as a function of decreasing pretreatment temperature but remains almost unchanged in the experiments conducted at the same residence temperature. When comparing experiment *Reference 10 L* with experiment *Reference 4 L*, both of which are performed at the same pretreatment temperature, no significant increase in the concentration of the components as a function of increased substrate loading is observed. This can most probably be due to a smaller amount of filtrate generated in experiment *Reference 4 L*, resulting in smaller amounts of each compound in total.

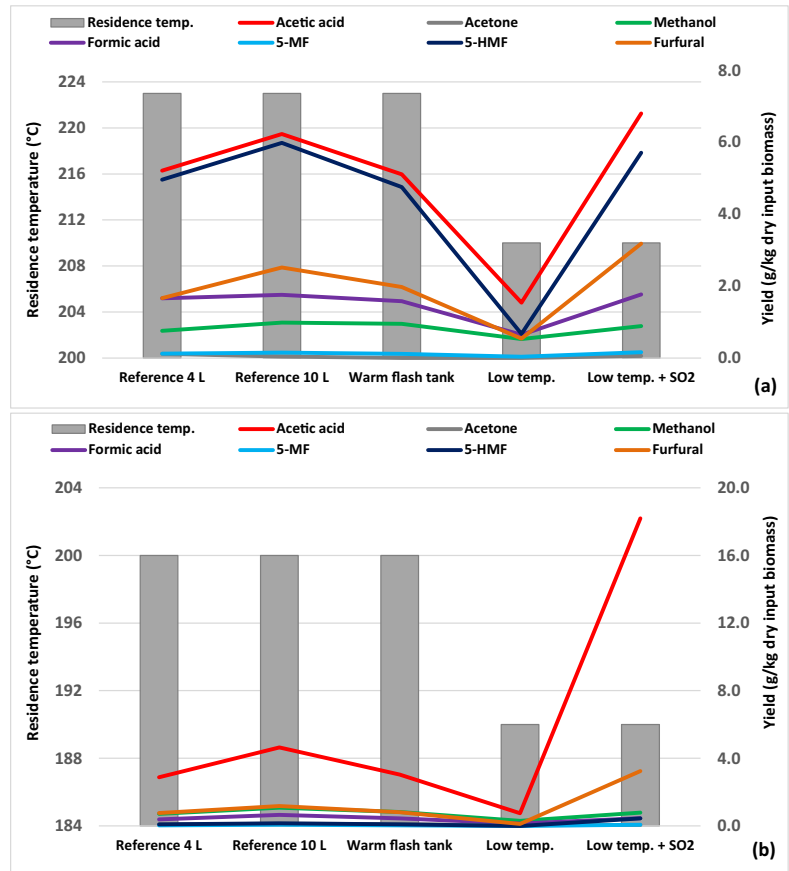
### 3.3.2 Yields on a feedstock basis

The relationship between the calculated yields of the major compounds in the process filtrates on an input weight basis and the residence temperature of the steam explosion processes is shown in Fig. 8. For the replicated samples, the average yield of each component is shown in Fig. 8.

As depicted in Fig. 8a, variations in the yield of the components in the different filtrate samples follow a similar trend. Acetic acid and 5-HMF have considerably higher yields than furfural, methanol, and formic acid. Acetone and 5-MF have the lowest yields in the process filtrates from the steam explosion of Norway spruce. The low yield of acetic acid, 5-HMF, and furfural in the filtrate sample was performed at low temperature and pressure, experiment *Low temp.* confirms less efficient depolymerization of the biomass at low temperatures, resulting in lower cleavage of



**Fig. 8** Schematic overview of the relationship between the yield of the components in the filtrate samples from steam explosion of Norway spruce (a) and birch (b) and the residence temperature (°C)



acetic acid from acetyl groups in the native biomass structure and thus less efficient hydrolysis and subsequent dehydration of hemicellulose units to furanic derivatives. The yield of acetic acid has been found to be quite similar, between 5.1 and 5.2 g/kg dry input biomass, in the filtrate samples from experiment *Reference 4 L* and *Warm flash tank*, using Norway spruce as feedstock. However, the highest acetic acid yield, 18.1–18.3 g/kg dry input biomass, was obtained in the filtrate sample from the experiment *Low temp. + SO<sub>2</sub>*, when birch was used as raw material. Moreover, the results indicated that a major part of the produced acetic acid remained adsorbed on the steam-exploded biomass, which makes an additional washing procedure after the steam explosion process worth considering for maximizing the recovery of acetic acid.

As shown in Fig. 8, the yield of 5-HMF is considerably higher in the filtrate samples from the steam-exploded Norway spruce compared to the filtrate samples from the steam explosion of birch, which is due to the high content of

galactoglucomanan in the softwood hemicellulose. A comparison of the yield of 5-HMF based on pretreatment conditions shows that the highest 5-HMF yields were obtained in the filtrate samples from the experiments *Reference 10 L* and *Low temp. + SO<sub>2</sub>*. Moreover, significant differences were observed between the composition of the filtrate sample from experiment *Reference 4 L* compared to the composition of the filtrate sample from experiment *Reference 10 L* using both feedstocks. The higher yields of the components in the filtrates from experiment *Reference 10 L* compared to experiment *Reference 4 L* indicate that higher amounts of the volatiles remain in the solid residues from experiment *Reference 10 L* most probably as a result of less efficient removal of volatiles during the pressure release stage at 10 L scale.

However, significantly higher yields of formic acid were observed for the process filtrates compared to the process effluents. Formic acid can be produced both from the elimination of formyl groups in the hemicellulose units and from the rehydration of 5-HMF in the aqueous reaction media.

5-HMF can undergo a rehydration process and decompose to formic acid and levulinic acid. However, the absence of levulinic acid in the aqueous product streams can most probably be related to secondary reactions including the formation of humins. The presence of sugar residues in the filtrate samples indicates incomplete decomposition of the carbohydrate fractions of the biomasses when using the investigated steam explosion conditions. However, the low standard deviations (<2%) measured for each identified component based on three repeated sample preparations of filtrate samples from the experiments *Reference 10 L* and *Low temp. + SO<sub>2</sub>*, again confirms the outstanding reproducibility of the reported sample preparation technique as well as the qNMR spectroscopic method used.

The results obtained in this study indicated that the filtrate samples obtained from steam explosion contained significant amounts of valuable platform chemicals that can be recovered for commercial use. Acetic acid, 5-HMF, furfural, and formic acid are the components with the highest yields in the filtrate samples from the steam explosion of Norway spruce, respectively, and acetic acid, furfural, and methanol are the components with the highest yields in the filtrate samples from the steam explosion of birch. The yields are sufficient to confirm that washing of steam-exploded biomass is worth performing for maximizing economic outputs from this type of biomass. On the other hand, washing steam-exploded biomass could perhaps influence the pelletizing properties of the biomass. Hence, additional analyses are required to ensure that physicochemical pellet properties like calorific value, impact and abrasion resistance, etc., are maintained. All in all, more research is needed to get a better understanding of the relationship between the pretreatment conditions and the generation of the identified organic components.

### 3.3.3 Analytical precision and accuracy for process filtrates

The 5-HMF signal at 4.70 ppm was excluded from the quantification due to the proximity of the methylene resonance to the H<sub>2</sub>O solvent peak. Spillover from the pre-saturated H<sub>2</sub>O resonance to the CH<sub>2</sub> resonance causes saturation of the methylene signal, consistently reducing its relative intensity, making it inaccurate for quantitative purposes. This is a good example of how the dynamic range problem can affect signal intensity when working with aqueous samples, as big solvent peaks can influence the signal intensity of adjacent signals [54]. In addition, the 5-MF <sup>1</sup>H signal at 9.33 was excluded from the calculation of the 5-MF concentration average in the filtrate samples due to deviating peak integral compared to the other 5-MF peak integrals. In addition, the 5-HMF <sup>1</sup>H signal at 9.46 ppm has also been excluded from the calculation of 5-HMF concentration averages in the filtrate samples from birch due to significantly lower peak integral relative to 5-HMF peak integrals at 7.54 and 6.68 ppm. Uncertainties

related to the integration values of 5-MF and 5-HMF can be associated with the relatively low concentrations of these components in the aqueous samples studied in this work. However, this illustrates the flexibility of the qNMR quantification, as the normalization of the peak areas to the specific protons providing the signal makes the exclusion of the more variable signal unproblematic. The measured concentration averages of furfural, 5-MF, and 5-HMF in the process filtrates based on 4, 3, and 2 <sup>1</sup>H signals, respectively, resulted in standard deviations of <4%, <34%, and <10%. The high standard deviations for the 5-MF and 5-HMF averages are caused by the low concentration of these compounds, which are lower than the quantification limit (1 mM) of the NMR instrument.

As shown in Table 4, the three repeated sample workups of two different filtrate samples resulted in standard deviations of <2% of each compound average, which again confirms the excellent reproducibility of the quantitative procedure/method reported here. The only exception was 5-MF with a standard deviation of <7%, which can be associated with the uncertainty related to the integration of the weak proton signals of 5-MF.

## 3.4 Implications of results for a steam explosion-based biorefinery

By applying the results from this research to real-world biorefineries and using estimated market values of the identified value-added products, it is possible to estimate the potential revenue each product can give to a biorefinery. A basic commercial-size steam explosion biorefinery, as being presently demonstrated in Norway [55], has the potential to produce upwards of 40,000 tons or 4 × 10<sup>7</sup> L of effluent each year, from which furfural and 5-MF are the major target products. The co-produced acetic and formic acid can be processed by bacteria to generate methane gas that can be burned with the low-boiling compounds, typically methanol, to improve the energy efficiency of the refinery.

Following the results from Section 3.2, the yearly production can be estimated to 204.2 tons of furfural (95% purity) and 5.2 tons of 5-MF, obtained from the treatment of Norway spruce using the *Low temp. + SO<sub>2</sub>* conditions, while approximately 243.4 tons of furfural (95% purity) and 3.6 tons 5-MF can be obtained from birch using the same conditions. For reaction conditions without acid catalysis, the highest concentrations are obtained from the *Warm flash tank* and *Reference 4 L* conditions with Norway spruce and give 173.5 tons of furfural (95% purity) and 6.0 tons of 5-MF, while similar conditions for birch are not worth estimating as the furfural and 5-MF concentrations are too low to have any commercial value.

If we assume that a commercial biorefinery can process 130,000 tons of biomass per annum and that from

**Table 4** Quantification data from three workup replicates of filtrate samples from experiment *Reference 10 L* and *Low temp. + SO<sub>2</sub>* from Norway spruce and birch, respectively

Biomass type	Experiment name	Concentration (mM)						
		Acetic acid	Acetone	Methanol	Formic acid	5-MF	5-HMF	Furfural
Norway spruce	<b>Reference 10 L p1</b>	46.10	0.30	13.75	16.94	0.61	21.09	11.62
	<b>Reference 10 L p2</b>	46.18	0.31	13.46	17.02	0.60	21.03	11.60
	<b>Reference 10 L p3</b>	46.11	0.30	13.67	16.94	0.62	21.17	11.69
	<b>Average</b>	46.13	0.30	13.63	16.97	0.61	21.10	11.64
	<b>σ</b>	0.04	0.004	0.15	0.05	0.01	0.07	0.05
	<b>Standard deviation (%)</b>	0.09	1.33	1.10	0.29	1.64	0.33	0.43
Birch	<b>Low temp. + SO<sub>2</sub> p1</b>	209.68	0.63	17.10	7.00	0.43	2.51	23.32
	<b>Low temp. + SO<sub>2</sub> p2</b>	212.25	0.62	17.30	7.00	0.43	2.52	23.59
	<b>Low temp. + SO<sub>2</sub> p3</b>	210.41	0.63	17.30	6.80	0.39	2.49	23.59
	<b>Average</b>	210.78	0.63	17.23	6.93	0.42	2.51	23.50
	<b>σ</b>	1.32	0.01	0.12	0.12	0.03	0.02	0.16
	<b>Standard deviation (%)</b>	0.63	1.59	0.70	1.73	7.14	0.80	0.68

every 3 kg of treated biomass can produce about 1 L of filtrate, the following amounts of chemicals can be extracted: 89.4 tons of furfural, 152.5 tons of 5-HMF, and 4.3 tons of 5-MF from Norway spruce and 103.1 tons of furfural, 13.9 tons of 5-HMF, and 2.2 tons of 5-MF from birch with *Low temp. + SO<sub>2</sub>*. As for the best non-catalyzed alternative, *Warm flash tank* with Norway spruce, 64.8 tons of furfural, 148.6 tons of 5-HMF, and 3.5 tons of 5-MF can be extracted annually.

Under the assumption that market prices for these compounds are stable, one can estimate the additional value of the biorefinery. From a refinery using the *Low temp. + SO<sub>2</sub>* condition with birch as feedstock, an estimated 866,000 \$/year from furfural, 64,000 \$/year from 5-HMF, and 235,000 \$/year from 5-MF can be added to the annual revenue of the biorefinery. Similarly, *Low temp. + SO<sub>2</sub>* condition with Norway spruce can add 735,000 \$/year from furfural, 702,000 \$/year from 5-HMF, and 391,000 from 5-MF. For the *Warm flash tank* conditions, on the other hand, potential profits are somewhat lower with estimated earnings from furfural, 5-HMF, and 5-MF of 596,000 \$/year, 684,000 \$/year, and 388,000 \$/year, respectively.

These results clearly show that extraction of furfural, 5-HMF, and 5-MF from effluents and filtrates has the potential to drastically increase the profit margins of modern biorefineries. It also shows that more value can be extracted from Norway spruce than from birch and that depending on the cost, using SO<sub>2</sub> as an acid catalyst may not increase the revenue from Norway spruce, but is indicated to be able to extract additional value from birch.

## 4 Conclusion

The results presented in this paper show that the aqueous product streams generated from the steam explosion of woody biomass contain platform chemicals of high value that are suitable for recovery for commercial use. The most abundant compounds identified in the process effluents were acetic acid, methanol, formic acid, 5-methylfurfural (5-MF), and furfural, while the most abundant components identified in process filtrates were acetic acid, acetone, methanol, formic acid, 5-methylfurfural (5-MF), 5-hydroxymethylfurfural (5-HMF), and furfural. These platform chemicals can be recovered and utilized in the production of other value-added chemicals, medicines, biofuels, polymers, bioplastics, additives, etc. In addition, filtrate samples contain considerable amounts of sugar residues that were not addressed in this study.

Acetic acid (0.1–0.50 g/kg dry input biomass) and furfural (0.1–1.0 g/kg dry input biomass) were found to be the components with the highest yields in the process effluents. The use of SO<sub>2</sub>-gas in addition to steam in the steam explosion processes conducted at low residence temperatures led to more efficient hydrolysis of hemicellulose units present in the biomass, resulting in a higher concentration (mM) and yield (g/kg dry input biomass) of furfural in the process effluents. However, the problems associated with the use of SO<sub>2</sub> do not make the pretreatment beneficial in a full-scale commercial biorefinery. Additionally, with respect to the investigated parameters, birch has proven to have an advantage since it required lower pretreatment

temperature with regard to furfural production. Furthermore, results obtained from process filtrates indicated that acetic acid (0.8–18.3 g/kg dry input biomass), 5-HMF (0.1–6.0 g/kg dry input biomass), furfural (0.1–3.3 g/kg dry input biomass), formic acid (0.1–1.8 g/kg dry input biomass), and methanol (0.3–1.1 g/kg dry input biomass) were the components with highest concentrations in the process filtrates. The highest yield of these components was achieved in the experiments performed using SO<sub>2</sub>-gas as an acid catalyst. The yield of 5-HMF was considerably higher in the filtrate samples from the steam-exploded Norway spruce compared to filtrate samples from the steam-exploded birch, which is consistent with the high content of hexoses in the softwood hemicellulose. However, the yield of furfural in the filtrate sample from the experiment *Low temp. + SO<sub>2</sub>* from both feedstocks was quite similar.

In order to approach optimal conditions for this biorefinery concept, which aims for simultaneous production of high-quality brown pellets (Arbaco pellets) and value-added platform chemicals recovered from the process effluents and filtrates, further in-depth investigations are required. The furfural and 5-HMF recovery must be balanced against the physicochemical properties of the pellets achieved. The result presented in this study shows that the steam explosion conditions strongly influence the amounts of furfural and 5-HMF produced in the pre-treatment step. The results also suggest that it is possible to drastically increase the concentrations of the targeted compounds by making only moderate adjustments to the process conditions.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s13399-022-02712-w>.

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**Author contribution** The experimental work was carried out by Solmaz Ghoreishi and Dag Helge Hermundsgård. The writing was mainly carried out by Solmaz Ghoreishi in collaboration with Camilla Løhre and Tanja Barth. Joakim Lindgaard Molnes has contributed with graphics and text revision. Mihaela Tanase-Opedal participated in the planning of steam explosion pretreatment in Lund and worked with the raw materials and the steam-exploded biomass. Rune Brusletto participated in the development of the concept and evaluation of the results reported in the manuscript.

