

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY  
LUT School of Engineering Science  
Degree Program of Chemical Engineering

Master's Thesis  
2017

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**Pretreatment of Wheat Straw for Fast Pyrolysis by Recirculation of by-products**

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# TIIVISTELMÄ

KIT:ssä (Karlsruhe Institute of Technology, Saksa) kehitetty bioliq® konsepti on kolmivaiheinen konversioprosessi toisen sukupolven drop-in biopolttoaineille, jotka tuotetaan biojätteestä kuten vehnän oljista. Ensin biomassa konvertoidaan liikuteltavilla nopeilla pyrolyysiyksiköillä energiatiheäksi synteettiseksi bioraakaöljyksi (engl. *biosyncrude*), bioöljyn ja hiiltyneen oljen seokseksi. Tämä liete syötetään isoon 8 MPa:iin paineistettuun kaasuvirtaussekoittimeen, jolla tuotetaan tervavapaata kaasua. Lopuksi kaasu konvertoidaan DME (Dimethylether) synteesillä halutuksi polttoaineeksi.

Tämä työ käsittelee ensimmäistä vaihetta, nopeaa pyrolyysiä. Tämä ensimmäinen muunnos suoritetaan 500 °C kaksoisruuvisekoitusreaktorissa. Hienonnettu biomassa konvertoidaan termokemiallisesti kuumaksi pyrolyysihöyryksi, kaasuksi ja hienoksi hiileksi sekunneissa. Kiinteät partikkelit erotetaan toisistaan sykloneilla ennen kaksivaiheista höyryn kondensointia, jolla tuotetaan orgaanista sekä vesipitoista kondensaattia. Orgaaninen kondensaatti on päätuote, kun taas vesipitoisella kondensaattilla on heikommat ominaisuudet kaasutukseen (suuri vesipitoisuus, matala lämmitysarvo ja matala hiilipitoisuus). Vesipitoinen kondensaatti kuitenkin sisältää merkittäviä määriä orgaanisia happoja, joita voidaan hyödyntää muissa käyttökohteissa. Yksi mahdollinen käyttökohde voisi olla korkean tuhkapitoisuuden omaavien olkien demineralisaatio.

Tämän työn tavoite on testata nopeasta pyrolyysistä saadun vesipitoisen kondensaatin vaikutusta oljen esikäsitteilyä ja sen vaikutusta koko prosessiin.

- Esikäsitteily kehittäminen ja karakterisointi
- Esikäsitteilytuotteiden (nesteet, kiintoaineet) karakterisointi
- Esikäsitteily vehnäöljen pyrolyysikokeet
- Prosessitehokkuuden kokonaisvaltainen tutkiminen simuloimalla

Voidaksemme päätellä, onko alkukäsittelyprosessi toteuttamiskelpoinen, arvioimme sen energiankulutuksen ja vertasimme sitä ylimääräisen orgaanisen kondensaatin energiamäärään. Valitettavasti alkukäsittely ei ole toteuttamiskelpoinen, koska alkukäsittelyn arvioitu energiankulutus on 414kW, kun taas ylimääräisen orgaanisen kondensaatin energiamäärä on 291 kW. Toisena mahdollisuutena oli alkukäsittelyn hahduttamisen korvaaminen aurinkokuivauksella, mikä muuttaa tilannetta dramaattisesti, koska alkukäsittelyyn tarvittava energia tippuisi 57 kW:iin. Toisinsanoen, tämä olisi 19,25%:in lisäys vehnäoljien tuottamaan energiaan. Tämä saattaisi oikeuttaa alkukäsittelyprosessin. Kuitenkin, aurinkokuivauksen käyttöä pitää vielä arvioida, koska sääolot eri

maissa ja alueilla eivät välttämättä ole sopivia menetelmälle. Lisäksi alkukäsittely tuottaa jätevettä, jota voitaisiin käyttää kastelussa, muuten se täytyy käsitellä. Tämä seikka vaatii lisäarviointia.

## ABSTRACT IN ENGLISH

The bioliq® concept developed at KIT is a three-step conversion process for the production of 2<sup>nd</sup> generation drop-in biofuels from biomass waste such as e.g. wheat straw. First, biomass is converted by decentralized fast pyrolysis units to yield energy dense biosyncrude, a mixture of bio-oil and char. This slurry is the feed for large-scale pressurized entrained flow gasification at 8 MPa to yield producer gas free of tars. The gas is finally converted by DME (Dimethyl ether) synthesis to yield designer fuels.

The given task is set in the first step, fast pyrolysis. This initial conversion is performed in a twin-screw mixing reactor at 500 °C. The comminuted biomass feed is thermochemically converted to hot pyrolysis vapors, gas, and char fines within seconds. Solid particles are separated by cyclones prior to a two-step condensation of the vapors to yield an organic and an aqueous condensate. The organic condensate represents the main product whereas the aqueous condensate has less favorable characteristics for subsequent gasification (high water content, low heating value, and low carbon content). However, the aqueous condensate contains significant amounts of organic acids which open up the potential for other uses. One possible use could be the demineralization of wheat straw with high ash content.

The aim of this work is to test the effect of wheat straw pretreatment with aqueous condensate obtained from fast pyrolysis and its effect on the overall process efficiency.

- Development and characterization of pretreatment method
- Characterization of pretreatment products (liquid, solid)
- Pyrolysis experiments with pretreated wheat straw
- Simulation to investigate effects on overall process efficiency

In order to know if the pretreatment process is feasible, it was estimated the energy consumption of the pretreatment process and compared it with the energy content in the extra organic condensate. Unfortunately, the pretreatment is not feasible because the estimated energy of the pretreatment is 414kW while the energy content in the extra organic condensate can produce 291kW. However, it was proposed to replace the evaporation of the pretreatment process by a sun drying which turns the situation around dramatically because the energy consumed by the pretreatment would be 57kW. In other words, this is an increase of 19.25% of the total energy produced by wheat straw. This may justify the pretreatment process. Nevertheless, the implementation of sun-drying should be evaluated since weather conditions could be not favorable the whole year in all countries or regions. In addition, the pretreatment process produces waste water which could be used for irrigation or they must be treated, this point should be evaluated in detail.

## ABSTRACT IN GERMAN

Das am KIT entwickelte bioliq®-Konzept ist ein dreistufiges Umwandlungsverfahren zur Herstellung von Biokraftstoffen der zweiten Generation aus Biomasseabfällen, wie z.B. Weizenstroh. Zuerst wird Biomasse durch dezentrale Schnellpyrolyse-Anlagen in bioSynCrude®, eine Mischung aus Bioöl und Kohle, umgewandelt. Diese zeichnet sich durch eine hohe Energiedichte bei gleichzeitig hoher erreichbarer Energieausbeute aus. Die Schlämme dient als Einspeisung einer großvolumigen, unter Druck stehende Flugstromvergasung bei der bei einem Druck von 8 MPa ein Erzeugergas frei von Teeren produziert wird. Das Gas wird schließlich durch DME-Synthese(Dimethylether) umgewandelt, wodurch die Designer-Kraftstoffe erzeugt werden.

Der erste Teil der Aufgabe befasst sich mit der Schnellpyrolyse. Dabei erfolgt die anfängliche Umwandlung in einem Doppelschnecken-Mischreaktor bei 500 ° C. Die zerkleinerte Biomasse wird innerhalb von Sekunden thermochemisch in heiße Pyrolyse-Dämpfe, Gas- und Blei-Feinstoffe umgewandelt. Feste Partikel werden durch Zykclone vor einer zweistufigen Kondensation der Dämpfe getrennt, um ein organisches und ein wässriges Kondensat zu ergeben. Das organische Kondensat stellt das Hauptprodukt dar, während das wässrige Kondensat für die anschließende Vergasung (hoher Wassergehalt, geringer Heizwert und niedrigem Kohlenstoffgehalt) weniger günstige Eigenschaften aufweist. Das wässrige Kondensat enthält jedoch erhebliche Mengen an organischen Säuren, die das Potenzial für andere Verwendungen erschließen. Eine mögliche Verwendung könnte die Demineralisierung von Weizenstroh mit hohem Aschegehalt sein.

Ziel dieser Arbeit ist es, die Wirkung der Weizenstrohvorbereitung mit wässrigem Kondensat aus der schnellen Pyrolyse und deren Auswirkung auf die gesamte Prozesseffizienz zu testen.

- Entwicklung und Charakterisierung der Vorbereitungsmethode
- Charakterisierung von Vorbereitungsprodukten (flüssig, fest)
- Pyrolyseexperimente mit vorbereitetem Weizenstroh
- Simulation zur Untersuchung von Auswirkungen auf die gesamte Prozesseffizienz

Um herauszufinden, ob der Vorbereitungsprozess durchführbar ist, wurde der Verbrauch der benötigten elektrischen Leistung des Vorbereitungsprozesses abgeschätzt und mit dem in elektrische Leistung umwandelbaren Energiegehalt im extra organischen Kondensat verglichen. Die Vorbereitung auf diese Weise ist nicht möglich, da die geschätzte benötigte elektrische Leistung der Vorbereitung 414 kW beträgt, während der Energiegehalt im extra organischen Kondensat nur zu einer elektrischen Leistung von 291 kW ausreicht. Es wurde jedoch vorgeschlagen, die Verdampfung

des Vorbehandlungsprozesses durch eine Sonnentrocknung zu ersetzen, die die Situation drastisch verändern würde. Für die Vorbehandlung würde auf diese Weise nur noch eine elektrische Leistung von 57 kW benötigt werden. Der Anstieg beträgt somit 19,25% der Gesamtenergie, die durch Weizenstroh erzeugt wird. Dadurch könnte der Vorbehandlungsprozess gerechtfertigt werden. Trotzdem sollte die Umsetzung der Sonnentrocknung ausgewertet werden, da die Wetterbedingungen das ganze Jahr in allen Ländern oder Regionen nicht günstig sein könnten. Darüber hinaus produziert das Vorbehandlungsverfahren Abwässer, die für die Bewässerung verwendet werden können oder die Abwässer müssten weiter behandelt werden. Dieser Punkt sollte im Detail ausgewertet werden.

## ACKNOWLEDGEMENTS

I should say that I am blessed because I received a lot of help to complete my thesis, without this help I would not have been able to complete it as satisfactory as I did. I would like to express my deepest gratitude to **Dr. Axel Funke** who gave me not only the opportunity to work with him but also the confidence to apply my ideas and knowledge; his guidance and experience were vital in this project. I would like to thank the KIT laboratory staff, especially **Daniel Richter and Pia Griesheimer**. They were so useful.

I also express my gratitude to **Prof. Tuomas Koironen** because he was really patient and flexible with me. My ex-coworkers and friends in Mexico, Finland, USA and Germany who enriched my research from various perspectives and helped me on topics in regarding this project.

Finally, I would like to thank my mom **Emilia Chavando, Sonia Kotenko** and **Fabiola Villicaña** for the emotional support which was crucial to finish my thesis.

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# LIST OF SYMBOLS AND ABBREVIATIONS

## General

- AAEMs: alkali and alkaline earth metals (mg)
- FC: Fixed carbon (% w dry basis)
- VM: Volatile matter (% w dry basis )
- GHG: Greenhouse gas
- ILUC: Impact: indirect land use change
- DME: Dimethyl ether
- Char<sub>d</sub>: Char dry basis (%)
- Char<sub>ad</sub>: Char as determined (%)
- WSm : Wheat straw moisture (%)
- OC<sub>d</sub>: Organic condensate dry basis (%)

## Experimentation

- AC: Aqueous condensates
- WS: Wheat straw
- WS1: Untreated wheat straw

## Washing

- WS2: WS1 washed with fresh water
- WS2A: WS1 washed with L1
- WS2B: WS1 washed with L1A
- WS2C: WS1 washed with L1B
- WS2D: WS1 washed with L1C
- L1: Liquors from the washing process to obtain WS2
- L1A: Liquors from the washing process to obtain WS2A
- L1B: Liquors from the washing process to obtain WS2B
- L1C: Liquors from the washing process to obtain WS2C
- L1D: Liquors from the washing process to obtain WS2D
- WS2': WS1 washed with L3D'
- L3D'': Liquors from the washing process to obtain WS2'

## Leaching at room temperature

- WS3: WS2 leached with AC at room temperature and rinsing with fresh water
- WS3A: WS2 leached with AC at room temperature and rinsing with L3
- WS3B: WS2 leached with AC at room temperature and rinsing with L3A
- WS3C: WS2 leached with AC at room temperature and rinsing with L3B
- WS3D: WS2 leached with AC at room temperature and rinsing with L3C
- L2: AC from the leaching process to obtain WS3
- L3: Liquors from the rinsing process to obtain WS3
- L3A: Liquors from the rinsing process to obtain WS3A
- L3B: Liquors from the rinsing process to obtain WS3B
- L3C: Liquors from the rinsing process to obtain WS3C
- L3D: Liquors from the rinsing process to obtain WS3D

## Leaching at 60°C

- WS3': WS1 leached with AC at 60 °C and rinsing with fresh water

- WS3A': WS1 leached with AC at 60 °C and rinsing with L3'
- WS3B': WS1 leached with AC at 60 °C and rinsing with L3A'
- WS3C': WS1 leached with AC at 60 °C and rinsing with L3B'
- WS3D': WS1 leached with AC at 60 °C and rinsing with L3C'
- L2': AC from the leaching process to obtain WS3'
- L3': Liquors from the rinsing process to obtain WS3'
- L3A': Liquors from the rinsing process to obtain WS3A'
- L3B': Liquors from the rinsing process to obtain WS3B'
- L3C': Liquors from the rinsing process to obtain WS3C'
- L3D': Liquors from the rinsing process to obtain WS3D'

## Mass balance

- AC: Aqueous condensates
- AC-L: Aqueous condensates for leaching
- FW: Freshwater
- RW: rinsing water
- R-AC: Recirculate Aqueous condensates
- T-WS: Treated wheat straw
- WAC: Waste aqueous condensates
- WS: Wheat straw
- WS-C: wheat straw from centrifuge
- WS-E: wheat straw from evaporator
- WS-P: wheat straw for pyrolysis process
- W-C: Water from centrifuge
- W-E: Water from the evaporator
- W-R: Water from rinsing
- W-M: Water Mixture
- WW: Wastewater
- AR: Ash removal

## Pre-design of the equipment

- $t_{\text{box}}$ : time for moving a box (h)
- $t_s$ : Duration time of the leaching or rinsing step (h)
- $N_{\text{box-s}}$ : Boxes for the washing
- $WS_{\text{Box}}$ : wheat straw per box (kg)
- $F_{\text{ws}}$ : flow rate of the wheat straw kg/h
- $V_{\text{box}}$ : volume of the box ( $\text{m}^3$ )
- $N_{\text{B}}$ : Number of boxes
- $\rho_{\text{ws}}$ : Density of wheat straw ( $\text{kg}/\text{m}^3$ )
- $D_{\text{F}}$ : Design factor
- $W$ : potential energy (kW)
- $m$ : mass (kg)
- $g$ : gravity constant ( $\text{m}/\text{s}^2$ )
- $h$ : height (m)

- Ec: Energy content (MJ/kg)
- Ee: Extra energy (MJ/kg)
- Ep: Energy from a pretreated wheat straw (MJ/kg)
- Eu: Energy from an untreated wheat straw (MJ/kg)
- Ec<sub>o</sub>: Energy content in organic condensate (MJ/kg)
- Ec<sub>c</sub>: Energy content in organic condensate (MJ/kg)
- Y: yields (kg product/kg starting material x 100 %)
- Y<sub>o</sub>: Yield of organic condensate (kg organic condensate/kg starting material x 100 %)
- Y<sub>c</sub>: Yield of char (kg char/kg starting material x 100 %)
- HVV<sub>o</sub>: higher heating value of organic condensate (MJ/Kg)
- HVV<sub>c</sub>: higher heating value of char (MJ/Kg)

# 1 INTRODUCTION

By 2050 the world population would reach 9.7 billion ([UN,2017a](#)) and it is estimated that the vehicles on the road would be 2 billion ([Neste Oil, 2017](#)) that may carry problems related to climate change.

One available solution is the use of advanced biofuels which are those produced from lignocellulosic feedstocks, for example, wheat straw/corn stover/bagasse, wood-based biomass or non-food crops such as grasses, miscanthus, and algae. Advanced biofuels have lower CO<sub>2</sub> emission and higher GHG reduction when its life cycle assessment is compared with the life cycle assessment of fossil fuels ([Neil Bird, 2003](#)). According to Päivi Paakkari, a business development manager from Neste Oil “Straw is an agricultural residue that has a lot of potentials”. She contends that “the biggest thing is wheat straw is an underused material in Finland and in most countries and a significant amount of straw can be collected from the fields in a sustainable manner so it doesn’t harm the soil structure” ([Neste Oil, 2017](#)).

In this thesis, a pretreatment of wheat straw for fast pyrolysis by recirculation of byproducts were further investigated. In order to decrease the number of alkali and alkaline earth metals (AAEMs). Removing AAEMs from biomass leads to increase organic condensate and sugar yields ([S.R.G. Oudenhoven, 2016](#)). Different pretreatment methods to decrease the number of AAEMs from biomass have been studied. For example, Oudenhoven used synthetic byproducts. Others dilute sulfuric acid or organic acids such as maleic, oxalic, succinic acid, etc, ([Gizem Barisik, 2016](#)). However, these pretreatments imply an additional cost for the acids or for producing synthetic byproducts. In this thesis were used real byproducts also called aqueous condensates (AC).

To further develop the pretreatment, two factors were examined that could make the pretreatment process reliable, sustainable and profitable. These factors are (1) Water consumption during the process and (2) Energy consumption during the process.

To address these factors, the pretreatment process and the products of the pretreatment process were characterized. Next, the pretreatment process was related with the pyrolysis process in order to look for efficiencies in the overall process by recirculation of energy and water. Finally, the reactor yields using a pretreated wheat straw were contrasted with the reactor yields of a non-pretreated wheat straw.

## 1.1 Fossil Fuels and Sustainability

The seventh sustainable development goal is to ensure access to affordable, reliable, sustainable and modern energy for all ([UN, 2017b](#)).

Energy is vital for any advancement in technology, education, industrialization, health, etc. In other words, progress is linked with energy and its demand is increasing not only in developed countries but also in poor and developing countries since the global population with access to electricity has increased from 79 percent in 2000 to 85 percent in 2012 and it will continue increasing since there are still 1.1 billion people without energy access. ([UN, 2017c](#)). However, the production and consumption of energy has led to environmental problems ([UN, 2017d](#)) and an increased in the CO<sub>2</sub> emissions rate that according to Christine Lagarde, Managing Director International Monetary Fund, they are related to the climate change, she said that "The science is sobering—the global temperature in 2012 was among the hottest since records began in 1880. Make no mistake: without concerted action, the very future of our planet is in peril." ([Christine Lagarde, 2013](#)).

On 12 December 2015, some countries adopted the [Paris Agreement](#) at the [COP21 in Paris](#) in order to agree to work in the global temperature rise ([UN, 2017e](#)). Some of the agreements on climate change are:

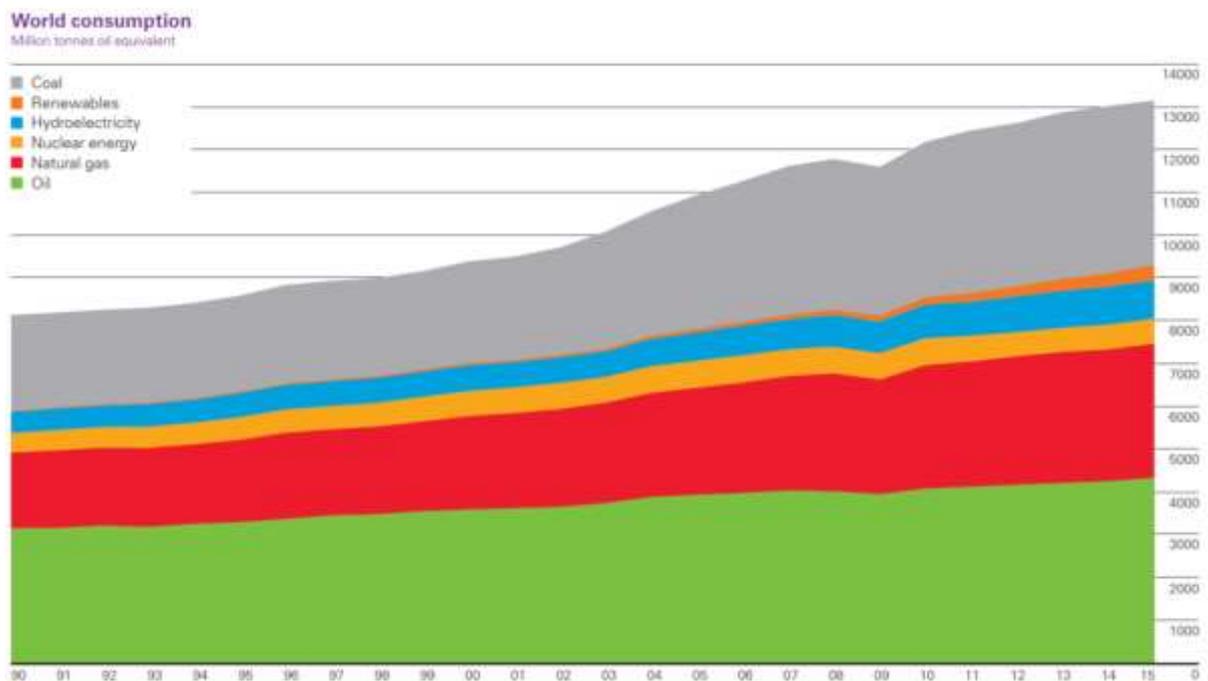
- *“Long-term temperature goal (Art. 2) – The Paris Agreement, in seeking to strengthen the global response to climate change, reaffirms the goal of limiting global temperature increase to well below 2 degrees Celsius while pursuing efforts to limit the increase to 1.5 degrees”* ([UN, 2017e](#)).
- *“Global peaking (Art. 4) –To achieve this temperature goal, Parties aim to reach global peaking of greenhouse gas emissions (GHGs) as soon as possible, recognizing peaking will take longer for developing country Parties, so as to achieve a balance between anthropogenic emissions by sources and removals by sinks of GHGs in the second half of the century”* ([UN, 2017e](#)).
- *“Finance, technology and capacity-building support (Art. 9, 10 and 11) – The Paris Agreement reaffirms the obligations of developed countries to support the efforts of developing country Parties to build clean, climate-resilient futures, while for the first time encouraging voluntary contributions by other Parties. Provision of resources should also aim to achieve a balance between adaptation and mitigation. In addition to reporting on finance already provided, developed country Parties commit to submitting indicative information on future support every two years, including projected levels of public finance”* ([UN, 2017e](#)).

Considering these agreements and that more people are accessing to energy, it is vital to reduce the consumption of fossil fuels replacing them for renewable fuels. Figure 1 presents the world primary energy consumption in 2015. We can clearly see a small increment in renewable energy consumption.

While, the energy consumption of coal, natural gas and oil continue increasing that means that the potential of energy consumption by renewable is big.

The primary energy consumption by the fuel of some countries is presented in Table 1. Mexico’s energy consumption by renewable in 2014 was 3 of 190 (1.6%) and in 2015 3,5 of 180 (1.9%). Finland’s energy consumption by renewable in 2014 was 2.9 of 26.3 (11%) and in 2015 3.1 of 25.9 (12%). Germany’s energy consumption by renewable in 2014 was 32.3 of 311.9 (10.4%) and in 2015 40 of 320 (12.5%). Germany’s energy consumption by renewable could cover easily the whole demand of Finland’s energy consumption.

On the other hand, US’s energy consumption by renewable in 2014 was 66.8 of 2013 (2.9%) and in 2015 71.7 of 2280 (3.14%). China’s energy consumption by renewable in 2014 was 59.9 of 2970 (1.74%) and in 2015 62.7 of 3014 (2%). Unfortunately, the countries that consume more energy are some of the countries that don’t take advantage of the renewable energy.



**Figure 1: World primary energy consumption 2015. Source ([BP Statistical Review of World Energy, June 2016](#)).**

**Table 1. Primary energy consumption by fuel. Source ([BP Statistical Review of World Energy, June 2016](#)).**

	2014								2015						
	Oil	Natural Gas	Coal	Nuclear energy	Hydro-electricity	Renewables	Total		Oil	Natural Gas	Coal	Nuclear energy	Hydro-electricity	Renewables	Total
China	526.8	169.6	1949.3	30.0	242.8	51.9	2970.3	559.7	177.6	1920.4	38.6	254.9	62.7	3014.0	
US	838.1	692.7	453.8	453.8	59.3	66.8	2300.5	851.6	713.6	396.3	189.9	57.4	71.7	2280.6	
Germany	110.4	64.0	78.8	22.0	4.4	32.3	311.9	110.2	67.2	78.3	20.7	4.4	40.0	320.6	
Mexico	85.2	78.1	12.8	2.2	8.6	3.0	190.0	84.3	74.9	12.8	2.6	6.8	3.5	185.0	
Finland	8.6	2.3	4.1	5.4	3.0	2.9	26.3	8.3	1.9	3.5	5.3	38	3.1	25.9	

Note: Units measured in million tonnes of fuel  
 Primary energy consumption in other countries is presented in Appendix A.

## 1.2 Biomass

According to Donald L Klass biomass is defined “as non-fossil, energy-containing forms of carbon and includes all land- and water-based vegetation and such materials as municipal solid wastes, forestry and agricultural residues, municipal biosolids, and some industrial wastes. In other words, biomass is all non-fossil organic materials that have an intrinsic chemical energy content” ([Donal.L Klass, 1998](#)).

Biomass is normally characterized by some physical and chemical properties such as ash content, bulk density, moisture, heating value, volatile fraction and chemical composition. The biomass acceptability as an energy source is based on those characteristic. ([Rupam Kataki, 2015](#)).

The chemical energy is in fixed carbon (FC) and volatile matter (VM) which is an index of the gaseous fuels present. Both characteristics VM and FC show the combustible fraction and they are an indicator of the value of the fuel. If carbon sequestration is the goal through pyrolysis, the higher the fixed carbon content the better. While for gasification lower fixed carbon is best because it is more that can volatilize to syngas. The chemical composition determines the concentration of carbon, hydrogen, nitrogen, sulfur, chlorine, and oxygen, present in the fuel. While, the biochemical composition determines the percentage of cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other compounds ([Rupam Kataki, 2015](#)).

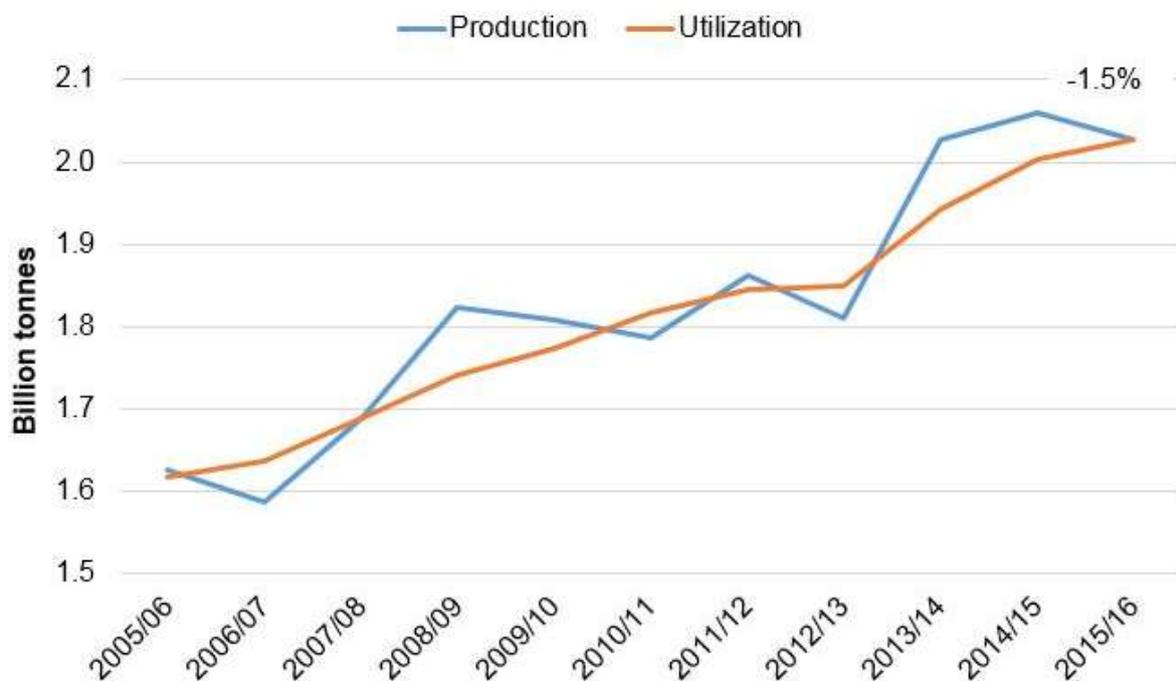
Biomass feedstock can classify into three categories: first generation, second generation, and third generation, respectively ([European biofuels, 2017](#)).

- **First Generation**, - The fixed carbon (FC) and volatile matter (VM) in this generation is sugar, lipids, and starches directly extracted from a plant, for example, corn, wheat, rice, potatoes, cassava, sorghum, sugarcane, etc. The biggest disadvantage of this generation is the feedstock is edible and it is seeing as a competitor with food. However, the use of 1<sup>st</sup> generation biofuels are used worldwide today because
- **2nd Generation** The fixed carbon (FC) and volatile matter (VM) in this generation is cellulose, hemicellulose, lignin or pectin, for example, agricultural and forestry residues such as wheat straw, the biggest disadvantage here feedstocks are too expensive and complex to present a business case today. In addition, some feedstocks like wheat straw present logistics problems.
- **3rd Generation** - The fixed carbon (FC) and volatile matter (VM) in this generation are derived from an aquatic autotrophic organism (e.g. algae).

Biomass is a renewable energy source and, and its utilization as feedstock for biofuel adds less CO<sub>2</sub> is to the atmosphere ([Kersten SRA, 2007](#)). This thesis focuses on 2<sup>nd</sup> Generation feedstocks to be precise wheat straw.

### 1.3 Wheat Straw

Wheat was one of the first domesticated food crops and it has been consuming for the major civilizations of Europe, West Asia, and North Africa since 8 000 years. Today, wheat continues being one of being the most important food grain source for humans and its production and consumption is increasing over the years (FAO, 2017). Figure 2 presents the production and utilization of wheat.



**Figure 2: World wheat and coarse grains production and utilization Source (FAO).**

The production of wheat produces byproducts and one of them is the wheat straw which is mainly used as fertilizer and to feed farm animal (J. M. Suttie, 2000). However, it is possible to add value to wheat straw by the production of biofuels using wheat straw as a raw material ([Alfani, F 2000](#), [Ballesteros I, 2006](#), [F. Talebnia 2010](#), [T. Mani, 2010](#), [Agro Business Park, 2011](#)). In addition, the residue/crop ratio is 1.3 which makes the raw material quite available ([Talebnia F, 2010](#)).

The composition of biomass varies depending both on the species and the geographic location in which it has been grown. Nevertheless, in general, crop residues, such as cereal straws, consist of five main components: cellulose, hemicellulose, lignin, extractives and ash ([Jennifer Ruth Dodson, 2011](#)). Table

2 and 3 present the chemical composition of the wheat straw and the proximate analysis of wheat straw respectively.

**Table 2: Chemical composition of wheat straw. Source (R. M. Rowell, 2014).**

Component	Yield (% wt. db.)
Cellulose	29-51
Hemicellulose	26-32
Lignin	16-21
Ash	4.5-9
Silica	3-7

Note: db. (Dry basis)

Fuel analysis based upon VM (Volatile Matter) content, ash, and moisture, with the FC (Fix Carbon) determined by difference, is termed the proximate analysis of a fuel. Elemental analysis of a fuel, presented as C, N, H, O, and S, together with the ash content, is termed the ultimate analysis of a fuel. The ratio of FC to VM provides an indication of the ease with which the solid fuel can be ignited and subsequently gasified, or oxidized, depending on how the fuel is to be converted ([Capitalenergy, 2017](#))

**Table 3: Proximate analysis of wheat straw. Source ([B.M Jenkins,1998](#)).**

Component	Yield (% wt. db.)
Fixed Carbon	17,71
Volatile Matter	75,27
Ash	7,02

Note: db. (Dry basis)

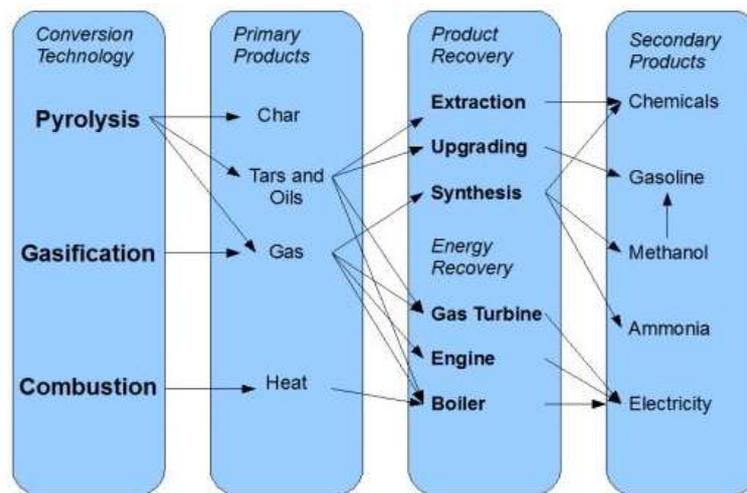
## 1.4 Biomass Thermal Conversion Technology

A good way to recover the energy content in biomass is using thermochemical conversion processes. There are mainly three thermochemical conversion processes combustion, gasification, and pyrolysis ([A.V. Bridgwater, 1994](#)). Figure 3 presents the mass thermal conversion schematically.

- Combustion burns biomass directly with excess oxygen at 800–1000 °C and the outcomes are just heat and this heat can be converted to mechanical power and electricity. It is already a well-known commercial technology and combustion technology is widely available at domestic, small industrial, and utility scales ([Zhongyang Luo and Jingsong Zhou, 2017](#)).
- Gasification converts biomass into useful convenient gaseous fuels or a combustible gas mixture through partial oxidation of biomass at high temperatures of 800–900 °C. Gasification

of biomass also involves removal of oxygen from the gas to increase its energy density ([Zhongyang Luo and Jingsong Zhou, 2017](#)) ([Prabir Basu, 2010](#)).

- Pyrolysis is a thermal destruction of biomass in the absence of air/oxygen. Pyrolysis of biomass starts at 350–500 °C and goes to 700 °C with the liquid oil, gases, and solid products. Pyrolysis of biomass is one of the most efficient technologies that are used to produce biofuels. The process uses either argon or nitrogen gas. The process yields are bio-oil, solid residue, and gaseous products ([Zhongyang Luo and Jingsong Zhou, 2017](#)).

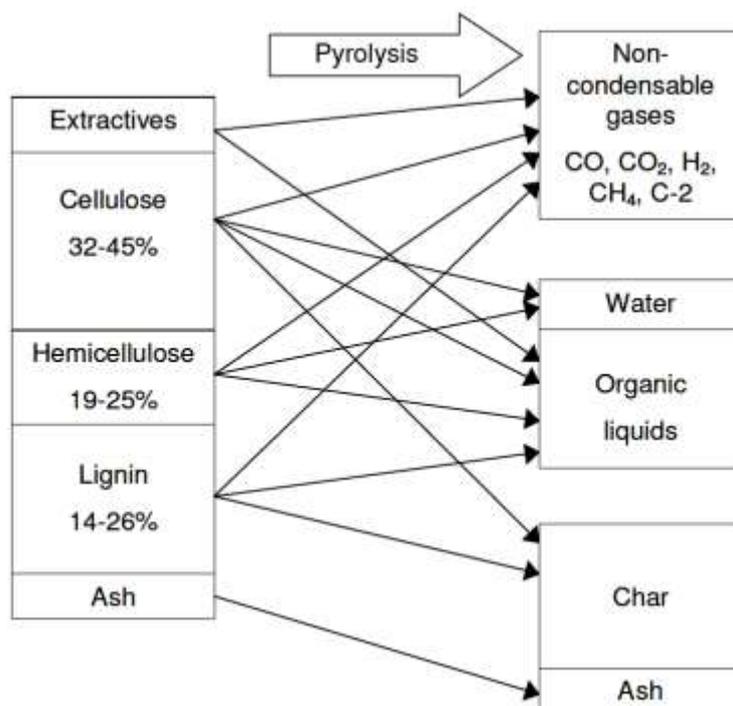


**Figure 3: Biomass thermal conversion.** Source ([A.V. Bridgwater, 1994](#))

## 1.5 Pyrolysis

Pyrolysis is the thermal decomposition of organic components in the absence of air. Different products are obtained such as liquid fraction, char, and gas. Several different technologies have been developed using different temperatures or different heating rates to influence the product composition ([D.L Klass, 1998](#)).