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## Declarations

**Conflict of interest** The authors declare no competing interest.

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# Paper II

Steam explosion of lignocellulosic residues for co-production of value-added chemicals and high-quality pellets

**Authors:**

Mihaela Tanase-Opedal, Solmaz Ghoreishi, Dag H. Hermundsgård, Tanja Barth, Størker T. Moe and Rune Brusletto

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# Steam explosion of lignocellulosic residues for co-production of value-added chemicals and high-quality pellets

Mihaela Tanase-Opedal<sup>a,\*</sup>, Solmaz Ghoreishi<sup>b</sup>, Dag Helge Hermundsgård<sup>b</sup>, Tanja Barth<sup>b</sup>, Størker T. Moe<sup>c</sup>, Rune Brusletto<sup>d</sup>

<sup>a</sup> RISE PFI AS, Høgskoleringen 6B, N-7491, Trondheim, Norway

<sup>b</sup> University of Bergen, Department of Chemistry, Allegaten 41, N-5007, Bergen, Norway

<sup>c</sup> Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering, Sem Sælandsvei 4, N-7491, Trondheim, Norway

<sup>d</sup> Arbaftame AS, Henrik Ibsens Gate 90, N-0230, Oslo, Norway

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## ABSTRACT

The demand of pellets as energy carrier and the competitiveness of wood biomass are the drivers for finding alternative raw materials for production of pellets. The aim of this study was to investigate the steam explosion of lignocellulosic residues such as, straw, sawdust birch, sawdust spruce, GROT (mixture of 30 % bark and 70 % industrial chips), and their mix to co-production of value-added chemicals and high-quality pellets. The raw materials were first impregnated with water/acetic acid prior to steam explosion process, while leaching and washing of steam exploded biomass was used to reduce the ash content. The value-added chemicals were extracted with MIBK, and a gas chromatography was used to determine which value-added chemicals are present in the MIBK filtrates after extraction of the steam exploded biomass. Thermogravimetric analysis and Fourier transform infrared spectroscopy, elemental analysis, calorific values, compression strength and density were used to assess and compare the quality of steam exploded biomass and pellets quality. The results from the extraction experiments shows that furfural, HMF, vanillin, syringaldehyde and coniferaldehyde are the most value-added chemicals extracted from lignocellulosic residues where higher yield of the valuable chemicals was obtained when the biomass was presoaked in acetic acid. The ash content was reduced by 83 % for straw material by washing and leaching of steam exploded straw material when the biomass was presoaked in acetic acid. High quality pellets with high calorific value (20 MJ/kg), high compression strength (228 kN/m), high density (1300 kg/m<sup>3</sup>) and low ash content (0,06 %) were produced from sawdust spruce and GROT:Spruce mix used in our study. Based on our results, we can therefore suggest that steam explosion process of lignocellulosic residues improves the quality of the biomass to pellets production and at the same time open for the possibility to produce value-added chemicals.

## 1. Introduction

Lignocellulosic biomass for co-production of high value chemicals and solid fuel in an integrated biorefinery concept plays an important role towards a more sustainable society. The increase in energy and oil prices, and taxes on carbon dioxide emissions from fossil fuels, results in the necessity of finding sustainable energy sources to combat climate change. As such wood pellets based on cutter shavings and sawdust have been intensively used as an energy source during the last decade. With a continuously increasing demand for pellets the supply of sawdust will be insufficient. Therefore, the mobilization and deployment of low-grade

materials, such as residues from forestry and agricultural materials, are promising materials to be explored for pellet production [1,2].

The competition on wood biomass is the driving force for introducing low value residual raw materials from agriculture and forestry which can contribute to the volume and economy. The large volume availability of forest residues after logging and thinning, such as bark, branches and tops but also residues from agricultural could potentially be a sustainable low carbon fuel [3]. Sawdust is defined as a by-product from sawmill industry [4], where per today is used as an energy source internally in the mill or it can be sold as raw material for briquetting/pellets. As such, sawdust represents a potential renewable

\* Corresponding author.

E-mail address: [mihaela.tanase@rise-pfi.no](mailto:mihaela.tanase@rise-pfi.no) (M. Tanase-Opedal).

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feedstock for production of solid fuel and chemicals while reducing the environmental impact of sawdust waste from sawmill industry. Agricultural feedstocks are abundant lignocellulosic biomass with a similar chemical composition to wood biomass, which alone or mix of them could be used as a source of biochemicals and solid fuel [5–8]. However, when agricultural biomass resources are used as a source of energy carrier, there are some bottlenecks to be taken in consideration such as, handling and transport, high ash and moisture content [9–13]. Generally, ash related issues include slagging, agglomeration, corrosion, etc. To reduce the ash content in the pretreated biomass is often necessary to introduce a washing step. Washing and leaching of agricultural biomass depends on several properties [14–16]. Literature studies indicates a reduction of the ash content and subsequently an increase in combustion quality of wood pellets after washing and densification of the material [10,17–20]. As such, a mix of high lignin content wood material and agricultural rest material have been described in the literature as a promising mix material to produce pellets with high strength and durability; high combustion rate and low ash content [11,12,21,22].

Due to the recalcitrance of the residual wood material, a pretreatment method is needed to disrupt the lignocellulosic structure. The selection of the pretreatment method should be aligned to the type and structure of the feedstock and the desired products. As such, steam explosion is described in the literature as a promising pretreatment method of lignocellulosic biomass due to its advantages [23–38]. The pretreatment effectiveness of steam explosion process of lignocellulosic biomass depends on the type of biomass and process variables [33]. Acid catalyzed steam explosion process can be used to increase the kinetic of hemicellulose solubilization at temperatures below 200 °C and still maintaining the concentration of inhibitory compounds at a minimum level [39]. Steam explosion with/without acid catalyst has been intensively studied in the last years. The role of the catalyzed in the steam explosion process is to increase the recovery of soluble sugars [40–42]. The optimization of the steam explosion process conditions, such as temperature, time and catalyst are necessary to obtain high sugar yields and high-quality pellets [43]. The highest yield of sugars was obtained by using lower dosage of sulfuric acid in one-stage steam pretreatment process [44].

The steam exploded lignocellulosic biomass has been used to produce pellets, demonstrating very good results regarding high density and energy content, bonding properties (pellet and particle strength), bulk density and well as improving greatly the homogeneity and hydrophobicity of the pellets [45–47,48,49]. In addition, steam exploded pellets were found to have enhanced storage and handling properties (less dust and mechanically durable pellets) [48–51]. The quality of the pellets depends on the process and feedstocks variables [10], chemical composition of the lignocellulosic biomass [2] and moisture content of the pretreated biomass, as the water content contribute to the binding properties [52–54]. However, the moisture content must be balance since a very high moisture content will have a negative effect on pellets mechanical properties and density [52,55,56]. Greinert et al. [57] observed that an increase in the humidity of pellets resulted in a decrease in the average calorific value of biomass. As such, large scale implementation of wood pellets as a solid fuel represents a change in the energy system that will have both economic and environmental consequences.

This work aims to provide insights in the use of a steam explosion pretreatment process of low value and abundant, high ash residual lignocellulosic materials to co-produce value-added chemicals and high-quality pellets. This contributes to broaden the limited knowledge of such processing by further generating data on the effect of presoaking of lignocellulosic biomass in water/acetic acid before steam explosion, on chemical and elemental composition, ash content and chemical extraction from lignocellulosic biomass. Moreover, this study includes data on pellets characterization, such as compression strength, calorific value, density, mass loss and the release of gasses during pyrolysis. The highest mass loss is identified at the maximum peak in the thermo-differential

analysis (DTG) curves. Understanding these characteristics support the potential for using pellets produced from lignocellulosic residues to replace coal in power plants.

## 2. Materials and methods

### 2.1. Chemicals

Methyl isobutyl ketone (MIBK) and hexadecane were purchased from Merck KGaA (Darmstadt, Germany), acetic acid and used without any further purification.

### 2.2. Sample preparation/feedstock

The lignocellulosic residues used in our study were: sawdust birch collected from Vanhälls Såg AB, sawdust spruce collected from Arbaflame AS, GROT prepared at RISE PFI (mix of 30 % bark and 70 % industrial spruce chips) and straw samples collected from a farmer in Trondheim (barley grain). A schematic draw of the designed steam explosion pretreatment process, followed by leaching and washing and MIBK extraction for co-production of value-added chemicals and high-quality pellets is presented in Fig. 1.

Both straw and GROT material were grounded using a hammer mill with a hammer mill screen size of 10 mm. All the materials were analyzed for the particle size distribution, moisture content and bulk density. In our study we used different mix of the materials (20 samples in total), as shown in Table 1. Before steam explosion all the mixtures were presoaked with 1 % acetic acid in water and water for 12 h, at room temperature. The excess of water was filtered off after soaking. The solid material was further collected in plastic bags for conditioning before steam explosion. The humidity of the material before steam explosion was 18–19 % for residual straw material, 34 % for sawdust birch, 32 % for sawdust spruce and 38 % GROT material.

### 2.3. Steam explosion process

Steam explosion trials were performed on a large pilot scale at Lund University Biobased Industry Research Center (LUBIRC), in Sweden [35]. The capacity of the steam explosion reactor is 4L. The chosen process conditions were the reference process used at Arbaflame and one lower temperature than the reference conditions. Prior to each pretreatment the steam explosion reactor was preheated at high temperature. The steam added to the reactor depends on the degree of filling. The optimal filling level used in Lund is 70 %, as a higher degree of filling leads to uneven heat transfer and variable conversion of the material. The desired treatment temperature was achieved by adjusting the reactor pressure. The hardwood materials and their mix were treated at two different temperatures and pressures (200 °C and 1.8 MPa; 190 °C and 1.3 MPa) for 8 min, while the softwood materials and their mix were treated at 223 °C and 2.4 MPa and 210 °C and 2.0 MPa for 8 min. The pretreated materials were collected in plastic bags and stored at 4 °C until further use.

### 2.4. Washing and leaching of the steam exploded biomass

The steam exploded materials were further dewatered by using filtration with a vacuum pump. The weight of the filtrate and the weight of the biomass was taken to calculate the yield. The chemical composition of the liquid fractions was determined, and the results will be published in a separate paper. The solid materials were then washed (100 g steam exploded material) with deionized water to obtain a consistency of 15 % and mixed well for 1 h at room temperature. When the mixing time was over, the mixture was filtered with a vacuum pump. The ash content was analyzed for both the filtrate and the filter cake. The ash content of all the pretreated material was quantified at 525 °C and 900 °C according to ISO 1762 and ISO 2144.

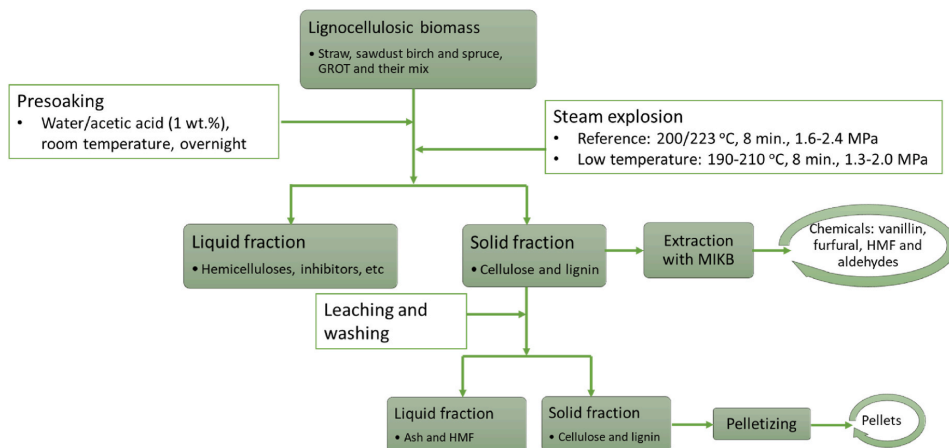


Fig. 1. Schematic drawing of the designed pretreatment process for co-production of value-added chemicals and high-quality pellets.

Table 1

Overview of the steam explosion experimental setup in Lund (all the experiments were done with a constant amount of dried biomass, 400g dried material; constant residence time of 480 s at various temperatures and pressures).

Sample name	Mixing, %	Impregnation	Experiment name	Residence temp, °C	Residence pressure, MPa
Straw	100	Water	Reference	200	1.6
			Low temperature	190	1.3
Straw	100	1 % acetic acid in water	Reference	200	1.6
			Low temperature	190	1.3
Straw:birch	10:90	Water	Reference	200	1.6
			Reference	200	1.6
			Low temperature	190	1.3
Straw:birch	10:90	1 % acetic acid in water	Reference	200	1.6
			Reference	200	1.6
			Low temperature	190	1.3
GROT:Spruce	10:90	Water	Reference	223	2.4
			Reference	223	2.4
			Low temperature	210	2.0
GROT:Spruce	10:90	1 % acetic acid in water	Reference	223	2.4
			Reference	223	2.4
			Low temperature	210	2.0
Birch	100	1 % acetic acid in water	Reference	200	1.6
Spruce	100	1 % acetic acid in water	Low temperature	210	2.0
			Reference	223	2.4
Birch	100	1 % acetic acid in water	Low temperature	210	2.5

### 2.5. Pellets production and pellets properties

The washed steam exploded materials were dried in controlled conditions before pelletizing. The target moisture content was between 8 and 10 %. The pellets were formed by a single pelletizer equipment (Zwick Roell) at RISE PFI laboratory under controlled temperature of 80 °C, maximum force of 9 kN and testing speed of 10 mm/min. Pellet properties such as length, width, density, and compression strength were collected during this measurement. The pellets were compressed until 10 % drop of maximum force was registered. The compression strength is defined as the force at breakage when a pellet is placed between two metal plates and compressed at a fix strain rate while force and distance are recorded. Six individual pellets were produced from each biomass material described in Table 1. The 10 mm hole of the cylinder was filled with approximately 5 g sample, then pressed by a piston connected with hydraulic press and hold for 90 s.

### 2.6. Thermogravimetric analysis (TGA-FTIR)

Thermogravimetric analysis (TGA) was used to characterize and

evaluate the thermal behavior of the pellet samples and weight loss at 35–900 °C at a constant heating rate of 10 °C/min in inert atmosphere of N<sub>2</sub> (nitrogen flow of 60 mL/min). Decomposition of the samples occur at high temperature and the gasses released were collected and measured with FT-IR 530-4000 cm<sup>-1</sup>.

### 2.7. Biomass extraction with methyl isobutyl ketone (MIBK) and sample preparation for GC-MS (gas chromatography-mass spectrometry) analysis

Approx. 5 g of the steam exploded biomasses were extracted with 10 mL MIBK for 20 h to investigate which chemicals that can be extracted from the steam exploded biomasses. After 20 h, the samples were filtered and washed with 10 mL of additional MIBK. Filtrates were analyzed by GC-MS and yields were measured as mg/kg dry steam exploded (STEX) biomass.

### 2.8. Carbohydrate and lignin analysis of the raw material and steam exploded biomass

The total amount of extractives in the raw materials were determined

gravimetrically according to SCAN-CM 49:3 “Content of acetone soluble matter”. Further, groups of wood extractives were quantified after silylation using GC-FID (gas chromatography with flame ionization detector, GC 7890A from Agilent Technologies). Fatty acids, resin acids, sterols, lignans, steryl esters and triglycerides were separated on a DB-1 capillary column (7.5 m-0.55 mm id, 0.15 µm film) using helium as the carrier gas.

The carbohydrate and lignin analysis of untreated and pretreated biomass was carried out based on the NREL method for structural carbohydrate and lignin analysis in biomass [58]. The samples were air dried to a moisture content less than 10 %. Furthermore, 10 mg of sample was taken in a reaction tube and mixed thoroughly with 3 mL of 72 % H<sub>2</sub>SO<sub>4</sub>. The tube was then placed in the Laboshake at 30 °C and incubated for 60 min with mixing the sample every 5–10 min. After incubation, the tube was removed, and the content of the tube was transferred to a 100 mL pyrex glass and diluted with 84 mL distilled water to make the acid concentration be 4 %. The sample is then autoclaved at 121 °C for 1 h. The sample is removed and cooled to room temperature. The sample is then neutralized until pH 5–6 with CaCO<sub>3</sub> followed by filtration through a pre-weighed filter paper. The neutralized samples were analyzed using HPLC (high performance liquid chromatography). The filter paper and the undissolved content was dried in an oven at 105 °C overnight and the acid soluble and insoluble lignin was analyzed gravimetrically. The liquid fraction was analyzed for acid soluble lignin before neutralization using UV/Vis spectrometry at a wavelength of 205 nm.

### 2.9. High performance liquid chromatography (HPLC)

The prepared sugar filtrate samples (described in the previous paragraph) were subsequently filtered using syringe-filter with 0.22 µm and the filtrates were analyzed by High Performance Liquid Chromatography (HPLC, Agilent Hi-Plex Pb, 7.7 × 300mm, 8 µm column). The mobile phase was water; the flow rate was 0,6 mL/min; and the column and refractive index detector (RID) temperature was set at 70 °C.