The primary products of hemicellulose and cellulose are condensable vapors and gas. Lignin decomposes to liquid, gas and solid char products. While extractives contribute to liquid and gas products. Ashes remain in the char. Figure 4 presents a schematic distribution of the pyrolysis process.



**Figure 4: Schematic distribution of the pyrolysis process.** (Gomes Fonseca, 2015)

## 1.6 Alkali and Alkaline Earth Metallic Species (AAEMs)

Agricultural residue (straw residues, husk residues etc.) contains considerable amounts of alkali and alkaline earth metallic species (AAEMs) such as sodium, potassium, calcium, magnesium, etc (Song Hu, Long, 2015). They affect negatively the yields of the organic condensate by increasing the formation of biochar and gaseous species (S.R.G. Oudenhoven, 2016, Scott W, 2016, Mourant D., 2011, Di Blasi, 2009, R. Fahmi, 2007).

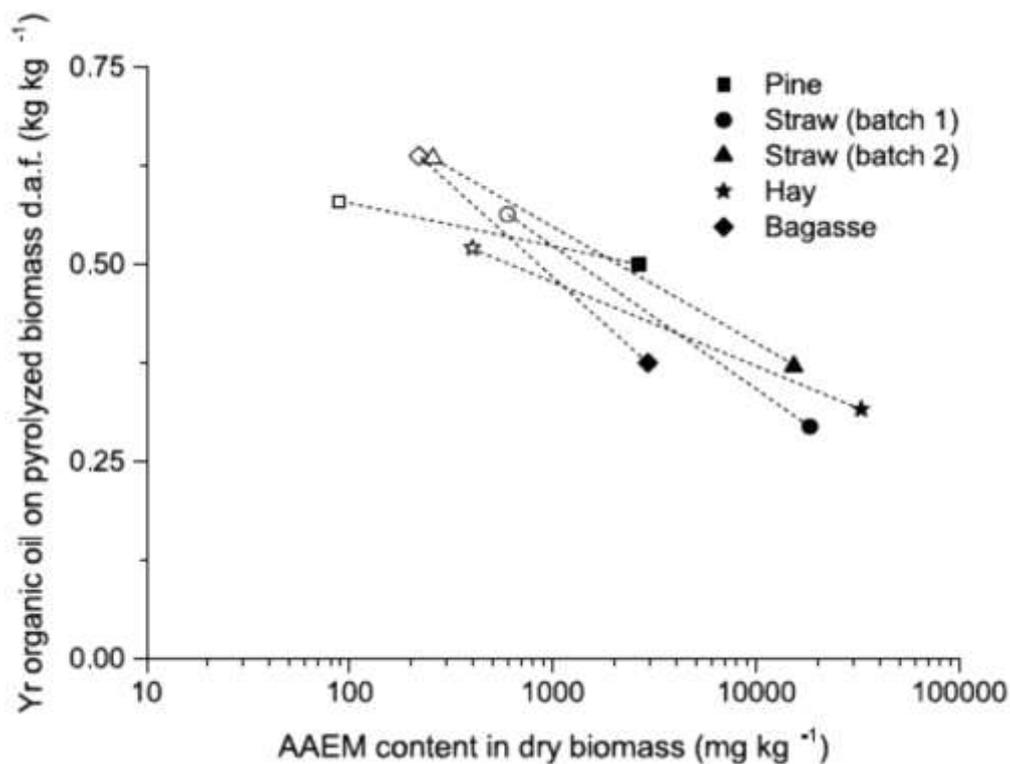
### 1.6.1 Removing AAEMs

Alkali and alkaline earth metals, in combination with other elements such as silica and sulfur, and facilitated by the presence of chlorine, are responsible for many undesirable reactions (Jenkins, 1996). These serial of reactions are complex and there is not much information about them (S.R.G. Oudenhoven, 2016).

There are pretreatments to reduce the concentration of AAEMs in biomass, for example washing with water. This pretreatment can remove troublesome elements in biomass such as potassium, sodium and other soluble water components (Jenkins, 1996). Other pretreatments are leaching with organic acids such as:

- Different acetic Acid concentrations ([K.L. Chin, 2015](#)).
- Maleic, oxalic, succinic acid, etc. ([Gizem Barisik, 2016](#)).
- Dilute hydrochloric acid, dilute sulfuric acid, dilute oxalic acid ([Zhang T, 2013](#)).
- Synthetic aqueous condensates ([S.R.G. Oudenhoven, 2016](#)).

According to Oudenhoven, chlorine is a major factor in ash formation because it facilitates the mobility of many inorganic compounds such as potassium. In addition, Chlorine may affect operation by corrosion. While, alkalis often form sulfates ([S.R.G. Oudenhoven, 2016](#)). Pyrolysis of acid leached biomasses resulted in a large increase of the organic oil yield compared to the untreated biomass. Figure 5 presents organic oil yield as a function of the AAEM content of the feed ([S.R.G. Oudenhoven, 2016](#)).



**Figure 5: Organic oil yield as a function of the AAEM content of the feed. The organic oil yield is expressed on basis of biomass fed to the pyrolysis reactor ([S.R.G. Oudenhoven, 2016](#)).**

Oudenhoven was able to reduce the number of ashes from a sample of wheat straw by leaching it with synthetic aqueous condensates. As it can be seen in Table 4, Oudeenhoven removes 62.5% of the total ashes from a sample of wheat straw with 6% of ashes of the total wheat straw mass. While in the second batch the ash removal was 37.5% from a sample of wheat straw with 8% of ashes of the total wheat

straw mass [S.R.G. Oudenhoven, 2016](#)). The composition of the synthetic aqueous condensates that Oudenhoven used are presented in Table 5 and they are compared with real aqueous condensates. The full composition of the real aqueous condensates is presented in Appendix B.

**Table 4: Biomass composition before and after acid leaching according to Oudenhoven Source ([S.R.G. Oudenhoven, 2016](#))**

	Straw (Batch 1)			Straw (Batch 1)		
	Initial (% of the total mass of WS)	Final (% of the total mass of WS)	Ash removal %	Initial (% of the total mass of WS)	Final (% of the total mass of WS)	Ash removal %
Compositional analysis, mass fraction in biomass d.a.f. (dry, ash free) (kg kg <sup>-1</sup> )	6	2	62.5	8	5	33.33

Note: d.a.f. (dry, ash free) refers to the composition of *biomass* excluding all water and ash content

**Table 5: Chemical composition of the synthetic aqueous condensates and KIT aqueous condensates**

Component	Synthetic mixture (Oudenhoven)	Real Aqueous Condensates (KIT)
Acetic acid (wt%)	10	4.165
Acetol (wt%)	-	2.956
Ethanol (wt%)	3.75	-
Methanol	-	0.944
Acetone (wt%)	3.75	-
Propionic acid (wt%)	1.5	0.449
Guaiacol (wt%)	1.5	0.24
Other organics (wt%)	-	-
water (wt%)	79.5	87.42

Note: the

As it can be seen the aqueous condensates used by Oudenhoven are different than the aqueous condensates used in this thesis.

## 2 EXPERIMENTAL SETUP AVAILABLE AT KIT AND PRETREATMENT

Biomass is a renewable source of carbon and it can be converted into biofuels by thermochemical processes. The Institute of Catalysis Research and Technology (IKFT) in Karlsruhe Institute of Technology (KIT) has made substantial contributions in renewable energy field by pyrolysis of biomass. KIT has different experimental setup for pyrolysis experiments such as the bioliq® and the fluidized bed reactor; the following sections describe them briefly since a hot stream from the bioliq® process is considered for heating the aqueous condensates produced in the bioliq® and they were used to leach wheat straw. In addition, pyrolysis experiments were performed in the fluidized bed reactor.

### 2.1 Process in the Bioliq® Pilot Plant

The aim of the bioliq® process is the conversion of biomass such as wood or agricultural residues into synthetic fuels or other organic chemicals. The first stage of the bioliq® process is to create a web of multiple decentralized pyrolysis plants able to convert biomass into bio-slurry which is a mixture of organic condensates, aqueous condensates, and char produced in the pyrolysis process. This bio-slurry has a higher energy than the straw ([Trippe, F., 2011](#)) and density similar to water. However, The bioliq® concept could make the logistics process more efficient and affordable since instead of transporting wheat straw which has a low density to a central plant for converting it into bio-slurry; decentralized pyrolysis plants would do it in the fields so it would transport bio-slurry and the decentralized pyrolysis plants rather than wheat straw. The second stage is the implementation of a large-scale gasification and synthesis plant that receives the bio-Syncrude and converts it into gasoline, DME (dimethyl ether) and other products. Figure 6 represents schematically the concept of the Bioliq process and Figure 7 presents bioliq® process.

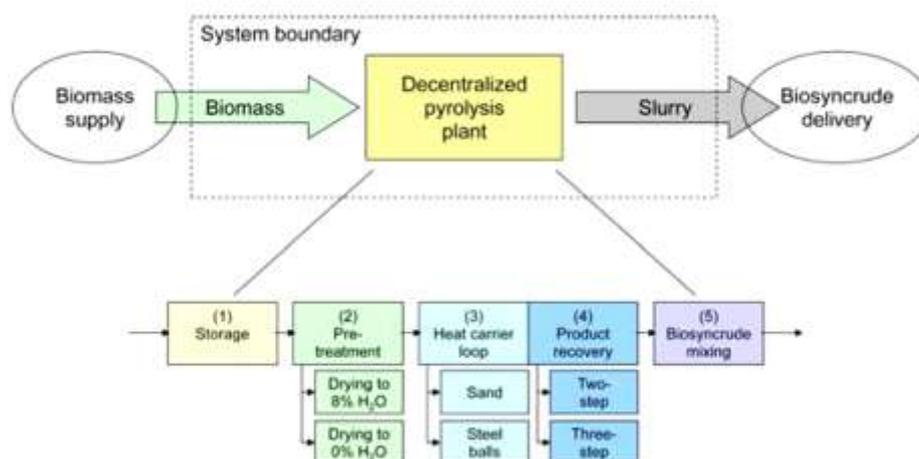
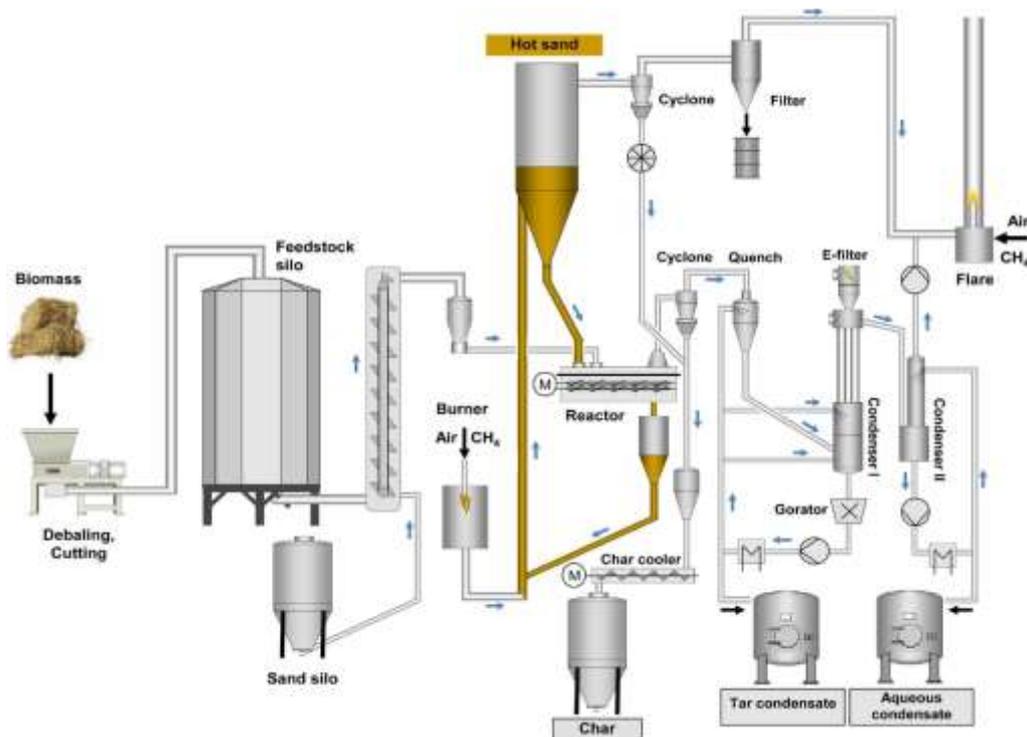


Figure 6: Bioliq® concept. Source ([Gomes Fonseca, 2015](#))

### 2.1.1 Bioliq® Process Description

Figure represents 7 the Bioliq® process where biomass is shed using grinds of 5 mm and stored in a silo and then biomass (500kg/h) goes into the twin-screw reactor where is heated at 515 °C, the biomass rate is controlled by a series of screws and lifts and the heat is supplied by hot sand which was heated through the combustion of the dry char produce in this process. The flue gases produced in the reactor pass through a cyclone which separates the char and the gas from the cyclone goes into a quenching cycle where it is sprayed with a cold organic condensate ; then the product is fed into the condenser I, where there is an electrostatic precipitator, to make sure the gas is clean of solids and liquids, the condensate is cooled and partially stored as a tar condensate. Lastly, the gas is fed to a the condenser II, with a quenching spray system which works with glycol and water -20°C, then the gas is removed from the top, while, the aqueous condensate is cooled and stored as aqueous condensates. The organic condensate is kept at a temperature similar to its product exit value to keep the viscosity low enough to be easily pumped. The aqueous condensate is separated at a low temperature and therefore doesn't require cooling.



**Figure 7: Bioliq® process. Source (Cornelius Pfitzer, 2016)**

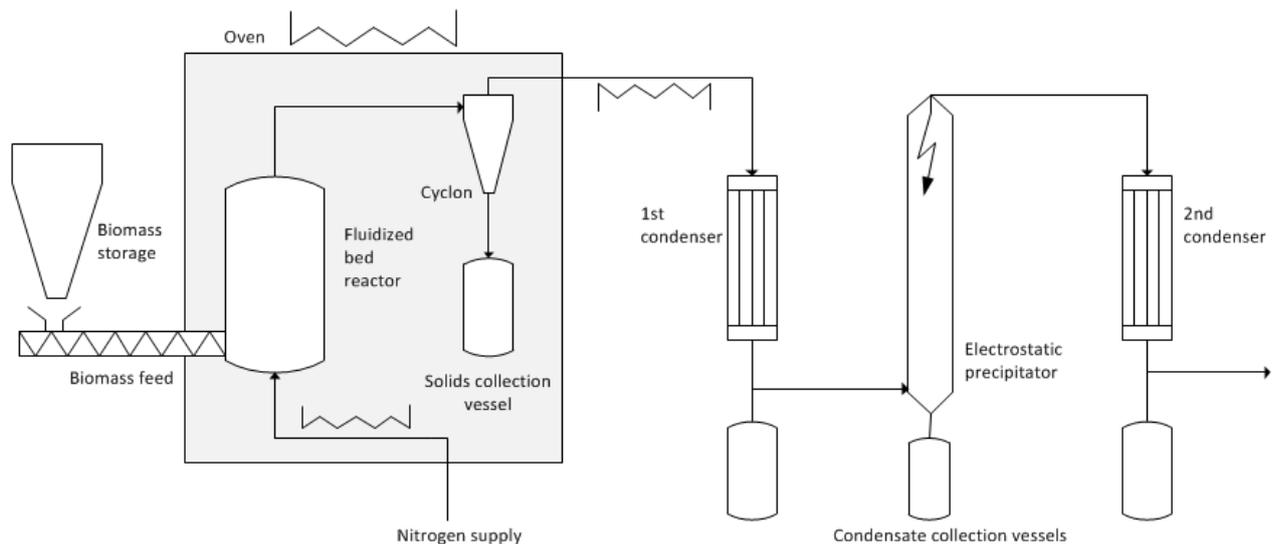
### 2.2 Fluidized Bed Reactor

The fluidized bed reactor (FBR) has been designed to pyrolyze 100-200 g of biomass within 1-2 h of operation.

The product recovery is similar to that of the larger pyrolysis plants like the bioliq® and it separates char, organic condensate, and aqueous condensate. Figure 8 represents a simplified scheme. Some

pyrolysis experiments were performed in the fluidized bed reactor with pretreated wheat straw and with untreated wheat straw. These experiments are described in Chapter 3.

Biomass is fed into the biomass storage then, a screw conveyor transports the biomass into the reactor which contains sand. The reactor, the cyclone, and the solids collection vessel are inside an oven which provides heat. The system is heated at 515 °C and a stream of nitrogen is fed to the reactor. After some time some gases and char are produced. The char is contained in the cyclone and the solids collection. While the gases are carried by the nitrogen and goes to the first condenser. In the first condenser organic liquid is collected, then the gases continue going through the system and in the electrostatic precipitator some char and more organic condensate stay. After the gas goes to a second condenser where AC is collected.



**Figure 8: Simplified flow scheme of the fluidized bed reactor test rig. Source (Axel Funke, 2017)**

### 2.3. Pretreatment Process Proposal

In this section, it is assumed that the pretreatment process will be added into the bioliq® process in order to reduce the number of ashes contained in wheat straw and increase the reactor yields.