### 2.10. Elemental analysis

All samples, including the starting feedstocks and the steam exploded biomasses before and after extraction with MIBK, were analyzed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as the carrier gas. The amount of oxygen was calculated by the difference of CHN. Results from elemental analysis have been used to measure the higher heating values (HHV) of the different materials using the equation below (Eq. (1)), where C<sub>A</sub>, H<sub>A</sub>, N<sub>A</sub>, S<sub>A</sub>, and O<sub>A</sub> are the wt.% of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively. Since the instrument used for this analysis was not calibrated for sulfur, the sulfur content has been assumed to be zero.

$$\begin{aligned} HHV \text{ (MJ kg}^{-1}\text{)} &= (0.3404 * C_A) + (1.2432 * H_A) + (0.0628 * N_A) \\ &+ (0.1909 * S_A) - (0.0984 * O_A) \end{aligned} \quad \text{Eq. 1}$$

### 2.11. Gas chromatography–mass spectroscopy of the filtrates obtained from the extraction with MIBK

0.5 mL of each sample was added 0.5 mL of an internal standard solution (10 µL/L), giving a hexadecane concentration of 5 µL/L. The samples were analyzed using an Agilent Technologies 7890A GC system with an autosampler coupled with an Agilent 5977A mass-selective detector (MSD). The injection was run in the splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 µm i.d. and thickness of 0.25 µm from Agilent Technologies. The following GC–MS instrumental conditions were applied: Start temperature: 40 °C (held for 5 min), heating rate 1: 6 °C/min to 280 °C, and heating rate 2: 40 °C/min to 300 °C (held for 5 min). The GC–MS interphase valve delay was set to 4.60 min and the MS detector was operated in the positive mode at 70 eV

with an ion-source temperature of 250 °C. Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

The estimated yield of each identified component, given as mg/kg dry input biomass, was calculated according to Eqs. (2)–(5). The unknown densities of the compounds have been assumed to be like 1.00 g/L.

$$[A] \left( \frac{\mu\text{L}}{\text{L}} \right) = \frac{A_A * 5 \left( \frac{\mu\text{L}}{\text{L}} \right)}{A_{IS}} \quad \text{Eq. 2}$$

$$[A] \left( \frac{\text{g}}{\text{L}} \right) = \frac{[A] \left( \frac{\mu\text{L}}{\text{L}} \right) * D \left( \frac{\text{g}}{\text{mL}} \right)}{1000} \quad \text{Eq. 3}$$

$$m_A \text{ (g)} = [A] \left( \frac{\text{g}}{\text{L}} \right) * V_{\text{frac.}} \text{ (L)} \quad \text{Eq. 4}$$

$$\text{yield} \left( \frac{\text{mg}_A}{\text{kg}_{\text{dry input biomass}}} \right) = \frac{m_A \text{ (g)} * 1000}{m_{\text{dry input biomass}} \text{ (kg)}} \quad \text{Eq. 5}$$

where A<sub>A</sub> is the area below the top for each identified component.

## 3. Results and discussion

The results from the solid fractions are presented in this paper and the results from the liquid fractions will be presented in a separate paper.

### 3.1. Characterization of the raw materials

The results from the chemical characterization of the raw materials used in this study shows that the chemical composition varies among different types of biomasses, as straw raw material and sawdust birch contains more xylose compared with sawdust spruce where mannose is the predominant of the hemicellulose sugars. The lignin and extractives content are also different, sawdust spruce contains more lignin compared to sawdust birch and straw, while extractives content is higher for straw compared to sawdust birch and spruce as seen in Table 2. The chemical composition is important for production of high-quality pellets. High lignin content in sawdust spruce is beneficial for high mechanical strength of the pellets because of lignin’s good binding ability, while high extractive content in straw has a negative effect on the bonding ability [48]. However, high extractives content has been shown to have a positive effect on high heating value [59–61].

Presoaking resulted in a biomass having a dry matter of 18–19 %, 34 %, 32 % and 38 % for straw, sawdust birch, sawdust spruce and GROT, respectively. The initial moisture content of the sample is a determining factor in the effectivity of steam explosion pretreatment, since it impacts the ability of heat and chemicals to permeate the biomass [62]. Steam explosion pretreatment decreased the dry material content of all samples to 9–11 %, 15 %, 17–25 %, and 16–23 % for their mix which indicates that the steam exploded materials contains significant amount of water. Washing and leaching of the steam exploded biomass resulted in an increase in the dry matter 14–16 %, 40 %, 38 %, 24–36 % for straw, sawdust birch, sawdust spruce and their mix. Moisture content of steam exploded biomass is an important parameter in industrial applications, as less energy will be required for the drying of the material before pelletizing process. The effect of biomass moisture content prior pelletization process has been well studied in the literature [48]. Solid yield results after steam explosion from our study showed a very large variation for all samples, with highest solid yield of 96 % for straw residue and the lowest yield of 71 % for birch. The yield for sawdust spruce samples was 81 %, while for the GROT:Spruce mix varied between 82 and 93 % with the lowest yield for the samples presoaked in

**Table 2**  
Chemical composition of raw materials used in this study.

Sample name	Moisture content, %	Carbohydrate as anhydrosugars, %					Total lignin, %	Extractives, %	Ash, %
		Glucose	Mannose	Xylose	Galactose	Arabinose			
Straw	89 ± 0,09	39 ± 1,9	0,5 ± 0,01	19 ± 1,4	2,1 ± 0,36	2,5 ± 0,01	24 ± 0,6	2,3 ± 0,9	5,7 ± 0,29
Sawdust birch	62 ± 0,12	45 ± 2,0	1,3 ± 0,05	22,6 ± 1,8	0,5 ± 0,01	1,3 ± 0,2	25 ± 2,6	1,6 ± 0,7	0,2 ± 0,8
Sawdust spruce	44 ± 1,5	46 ± 0,13	13 ± 0,08	7 ± 0,06	2,37 ± 0,15	1,98 ± 0,06	29 ± 0,2	1,3 ± 0,4	0,2 ± 0,2

acetic acid. The same trend was observed for Straw: Birch mix with a yield between 74 and 94 %, lowest for the samples presoaked in acetic acid. Based on these results we would expect a higher removal of hemicellulose content. However, the chemical composition of solid lignocellulosic residues after steam explosion does not support this affirmation.

### 3.2. Ash content in the raw materials and in the steam exploded biomass

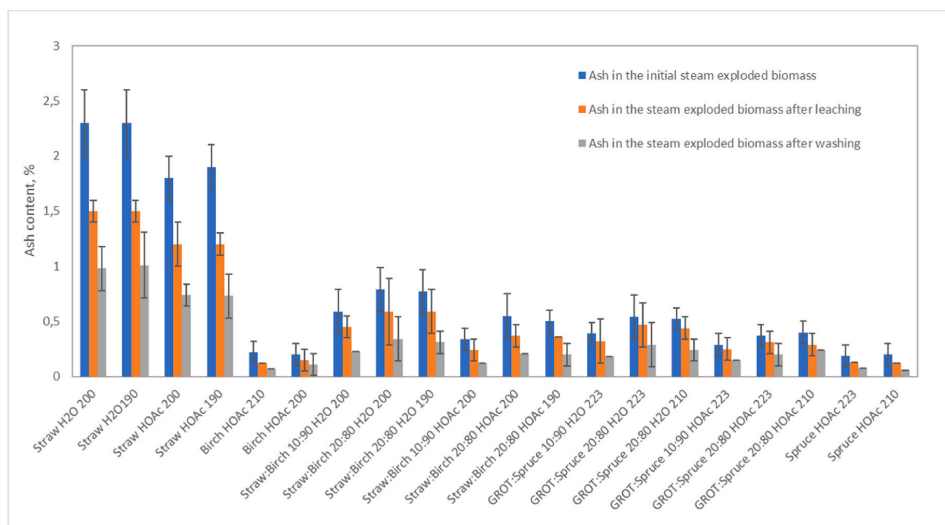
Ash content of all the steam exploded biomass samples is shown in Fig. 2. The ash content of initial straw biomass was found to be 5.7 %, which is much higher than that of wood biomass at 0.2 %. This is not unexpected, since straw contains minerals which contribute to the ash content. However, after steam explosion pretreatment the ash content decreased from 5.7 to 2.3 % for straw material impregnated with water and even more for the material impregnated with acetic acid, decreasing from 5.7 % to 1.8 %. As such, steam explosion of high ash content biomass is beneficial for ash removal. Furthermore, after washing and leaching the ash content decreased even more for presoaked water samples from 5.7 % to 0.98 % and for the presoaked acetic acid samples from 5.7 % to 0.73 %. Our results indicate that an acid washing is more beneficial to reduce the ash content compared to only water washing from lignocellulosic residues. This conclusion is in accordance with literature results [63]. Problems associated with ash is important when biomass is considered for pellets production. For burning of the wood pellets very low ash content is wanted, as the ash content is directly correlated to how often the oven/stove needs to be cleaned. According to CEN Standard [64], the allowable ash content of non-woody pellets is 6 %.

The mineral composition presents in the ash from combustion of

wood pellets is related to slagging problem. The ash content of the hardwood and softwood is generally low, and the mineral composition in the clean wood fibers will not contribute to slagging. However, when clean hardwood is combined with straw and clean softwood fibers are combined with bark the ash content will increase and the mineral content in the mixed hardwood and mixed softwood can contribute significantly to the slagging problem. Therefore, introducing an extra washing step is essential to remove the ash content from the steam exploded biomass, which is important when the biomass is to be used for pellets production.

### 3.3. Characterization of the steam exploded biomass

The chemical composition of steam exploded materials determined on a dry weight basis is shown in Fig. 3. The results show an overall decrease in hemicellulose content and an increase in glucose and lignin content after steam explosion for all 20 samples investigated in our study. However, the decreased in hemicellulose content was not as expected for straw, birch and Straw: Birch mix samples. The most significant hemicellulose removal was observed for steam exploded spruce and Spruce: GROT mix, while glucose content of pretreated material increased to 50 w% and lignin content increased to 40 w% at 223 °C, 8 min, 2.4 MPa. As such, we believe that explosion temperature has a significant effect on both ash and hemicelluloses content removal for all the samples. Iroba et al. [65] showed that steam explosion temperature significantly affected the changes associated with hemicellulose content in the pretreated material. Increased lignin content after steam explosion has been reported in the literature [66–68]. Other possible explanations for increased lignin content have been associated with the formation of pseudo-lignin as a result of condensation reactions [38].



**Fig. 2.** Ash content initial in the initial steam exploded biomass, in the biomass after dewatering (washing and leaching) and in the biomass before pelletizing. The coding of the samples refers to Table 1.



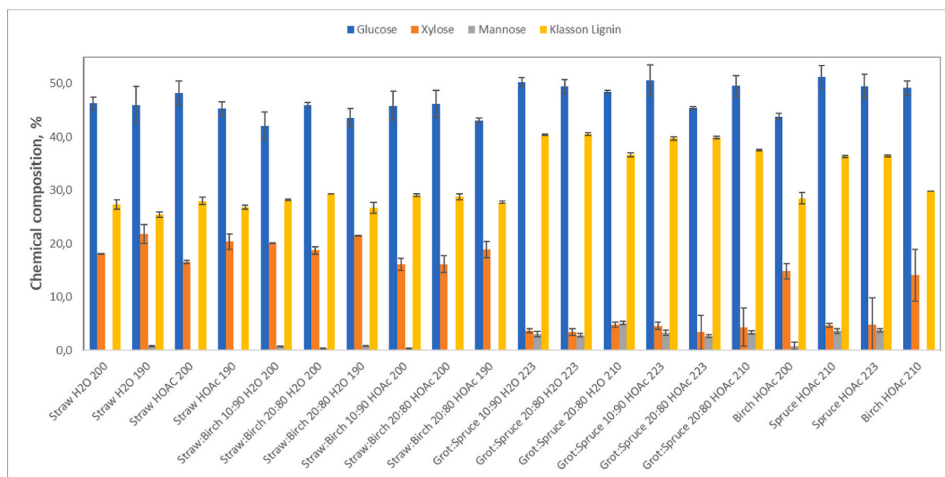


Fig. 3. The chemical composition of the steam exploded biomass. The coding of the samples refers to Table 1.

### 3.4. Elemental composition of steam-treated biomasses

The Van Krevelen diagram in Fig. 4 displays H/C and O/C ratios of both initial and steam exploded biomasses. The results show significant differences in hydrogen and oxygen contents between the different starting feedstocks. The untreated straw has the highest hydrogen and oxygen content compared to untreated birch and spruce. Birch and spruce have almost the same hydrogen content, while the oxygen content is considerably higher for birch which can be explained by the

higher content of carbohydrates in this feedstock. The Van Krevelen diagram in Fig. 4 also depicts clear differences between the steam-treated biomasses, resulting in three distinct groupings. In most of the cases, a significant reduction in the oxygen content of the steam-treated biomasses has been observed compared to the starting biomasses, which indicates high lignin content in the steam exploded pretreated materials. This agrees with the results from chemical composition of steam exploded materials, where steam-treated spruce from the experiment Spruce HOAc 223 contains the lowest oxygen amount and steam-treated

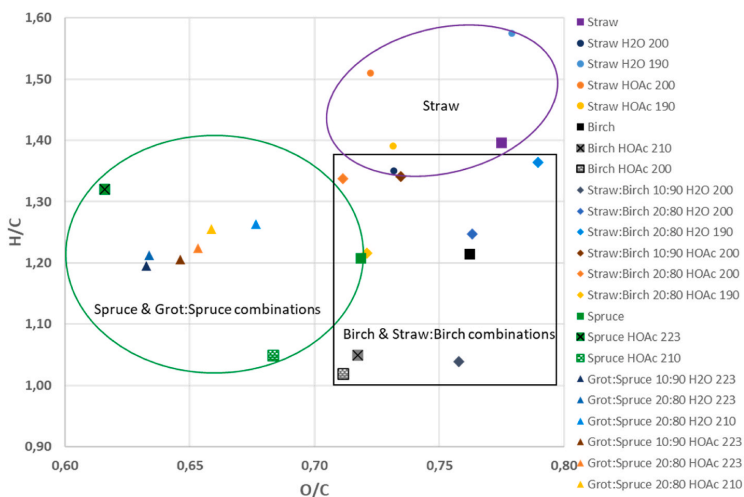


Fig. 4. Van Krevelen diagram shows H/C ratio and O/C ratio of all untreated feedstocks and steam-treated biomasses produced from different steam explosion processes. The coding of the samples refers to Table 1.

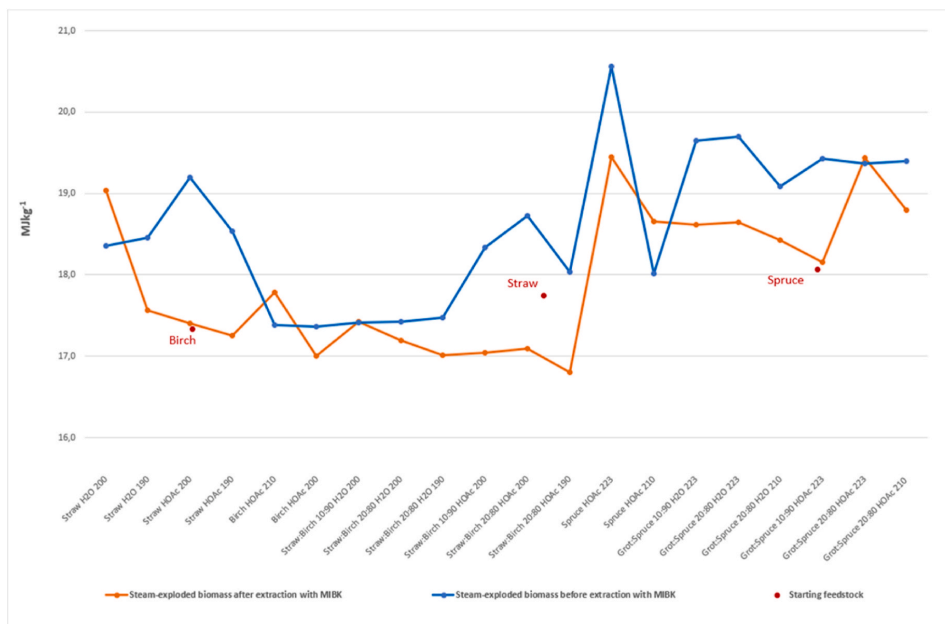


Fig. 5. Estimated HHV (MJ/kg) for the steam-exploded biomasses before and after extraction with MIBK. The coding of the samples refers to Table 1.

straw from the experiment Straw H<sub>2</sub>O 190 contains the highest hydrogen amount. However, in more detail statistical analysis are necessary to support our results.

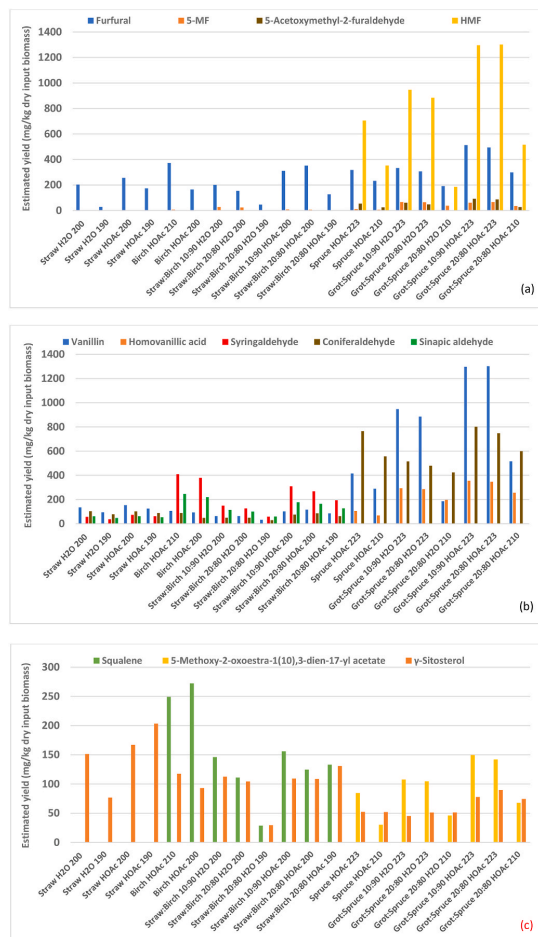
### 3.5. Higher heating value (HHV) of the steam explosion pretreated biomass

The determination of HHV is essential due to the use of the biomass treated by steam explosion to produce pellets. The untreated spruce had the highest HHV of 18 MJ/kg followed by untreated straw which had higher HHV than birch 17.8 MJ/kg and 17.2 MJ/kg, respectively. As shown in Fig. 5, the steam explosion process increases the HHV values for all the pretreated biomasses. Furthermore, extraction with MIBK has resulted in lower HHV in most of the cases. This may be due to the removal of the less volatile components that have been adsorbed to the steam-exploded biomasses. The results presented in Fig. 5 indicate that softwoods have a higher HHV compared to hardwoods, which is consistent with the literature [69]. In general, biomasses treated at lower temperatures have lower HHV than biomasses treated at higher temperatures, especially when it comes to biomasses impregnated with acetic acid. The overall result indicates that spruce is a better option to be used as raw material in the production of pellets compared to the other two woody biomasses. The highest HHV is obtained from experiment Spruce HOAc 223 before extraction with MIBK.