The main stages of the pretreatment process are the following:

- **Washing:** wheat straw is washed with water to remove mainly potassium and sodium since, for some high AAEM biomass feedstocks, a number of aqueous condensates produced in the pyrolysis process may not be sufficient to dissolve a significant amount of AAEMs ([S.R.G. Oudenhoven, 2016](#)).

- Leaching: washed wheat straw is leached with the aqueous condensate produced in the pyrolysis process to remove more AAEMs.
- Rinsing: after the leaching, wheat straw is rinsed with water.
- Dewatering by centrifugation or pressing: removing water by mechanical means is crucial since the energy required for mechanical dewatering is much lower than the energy required for evaporation.
- Evaporation: Finally the remaining water in the wheat straw is evaporated to obtain a wheat straw with the same moisture content than a non-pretreated wheat straw.

In order to characterize the pretreatment process and look for optimizations washing and leaching experiments at different conditions were performed. Chapter 3 describe the experiments performed and the conditions of those experiments.

## 3 EXPERIMENTATION AND PROCESS CONDITIONS

### 3.1 Laboratory Analyses

Table 6 contains the analytical methodology used to determinate the moisture content, higher heating value, ash content and so on.

**Table 6: Analytical Methodology**

	<b>Biomass</b>	<b>Char</b>	<b>Organic Condensate</b>	<b>Aqueous Condensate</b>
<b>Moisture content</b>	DIN EN 14774-3: (prEN ISO 18134) Drying at 105 °C; (±0.2 %)	DIN EN 14774-3: Drying at 105 °C; (±0.1 %)	Volumetric Karl-Fischer-Titration (MetOH with Hydranal-Composit-V) (±1.5 %)	Volumetric Karl-Fischer-Titration (MetOH with Hydranal-Composit-V)
<b>Higher Heating Value</b>	DIN EN 14918: Bomb calorimeter (±100 J g <sup>-1</sup> )	DIN 51900-2/3: Bomb calorimeter (±200 J g <sup>-1</sup> )	DIN EN 14918: Bomb calorimeter (±50 J g <sup>-1</sup> )	-
<b>Ash Content</b>	DIN EN 14775 (prEN ISO 18122): 60 min @ 250 °C, 120 min @ 550 °C (atmospheric conditions) (±0.2 %)	DIN EN 14775 (prEN ISO 18122): 60 min @ 250 °C, 120 min @ 550 °C (atmospheric conditions) (±0.5 %)	-	-
<b>Carbon, hydrogen, and nitrogen contents</b>		DIN 51732: Elemental analysis without correction of water content	DIN EN 15104: Elemental analysis without correction of water content	DIN EN 1484 TOC
<b>Solids content</b>	-	IKFT Method (Extraction with MethOH) (±0.5 %)	IKFT Method (Extraction with MethOH) (±1.5 %)	-
<b>COD</b>	-	-	DIN ISO 15705	

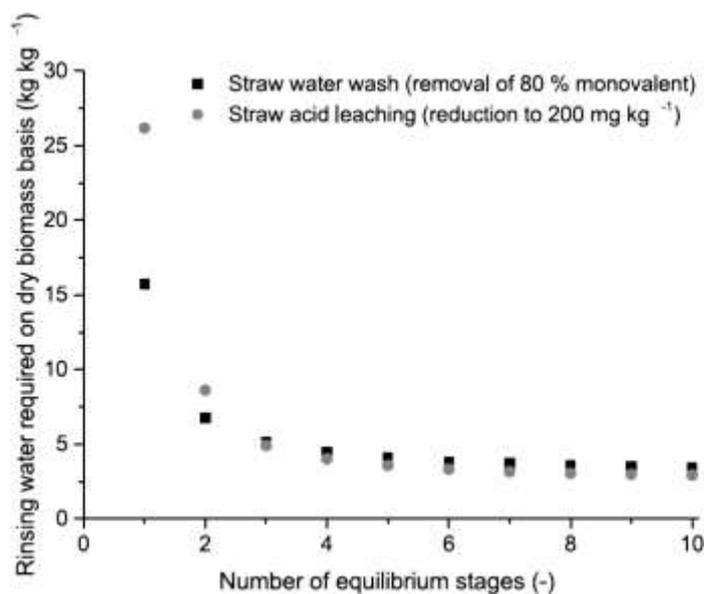
## 3.2 Determination of the Experimental Conditions

In this section, the experiments performed are described as well as the experimental conditions which were considered for the pre-design of the equipment and optimization of the process.

### 3.2.1 Water Required for the Washing and Rinsing Step

To wash a sample of wheat straw basically wheat straw and water are mixed inside of a beaker. The amount of water and wheat straw was determined by Figure 9. As it can be seen in Figure 9 the water required to wash one kilogram of wheat straw is 17kg considering 1 stage. While the amount of water required to rinse 1kg of wheat straw is 27kg considering one stage, The concept of stages is described in this chapter.

It is worth to mention that It was tried to wash wheat straw with less but it was unpractical because wheat straw absorbs around 85/15 its weight and agitate wheat straw with less water is almost impossible.

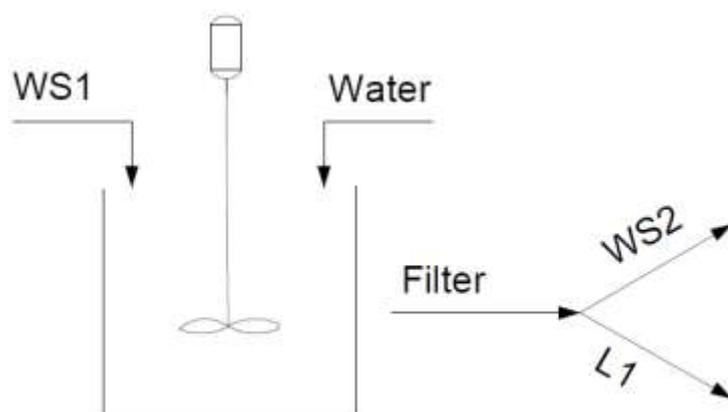


**Figure 9.** The amount of washing and rinsing water required versus the number of stages.  
Source ([S.R.G. Oudenhoven, 2016](#)).

### 3.2.2 Determination of Washing Time

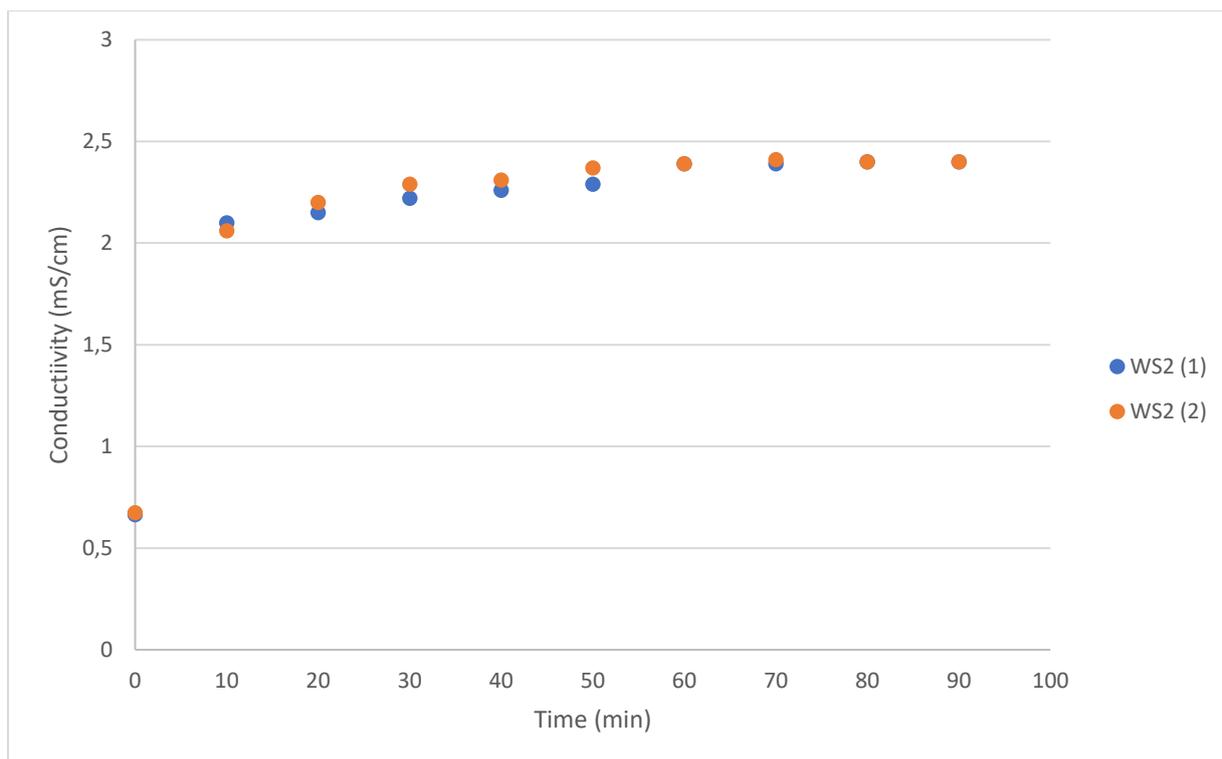
To determine the washing time a sample of wheat straw was washed considering the ratio 17 kg of water per 1 kg of wheat straw. In addition, the conductivity of the water was measured over the time. The following steps were performed to wash a sample of wheat straw and Figure 10 represents these steps schematically.

1. 5g of wheat straw (**WS1**) were mixed with 80ml of water in a 0.5l beaker
2. After that, the sample was stirred with a magnetic bar.
3. The conductivity was measured for 90 minutes.
4. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2 (**WS2**).
5. The final water from the washing process was called liquors one (**L1**).



**Figure 10: Normal washing Procedure.**

As it can be seen in Figure 11, the conductivity of water is increasing over the time because wheat straw releases AAEMs such as sodium, potassium, etc. Those AAEMs are dissolved into the water thus its conductivity increases. There are no significant changes in the conductivity after 60 minutes. So it may be concluded that the washing time is 60 min.



**Figure 11: Washing time, conductivity vs time**

**Note: The number between the brackets is the experiment number**

### 3.2.3 Determination of Leaching Time

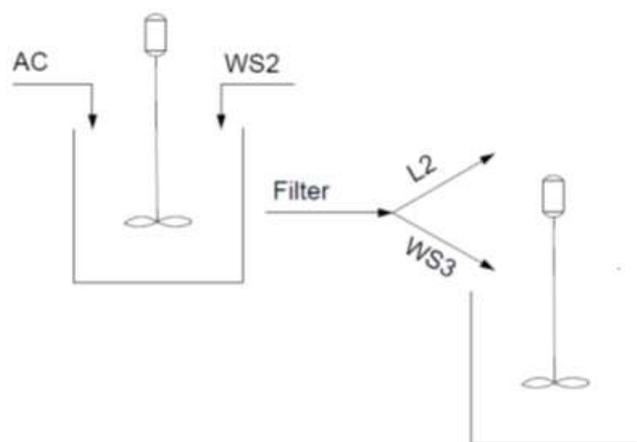
Similarly, to determine the leaching time a sample of washed wheat straw and aqueous condensate were mixed inside of a beaker considering that the ratio liquid/wheat straw to have a proper agitation is 17kg. In addition, it was also considered that normal wheat straw (WS1) absorbs 85/15 its weight so, 5g of normal wheat straw after washing will contain around 28g of water thus 52g of aqueous condensates are enough to leach a sample of washed wheat straw. In other words, a ratio of 10.4kg of aqueous condensate per kg of wheat straw.

The following steps were performed to leached a sample of washed wheat straw (WS2) and Figure 12 represents these steps schematically.

1. Approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of aqueous condensates in a 0.5l beaker.
2. After that, the sample was stirred with a magnetic bar.
3. The conductivity was measured for 90 minutes
4. Next, the sample was drained for 5 min and put it again in a 0.5l baker to prepare it for the rinsing step and obtain a rinsed wheat straw called WS3. For pragmatic reasons, we called these

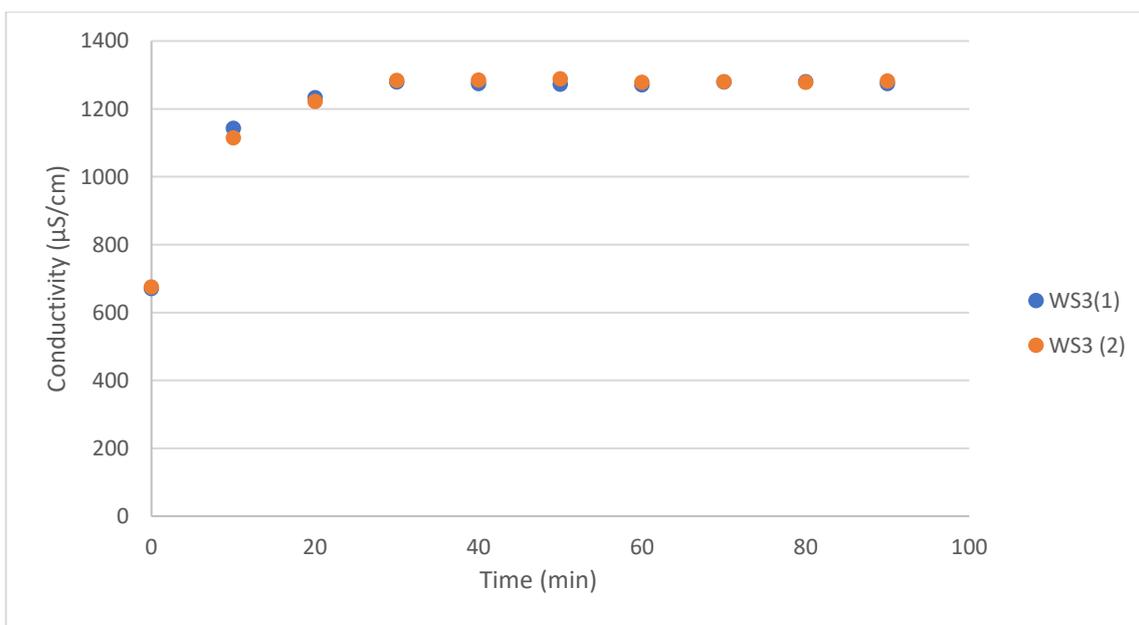
two samples as WS3 since the leaching and rinsing will be performed in the same equipment as it will be presented in the next chapters.

5. The final aqueous condensate from the washing process was called liquors 2 (L2).



**Figure 12: Leaching Procedure**

As it can be seen in Figure 13, the conductivity of aqueous condensates is increasing over the time because wheat straw releases AAEMs. Those AAEMs are dissolved into the aqueous condensate thus its conductivity increases. There are no significant changes in the conductivity after 60 minutes. So it may be concluded that the leaching time is 60 min.



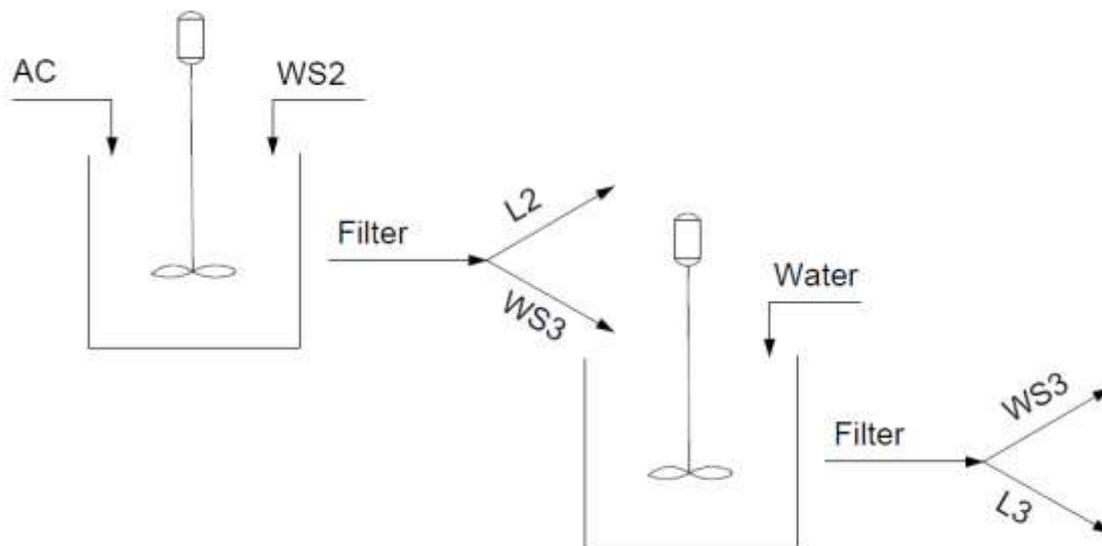
**Figure 13: Leaching time, conductivity vs time**

**Note: The number between the brackets is the experiment number.**

### 3.2.4 Determination of Rinsing Time

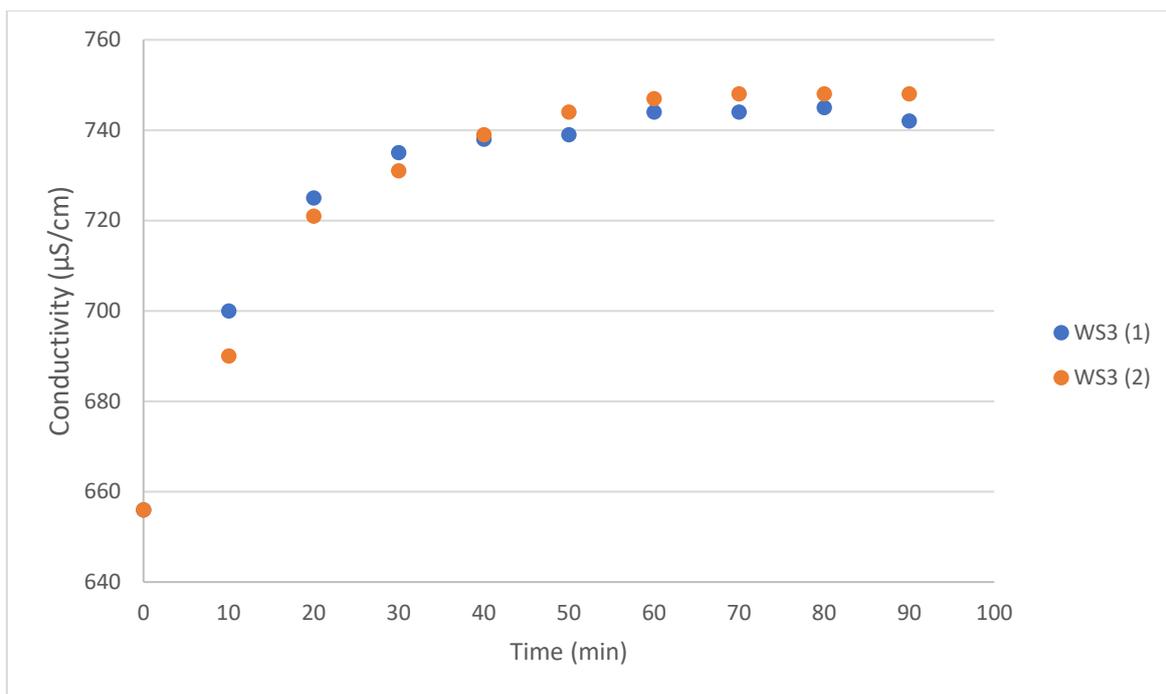
Similarly, to determine the rinsing time a sample of leached wheat straw and water were mixed inside of a beaker considering the ratio 27 kg of water per 1 kg of wheat straw. In addition, the conductivity of the water was measured over the time. The following steps were performed to rinse a sample of wheat straw and Figure 14 represents these steps schematically.

1. The sample prepared in step 4 in the leaching step was mixed with 135ml of water since as
2. After that, the sample was stirred with a magnetic bar.
3. The conductivity was measured for 90 minutes
4. Next, the sample was drained for 5 min. and called it as WS3.
6. The final water from the rinsing step was called liquors 3 (L3).



**Figure 14: Rinsing step procedure**

As it can be seen in Figure 15, the conductivity of water is increasing over the time because wheat straw releases AAEMs. Those AAEMs are dissolved into the aqueous condensate thus its conductivity increases. There are no significant changes in the conductivity after 60 minutes. So it may be concluded that the rinsing time is 60 min.

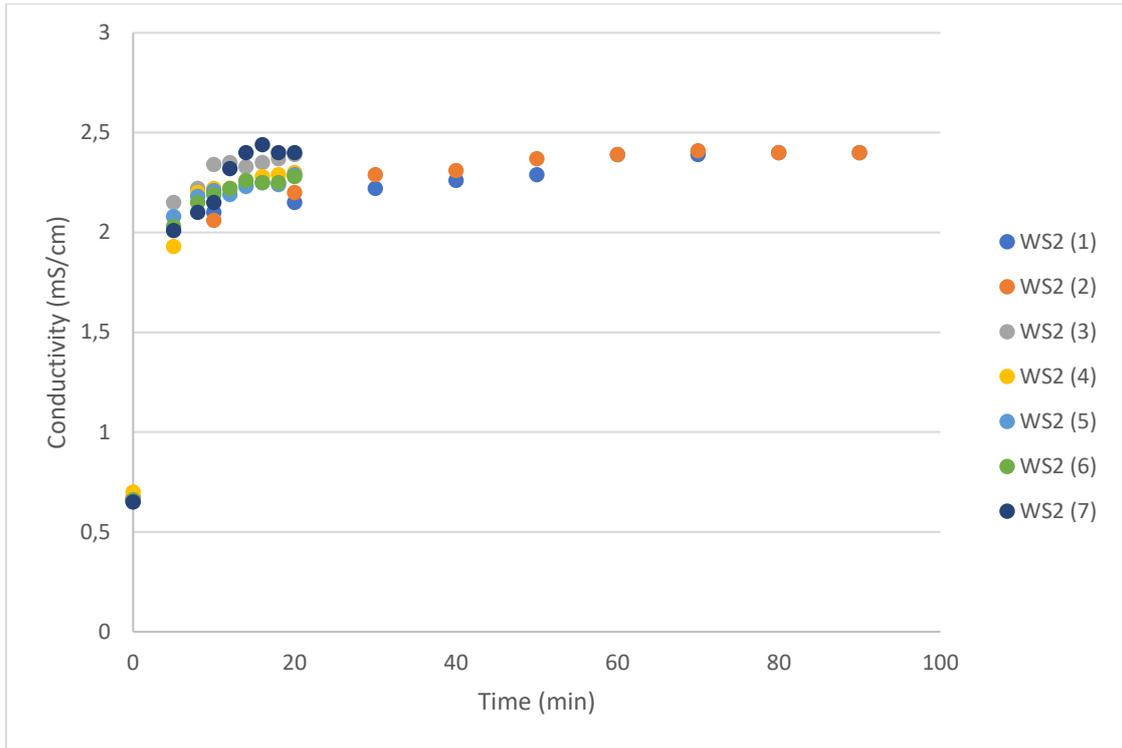


**Figure 15: Rinsing time, conductivity vs time**

**Note: The number between the brackets is the experiment number.**

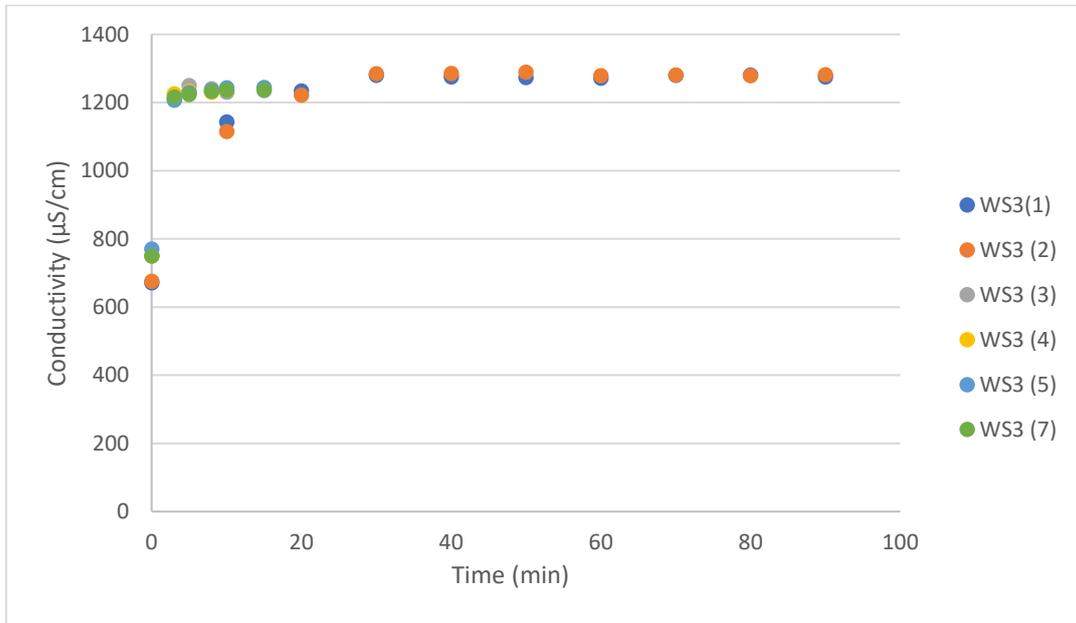
### 3.2.5 Improving Washing Time

Here the agitation of the washing, leaching, and rinsing was improved by using a stirring device at 150rpm. Figure 16 presents the same levels of the conductivity of the samples 1 and 2 after 60 minutes were reached by the other samples in between 10 and 20 minutes.

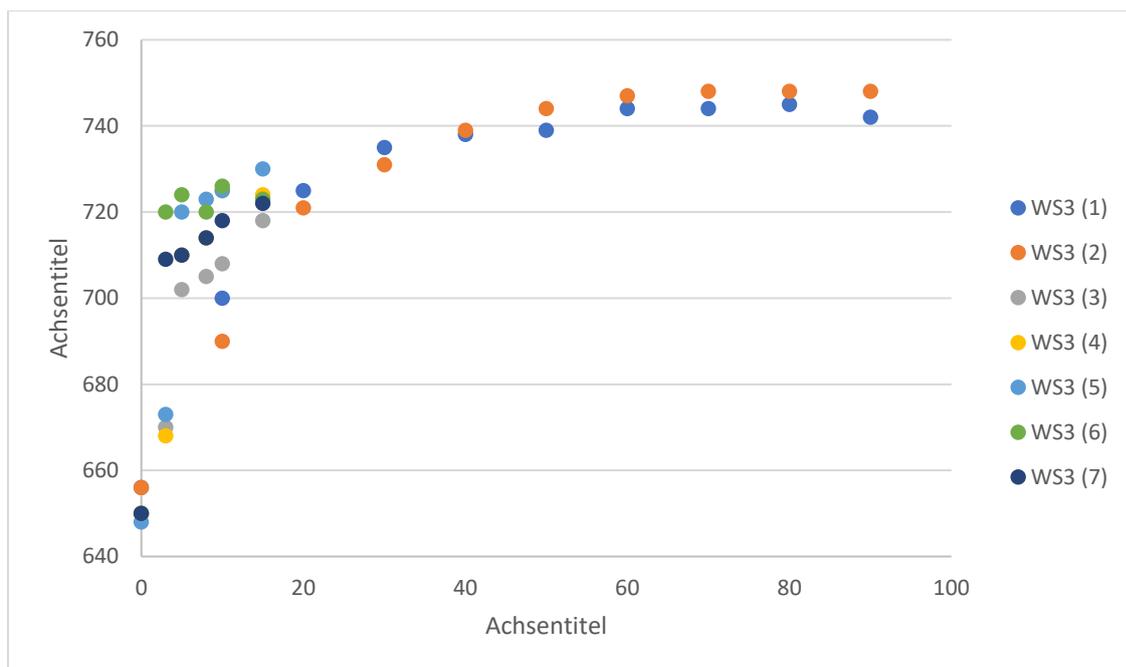


**Figure 16: Improving washing time**  
**Note: The number between the brackets is the experiment number.**

Base on this information, it is assumed that the washing time will be around 15 minutes. For the leaching and the rinsing steps, the behavior was similar as it can be seen in Figures 17 and 18.



**Figure 17: Improving washing time**  
**Note: The number between the brackets is the experiment number.**



**Figure 18: Improving the rinsing time**  
**Note: The number between the brackets is the experiment number.**

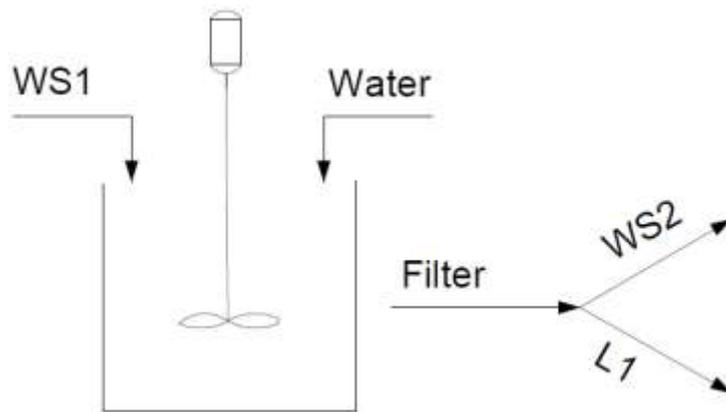
### 3.3 Washing Experimentation

According to Oudenhoven, a number of aqueous condensates produced within the pyrolysis process may be not sufficient to dissolve both the mono (K + Na) and divalent (Mg + Ca) AAMs so a washing step is required. This section presents the procedure performed for a normal washing and for different washings which were performed to look for optimizations in the process.

#### 3.3.1 Normal Washing

The following steps were performed for a normal washing and Figure 19 represents schematically the procedure.

1. 5g of **wheat straw (WS1)** were mixed with 80ml of water in a 0.5l beaker
2. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2 (**WS2**).
4. The final water from the washing process was called liquors one (**L1**).



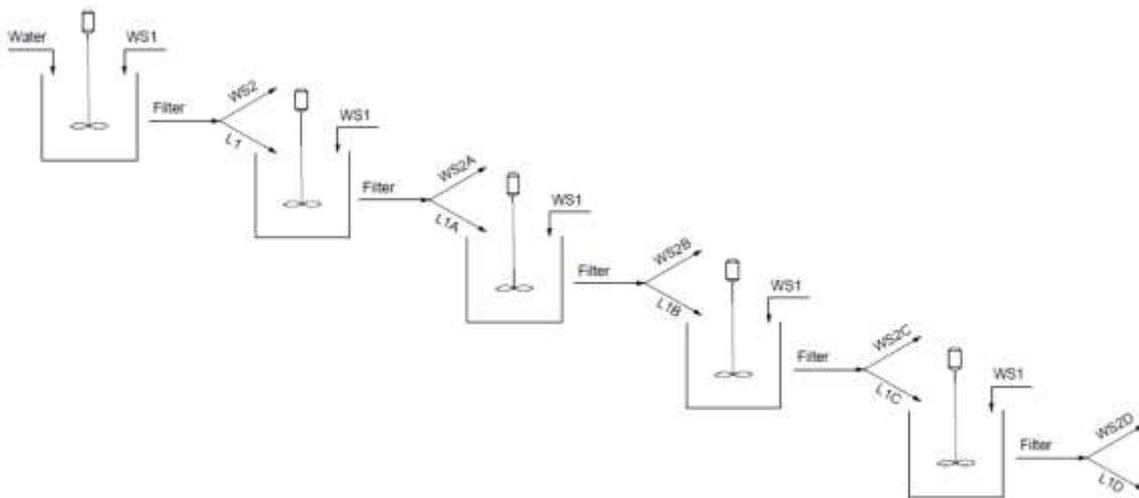
**Figure 19: Normal washing Procedure.**

### 3.3.2 Washing with Washing Water Recirculation

The objective here was to determinate the number of stages of the washing step. A stage here is the number of times that water from one sample to another sample is recirculated. The next steps were performed for a washing with washing water recirculation and Figure 20 presents a simplified schematic of these steps.

1. 5g of **wheat straw (WS1)** were mixed with 80ml of water in a 0,5L beaker
2. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2 (**WS2**). This was the first stage.
4. The final water from the first washing was collected and called liquors one (**L1**).
5. For the second stage, 5g of **wheat straw (WS1)** were mixed with 80ml of L1
6. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
7. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2A (**WS2A**). This was the second stage.
8. The final water from the second washing was collected and called liquors 1A (**L1A**).
9. For the third stage, 5g of **wheat straw (WS1)** were mixed with 80ml of L1A
10. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.

11. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2B (**WS2B**). This was the third stage.
12. The final water from the third washing was collected and called liquors 1B (**L1B**).
13. For the fourth stage, 5g of **wheat straw (WS1)** were mixed with 80ml of L1B
14. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
15. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2C (**WS2C**). This was the fourth stage.
16. The final water from the fourth washing was collected and called liquors 1C (**L1C**).
17. For the fifth stage, 5g of **wheat straw (WS1)** were mixed with 80ml of L1C
18. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
19. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2D (**WS2D**). This was the fifth stage.
20. The final water from the fifth washing was collected and called liquors 1D (**L1D**).

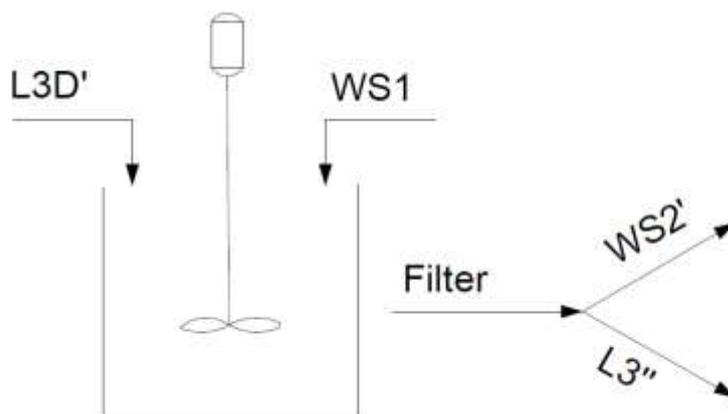


**Figure 20: Washing with washing water recirculation**

### 3.3.3 Washing with L3D' (Rinsing water)

The objective of this experiment was to wash a sample of WS1 with the residual water from the rinsing step after 5 stages (L3D'). The next steps were performed for a washing with L3D' and Figure 21 presents a simplified version of these steps.

1. 5g of wheat straw (WS1) were mixed with 80ml of L3D' in a 0.5L beaker
2. After that, the sample was stirred with a stirred device at 150rpm for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and labeled it as wheat straw sample 2' (WS2').
4. The final water from the washing process was called liquors 3'' (L3'').



**Figure 21: Washing with L3D'**

### 3.4 Leaching WS2 and Rinsing Experimentation

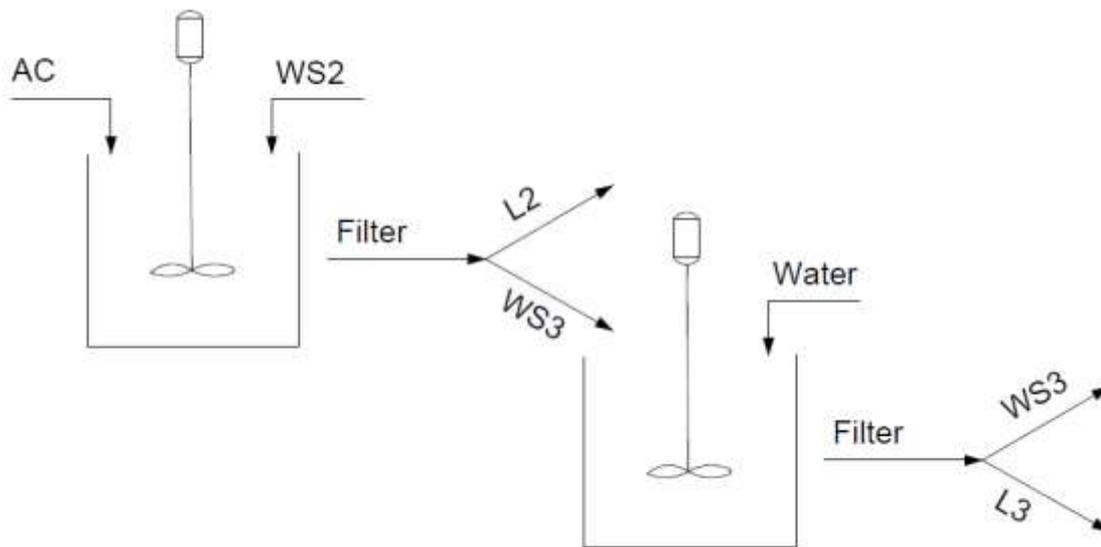
The objectives of these experiments were to know the number of ashes that we can remove by leaching at room temperature and a normal rinsing as well as to look for optimizations in the process by changing the normal procedure. The following sections present what it was performed.