### 3.6. Molecular composition of MIBK filtrates

The more volatile compounds of the filtrates have been identified using GC–MS analysis. The filtrates comprise a complex mixture of furanic and phenolic compounds, aldehydes and terpenes and sterols as shown in Appendix (FIG A1 and Table A1). The chromatograms shows that the composition of the filtrates is different and strongly dependent on the type of starting feedstock. The quantitative results for some of the most valuable components identified by GC-MS analysis are given in Fig. 6. The yields of all the identified components increases as a function of increased pretreatment temperature, confirming more efficient depolymerization of the lignocellulosic polymers under more severe conditions. Moreover, use of acetic acid as an impregnation agent has contributed to a more extensive depolymerization of the biomasses. As depicted in Fig. 6(a), furfural is the only furanic compound that is present in all the filtrate samples, regardless of biomass type. Furfural is a key platform chemical produced from acid-catalyzed dehydration of C5 sugars derived from biomass, mainly xylose. Furfural can further be converted into fuels and value-added chemicals which are widely used in oil refining, plastics, pharmaceutical, and agrochemical industries, making the recovery of furfural from steam-exploded biomasses before pressing the masses into pellets beneficial.

MIBK filtrates from spruce contains both hydroxymethylfurfural (HMF) and 5-Acetoxyethyl-2-furaldehyde, dehydration compounds derived from hexose sugars. The chemical composition of the steam exploded biomass indicated higher amounts of hexose sugars (glucose



**Fig. 6.** Column diagrams showing the estimated yields (mg/kg) of furanic compounds (on the top), phenolic compounds (in the middle), and terpenes and sterols (at the bottom) extracted from the steam exploded biomasses. The coding of the samples refers to Table 1.

and mannose) in the Spruce and Grot:Spruce combinations compared to Birch and Straw: Birch combinations. Hydroxymethylfurfural is considered one of the top 10 value-added bio-based chemicals by the US DOE. HMF and its derivatives are valuable precursors to produce bioplastics, biopolymers, and biofuels.

Compounds quantified in Fig. 6(b) are lignin-derived phenolic components. Filtrate samples from steam-exploded Straw contained significantly lower amounts of lignin-derived phenolic compounds compared to Spruce and Birch which is due to the lower content of lignin in Straw compared to the other two feedstocks. Vanillin, homovanillic

**Table 3**

Properties of the pellets produced using different pressures during the pelletizing.

		Straw: Birch 20:80 H2O 200	Straw: Birch 20:80 HOAc 200	Birch HOAc 210	Spruce HOAc 223
pressed with maximum force of 800 N	Calorific value, MJ/kg	19 ± 0.08	19 ± 0.16	19 ± 0.26	20 ± 0.31
	Compression strength, kN/m	29 ± 1.4	34 ± 1.04	31 ± 1.5	52 ± 4.04
	Density, kg/m <sup>3</sup>	969 ± 72.2	953 ± 14.3	916 ± 14.9	972 ± 72.3
pressed with maximum force of 9000 N	Calorific value, MJ/kg	19 ± 0.7	19 ± 0.25	19 ± 0.29	20 ± 0.11
	Compression strength, kN/m	149 ± 6	133 ± 7	129 ± 4	172 ± 20
	Density, kg/m <sup>3</sup>	1292 ± 7	1277 ± 9	1226 ± 6	1275 ± 7

acid, and coniferaldehyde are the components with highest yields in the filtrate samples from spruce containing feedstocks, while syringaldehyde and sinapic aldehyde are the major components quantified in the filtrate sample from birch containing feedstocks. Vanillin, homovanillic acid, and coniferaldehyde are derived from coniferyl alcohol units in the lignin structure, while syringaldehyde and sinapic aldehyde are derived from sinapyl alcohol units. This observation was expected since softwood lignin contains more guaiacyl units and hardwood lignin contains a mixture of guaiacyl and syringyl units. The presence of two methoxy groups in the syringaldehyde and sinapic aldehyde structure contributes to higher oxygen content in hardwood biomasses. This result is consistent with the result obtained by elemental analysis where Birch and Straw: Birch biomasses have shown to have higher O/C ratios compared to Spruce and Grot: Spruce biomasses. Vanillin which has been shown to be the highest yielding lignin-derived compound from Spruce is a valuable chemical widely used in the production of food, pharmaceuticals, medicines, and as a flavoring agent. In addition, the filtrates contained small amounts of sterols and terpenes. As shown in Fig. 6(c), squalene which is a triterpene has only been identified in the filtrate samples from Birch. Natural squalene is widely used in the cosmetics, and has multiple benefits for the skin, including being an excellent moisturizer.  $\gamma$ -sitosterol which contains a core skeleton of cholesterol is one of the representative phytosterols found in plants and has been identified in all the samples. All in all, recovery of furfural, HMF, vanillin, syringaldehyde, and coniferaldehyde as the most valuable components extracted from the steam-exploded biomass must be balanced against the physicochemical properties of the pellets achieved.

### 3.7. Densification of steam exploded material (pelletization)

The lowest bulk density in our study was found to be 47 kg/m<sup>3</sup> for straw material compared to sawdust birch 101 kg/m<sup>3</sup> and 145 kg/m<sup>3</sup> for sawdust birch. Low bulk density and inhomogeneous structure of the lignocellulosic biomass are considered as problematic when the biomass is to be used as fuel [48]. Densification of lignocellulosic biomass has been previously shown in the literature [70] to have a positive effect on homogeneity of the biomass and increase in the calorific value. The pellets properties result from an initial study is given in Table 3. The

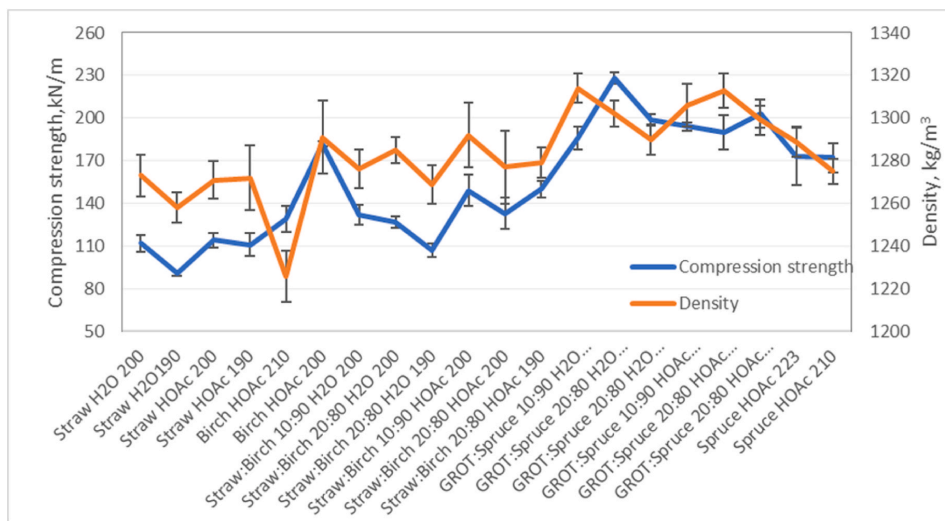


Fig. 7. Compression strength and calorific value of steam exploded biomass measured as a function of pellets density.

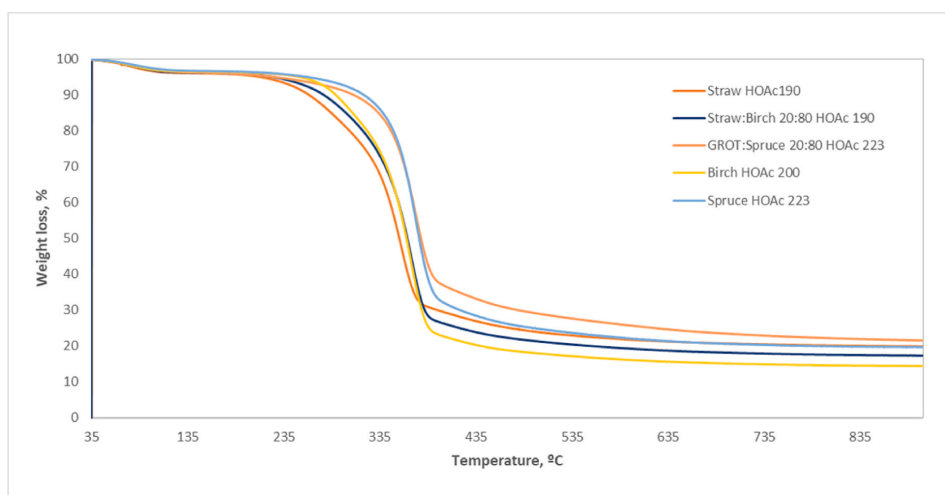


Fig. 8. Weight loss as function of temperature.

results shows that the mechanical properties, such as pellets density and compression strength are strongly correlated to the maximum force (pressure) that has been applied under pelletization process. As such, pellets density and compression strength increased with the pressure increase applied under the pelletization. Based on these results, we decided to use a pressure of 9 kN to produce pellets from all the steam

exploded materials described in Table 1.

Results on the physical properties of the pellets produced in this study are summarized in Fig. 7. The highest compression strength was measured to be between 172 and 228 kN/m at the highest density 1314 kg/m<sup>3</sup> for pellets made from both spruce and spruce/GROT mix with a high calorific value of 20 MJ/kg. We believe that the high mechanical

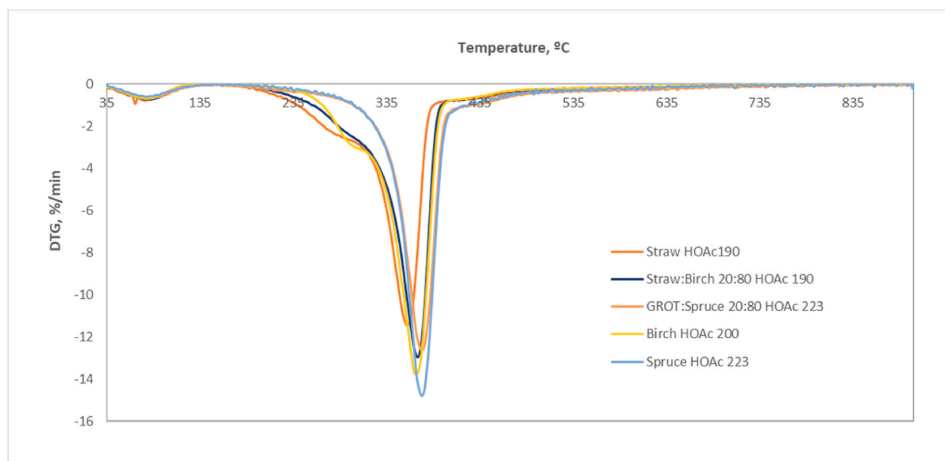


Fig. 9. Thermal decomposition (DTG curves) for steam exploded biomass samples. The coding of the samples refers to Table 1.

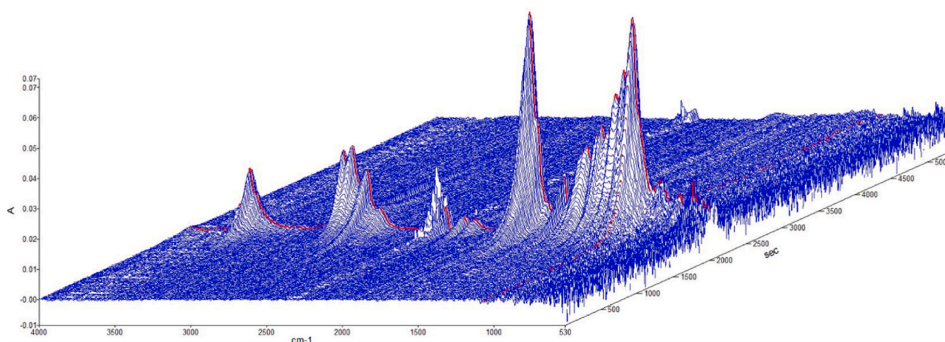


Fig. 10. Three dimensional plots of TGA-FTIR spectra of spruce pellets samples. The gasses recorded in our study from left to right are H<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, CO, and organic components, aldehydes and acids (C=O), alkanes (C-C) and ethers (C-O-C).

strength of both sawdust spruce and GROT:mix samples is due to the high content of lignin. At high temperature, lignin softness and flows which will have positive effect on fiber binding resulting in pellets with high mechanical strength. A lower calorific value of 18–19 MJ/kg was measured for straw and mix of straw:birch at lowest density. Greinert et al. [57], reported similar calorific values for pellets made from straw and willow wood, ranging from 17.3 to 20.1 MJ/kg. The initial calorific values of the raw materials were 17 MJ/kg and 18 MJ/kg for straw, sawdust birch and sawdust spruce, respectively. Hence, the steam explosion followed by washing and leaching, and pelletization of biomass increases the calorific value for all biomass samples, most probably due to the ash removal and increased in carbon content [2].

### 3.8. Mass loss and thermal stability of pellets

The mass loss as function of temperature is shown in Fig. 8. Results from the weight loss of pellets at 900 °C showed the highest weight loss for pellets made from sawdust birch (14–15 %), while for all the other pellets made from spruce, straw and mix of materials the weight loss is nearly in the same the range of 19–22 %. A very small weight loss is observed before 135 °C, and this is due to the moisture and volatile compounds evaporation. The weight loss and DTG curves (Fig. 9) shows a significant mass loss and the main stage of thermal decomposition for all the samples at 350–400 °C. There has been observed a slightly difference in the mass loss and the height and position of the peak between pellets made from straw and Straw:birch mix and pellets made from sawdust spruce and GROT:Spruce mix, respectively. The results shows that the mass loss and the thermal decomposition occur at lower

temperature for pellets made from straw and Straw:birch mix and pellets made from sawdust spruce and GROT:Spruce mix. This difference could be explained by the different chemical composition in the materials, higher amount of hemicellulose sugars and lower amount of lignin in the straw and straw:birch mix material compared to spruce material.

TGA-FTIR results of steam exploded spruce pellets is shown in Fig. 10. The FTIR spectra indicates that the gases generated during the thermal degradation of pellets samples were similar to the results reported in the literature [71,72]. The components identified during the combustion of the pellets depends on the chemical composition of the material, since hemicellulose and cellulose have different combustion range than lignin. As we saw in Figs. 9 and 10, at temperature range 135–200 °C moisture and volatile compounds evaporation take place and the release of H<sub>2</sub>O, CO, CO<sub>2</sub> occur for all pellets samples. Below 200 °C, all samples perform similarly independently of the gas atmosphere. With further temperature increase, the samples start to lose mass at a higher rate in the oxidizing atmosphere due to a reaction with O<sub>2</sub> and desorption of oxidized species (CO and CO<sub>2</sub>) [70]. As we mention before in this article, it seems that moisture content of the pellets is an important parameter in the combustion process. At higher temperature, between 380 and 400 °C the thermal degradation of hemicelluloses and cellulose occurs, and this can be seen in the release of CO<sub>2</sub> and CH<sub>4</sub> [71]. At temperature range of 500–800 °C, the released gasses observed for all samples analyzed in this study were high molecular weight carbonaceous products due to the thermal degradation of lignin. Overall, this study revealed that the combustion of pellets made from steam exploded straw, birch, spruce and their mix resulted in low emission of gases. Thus, co-combustion of steam exploded biomass with coal is an attractive option to consider for power plants for energy generation because of the major environmental benefits.

#### 4. Conclusions

The result from this study shows that the steam explosion biomass had a positive effect on both ash and hemicellulose content removal, while the lignin and glucose content increased in the solid fraction. This effect was more pronounced at high temperature compared to low temperature. Leaching and washing can be considered as an important process step for the steam pretreated lignocellulosic residues as this step was shown to reduce the ash content by 80 % for the straw samples. The elemental analysis results of all pretreated biomass show an increase in H/C content along with decrease O/C content after steam explosion. This may be seen also in the formation of CO<sub>2</sub> and H<sub>2</sub>O in the released gasses during decomposition of samples (TGA-FTIR spectra). However, some more statistical analysis is needed.

The yield of the extracted components (furfural, HMF, vanillin, syringaldehyde and coniferaldehyde) is strongly affected by the steam explosion conditions, such as temperature and the presence of catalysts. Higher yield of value-added chemicals was found in MIBK filtrate samples produced from biomasses presoaked in acetic acid compared to biomasses presoaked only in water. The results indicate that it is possible to produce value-added chemicals from steam exploded biomass, while still producing high-quality pellets.