#### 3.4.1 Leaching at Room Temperature and Normal Rinsing Experimentation

The following steps were performed for a leaching at room temperature and normal rinsing. Figure 22 presents a simplified version of these steps.

1. Approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of aqueous condensates in a 0.5l beaker. This 33g of WS2 contain 5g of WS1 and 28g of water since wheat straw absorbs approximately 85/15 its weight. As it was discussed in section 3.2.1 the ratio 17kg of water per kilogram of wheat straw was suitable to have a proper agitation so considering that WS2 contains 28g of water it is necessary to add 52g of liquid to have a proper agitation in this case this liquid was aqueous condensates. The flow rate then is 10.4kg of AC per kg of wheat straw.

2. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of water since as it was discussed in section 3.2.1 the water required for the rinsing step is 27kg of water per kilogram of wheat straw. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
4. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
5. Next, the sample was drained for 5 min. and called it as WS3.
6. The final water from the rinsing step was called liquors 3 (**L3**).



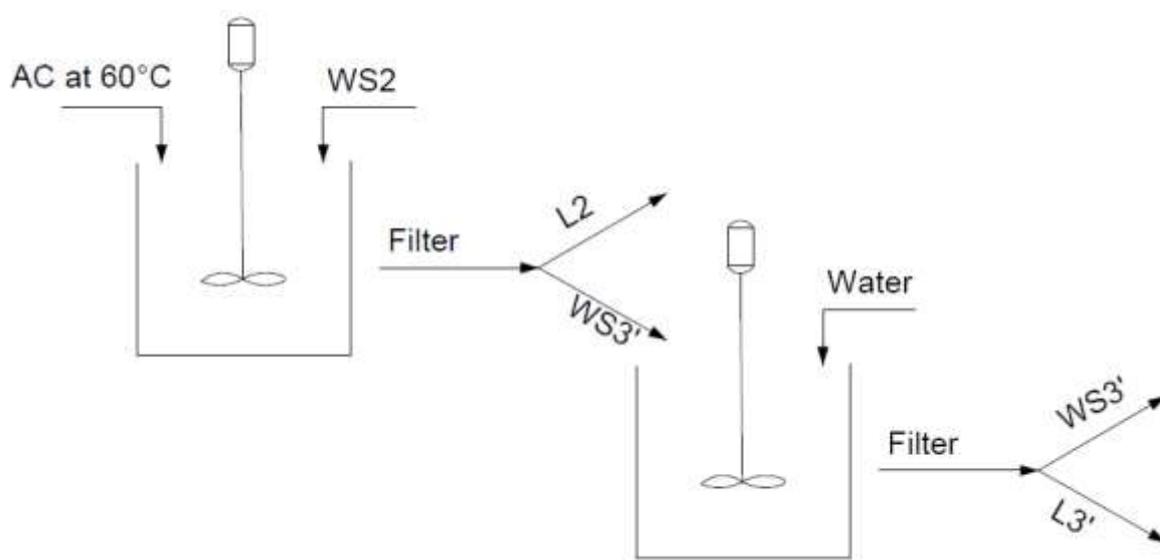
**Figure 22: Leaching using AC at room temperature and normal rinsing**

### 3.4.2 Leaching at 60 °C and Normal Rinsing Experimentation

As it was said in Chapter 2 a hot stream from the bioliq® process would be used to heat aqueous condensates. Aspen was used to determinate the temperature that aqueous condensate can reach with this hot stream as it is presented in section 6.2.3. The following steps were performed for a leaching at room temperature and normal rinsing. Figure 23 presents a simplified version of these steps.

1. Approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of aqueous condensates at 60 °C in a 0.5l beaker.

2. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of water. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
4. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
5. Next, the sample was drained for 5 min. and called it as WS3'.
6. The final water from the rinsing step was called liquors 3' (**L3'**).



**Figure 23: Leaching at room 60 °C temperature and normal rinsing**

### 3.4.3 Leaching at 60 °C and Rinsing Water Recirculation Experimentation

The objective of this experiment was to leach a sample of wheat straw 2 at 60 °C and recirculate the water from the rinsing stage and the aqueous condensates in order to simulate a Bollman extractor. The following steps were performed for a leaching at room temperature and rinsing water recirculation. Figure 24 presents a simplified version of these steps.

1. Approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of aqueous condensates at 60 °C in a 0.5L beaker.

2. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
3. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of water. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
4. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
5. Next, the sample was drained for 5 min. and called it as WS3'. This is the first stage.
6. The final water from the rinsing step was called liquors 3' (**L3'**).
7. For the second stage, approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of the aqueous condensates at 60 °C in a 0.5l beaker. Those aqueous condensates were those that were used to leach a sample of WS2 in the first stage.
8. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
9. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of L3'. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
10. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
11. Next, the sample was drained for 5 min. and called it as WS3A'..
12. The final water from the rinsing step was called liquors 3A' (**L3A'**).
13. For the third stage, approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of the aqueous condensates at 60 °C in a 0.5l beaker. Those aqueous condensates were those that were used to leach a sample of WS2 in the second stage.
14. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
15. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of L3A'. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
16. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
17. Next, the sample was drained for 5 min. and called it as WS3B'.
18. The final water from the rinsing step was called liquors 3B' (**L3B'**).
19. For the fourth stage, approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of the aqueous condensates at 60 °C in a 0.5l beaker. Those aqueous condensates were those that were used to leach a sample of WS2 in the third stage.
20. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
21. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of L3B'. The final aqueous condensate from the washing process was called liquors 2 (**L2**).

22. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
23. Next, the sample was drained for 5 min. and called it as WS3C'.
24. The final water from the rinsing step was called liquors 3B' (**L3C'**).
25. For the fifth stage, approximately 33g of washed **wheat straw (WS2)** were mixed with 52ml of the aqueous condensates at 60 °C in a 0.5l beaker. Those aqueous condensates were those that were used to leach a sample of WS2 in the fourth stage.
26. After that, the sample was stirred with a stirring device for 15 minutes and the conductivity was measured over the time.
27. Next, the sample was drained for 5 min and put it again in a 0.5l baker to mix it with 135ml of L3C'. The final aqueous condensate from the washing process was called liquors 2 (**L2**).
28. After that, the sample was stirred with a stirring device at 150rpm for 15 minutes and the conductivity was measured over the time.
29. Next, the sample was drained for 5 min. and called it as WS3D'.
30. The final water from the rinsing step was called liquors 3B' (**L3D'**).

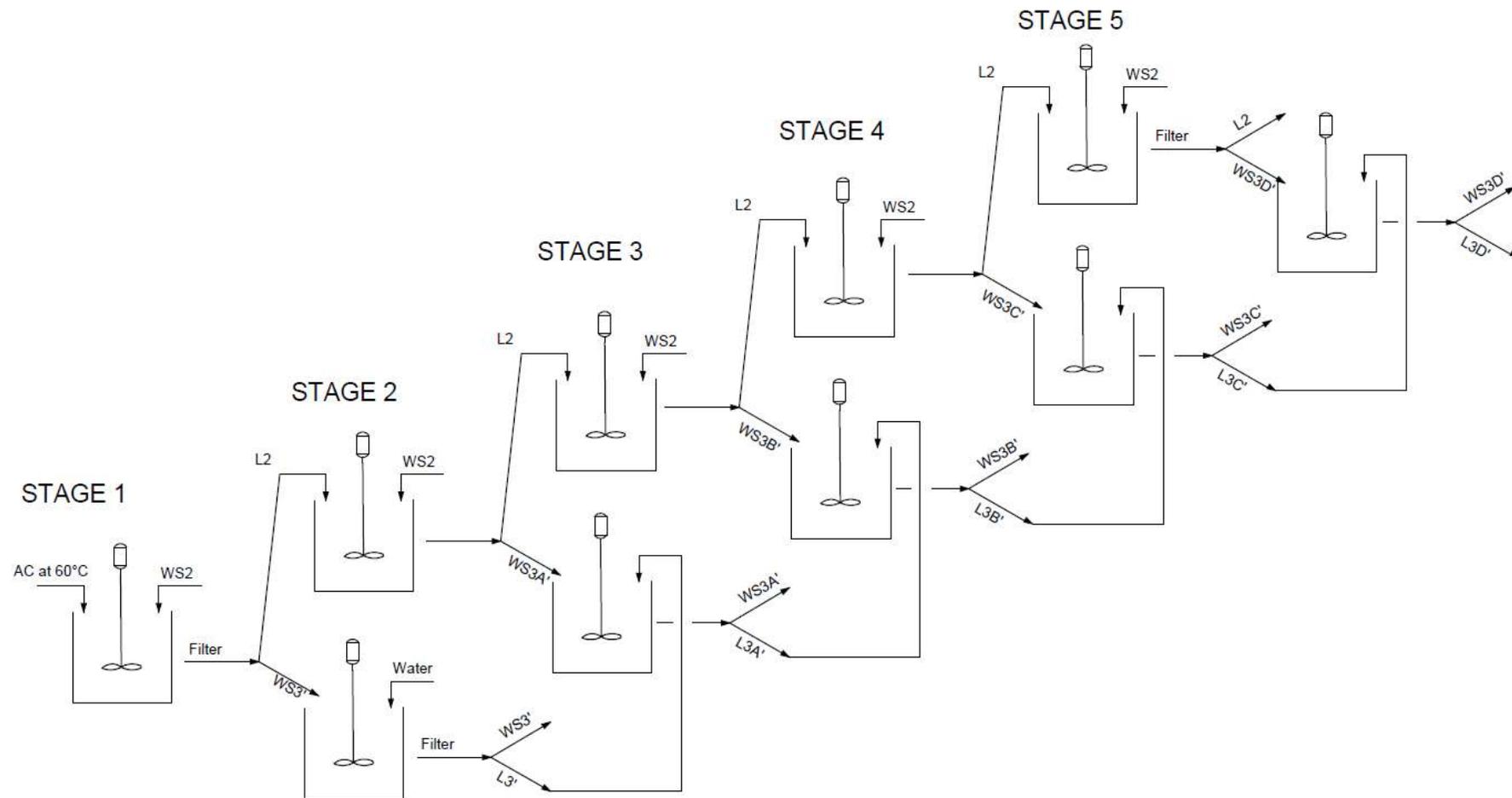


Figure 24: Leaching at 60 °C temperature and rinsing water recirculation

### 3.4.4 Leaching at 60°C and Pressing Experimentation

The objective of this experiment was to know the number of ash removal from a pretreated wheat straw sample if we remove water by mechanical means.

1. Leach a sample like in section 4.4.2
2. Use a press to remove water from a wheat straw and compare the ash removal with the initial sample.

### 3.5 Pyrolysis Experiment

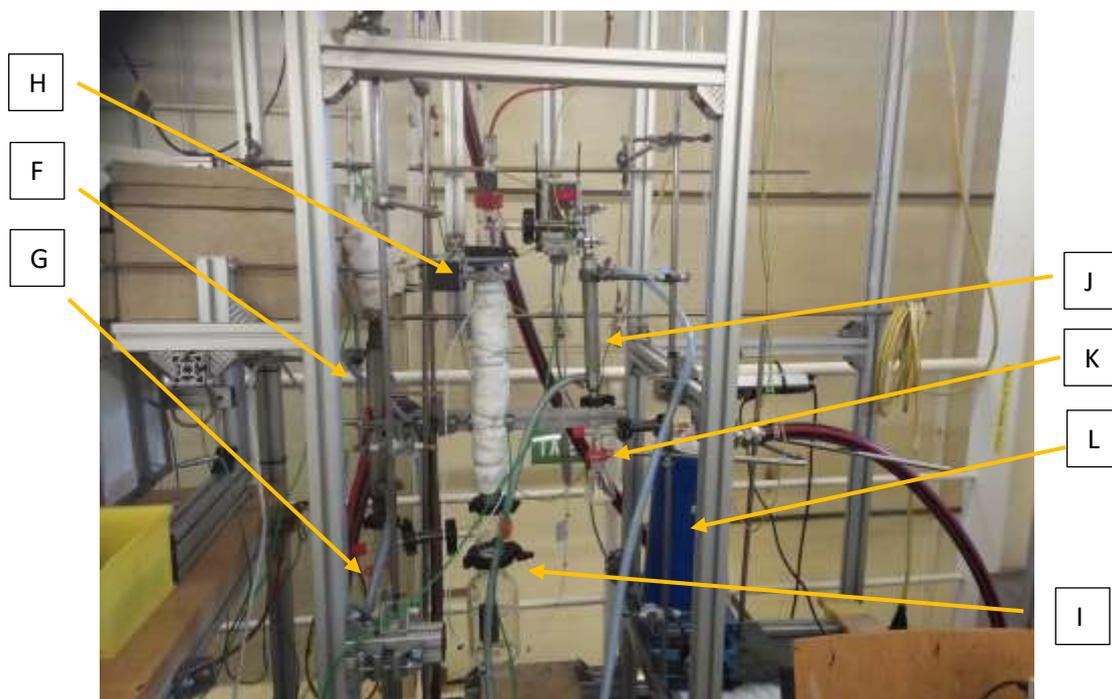
It was performed 3 pyrolysis experiments in the fluidized bed reactor with pretreated wheat straw and 3 with untreated in order to compare the reactor yields.

1. The first step is to install the system, Figures 25 and 26 present the fluidized bed reactor



**Figure 25: First part of the fluidized bed reactor**

- A) Motor for the screw conveyor
- B) Motor for moving wheat straw
- C) Biomass storage
- D) Oven, It contains the reactor cyclone and solids collector
- E) Filter



**Figure 26: Second part of the fluidized bed reactor**

- F) First condenser
- G) Organic condensate collector 1
- H) Electrostatic precipitator
- I) Organic condensate collector 2
- J) Second condenser
- K) AC condensate collector 1
- L) Gas tramp 1

2. Introduce 100g of untreated or treated wheat straw in the biomass storage
3. Charge the reactor with 40g of sand
4. Connect the cooling water to the device adapted to keep the biomass at 20 °C before going to the reactor.
5. Set a temperature of 515°C for the oven
6. Set a temperature of 515 °C for the box with the filter
7. Set a temperature of 100 °C for the electrostatic precipitator (This allows water to continue going through the system)
8. Set 10 V for the electrostatic precipitator
9. Feed approximately 700 l/min of nitrogen
10. Set a temperature of 20°C for the first condenser
11. Set a temperature of 5°C for the second condenser
12. Set a temperature of 0°C for the first tramp
13. Set a temperature of -20°C for the second tramp
14. Wait for 1 or 2 hrs
15. Collect and quantify the products

## 4 EXPERIMENTATION RESULTS AND ANALYSIS

### 4.1 Washing Results

#### 4.1.1 Normal Washing Experimentation Ash Removal

The objective of this experiment was to know the number of ashes that it can be removed by washing wheat straw with fresh water.

The ash removal of the samples WS2 (1) and WS2 (2) was 7.6% and 13.7% respectively. Those samples were used to determinate the washing time in section 3.2.2. The results of the ash removal of those samples demonstrate that the agitation at 150rpm improved the washing time since in the next experiments presented in Table 7 the washing time was 15min and the ash removal was similar to WS2 (1) and WS2(2).

**Table 7: Ash removal of a normal washing**

	<b>WS2 (3)*</b>	<b>WS2 (4)*</b>	<b>WS2 (5)*</b>	<b>WS2 (6)**</b>	<b>WS2 (7)**</b>
Ash removal %	10.6	12.3	16.5	13.8	14.6

\*\* The initial ash content was 6.2% of the total wheat straw mass.

\*\* The initial ash content was 6.5% of the total wheat straw mass.

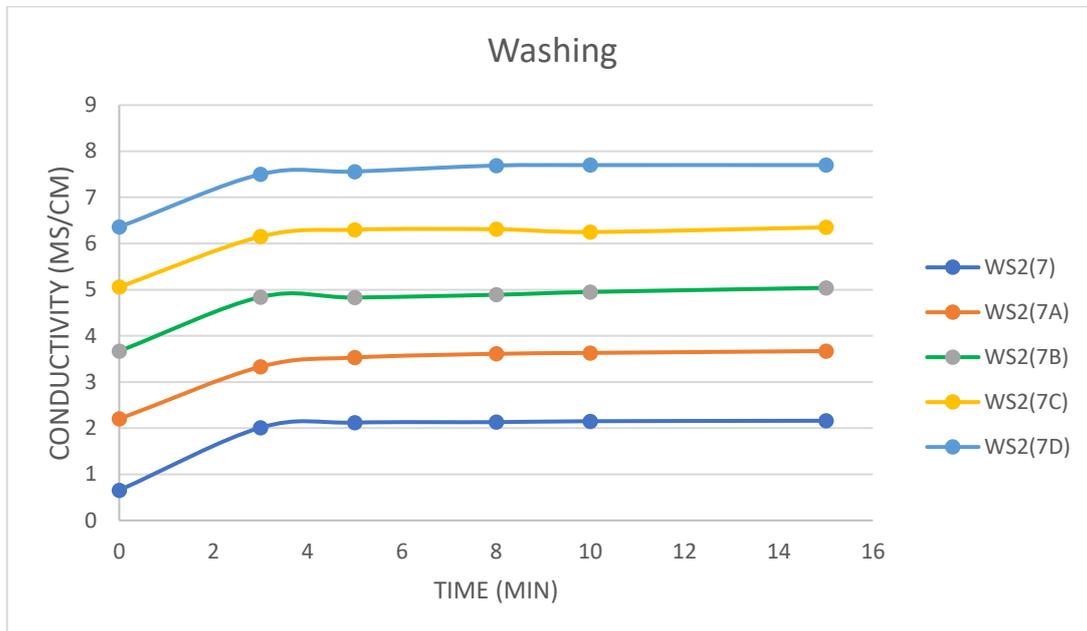
Note the number between the brackets is the experiment number

#### 4.1.2 Washing with Washing Water Recirculation Aash Removal

The objective of these experiments was to know the number of stages of the washing step. Table 8 presents that after the first stage, the ash removal is decreasing, even though in Figure 27 the conductivity from one sample to other is increasing which may indicate that there is ash removal. Paradoxically, in the last two stages, we added ashes. This situation could be due to wheat straw absorbs water around 85/15 times its weight and after each stage, the washing water contains more ashes. Based on this information, we can conclude that the maximum number of stages for the washing is 2 since there could be some high AAEM biomass feedstocks and the water used to wash the second sample could add ashes to the third sample.