The pellets produced from all lignocellulosic residues investigated in our study showed high compression strength, high calorific value and high density. Thus, our results suggests that pellets produced from

abundant, low value and high ash lignocellulosic residues can be used to provide pellets of sufficiently high quality for use as a substitute for coal in combustion-based processes. However, industrial steam explosion trials of lignocellulosic residue to produce pellets and combustion trials of industrial pellets must be done to support our hypothesis. As such, we believe that the present study demonstrated not only the possibility of maximizing carbon content in the solids, enhancing the kinetics of the reaction by introducing a presoaking step in very low acid acetic concentration, but also extracting chemicals from steam explosion biomass and washing of the ash content which has positive effect on producing high-quality pellets.

#### Ethical approval

Not applicable.

#### Founding

This work received founding from Arbaflame AS through the Research Council of Norway under grant agreement No 309970; No 309674 and PhD project No 321268.

#### Available data and materials

Not applicable.

#### CRedit authorship contribution statement

**Mihaela Tanase-Opedal:** Conceptualization, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Solmaz Ghoreishi:** Formal analysis, Writing – original draft. **Dag Helge Hermundsgård:** Formal analysis. **Tanja Barth:** Writing – review & editing. **Størker T. Moe:** Writing – review & editing. **Rune Brusletto:** Writing – review & editing.

#### Declaration of competing interest

The authors declare no competing interests and funding.

#### Data availability

No data was used for the research described in the article.

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Appendix A

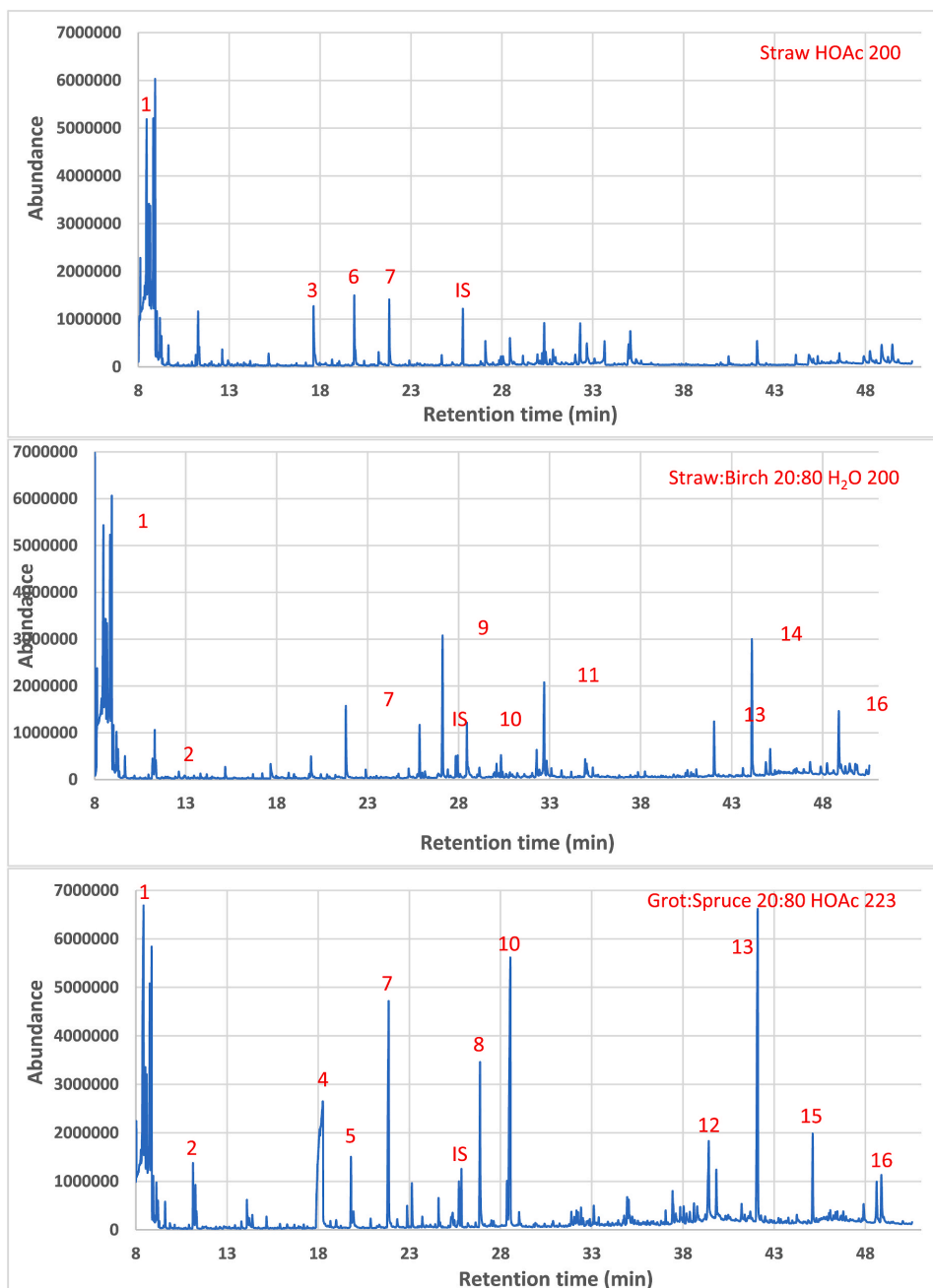

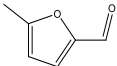
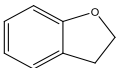
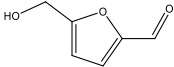
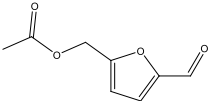
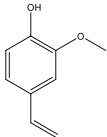
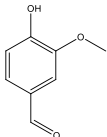
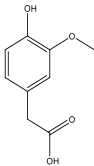
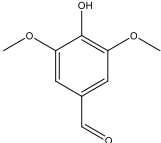


Fig. A.1. GC-MS chromatograms of the filtrate samples from experiment Straw HOAc 200 at the top, experiment Straw: Birch 20:80 H<sub>2</sub>O 200 in the middle, and experiment Grot: Spruce 20:80 HOAc 223 at the bottom.

**Table A.1**

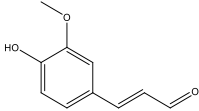
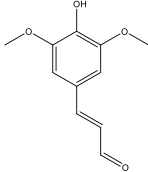
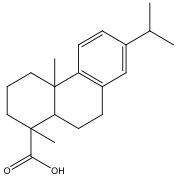
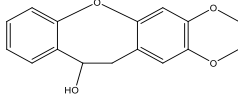
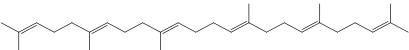
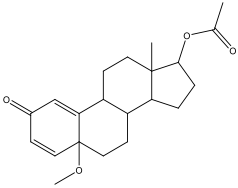
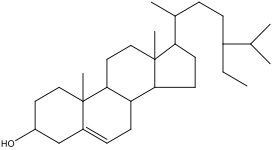
Overview of the main components identified in the filtrate samples from extraction of steam-exploded biomasses with MIBK.

Compound nr.	Compound name	Structure
1	Furfural	
2	5-Methylfurfural	
3	2,3-dihydrobenzofuran	
4	HMF	
5	5-Acetoxyethyl-2-furaldehyde	
6	2-Methoxy-4-vinylphenol	
7	Vanillin	
8	Homovanillic acid	
9	Syringaldehyde	

(continued on next page)



Table A.1 (continued)

Compound nr.	Compound name	Structure
10	Coniferaldehyde	
11	Sinapic aldehyde	
12	Dehydroabietic acid	
13	10,11-Dihydro-10-hydroxy-2,3-dimethoxydibenz(b,f)oxepin	
14	Squalene	
15	5-Methoxy-2-oxoestra-1(10),3-dien-17-yl acetate	
16	$\gamma$ -Sitosterol	

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# Paper III

Maximizing yields of furfural and 5-hydroxymethylfurfural in side streams from steam explosion of lignocellulosic residues

**Authors:**

Dag H. Hermundsgård, Solmaz Ghoreishi, Mihaela Tanase-Opedal, Størker T. Moe  
Rune Brusletto and Tanja Barth

**Manuscript:**

Submitted

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# Paper IV

Value generation from steam explosion of waste guayule bagasse

**Authors:**

Dag H. Hermundsgård, Mihaela Tanase-Opedal, Rune Brusletto and Tanja Barth

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# Paper V

Investigating solids present in the aqueous stream during STEX  
condensate upgrading—a case study

**Authors:**

Dag H. Hermundsgård, Solmaz Ghoreishi, Mihaela Tanase-Opedal, Rune Brusletto  
and Tanja Barth

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# Investigating solids present in the aqueous stream during STEX condensate upgrading—a case study

Dag Helge Hermundsgård<sup>1,2</sup> · Solmaz Ghoreishi<sup>1</sup> · Mihaela Tanase-Opedal<sup>3</sup> · Rune Brusletto<sup>2</sup> · Tanja Barth<sup>1</sup>

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## Abstract

Steam explosion (STEX) of woody biomass is an efficient pretreatment method in the production of water-resistant wood pellets. The STEX process also generates an aqueous condensate stream containing dissolved organic compounds, with furfural as the most abundant and valuable component. An industrial-scale recovery process for furfural and other organic by-products is therefore in the process of being developed and built. One challenge in the process has turned out to be the formation of solid particulate matter that can clog filters in the process unit. We have analyzed both the solid deposits and the fluids present at different points in the process unit to try to identify the origin of the particles using spectroscopic and chromatographic analysis, elemental analysis, and scanning electron microscopy.

The aqueous fluids deriving from condensed steam contain furfural and other small organic molecules, with a separate low-density organic layer occurring at some points. This layer largely consists of wood extractives, typically terpenoids. In addition, a heavy organic phase comprising mostly furfural was found at one sampling point. The particles comprise a black, largely insoluble material with a H/C ratio of 0.88 and an O/C ratio of 0.26 and a very low ash content. IR spectra show a low content of C–H functional groups, and chromatographic analysis supports an interpretation that the particles are dominantly furfural-sourced humin-like polymers with adsorbed or co-polymerized terpenoids. Particle formation has been reproduced in a laboratory setting with conditions similar to those in the full-scale process.

**Keywords** Biorefinery · Steam explosion · Condensate · Furfural · Terpenoids

## 1 Introduction

Increasing the use of renewable carbon-based resources requires the development of efficient biorefinery options to maximize the utilization of biomass feedstocks. In this context, a biorefinery for producing resilient black pellets and bio-based chemicals from wood as feedstocks has been established in Norway [1]. The concept comprises steam explosion (STEX) of sawdust for pellets production and recovery of bio-based chemicals from the condensed steam and wet steam-exploded mass. Furfural is the most important

product found in the condensed steam, and there is also an option for recovering 5-hydroxymethylfurfural (HMF) and sugars by washing and pressing the steam-exploded mass [2].

Establishing a novel, full-scale, efficient production plant is a challenge, and unexpected by-products can appear. In this case, the operation of the refinery unit for recovering furfural has been hampered by the formation of solid black particles that cause clogging of filters in the process flow, impeding the production rate of furfural and slowing down the water treatment. This reduces the production capacity of the refinery, as these are essential processes; hence, understanding the origin and formation pathway for the particles is crucial for developing suitable strategies for prevention.

The condensed steam from the STEX reactor contains the volatile fractions of extractives, such as terpenoids, and the reaction products from labile biomass polymers, especially those from hemicellulose. The feedstock also contains other extractives, such as fatty acids and resin acids that follow the steam-exploded biomass. Extractives are well

✉ Dag Helge Hermundsgård  
Dag.Hermundsgard@uib.no

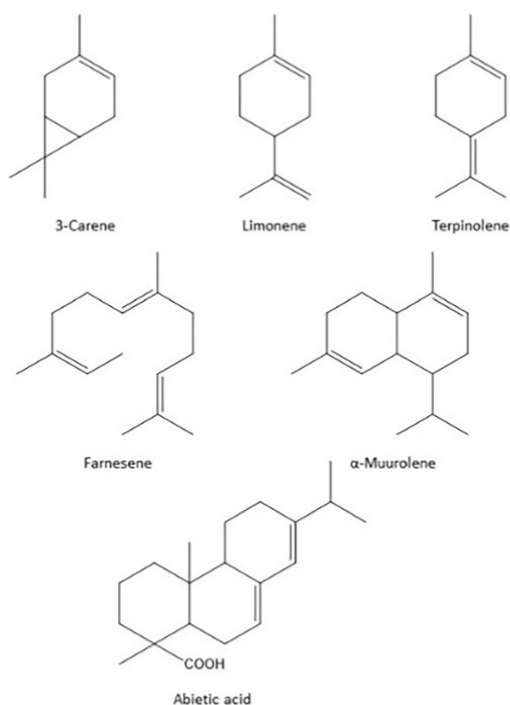
<sup>1</sup> Department of Chemistry, University of Bergen, Norway, Allégaten 41, N-5007 Bergen, Norway

<sup>2</sup> Arbaflame AS, Henrik Ibsens gate 90, N-0230 Oslo, Norway

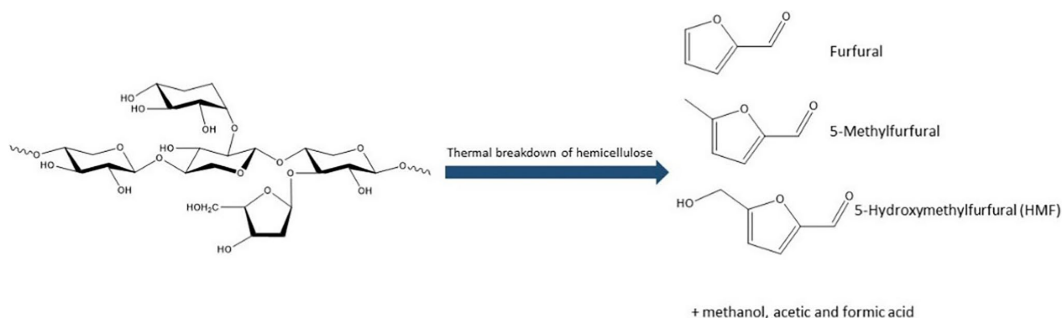
<sup>3</sup> RISE PFI AS, Høgskoleringen 6B, NO-7491 Trondheim, Norway

described in literature on the composition of wood, see, e.g., Fig. 1 [3], and the terpenoids comprise a large part of this compound class. They include hydrocarbon species and oxygen-containing structures with carbonyl, ether, and hydroxyl compounds, often with cyclic structures and some degree of unsaturation.

The products from the thermal breakdown of hemicellulose (Fig. 2) are also a source of reactive molecules in the



**Fig. 1** Examples of terpenoids found in wood extractives (adapted from Sjöström [3])



**Fig. 2** Furanic compounds produced from STEX of woody biomass

system. The furanic structures are prominent, like furfural and HMF, together with smaller molecules like methanol, acetic and formic acid, and acetone. Both the furans and the terpenoids can participate in polymerization reactions that can ultimately lead to black precipitates and are thus candidates as a source for the observed solid particles. One class of such particles, often termed *humins*, are solid condensation products which occur by random polymerization processes during acid-catalyzed dehydration of sugars [4]. Both pentose and hexose sugars, as well as furans like HMF, have been reported to contribute to the formation of humins, and although their formation routes and molecular structure are not fully established, research strongly suggests that humins from different sources will have differences in structure [5–7]. Formation of solid by-products like humins is a constant challenge in industrial processes, where they impede production and reduce operational efficiency, which leads to negative effects on the economics of the production process. Looking at results from the acid-catalyzed conversion of different sugar molecules to levulinic acid seems to suggest that humin formation cannot be prevented and a better understanding of their formation and how to handle them is therefore the key to reducing their undesirable effects [8–11].

In this work, black particles recovered from a filter in a side-stream processing unit for condensed steam at the ArbaOne plant have been analyzed in terms of composition and solubility, using a wide range of spectroscopic and chromatographic analytical procedures. The analytical results are evaluated in terms of suggesting a pathway for the formation of the particles from the organic components available in the condensate stream. Laboratory-scale experiments to replicate the formation of black particles have also been performed.

## 2 Materials and methods

All reagents and solvents were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification. All standard components are commercially available.

### 2.1 The steam explosion process

The steam explosion pretreatment was performed at the ArbaOne pelleting plant, operated by Arbaflame AS, located in the south-eastern part of Norway. A feedstock consisting of sawdust from a mixture of spruce and pine, both softwoods, in an unknown, variable ratio is treated with saturated steam in a large-scale 11.5-m<sup>3</sup> reactor with pressures of 19–23 bar and a reaction time of 500 s. Reaction temperatures reach between 212 and 222 °C during cooking, which is optimal for the production of water-resistant pellets. However, this temperature is also ideal for the formation of furanic compounds. These reaction conditions comprise a severity [12] of about 4.22 for the case of 212 °C up to 4.51 when the temperature reaches 222 °C.

During the decompression, high-pressure steam is released from the reactor and subsequently cooled in condensers and collected in the demister tank (Fig. 3). From the demister, the acidic condensate (pH 2.5–3) flows through a

skimmer tank, where a significant part of the extractives are removed from the liquid. The condensate is then fed through an ultra-filtration unit (UF), removing particles larger than 0.05 µm, to a temporary storage tank that feeds condensate through a distillation tower to separate furfural and low boilers from the aqueous condensate, as illustrated in Fig. 3.

The main components and typical concentrations of the condensate are as follows: furfural, 18.1 g/L; 2-acetylfuran, 0.2 g/L; 5-methyl furfural, 0.4 g/L; HMF, 0.4 g/L; acetic acid, 9.3 g/L; formic acid, 1.9 g/L; methanol, 5.5 g/L; and a small, but un-quantified, amount of residual sugars.

The distillation unit separates low boilers and furfural from the condensate in a continuous two-step process. The first column operates at 1100 mbar and in the range of 70–105 °C, where low boilers are removed from the condensate, and the second column operates at 150 mbar and between 50 and 56 °C and removes the furanic compounds, mainly furfural, from the condensate stream before the stripped condensate can be sent to the water treatment plant. While the black particles were first found in a strainer after the first column, a closer investigation uncovered that the actual earliest source of the black particles in the process stream is a heat exchanger that heats the condensate to a temperature of about 96–104 °C, before it enters the first column.

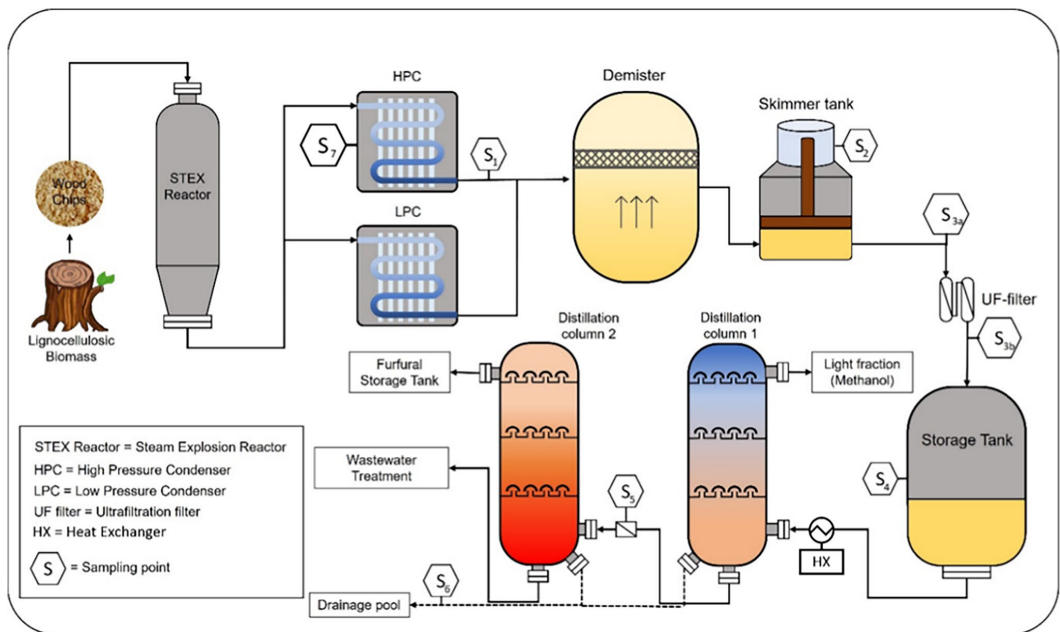


Fig. 3 Overview of ArbaOne process flow with sampling locations marked ([13, 14] recreated by Joakim L. Molnes)

## 2.2 Sampling

In order to get a better understanding of where the black particles originate, samples taken from several points in the process chain were analyzed. Figure 3 shows a simplified flowchart of ArbaOne's process chain, with markers showing the sampling points along the process chain. The sample information is given in Table 1.

## 2.3 Analysis of the black particles

### 2.3.1 FT-IR of black particles

A sample of the black particles (sample #5, Table 1) was crushed into a rough powder before being applied to an attenuated total reflectance (ATR) crystal, where a spectrum was acquired (Fig. 5).

### 2.3.2 Elemental analysis

Elemental analysis was performed on a sample of the black particles (sample #5, Table 1), and a van Krevelen diagram (Fig. 12) was created to compare the elemental composition of the black particles to that of relevant carbohydrates from lignocellulose, furans, and furfural-derived humins.

### 2.3.3 SEM

A sample of roughly crushed black particles (sample #5, Table 1) was coated with a thin layer of 60% palladium and 40% gold before being placed in a Fei Quanta 450 scanning electron microscope where pictures of the surface structure were taken (Fig. 6).

### 2.3.4 Ash content

The ash content of the black particles (sample #5, Table 1) was quantified with two parallels at 525 °C and 900 °C according to ISO 1762 and ISO 2144, respectively.

### 2.3.5 ICP-MS

A sample of 0.24 g of black particles (sample #5, Table 1) was dissolved into a homogeneous solution with 10 mL of concentrated nitric acid. Before analysis, the sample was diluted with 2% w/v HNO<sub>3</sub> to a dilution factor of 825. The sample of black particles was then analyzed for trace amounts of a range of elements (Al, Cr, Mn, Fe, Ni), with a Thermo Scientific Element XR high-resolution inductively coupled plasma mass spectrometer.

**Table 1** Overview of samples taken from the process line and what analysis was performed on the different samples. The sampling points are marked in the process sketch in Fig. 3

Sample #	Sample type (phase)	Location	Analysis	Additional notes
1	Condensate (liquid)	Condensate from the HPC outlet	FT-IR and GC-MS of the organic top layer	Analysis after fractionation
2	Skimmer tank product (organic liquid/solid particles)	Skimmer tank product container	NMR/IR	Product from the skimmer tank
3a	Condensate (liquid)	Before UF	Visually inspected (filtration)	No black particles were found
3b	Condensate (liquid)	After UF	Visually inspected (filtration)	No black particles were found
4	Brown particles (solid/semi-solid)	Storage tank	Particles were found, not enough for systematic analysis	Some brown particles were found when the tank was drained and inspected
5	Black particles (solid)	Filter before the inlet to column 2	Ash content, FT-IR, ICP-MS, SEM, GC-MS, Pyr-GC-MS, TGA-FTIR	The black particles were collected from the filter and analyzed in the state they were found
6	Black organic liquid (organic liquid)	Distillation unit drainage pipes	NMR, FT-IR	Black organic liquid found together with water/condensate
7	Black solid residue	HPC	FT-IR, TGA-FTIR, Pyr-GC-MS	Residue found during maintenance, somewhat resembling the black particles
8	Black solids	Laboratory	FT-IR	Solid material collected after laboratory experiments at various conditions

### 2.3.6 Pyrolysis GC–MS

Organic compounds in the samples were also characterized using pyrolysis GC–MS (pyrolysis gas chromatography–mass spectroscopy). Samples of 3–5 mg (sample #5 and #7, Table 1) were pyrolyzed at 600 °C in a reactor from Frontier Lab (3050TR).

### 2.3.7 TGA-FTIR

Thermogravimetric analysis was conducted on a NETZSCH STA 449F3 Jupiter instrument. Samples of 10 ( $\pm$  1) mg (sample #5 and #7, Table 1) were individually heated in an inert atmosphere of N<sub>2</sub>.

The evolved gasses from the TGA analyzer then entered a PerkinElmer Spectrum 3 FT-IR where an absorbance spectrum and a 3D surface plot were collected (Figure S5 and S6 in the supplementary file).

### 2.3.8 Solubility of black particles and Soxhlet extraction for GC–MS analysis

To perform a GC–MS analysis of the particles, an attempt was made to dissolve a small sample of particles in one of the three common solvents, acetone, ethyl acetate, and tetrahydrofuran (THF). The samples were stirred overnight (about 14 h), and though none of the solvents was able to fully dissolve all the material, THF was by visual inspection determined to be the best solvent (Figure S1 in supplementary material), and a Soxhlet extraction was performed.

When performing the extraction, 1.5 g of the black particles (sample #5, Table 1) was extracted with THF for 20 h using Soxhlet extraction. For analysis with GC–MS, 1 mL of the solution from the Soxhlet extraction was diluted with 10 mL THF.

In order to more thoroughly evaluate the solubility of the black particles (sample #5, Table 1), a range of common and less common solvents with different polarities were tested by weighing and adding a sample of black particles to the solvent and stirring for 24 h. The samples were then filtered with a 1.6- $\mu$ m pore size glass fiber filter, before the particles were weighed again and the dissolved mass calculated. Results from the solubility tests can be found in Table S3 in the supplementary file. It is important to note that the expanded solubility test has been done with a different batch of black particles than the rest of the experiments, due to a shortage of material from the initial batch. The visual difference between the batches can be seen in Figures S1 and S2 in the supplementary file.

Similarly, the solubility of the black residue from the HPC (sample #7, Table 1) was assessed, and it was shown

to be far more soluble in ethyl acetate than the black particles from the distillation unit, although it was not completely dissolved.

## 2.4 Analysis of other organic liquids and samples

### 2.4.1 FT-IR of organic samples

Samples of liquid organics from condensates (sample #1, Table 1), the skimmer tank (sample #2, Table 1), and the drainage pipes (sample #6, Table 1) were applied in small amounts to the ATR crystal with a glass pipette and an IR spectrum was acquired (Figs. 7 and S7 respectively).

### 2.4.2 Sample preparation and acquisition of qNMR spectra for NMR analysis

A portion of the black organic liquid (sample #6, Table 1) was prepared for qNMR analysis. Using 0.56 g of the organic liquid and adding 1.92 mL of deuterated chloroform (CDCl<sub>3</sub>, containing 0.03% TSP (3-(trimethylsilyl)propionic-2,2,3,3-d<sub>4</sub> acid)). Finally, 600  $\mu$ L of the prepared sample was then transferred to a 5.0  $\times$  103.5 mm Sample-jet NMR tube with an Eppendorf autopipette.

### 2.4.3 Fractionation of condensates

A condensate sample (sample #1, Table 1) of approximately 200 g was placed into a round-bottom flask and fractionated into 4 fractions using a rotary evaporator at 50 °C with decreasing pressure from 90 to 60 mbar. From the remaining non-volatile fraction, 0.1 g was dissolved in 9 mL EtOAc, with 1  $\mu$ L/L (IS) and analyzed by GC–MS.

## 2.5 Instrumental conditions

### 2.5.1 FT-IR instrumental conditions

The FT-IR spectra of the black particles and organic liquids from the condensate stream were acquired on a Thermo Fisher Nicolet iS5 instrument with an attenuated total reflectance (ATR) crystal. The main measurement features were a spectral range from 4000 to 400 cm<sup>-1</sup>, 16 scans, and a resolution of 4 cm<sup>-1</sup>.

### 2.5.2 Elemental analysis instrumental conditions

Elemental analysis was performed in CHNS mode with a VarioEL III from Elementar, using helium as carrier gas and calculating the oxygen amount by difference.

### 2.5.3 Instrumental conditions for the acquisition of NMR spectra

$^1\text{H}$  NMR analysis of the sample was performed on a 600-MHz Bruker AVANCE NEO NMR-spectrometer equipped with a QCI-P CryoProbe at 298 K. The pulse sequence applied was zg0 using a  $90^\circ$   $^1\text{H}$  pulse with a spectral width of 28 ppm, 128 k data points, 8 scans, and 0 dummy scans. The relaxation delay was set to 60 s to ensure complete relaxation between scans. The spectrum was zero-filled to 256 k data points and processed using a line broadening of 0.3 Hz.

### 2.5.4 SEM instrumental conditions

The Fei Quanta 450 scanning electron microscope is using a thermal field emission filament and has a range of 200 V–30 kV with a resolution of 0.8 nm at 30 kV for up to 1,000,000 $\times$  magnification. The microscope uses variable pressure and is fitted with a secondary electron detector and a backscatter detector.

### 2.5.5 ICP-MS instrumental conditions

Quantification of the sample is done with the use of external calibration curves (multi-element standard solutions prepared from certified single-element solutions from Spectrapure) and indium is used for internal standardization.

No relevant reference material was available, so as a direct control of the calibration curves and to monitor the performance during the analytical runs, certified reference material in the form of synthetic water, SPS-SW-2 from Spectrapure Standards AS, is analyzed repeatedly throughout the run.

### 2.5.6 Pyr-GC-MS instrumental conditions

The pyrolytic compounds were separated in the GC (7890B) using an Ultra ALLOY-1 capillary column (30 m–0.25 mm id, 2.0- $\mu\text{m}$  film) and identified using MS (5977B MSD), both from Agilent Technologies.

### 2.5.7 TGA-FTIR instrumental conditions

For each sample, using dynamic thermogravimetry, the TGA was triggered between 35 and 900  $^\circ\text{C}$ , in the inert  $\text{N}_2$  atmosphere. The purge nitrogen flowrate was set to 40 mL/min and the protective nitrogen flow to 60 mL/min.

With FT-IR, the evolved gasses from TGA were analyzed, with both an absorbance spectrum and a 3D surface

plot collected in the 530–4000- $\text{cm}^{-1}$  wavenumber range, with 32 scans per specimen.

### 2.5.8 GC-MS instrumental conditions

All samples prepared for GC-MS were analyzed on an Agilent Technologies 7890A GC system with an autosampler coupled with an Agilent 5977A mass-selective detector (MSD). The injection was run in splitless mode, with an injector temperature of 280  $^\circ\text{C}$ . A 30-m HP-5 ms column with 250  $\mu\text{m}$  i.d. and thickness of 0.25  $\mu\text{m}$  from Agilent Technologies was used. The following GC-MS instrumental conditions were applied: start temperature: 40  $^\circ\text{C}$  (held for 5 min), heating rate 1: 6  $^\circ\text{C min}^{-1}$  to 280  $^\circ\text{C}$ , and heating rate 2: 40  $^\circ\text{C min}^{-1}$  to 300  $^\circ\text{C}$  (held for 5 min). The GC-MS interphase valve delay was set to 4.60 min and the MS detector was operated in the positive mode at 70 eV with an ion-source temperature of 250  $^\circ\text{C}$ . Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

## 2.6 Preparation of reference samples

### 2.6.1 Reflux cooking of condensates

To replicate the formation of the black particles in a laboratory environment, several experiments were conducted with a total reflux system as to simulate conditions similar to the distillation unit at ArbaOne. Condensate samples (sample #1, Table 1) were heated under stirring in an attempt to generate solid humins for comparison with the black particles (sample #5, Table 1), in an experimental setup consisting of a round flask, submerged into an oil bath for heating, and a water-cooled spiral cooler attached to the flask.

For each experiment, a sample of condensate (sample #1, Table 1) of 75 mL was added to the round flask, heated to boiling, and held at boiling temperature for about 72 h.

### 2.6.2 Seeding with black particles and added furfural

To investigate what may cause further growth of the black particles, a sample of black particles (sample #5, Table 1), collected from the Arbaflame plant, was added to a condensate sample to work as seeding particles and boiled with the condensates as described in Sect. 2.6.1. In parallel, another 75 mL of the condensate sample with seeding particles was prepared, but in addition to a sample of seeding particles, 4 mL of furfural (Sigma-Aldrich, 99%) was also added to the round flask before the mixture was heated and boiled. In a similar experiment, the added furfural was replaced with an addition of 0.05 g of HMF.

Two control experiments were also performed, one with distilled water and one with condensate (sample #1, Table 1).



**Fig. 4** Picture of a sample of black particles found in the distillation unit (sample #5, Table 1)

**Table 2** Results from the determination of ash content in the black particles show similarly low ash values at both ISO standards

Standard	Ash value [%]	Temperature [°C]	Std dev
ISO 1762	0.14	525	0.01
ISO 2144	0.14	900	0.01

**Table 3** Results from ICP-MS analysis with 3 parallels of black particles show that they contain only trace amounts of inorganics

Trace elements		Al	Cr	Mn	Fe	Ni
mg/g of sample	Par 1	0.146	0.085	0.008	0.140	0.032
	Par 2	0.136	0.082	0.008	0.135	0.026
	Par 3	0.149	0.083	0.008	0.138	0.028
Average		0.144	0.083	0.008	0.138	0.027

**Table 4** Estimated elemental composition of the black particles, with H/C and O/C ratios from the two parallels of the elemental analysis

	Weight%				Per carbon	
	N	C	H	O	H/C	O/C
Black particles 1	1.5E-03	70.35	4.98	24.66	0.84	0.26
Black particles 2	8.9E-04	70.21	5.46	24.32	0.93	0.26

A 4-mL sample of furfural (Sigma-Aldrich, 99%) was added to both before the samples were heated for 72 h. This was done to control for how much, if any, of the solid matter generated from the humin experiment could be accounted for from self-polymerization of furfural.

## 3 Results

### 3.1 Characterization of particles

A sample of the black particles (sample #5, Table 1) that was collected from a filter at the inlet of the second distillation

column is shown in Fig. 4. The particles are dark black with a rough but shiny, almost metallic, surface.

#### 3.1.1 Ash and inorganic constituents

Ash analysis at 525 °C and 900 °C provides a rough estimate of the content of inorganic material. The results given in Table 2 show that the ash content is quite low, and these results are in agreement with the ICP-MS results (Table 3).

Identification of inorganic constituents in the particles was accomplished with ICP-MS analysis, after total dissolution of a particle sample in concentrated nitric acid. The results are given in Table 3.

The ICP-MS analysis shows a variety of metallic compounds where iron (Fe), aluminum (Al), nickel (Ni), and chromium (Cr) are most prominent. With the exception of aluminum, these are metals which are commonly used in black carbon steel, found in the reactor and piping at the ArbaOne plant. The low concentration of inorganics found in the black particles shows that the particles are organic in nature and supports a theory of humin formation as their source.

#### 3.1.2 Elemental analysis

The black particles from the distillation unit were analyzed to determine their elemental composition. The analysis was performed on the particles as received before extraction. The relationship between the carbon, oxygen, and hydrogen content that can be expected from humins is reported in the literature to be in the order of 55–65% carbon, 4–5% hydrogen, and 30–40% oxygen [10, 15–18]. The composition of the organic elements in the black particle sample (sample #5, Table 1) is shown in Table 4 and differs from the composition of humins by having a larger w% of carbon, with correspondingly lower oxygen content.



### 3.1.3 FT-IR spectra of the black particles

The FT-IR spectrum of the particles (sample 5, Table 1), as received, is shown in Fig. 5.