Section 8.5 describes the composition of the washing water after the first washing. The total number of ash content in the water after the first washing is around 0.046%. Assuming that in each stage water dissolves the same amount of ashes than the concentration of ashes in the washing water after the second stage would be 0.096%. Using a water with this ash concentration could be risky since the ash removal in the experiment 3<sup>rd</sup> stage is just 3%. So it will be considered just 2 stages for the washing step.

On the other hand, we observed that It is important to allow the washed wheat straw to drain the excess of water since this water contains dissolved ashes.



**Figure 27: Washing water recirculation conductivity in different stages**  
**Note the number between the brackets is the experiment number**

**Table 8: Ash removal of washing with recirculation of washing water**

	WS2 (7)	WS2A (7A)	WS2B (7B)	WS2C (7C)	WS2D (7D)
Ash removal %	14.6	8.0	3.1	-12.5	-21.9

\* The initial ash content was 6.5% of the total wheat straw mass.

Note the number between the brackets is the experiment number

#### 4.1.3 Washing with L3D' (waste rinsing water) Ash Removal

L3D' was used to wash a sample of WS1 and some ashes were removed as it can be seen in table 20. Base on this information the water from the rinsing process can be recirculated in order to reduce the amount of washing water required. However, this washing may not be as effective as a washing with fresh water because L3D' contains some ashes. In these experiments, we got an ash removal similar to wash with fresh water. This situation may be due to the initial ash content in the wheat straw was 6.2% and not 6.5% as in the other samples. In addition, according to Table 9 the ash content in L3D' is 0.059%

which is almost the half of the limit that was set in Section 4.1.2. However, washing with L3D' will be not considered. This decision is further supported in section 4.2.4.

**Table 9: Ash removal of washing with L3D'**

Experiment	WS2' (1)	WS2' (2)
Wheat Straw 1 (g)	5	5
L3D'	80	80
Ash removal %	15.6	13.8

\* The initial ash content was 6.2% of the total wheat straw mass.

Note the number between the brackets is the experiment number

## 4.2 Leaching Results

### 4.2.1 Leaching at Room Temperature and Normal Rinsing ash Removal

The objective of these experiments was to know the number of ashes that it can be removed by leaching a sample of washed wheat straw (WS2) at room temperature and then rinse them with fresh water.

The ash removal of samples WS3 (1) and WS3 (2) was 27.9% and 31.0% respectively. Those samples were used to determinate the leaching and rinsing time in section 3.2.2. and 3.2.3. The results of the ash removal of those samples demonstrate that the agitation at 150rpm improved the leaching and rinsing time since the next samples were leached and rinsed for 15 minutes in each step and the ash removal of those samples were similar to WS3 (1) and WS3 (2) as it can be seen in Table 10.

**Table 10: Ash removal of leaching at room temperature and normal rinsing results**

	WS3 (3)	WS3 (4)	WS3 (5)	WS3 (6)	WS3 (7)
Ash removal %	32.5	29.3	32.2	35.8	31.9

\* The initial ash content was 6.5% of the total wheat straw mass.

Note the number between the brackets is the experiment number

### 4.2.2 Leaching at 60 °C and Normal Rinsing Ash Removal

The objective here was to know the number of ashes removed by leaching at 60 °C and compare this number with a leaching at room temperature. Table 11 contains the ash removal results of leaching at 60 °C and normal rinsing results.

**Table 11: Ash removal of leaching at 60 °C and normal rinsing**

	WS3' (1)	WS3' (2)	WS3' (3)	WS3' (4)	WS3' (5)
Ash removal %	37.6	40.0	28.4	34.4	35.7

\* The initial ash content was 6.5% of the total wheat straw mass.

Note the number between the brackets is the experiment number

The average ash removal is 35.22%. If we compare the average removal of leaching at room temperature and leaching at 60 °C, we have almost 3% more ash removal.

#### 4.2.3 Leaching at 60 °C and Rinsing Water Recirculation Ash Removal

The objective of these experiments was to leach a sample of WS2 at 60 °C and recirculate the water from the rinsing stage and the aqueous condensates in order to simulate a Bollman extractor. Table 12 contains the results of the ash removal of a leaching at 60 °C and rinsing water recirculation. As it can be seen in Table 21 the ash removal was similar to the experiments without rinsing water recirculation. This situation is very beneficial for the process because this will save a lot of water as it can be seen in Chapter 5.

**Table 12: Ash removal of leaching at 60 °C and rinsing water recirculation.**

	WS3' (6)	WS3A' (6A)	WS3B' (6B)	WS3C' (6C)	WS3D' (6D)
Ash removal %	35.7	33.1	34.1	32.0	34.7

\* The initial ash content was 6.5% of the total wheat straw mass.

Note the number between the brackets is the experiment number

On the other hand, the conductivity of the aqueous condensate is increasing from one sample to another and even though there were no remarkable changes in the ash removal among these experiments, this increase in the conductivity may affect the performance of the pretreatment process so to minimize the effects the removal of aqueous condensate and the addition of fresh aqueous condensates in the flow rate of production is compulsory. In addition, the recirculation of L3D' to wash a sample of WS1 will be not considered.

#### 4.2.4 Leaching at 60 °C and Dewatering by Mechanical Means Ash Removal

The objective of this experiment was to know the number of ashes removed by dewatering from a sample of pretreated wheat straw. Table 13 presents the extra ash removal due to a dewatering by pressing at 8.1 MPa.

**Table 13: Ash removal of leaching at 60 °C and dewatering**

	WS3' (7)	WS3' (8)	WS3' (9)	WS3' (10)	WS3' (11)
Ash removal after Pressing	30.5	29.4	29.7	28.8	29.8
Extra ash removal	6.1	5.0	5.3	4.4	5.4

\* The initial ash content was 6.5% of the total wheat straw mass.

Note the number between the brackets is the experiment number

### 4.3 Pyrolysis Experiments Results

Table 14 and 15 contain the results of the reactor yields using a pretreated wheat straw and an untreated wheat straw respectively.

**Table 14: Pyrolysis experiment results with pretreated wheat straw**

Experiment	1*	2*	3*	Average*	Average**	Σ*
Char %	10.1	11.4	12.1	11	11.37	0.85
Organic Condensate %	41.0	43.4	40.5	42	40.97	1.32
AC %	14.5	14.6	13.1	14	9.82	0.69
Gas %	34.4	30.7	34.3	33	34.13	1.73

\* as determined

\*\* dry basis

**Table 15: Pyrolysis experiment results with untreated wheat straw**

Experiment	1*	2*	3*	Average*	Average**	Σ*
Char %	21.1	19.4	19.9	20	21.88	0.73
Organic Condensate %	15.3	17.2	15.0	16	15.56	0.99
AC %	23.2	21.7	22.7	23	6,02	0.78
Gas %	40.2	41.4	42.3	41	44.87	0.91

\* as determined

\*\* dry basis

As it can be seen in the previous tables, the difference between the organic condensate from an untreated and pretreated wheat straw is remarkable 42% and 16% conversion respectively. However, the char yields are also considerable different. This remarks are discussed in Chapter 6.

On the other hand, the tables 16 and 17 contain the Oudenhoven results using a pretreated WS and untreated wheat straw respectively.

**Table 16: Pyrolysis experiment results with pretreated wheat straw Oudenhoven. Source (Oudenhoven,2015)**

Experiment	1*	2**	Average
Char %	7	8	7.5
Organic Oil %	54	62	58
Water %	11	8	9.5
Gas %	28	22	25

Notes: dry basis. \*\* from a sample with an initial ash content of 6%. \*From a sample with an initial ash content of 8%

**Table 17: Pyrolysis experiment results with untreated wheat straw of Oudenhoven (Oudenhoven,2015)**

Experiment	1*	2**	Average
Char %	19	17	18
Organic Oil %	28	34	31
Water %	17	11	14
Gas %	36	38	37

Notes: dry basis. \*\* from a sample with an initial ash content of 6%. \*From a sample with an initial ash content of 8%

The results of Oudenhoven are presented in organic oil which is a combination of aqueous condensates and organic condensate without water in order to compare the results of this thesis with the Oudenhoven results, the water from organic condensate and aqueous condensate is subtracted and then results are summarized. According to section 7, the water content in the organic condensate using a pretreated wheat straw is 5.93% and in the aqueous condensate 29.8%. That means that our pretreated wheat straw produced **49.92% organic oil** and the pretreated wheat straw of Oudenhoven produced around 58% organic oil. This difference could be due to the temperature for leaching. It was used 60 °C in this thesis and the pretreatment process last 60 min. While in the Oudenhoven experiments the temperature was 90°C and the pretreatment process last for 120 min.

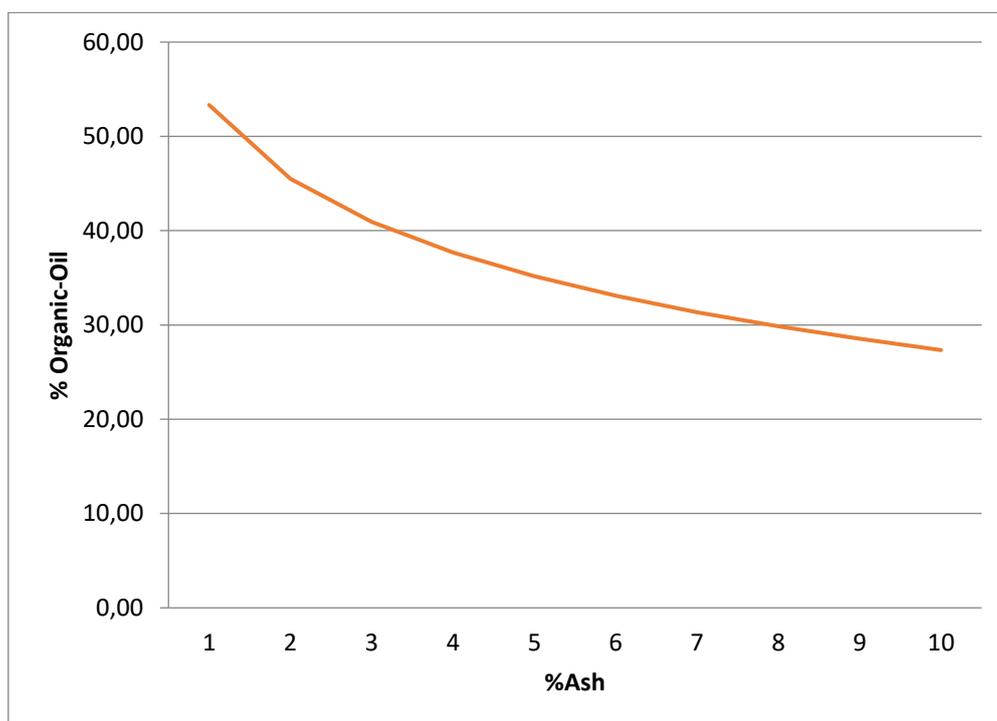
In regard to the untreated wheat straw the water content in the organic condensate 2.7% is and in the aqueous condensate 73.6% that means the organic oil produced by untreated wheat straw is 21.63%. The pretreatment increases the organic condensate from 21.64% to 49.92%. While the results of Oudenhoven were from 31% to 62%

KIT has performed pyrolysis experiments with different feedstock and a different number of ash content. The following regression was determined for the correlation of organic oil yield and the ash content of the feedstock (see Table 18 and Figure).

$$\%OrganigLiq = a * \ln(\%Ash) + b$$

**Table 18: Organic oil yield vs ash content**

	A	U <sub>a,95%</sub>	B	U <sub>b,95%</sub>	R <sup>2</sup>	RMSE	SSE
log <sub>10</sub>	-26,01	2,51	53,33	7,72	0,925	2,973	318
Ln	-11,29	1,1	53,33	7,72	0,925	2,973	318



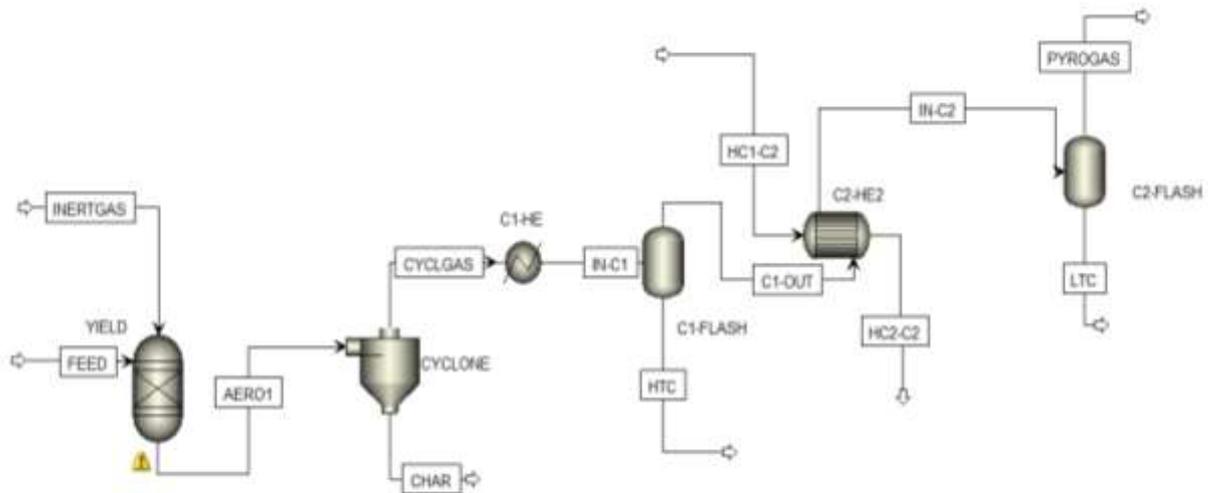
**Figure 28: Organic Oil Yield vs Ash Content. Source (KIT, IKFT)**

It has been removed around 30 to 40% the ash content from a sample of wheat straw with an initial ash content of 6.5% of the total mass of wheat straw. According to Figure 28 the expected amount of organic liquid should be around 37.5%. However, it was obtained 49.9%. This could be due to wheat straw is very heterogeneous and the ash content in some wheat straw should be lower. In addition, this curve was made of experimental data from different feedstock. On the other hand, Oudenhoven removed around 67% of the ashes from a sample with an initial ash content of 6% (([S.R.G. Oudenhoven, 2016](#))). If it is used the same figure, it is expected to obtain around 45.5% of organic liquid. However, he obtained 62%. It is clearly seen the this curve is not so accurate for wheat straw. However, it shows a good tendency of the behavior of organic oil vs ash content.

## 5 MASS BALANCE

### 5.1 Pyrolysis Process Mass Balance

The mass balance of the pyrolysis process was taken from an Aspen simulation ([Gomes Fonseca, 2015](#)). Figure 29 presents the diagram of the simulation and the Appendix F contains the detail of the streams.



**Figure 29: Pyrolysis process mass balance simulation diagram. Source ([Gomes Fonseca, 2015](#)).**

Appendix F presents the mass balance of the pyrolysis process. However, this mass balance is just an estimate since it may change if the ash content in wheat straw changes. According to Gomes Fonseca, the reactor of this simulation acts as a “black box system, feed with an inert and with fresh straw” and the simulation was made of experimental data.

In order to link the Gomes Fonseca mass balance with the pretreatment mass balance, the streams of the simulation were renamed as S1, S2 and so on. Figure 30 presents these changes and Figure 31 presents the pretreatment process diagram. It is useful to follow the mass balances with these diagrams and pay attention to the streams S10 and S6 in the pyrolysis process diagram since they go to the pretreatment diagram.