The spectra obtained from the black particle sample do not have strong absorption intensities, however finely crushed the particles were. The pattern indicates a strongly conjugated system. The lack of strong absorption bands in the C–H area is significant, indicating that saturated carbon groups are not frequent in the structure. The assignment of the major adsorption bands is given in Table S1 in the supplementary file.

### 3.1.4 SEM

Figure 6 shows two pictures of the surface of the black particles, taken with the scanning electron microscope at

3000 $\times$  and 10,000 $\times$  magnification, respectively. The image on the left shows both continuous areas with cracks and several noticeable spherical indentations and holes, which could indicate a porous structure. There are also areas with irregularly shaped debris and scattered spherical substances (magnified in the image on the right), resembling oily substances which could be the remains terpenoid compounds adsorbed to the surface of the black particles.

### 3.1.5 Pyrolysis GC–MS

Results from pyrolysis GC–MS analysis (Figure S3 in the supplementary file) showed that the volatile carbon constituents from both the black particles (sample #5, Table 1) and the dark residues (sample #7, Table 1) consist of various furanic species, phenolic groups, and terpene compounds. The data from pyrolysis GC–MS indicates that the particles

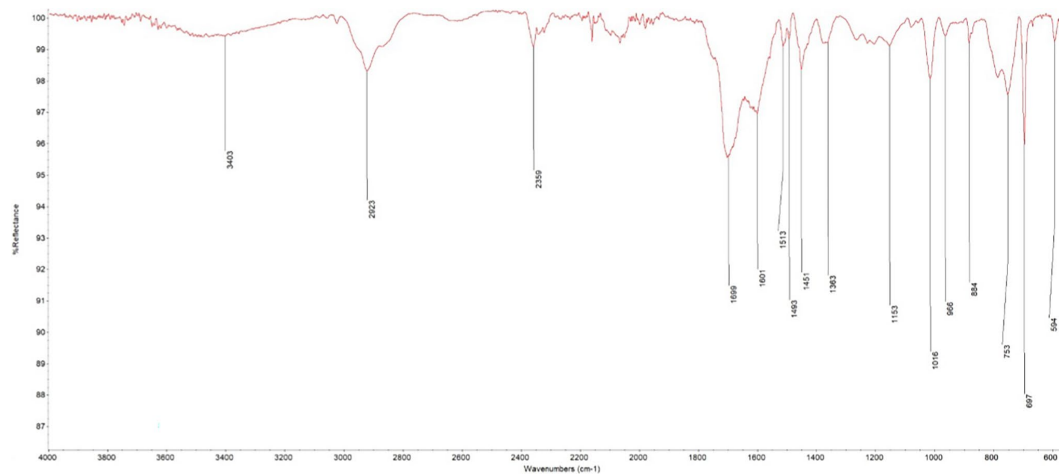
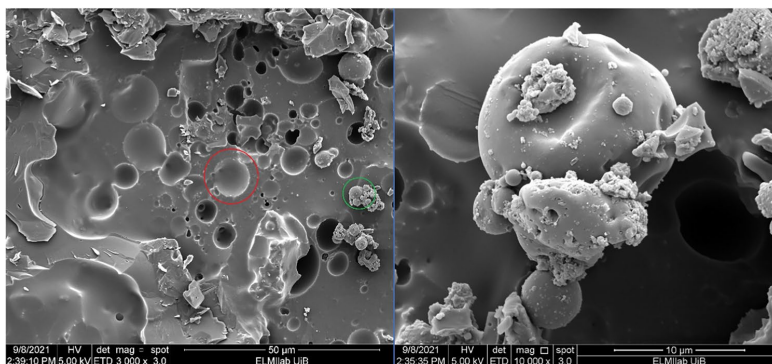


Fig. 5 IR spectrum of the black particles (sample 5, Table 1)

Fig. 6 Two SEM pictures. Black particles at 3000 $\times$  magnification. The red marker shows an indent on the surface and the green marker shows what may be terpenoids that have been adsorbed on the surface of the particles (L). One of the substances on the surface of the black particles at 10,000 $\times$  magnification (R)



consist of a furan-rich polymer network containing different oxygen functional groups and the results are in accordance with the literature results of van Zandvoort et al. [5] and support a hypothesis of humin formation as the source of the particles.

### 3.1.6 TGA-FTIR

Thermogravimetric analysis was used to study the thermal stability of the black particles, and Figure S4 in the supplementary file shows the TGA scans for both the black particles from the distillation unit (sample #5, Table 1) and from the solid dark residues found in the steam condenser (sample #7, Table 1). A mass loss of 14% from the black particles can be observed by 200 °C, which is mass loss attributed to the release of volatiles and humidity of the sample, and at the endpoint of 900 °C, a residual 20–22% of the mass remains present. In contrast to the particles, the dark residue from the condenser only shows a mass loss of 5% by 200 °C and approx. 40–43% at 900 °C, indicating a high ash content. The maximum rate of weight loss, identified by the highest intensity peak in the rate of weight change and represented by the dotted line, is found around 433 °C for both samples. The rate of mass loss for the black particles reaches approximately 5%/min at this temperature.

The high char yield for the dark particles from the reactor suggests that some condensation/polymerizations of formed fragments are possible. In addition, these results suggest that the dark residues from the HPC are very similar to what we would characterize as humins.

The evolved gasses released during TGA measurements were analyzed by FTIR. Water and CO<sub>2</sub> were the main gasses released during the mass loss, due to the release of volatile species. Water can be released as a by-product in condensation reactions, leading to losses in oxygenated functional groups. Because of this, CO<sub>2</sub> and H<sub>2</sub>O were filtered away from the TGA-FTIR spectrum in this analysis. CH<sub>4</sub> was detected at 2344 cm<sup>-1</sup> for the dark residues from the HPC, while in the spectrum for the dark particle from the distillation unit CH<sub>4</sub> can be identified at 2937 cm<sup>-1</sup> (see Figures S5 and S6 in the supplementary file). In the band range from 2170 to 2000 cm<sup>-1</sup>, there is the presence of gasses such as CO. The absorption peaks at 1740 cm<sup>-1</sup> correspond to the vibration of carbonyl groups C=O; acetyl and carboxyl groups present in hemicelluloses and cellulose. The peaks at 1430–1602 cm<sup>-1</sup> correspond to the vibration of the structure of aromatic ring (C=C) characteristic of cellulose and lignin [19].

### 3.1.7 Soxhlet extraction and solubility test

During the Soxhlet extraction with THF, which was determined to be the better of the solvent candidates from the

initial inspection, it was only possible to dissolve 23 wt% of the black particulate matter.

The most abundant compounds from the GC–MS analysis of the extracted material are given in Table S2 and comprise mostly oxygenated terpenoids which suggest that the terpenoids may not be an important constituent in the formation of the black particles, but rather are adsorbed to the particles' surface.

The initial solubility test and Soxhlet extraction showed that the particles were not easily soluble in common solvents (Figure S1 in the supplementary file). From the expanded solubility test, acetone, ethyl acetate, and dichloromethane gave the best results, being able to dissolve 32.5–33.7 wt% of the black particles (Table S3 in the supplementary file). From the two tests, it does seem that the particles from the new batch may have a small, but still significant increase in solubility, relative to the initial test and what was achieved from Soxhlet extraction with THF. The results from the expanded solubility test still show that the solubility of the black particles is fairly limited but may also indicate that the amount of terpenoids adsorbed to the surface of the particles can vary.

Several cleaning products, meant for industrial applications, have also been tested without providing any better results. The only medium that has been able to completely dissolve the black particles so far is nitric acid, which was able to fully dissolve the black particles over a period of 24 h in a concentration as low as 20%.

For the black residues (sample 7, Table 1), further investigation of solubility was deemed not necessary, as ethyl acetate proved sufficient for dissolving the majority of the residue.

### 3.1.8 Calorific value

The calorific value was determined for both samples, and the results show a lower calorific value of 26 MJkg<sup>-1</sup> for dark residues (sample #7, Table 1) from the HPC compared to the black particles from the distillation unit (sample #5, Table 1), calorific value 32 MJkg<sup>-1</sup>. Because of the calorific value and the TGA-FTIR results, the particles may have good fuel properties.

## 3.2 Characterization of other organic liquids and samples

### 3.2.1 Sampling

The function of the skimmer tank (sample point #2 from Fig. 3) is to remove oils, waxes, biomass residues, and resins like terpenoids from the aqueous product stream. These materials have been carried from the reactor with the condensate during the STEX decompression. From the analysis

of the skimmed organics, a major part of what is being removed here is terpenoids.

Samples of the condensate from both before and after passing the UF unit were inspected, but no black particles were found in the condensate stream. This implies that the particles either form after the filtration stage or are small enough that they can pass through the membrane and are invisible to the naked eye. Considering the pore size of the ultra-filtration unit, particle breakthrough is considered highly unlikely.

The temporary storage tank and the distillation unit are connected to enable recycling of the condensate. In such cases, the condensate could be heated and cooled several times, which could contribute to increase the polymerization reactions and by-product formation in the form of solid precipitates.

In the temporary storage tank, some similar particles with a dark brown color and oily/tar-like surface were found. As opposed to the black particles, these particles were liquidized and dissolved when heated in condensate. No further characterization was made since the sample was not large enough for further analysis.

### 3.2.2 FT-IR spectra

An infrared spectrum of the black organic liquid sample (sample #6, Table 1) was acquired and compared with a pure furfural sample, as shown in Figure S7. Peak assignments are given in Table S4.

The spectrum of black organic liquid found is mostly identical to that of a standard spectrum of furfural, with the exception of the small O–H stretch at  $3529\text{ cm}^{-1}$ . This impurity likely comes from the water in the condensate, mixing with the furfural.

The non-volatile bottom fraction from the fractionated condensate sample (sample #1, Table 1) was also analyzed by FT-IR, and the spectrum is given in Fig. 7. It is different from the spectra of the black particle sample, with strong C–H signals just below  $3000\text{ cm}^{-1}$ , indicating a terpenoid composition.

### 3.2.3 NMR

From the  $^1\text{H}$  NMR spectrum of the black organic liquid (Fig. 8), we identify one abundant compound with 4 peaks, corresponding with proton signals we expect to find from furfural. This further supports the idea that the black liquid is a separated phase of furfural.

Several smaller signals can be seen in the spectrum, and these correspond to 2-acetylfuran, 5-methylfurfural, and some other unidentified impurities. These signals are mostly the same as those found in the furfural standard. This supports the results from the FTIR analysis in that this liquid is furfural. The dark/black color is however interesting to note. Furfural, being a colorless liquid, will darken to yellow, brown, or even black when exposed to oxygen through oxidation and condensation reactions with furfural radical intermediates [20]. The concentration of these polymerized impurities will usually not constitute more than a minor fraction of the product, even in the case of completely black furfural.

Together, the FTIR and the NMR spectra highly suggest that the black liquid indeed is furfural, which has been darkened by impurities and supports the possibility of furfural polymerization as the source of the particles.

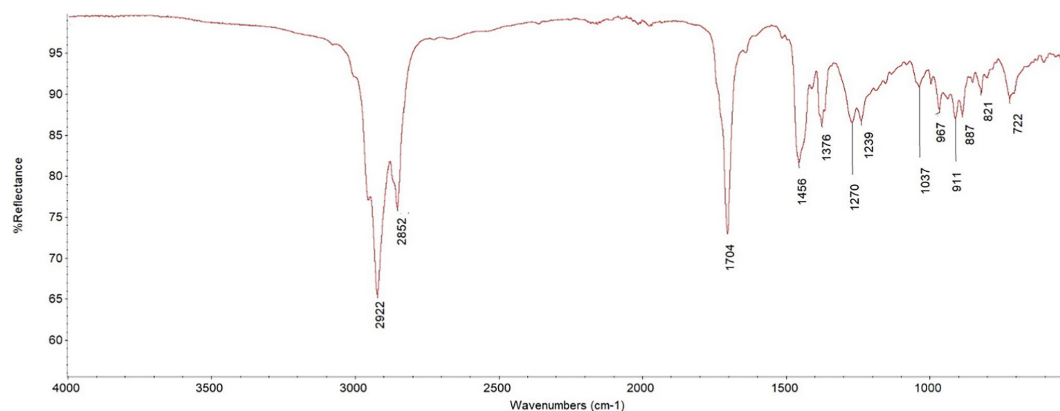
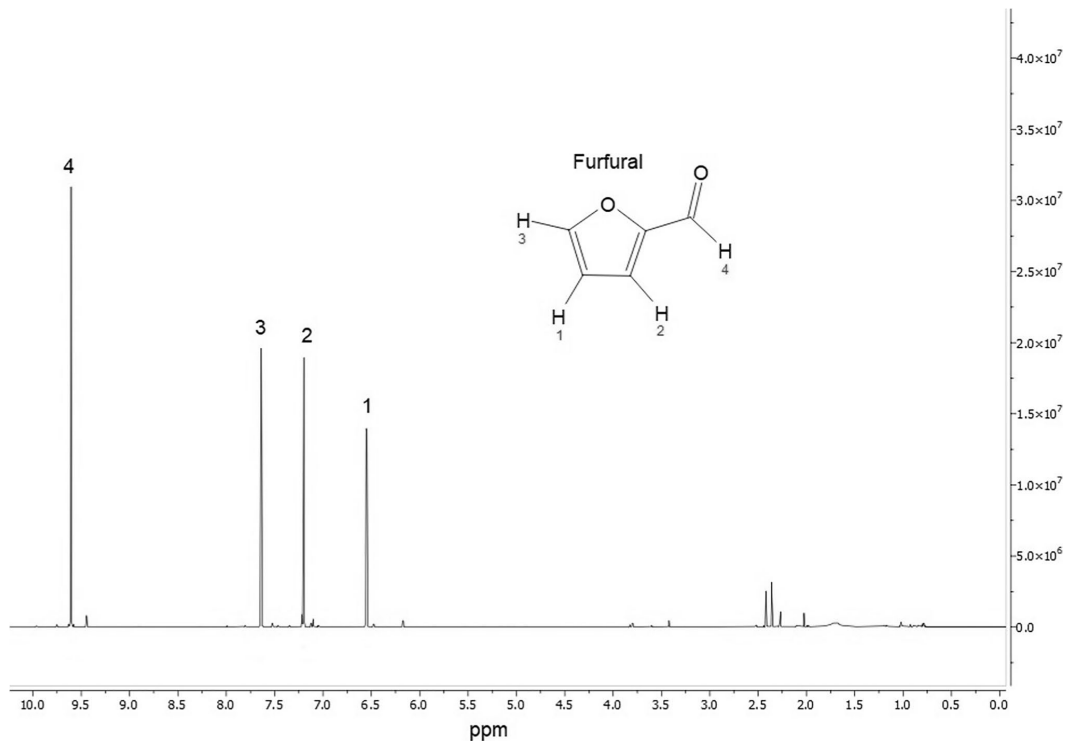


Fig. 7 Spectrum of the non-volatile 4th fraction, from the rotary evaporator fractionation, of a condensate sample (sample #1, Table 1)



**Fig. 8** Proton-NMR spectra of the black liquor, created with a 600-MHz NMR instrument. The most intense peaks assigned showing that it mainly consists of furfural

### 3.2.4 Fractionation of condensates and GC-MS results

From fractionation with the rotary evaporator, 4 separate fractions were created, where the residual fraction was non-volatile matter and comprised 3.1 wt% of the original condensate sample. In addition to the infrared spectrum given above (Fig. 7), this fraction was analyzed by GC-MS to determine the individual compounds present. The identified components are shown in Table S5 and found to be different terpenoid components from wood extractives.

Condensate samples collected from the outlets of HPC and LPC condenser units will sometimes have a thin yellow layer floating on top. The origin of the organic phase on top of the condensates is thus likely to be terpenoids from the wood biomass, but it also often contains biomass particles from the steam explosion.

### 3.3 Results from laboratory experiments

The laboratory experiments, listed in Table 5, gave some insights into what may cause the formation of the black particles found in the distillation unit.

Heating the condensate samples to their boiling point had some effects on the visual presentation of the condensate. The color changed from a light transparent yellow to a dark orange and the organic layer on top, consisting of terpenoids, thickened into a more viscous film. There were also some orange deposits staining the glass flask. However, the experiment did not produce any visible solid matter resembling the black particles and the results were therefore inconclusive.

To further investigate whether the black particles could be produced in the lab, two additional experimental variables were investigated. Firstly, a sample of black particles from the ArbaOne plant was added to the condensate sample before heating, to investigate whether we could

**Table 5** Results from laboratory experiments to replicate the formation of black particles. The table shows the input factors and the mass difference after the reaction. Furfural is denoted as FF in this table

Experiment/liquid medium	Seeding particles	Added furans	Weight of solids after heating	Mass difference	
1.1	Condensate	–	0.00	0.00	
2.1	Condensate	–	0.38	–0.07	
3.1	Condensate	4 mL FF	0.41	0.10	
2.2	Condensate	–	0.42	0.00	
3.2	Condensate	4 mL FF	0.55	0.09	
1.2	Dest. H <sub>2</sub> O	–	0.00	0.00	
4.1	Condensate	0.05 g HMF	0.45	0.01	
5.1*	Dist. H <sub>2</sub> O	–	4 mL FF	0.52	0.52
6.1*	Condensate	–	4 mL FF	0.30	0.30

\*Control experiments with only added furfural

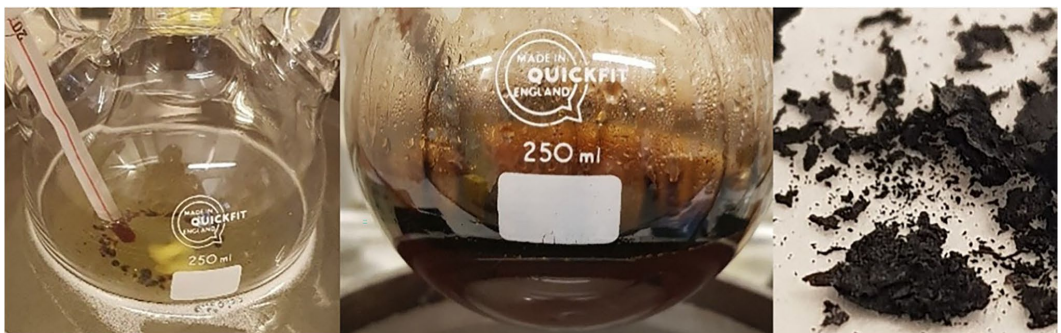
induce the growth of the particles with the condensates. Secondly, the furfural concentration was increased by adding a furfural standard (Sigma-Aldrich, 99%) to determine if black particle growth could be induced at any reasonable furfural concentration.

However, heating condensates with the addition of seeding particles had no positive effect on further generation of black particles, but rather a slight decrease in solid mass was found. In spite of this, increasing the concentration of furfural in the sample up to approx. 80 g/L by adding 4 mL of furfural before boiling resulted in a large increase in the solid material of similar character to the original black particles. A control test where furfural was added to both distilled water and a condensate sample and heated to boiling produced dark solid material deposits on the glassware in both instances. The solid residues from the experiments were then analyzed with FTIR (Fig. 9).

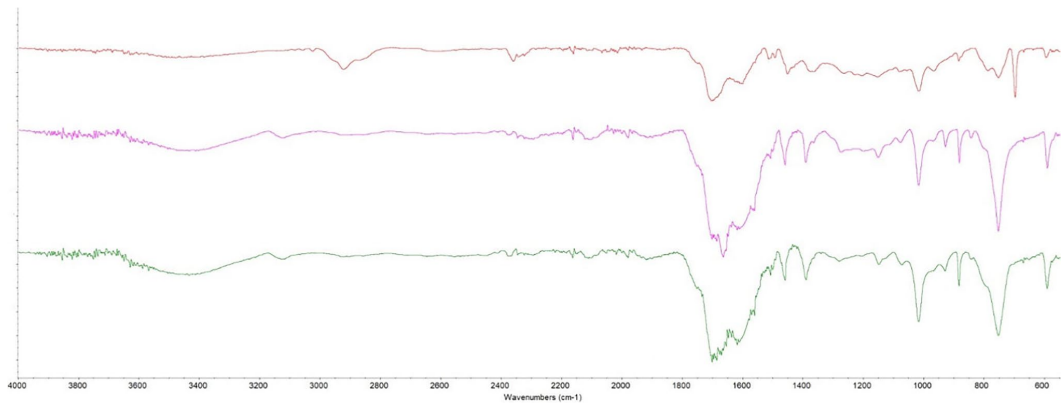
The FT-IR spectra in Fig. 10 show the similarities between the black residue created during laboratory experiments with furfural in water/condensate (pink and blue) and

the spectra acquired from the black particles (sample #5, Table 1 (orange)).

It is interesting to note how the yield of black residue varies by a large amount in these experiments. While some of the variation can be attributed to difficulty with removing all the solids from the flask without loss, the likely reason for the variation is that the furfural, which was added to the condensate samples in certain experiments, was mixed for an arbitrary amount of time, until it was visually homogeneous in the flask. However, it was observed that in the control experiments with distilled water and furfural, some furfural seemed to fall out of solution with the water and collect on the bottom in small droplets after beginning to heat the mixture. This may be caused by a too short mixing time but shows how furfural in a separate phase in an aqueous medium will increase the yield of solid black residue formed on the hot glass surface and strongly supports the hypothesis of the black particles being formed from polymerization of furfural. Figure 9 shows pictures of the progression of black particle growth from the control experiment, where furfural was added to distilled water.



**Fig. 9** Pictures showing the formation of black particles in laboratory experiments (experiment 6.1). Separate droplets of furfural collecting on the bottom (L). Black liquid and particle formation (M) dried particle residue retrieved from the flask (R)



**Fig. 10** Figure showing the similarities between residue from black particles from the distillation (top, orange), the control experiment with distilled H<sub>2</sub>O (middle, pink), and the unit condensate control experiment (bottom, green)

## 4 Discussion

The origin of the black particles was hypothesized to be either humins, polymerization of furfural, polymerization of terpenoids, or a co-polymerization of all three compound types. Analysis of the fluid samples (1, 2, 3, and 6) shows the presence of both furfural and terpenoids in the fluid stream, including the existence of a separated furfural phase found in a drainage pipe (sample 6). Furfural is known to readily polymerize to give a black solid [21] while terpenoids are a natural source of wood resins that with time can form insoluble amber.

From the GC–MS analysis of the fractionated condensate and the skimmer tank product (Fig. 7), wood extractives and especially terpenoids are among the most abundant compounds.

In the analysis of the soluble parts of the black particle sample, the components are shown to be dominated by terpenoids, both in direct GC–MS and PY–GC–MS. Most of the identified components contain oxygen, which increases their water solubility and explains why they are not removed in the skimmer tank together with the hydrocarbon terpenoid species. Hence, they are present in the post-skimmer process stream and can be a factor in the formation of black particles downstream in the system.

From the literature definition, humins are defined as by-products from the conversion of cellulose and its derivatives including sugars, HMF, and lactic acid. The humin yield will also generally increase with higher temperatures. In the condensate streams from the Arbaflame process, the concentrations of both HMF and sugars are very low, as they are not volatile and therefore generally stay with the steam-exploded biomass instead of following the steam from the reactor. Additionally, the distillation unit operates at temperatures

around 100 °C, which reduces the rates of the reactions that are involved in humin formation. When considering the total throughput of condensate over time, the total amount of sugar and HMF are larger. However, for these to be the primary cause of the black particles, a mechanism is needed where these molecules aggregate on the hot surface of the heat exchanger, which so far have not been shown.

Furfural on the other hand is the most abundant compound in the system, with a propensity for polymerization, and furfural is also the target product for the processing unit. Furfural is formed from hemicellulose sugars at the STEX conditions and is volatile with the steam. It thus follows the steam and is present as a dissolved component in the subsequently condensed aqueous stream. A separate organic phase comprising mostly furfural was also found in the process system, in the form of the dark-colored liquid tapped from a drainage pipe (sample #6). The processes leading to the formation of the separated furfural liquid phase are at present unknown but reflect that the furfural concentration in the aqueous stream must at times be above the solubility limit of 83 g/L. Furfural is thus an accessible source material for polymerization into solid particles. The black color of the particles is consistent with furan-based polymers, as darkening and black precipitates have been widely reported as a problem in furfural production and storage. A suggestion for the structure of the furfural polymer is given in Zeitsch [20] and reproduced here (Fig. 11).

The IR spectra of the particles from the refinery and laboratory experiments, as shown in Figs. 5 and 10, respectively, correspond well with the hypothesis of a furfural origin, as very limited absorption is found in the C–H areas. Terpenoids give strong adsorption around 3000 cm<sup>-1</sup>, as seen in Fig. 7 from the residual terpenoids from the condensate fractionation. As an example of a terpenoid polymer, reference

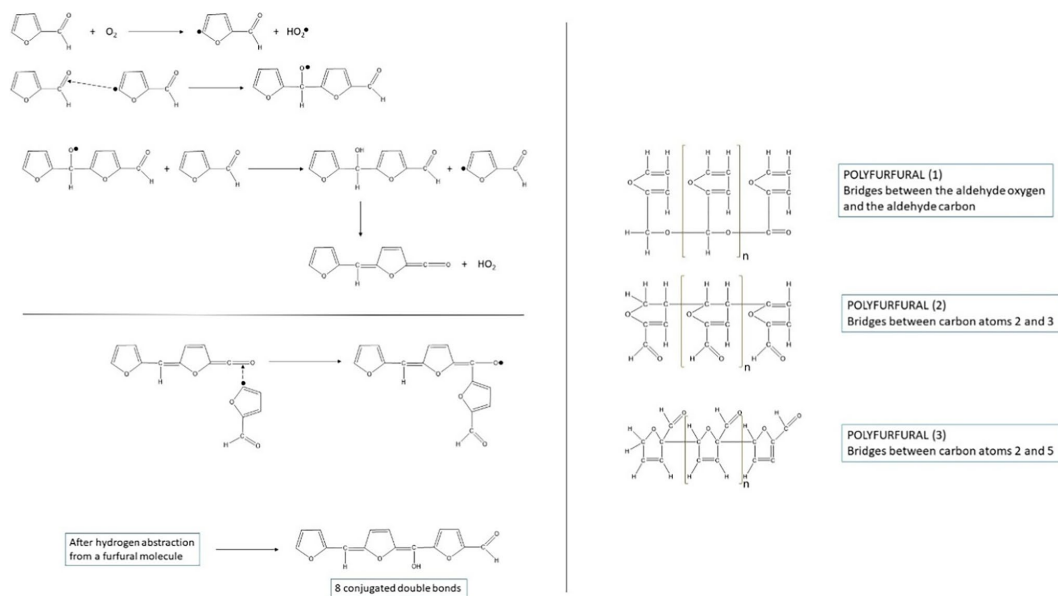


Fig. 11 Suggested reaction mechanism (L) and structures (R) for furfural polymers (adapted from Zeitsch 2000, 30–32 [20])

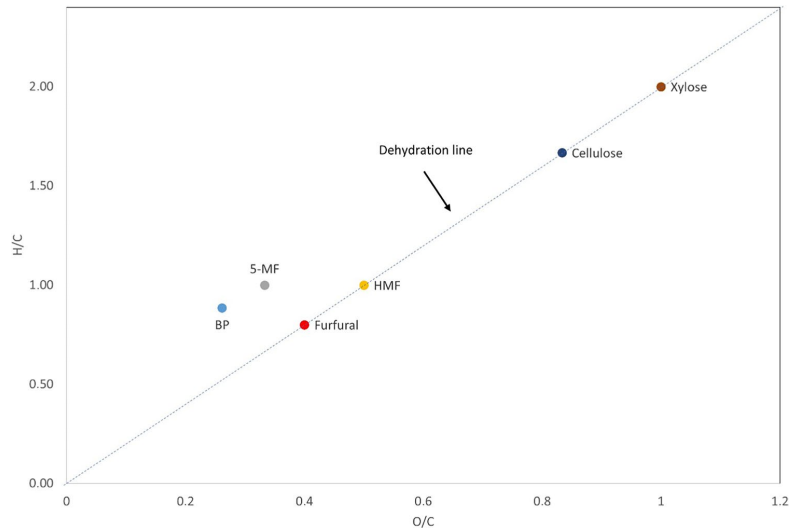
IR spectra of amber [22] also show strong IR adsorption in the C–H areas, which is not in agreement with the spectra acquired for the black particles in this analysis. Furfural is known to polymerize very efficiently at acidic conditions, and the pH of the condensate is in the area of 2–3 due to the presence of formic and acetic acid produced during hemicellulose degradation at STEX conditions [2]. The presence of catalysts can increase the propensity for polymerization. However, the ash content of the particle is low, and the inorganic constituents are quite limited, which does not support a hypothesis with the presence of active heterogeneous catalysts for this reaction. The polymerization of furfural is expected to be more efficient when the furfural is present as a separate organic phase, as found in sample 6 [23]. Even though no evidence of black particles was found before the distillation unit, there is a possibility that nucleation of the particles starts at an earlier phase, e.g., as humin formation, but that growth occurs at a low rate before they reach the distillation unit. Here temperatures are higher and the presence of heated surfaces where the nucleated particles can attach to and grow on increases. The ultra-filtration unit would however remove humin particles larger than  $0.05 \mu\text{m}$  before reaching the purification unit, suggesting that humin particles, which may be created during the STEX reaction, are not likely to reach the distillation unit.

Compared with humins formed during furfural production from xylose, the black particles have higher oxygen

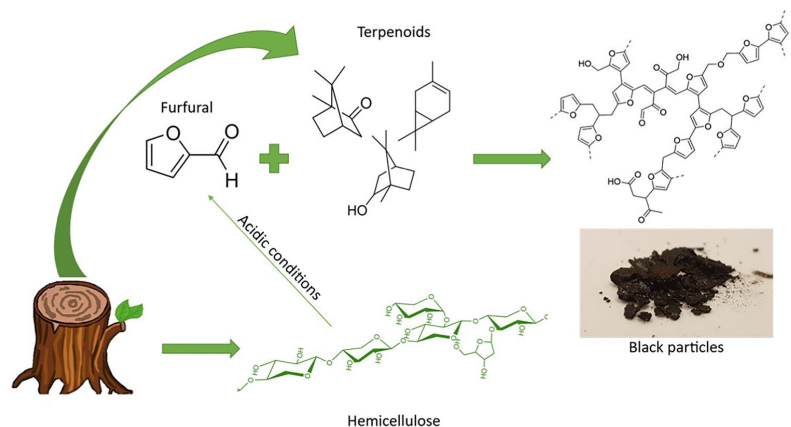
content and a corresponding lower carbon content. The hydrogen content is also very similar but slightly higher in the black particle sample. The theoretical H/C and O/C ratios for polymerized furfural are H/C = 0.8 and O/C = 0.4, according to the polymerization scheme provided in Zeitsch, which is not very different from the measured values for the black particles that average H/C = 0.88 and O/C = 0.26. Aside from these differences, the black particles share many similarities in both properties and apparent structure with both humins [24] and pseudo-lignins, which is another class of solid by-product. Pseudo-lignins are derived from condensation reactions between dehydrated polysaccharides, such as HMF and furfural, that take place during high-severity pretreatment of lignocellulosic biomass in the presence of acids (Fig. 12) [25].

A probable explanation for the terpenoids that have been observed in thermal and solvent extracts can be that they are adsorbed on the surface of the particles. Globules seen on the particle surface in the SEM pictures correspond well with the adsorbed terpenoids. A certain degree of co-polymerization of terpenoids into the primarily furfural-based solids is also possible, which would explain why the measured O/C ratio is lower than the theoretical ratio for a pure furfural polymer. However, the proportion must be quite limited since strong C–H adsorption bands are not seen in the IR spectra. A depiction of the suggested pathway for the formation of black particles from wood can be found in Fig. 13.

**Fig. 12** Van Krevelen diagram comparing the black particles (BP) from furfural production, furans (5-MF, HMF, and furfural) as well as cellulose and xylose (the figure is amended from Wang et al. [6])



**Fig. 13** Schematic overview of the suggested formation pathway for the black particles in the Arbaflame plant



## 5 Conclusions

Steam explosion of biomass and valorization of chemical by-products is a challenging process where the formation of unwanted solids is almost impossible to avoid. Understanding the conditions that lead to their formation and their chemical structure is therefore necessary for the ability to handle these undesirable solid residues and maintain a fully functional biorefinery.

Analyses performed on black particles found in the distillation unit of the ArbaOne plant, along with analyses of fluids from several different points throughout the

side-stream process chain, are presented in this paper and show that these insoluble particles, which have been formed on a heated surface, are of an organic nature and have humin-like characteristics. Our interpretation of the results shows that the black particles recovered from the distillation unit primarily consist of polymerized furfural with a certain amount of adsorbed terpenoids on the particle surface. Some aspects of the reaction mechanism, like the reaction kinetics, have not been investigated in depth in this work and are yet not fully understood. While the analysis of the recovered particles indicates that the structure incorporates organic compounds like terpenoids, laboratory experiments have found that no constituent other



than furfural is necessary for the formation of black solids to happen. A range of other compounds, like other furans and residual sugars, while not as prominent as furfural, can be found in the condensate stream. This permits the possibility that some of these could also be integrated into the complex polymer matrix of the particles.

To prevent the formation of black particles, it is suggested that the concentration of furfural in the condensate be below the saturation point for furfural in water. This also means that distilled furfural without sufficient purity should not be redistilled together with STEX condensate, as this may increase the furfural concentration above the saturation limit, creating a separate furfural phase that can polymerize to black particles. It is also suggested to implement routine cleaning of distillation equipment to limit the negative effects of black particle formation. The use of strong acids is preferred as they have shown to be effective, but solvents or good industrial cleaners may be used as the use of strong acids may not be practical in an industrial setting.

The similarities between the black particles, discussed in this paper, and the other dark solids reported in literature, such as humins and pseudo-lignins, are presumably not arbitrary. The resemblance emerges because of the requirement for very similar substrates and reaction conditions. How the black particles produced at the ArbaOne plant, during distillation of furfural, should be characterized in relation to humins, defined by their generation from catalytic conversion of cellulose and its derivatives, and pseudo-lignins, which arise from condensation reactions during high-severity, acidic pretreatment, is not within the scope of this paper. Moving forward, the focus should be on investigating the reaction kinetics of the furfural polymerization, to better understand the conditions necessary to trigger these polymerization reactions.

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**Author contribution** The experimental work was carried out by Dag Helge Hermundsgård, Solmaz Ghoreishi, and Mihaela Tanase-Opedal. Writing was carried out by Tanja Barth and Dag Helge Hermundsgård. Rune Brusletto developed the ArbaOne concept and implemented it in the production unit. Solmaz Ghoreishi and Mihaela Tanase-Opedal have also contributed with the text revision.

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## Declarations

**Conflict of interest** The authors declare no competing interests.

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