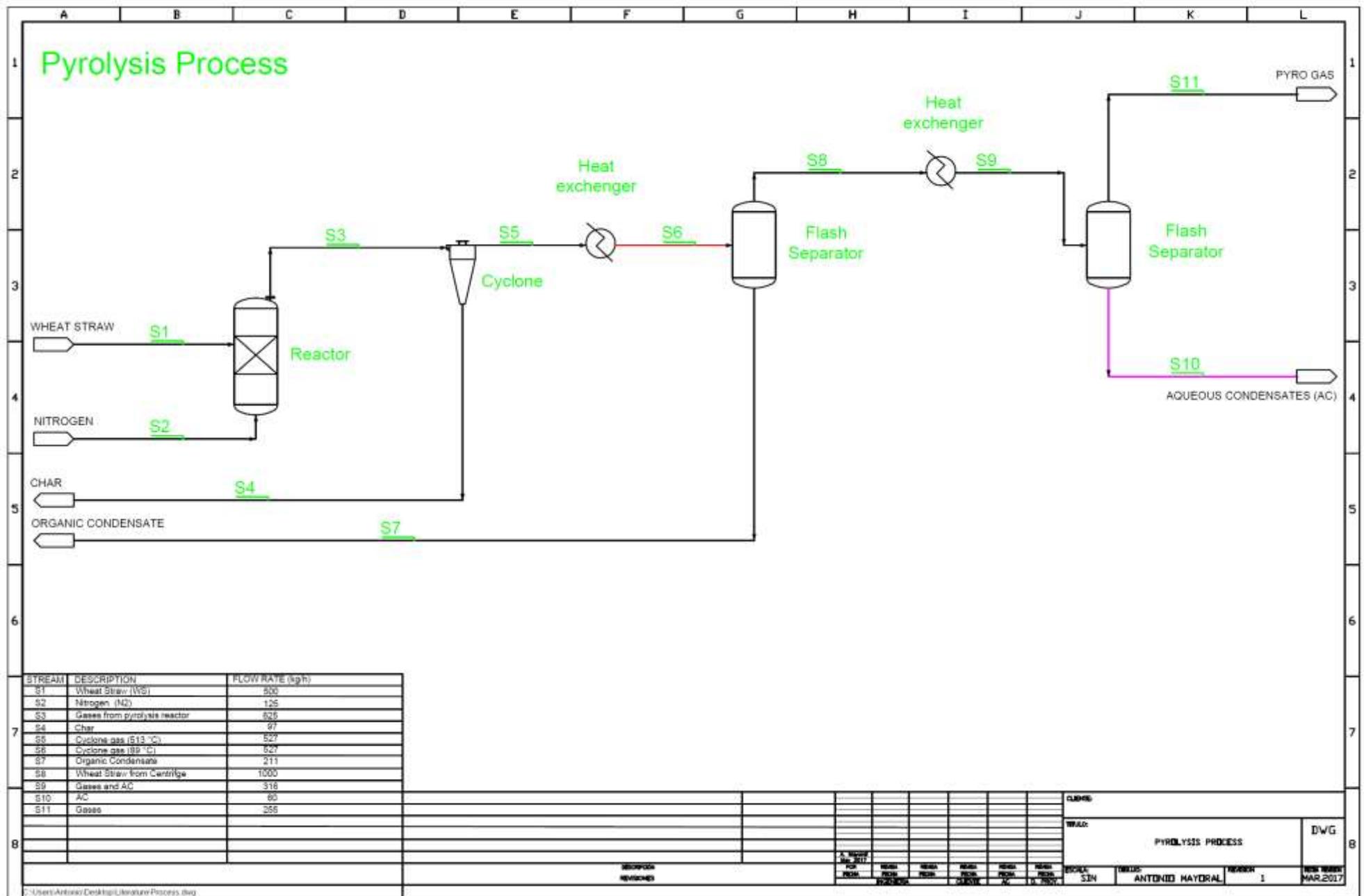


Figure 30: Pyrolysis process diagram

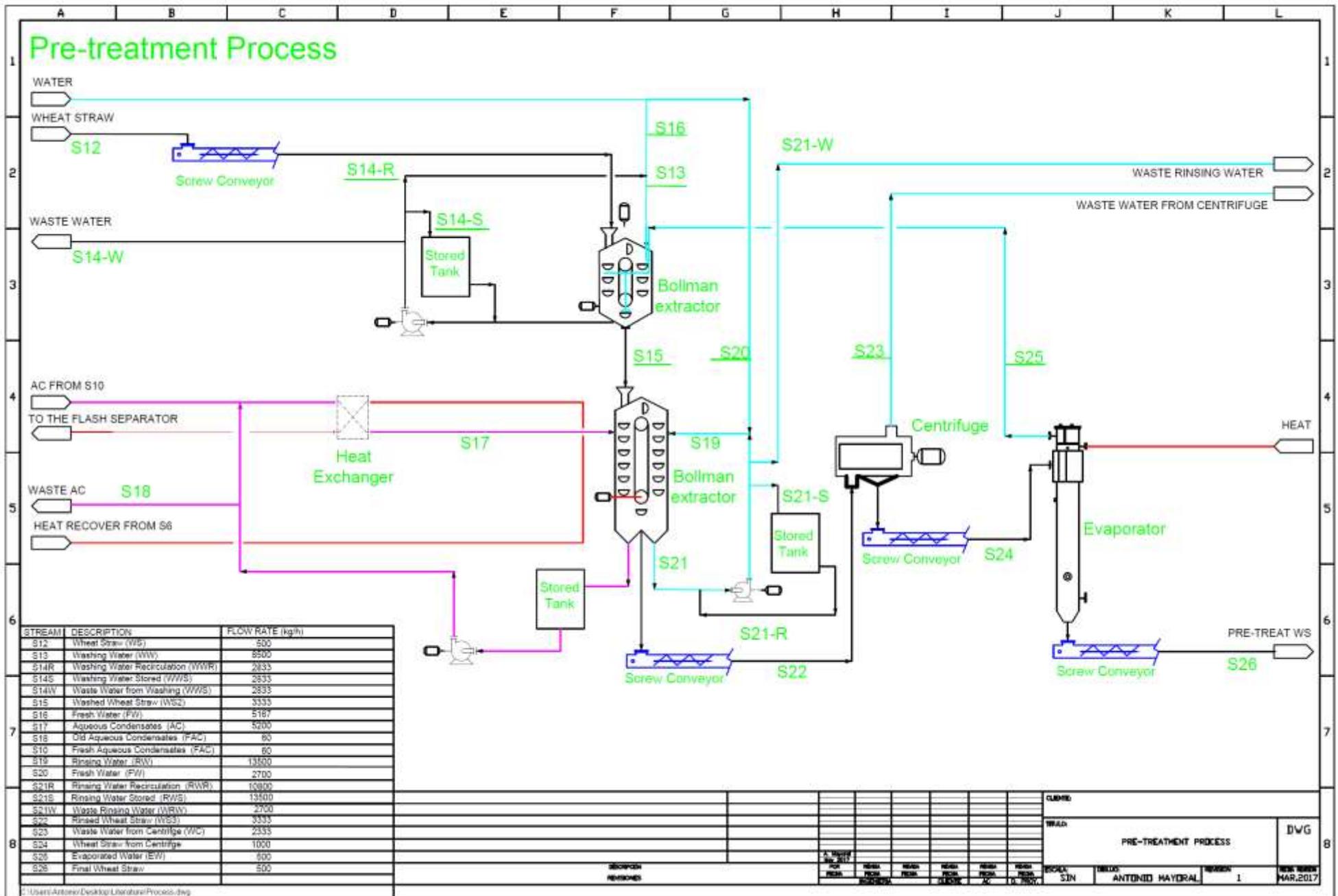


Figure 31: Pretreatment process diagram

## 5.2 Pretreatment Process Mass Balance

### 5.2.1 Washing

The amount of wheat straw (WS) considered for the mass balance is 500Kg/h so

$$S_{12} = 500kg \quad (5.1)$$

The pretreatment process diagram indicates that

$$S_{13} = S_{14R} + S_{16} \quad (5.2)$$

- Where  $S_{14R}$  represents the washing water recirculation (WWR)
- For the first stage  $S_{14R} = 0$  because there is no water to recirculate.
- $S_{16}$  is fresh water (FW)
- According to section 3.2.1, the water required to wash one kilogram of wheat straw (WS) considering 1 stage is 17kg in this case this 17kg of water is just fresh water because  $S_{14} = 0$
- $S_{13} = 500kgWS * 17 \frac{kgFW}{kgWS} = 8500kgFW$

However, as it can be seen in Section 4.1.2 it is possible to recirculate the washing water once so for the second stage the balance is:

$$S_{14R} = S_{13} - \left( S_{12} \frac{85}{15} \right) \quad (5.3)$$

Where 85/15 is the water absorbed by the wheat straw in the first stage.

And  $S_{16}$  for the second stage is

$$S_{16} = 8500 - S_{14R} \quad (5.4)$$

$S_{15}$  is washed wheat straw and it contains 85/15 its weight in water.

$$S_{15} = S_{12} + \left( S_{12} \frac{85}{15} \right) - AR \quad (5.5)$$

$AR$  = Ash removal, according to the experimentation the average ash removal of washing is around 15 % considering a wheat straw with an initial ash content of 6.5 % so that means that  $AR = S_{12} - (S_{12} * 0.065 * 0.15)$

To calculate  $S_{14-W}$  which represents the waste water from the washing step, the amount of water absorbed by the wheat straw is subtracted from the total water used ( $S_{13}$ ). This is just for the second stage because for the first stage there is no waste water since the water was recirculated to the second stage.

$$S_{14W} = S_{13} - \left( S_{12} \frac{85}{15} \right) \quad (5.6)$$

This is the mass balance for washing without evaporation. For the washing with evaporation, the water evaporated is recirculated to the washing step and this amount of water is always 500Kg. This value is calculated in Section 5.2.4 and 5.2.5

Tables 19 and 20 contains the mass balance for a washing without evaporation and with evaporation respectively.

**Table 19: Mass balance of the washing step without evaporation**

	S12	S13		S14		S15	
	S12	S16	S14-R	S14-S	S14-W	S15	
	WS (kg/h)	FW (kg/h)	WWR (kg/h)	WWS (kg/h)	WWW (kg/h)	WS (kg/h)	WW (kg/h)
1st stage	500	8500	0	5667	0	495	2805
2nd stage	500	2833	5667	0	5667	495	2805
Total	1000	11333	5667	5667	5667	995	5610
Flow rate (kg/h)	500	5667	2833	2833	2833	495	2805

**Table 20: Mass balance of the washing step with evaporation**

	S12	S13		S14		S15		S25
	S12	S16	S14-R	S14-S	S14-W	S15		S25
	WS (kg/h)	FW (kg/h)	WWR (kg/h)	WWS (kg/h)	WWW (kg/h)	WS (kg/h)	WW (kg/h)	WE (kg/h)
1st stage	500	8013	0	5667	0	495	2805	487
2nd stage	500	2346	5667	0	5667	495	2805	487
Total	1000	10359	5667	5667	5667	990	5610	974
Flow rate (kg/h)	500	<b>5180</b>	2833	2833	<b>2833</b>	495	2805	487

## 5.2.2 Leaching

Section 3.4.1 indicates that 10.4kg of AC is needed to leach a kilogram of wheat straw so

$$S_{17} = S_{12} * 10 \frac{kgAC}{kgWS} \quad (5.7)$$

- $S_{17} = 500kg * 10.4 \frac{kgAC}{kgWS} = 5200AC$

According to the mass balance of the pyrolysis process 500kg of wheat straw produces 60kg of AC. That means that it would be needed to concentrate the aqueous condensates of 430 ton of wheat straw. For the mass balance it is considered that the 5200kg of AC have been already concentrating.:

$$S10 = 60kgAC \quad (5.8)$$

In order to maintain the mass balance and the AC as fresh as possible each time that the process receives 60kg of AC the process removes 60 kg of old AC

- $S18 = 60kgAC. \quad (5.9)$

This amount depends on the yields of the reactor, if the process receives less AC then it will remove the same amount that it receives.

### 5.2.3 Rinsing

According to section 3.2.1, the water required to rinse one kilogram of wheat straw (WS) considering 1 stage is 27kg so

$$S19 = (S12 - AR) * 27 \frac{kgFW}{kgWS} \quad (5.10)$$

- $S19 = 500kgWS - 5kgash * 27 \frac{kgFW}{kgWS} = 13365kgFW$

According to the pretreatment diagram

$$S19 = S20 + S21 \quad (5.11)$$

Where S20 is fresh water and S21R rinsing water recirculate (RWR). For the first stage S21R = 0 because there is no water to recirculate.

As it was demonstrated in Section 4.2.3 is possible to recirculate rinsing water 5 times without any problem so that means that S19 in the second, third, fourth and fifth is 0 because fresh water is not needed. While S21R will be 13365 for those stages.

The pretreatment diagram presents that S21S is the stored water for the rinsing step

$$S21S = S20 + S21R \quad (5.12)$$

- And the waste water from the rinsing step S21W = 0 in the stages 1,2,3 and 4 because the water is recirculated. S21W = 13500 in the 5<sup>th</sup> stage.

S22 is the wheat straw after the rinsing and it contains 85/15 rinsing water. In addition, after the rising the pretreatment process has removed around 40% of the initial ash content considering a wheat straw with an initial ash content of 6.5%. Table 21 contains the mass balance of the rinsing step.

**Table 21: Mass balance of the rinsing step**

	S15		S19		S21		S22	
	S15		S20	S21-R	S21-S	S21-W	S22	
	WS (kg/h)	WW (kg/h)	FW (kg/h)	RWR (kg/h)	RWS (kg/h)	WRW (kg/h)	WS (kg/h)	RW (kg/h)
1st stage	495	2805	13365	0	13365	0	487	2760
2nd stage	495	2805	0	13365	13365	0	487	2760
3rd stage	495	2805	0	13365	13365	0	487	2760
4th stage	495	2805	0	13365	13365	0	487	2760
5th stage	495	2805	0	13365	13365	13365	487	2760
Total	2475	14167	13365	53460	66825	13365	2435	13798
Flow rate (Kg/h)	495	2805	<b>2673</b>	10692	13365	2673	487	2760

### 5.2.4 Dewatering

According to Li Wang ,dewatering by mechanical means can reduce moisture from an initial 80% wet basis immediately after leaching to as low as 50% wet basis. So we can assume that we will have a wheat straw wet basis after the centrifugation of 50% (Li wang 2013). That means that the water remove by the centrifuge will be around

$$S23 = (S12 - TAR) - \left( (S12 - TAR) \frac{85}{15} \right) \quad (5.13)$$

TAR is the total ash removal, according to the experimentation, the total ash removal goes from 30 to 40% from wheat straw with an initial ash content of 6.5% . So that means that TAR = S12\*0.065\*4

And the wheat straw after centrifugation has 50% moisture

$$S24 = S12 + (S12 * 0.5) \quad (5.14)$$

### 5.2.5 Evaporation

For the evaporation it was considered that all the water was evaporated:

$$S25 = S24 * 0.5 \quad (5.15)$$

This water is recirculated to washing process

Finally, S26 is the Pretreat wheat straw

$$S26 = S24 * 0.5 \quad (5.16)$$

This is the stream that will go to the pyrolysis process. Table 22 contains the mass balance for dewatering and evaporation

**Table 22: Mass balance of dewatering and evaporation step**

	S23	S24		S26
	S23	S24		S26
	WC (Kg/h)	WS (Kg/h)	RWR (Kg/h)	PW (Kg/h)
1st stage	2318	487	487	487
2nd stage	2318	487	487	487
3rd stage	2318	487	487	487
4th stage	2318	487	487	487
5th stage	2318	487	487	487
total	11590	2435	2435	2435
Flow rate (Kg/h)	2318	487	487	487

### 5.3 Water Consumption by the Pretreatment

One important factor of the pretreatment process is the water consumption, to optimize the process recirculation of washing water and rinsing water was analyzed. Figure 32 presents how this recirculation or stages affects the water consumption.

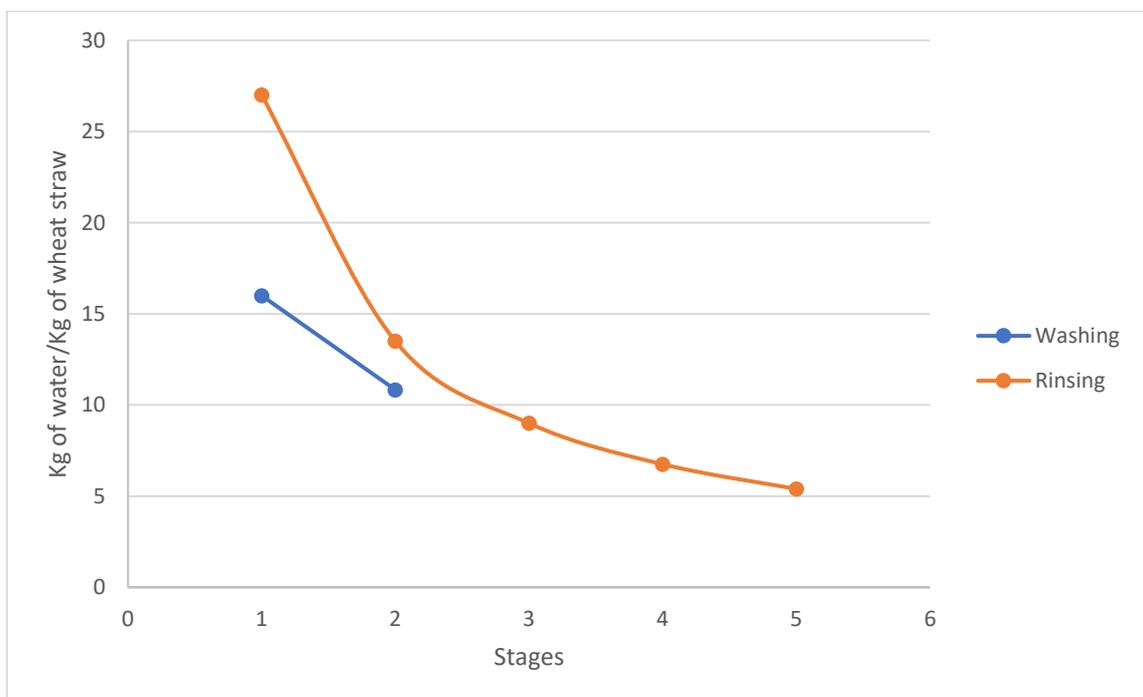


Figure 32: Water Required for Washing and Rinsing

It is clearly seen that the recirculation of water has reduced the fresh water required dramatically if 2 stages for washing and 5 stages are considered. Table 23 contains the results of the total water consumption of 2 stages for washing and 5 stages for rinsing are implemented.

Table 23: Total water consumption for the pretreatment process

	With evaporation	Without evaporation
Total Fresh water (kg/h)	7853	8340
Waste water from washing (kg/h)	2833	2833
Waste water from centrifuge (kg/h)	2310	2318
Water rinsing water (kg/h)	2673	2673
Total waste water (kg/h)	7816	7824

## 6 PREDESIGN OF THE EQUIPMENT

The objective of this chapter is to estimate the energy that the process will be required, the pre design of the equipment is just to have an idea of this energy.

### 6.1 Washing

#### 6.1.1 Bollman Extractor for the Washing Step

The washing step is performed in a Bollman extractor. Figure 33 presents the predesign of the Bollman extractor. To pre design the equipment, it was considered the following aspects which were set in previous chapters.

- The flow rate of pretreated wheat straw is 500kg/h
- The washing step last 15 minutes

The number of boxes depends on the flow rate of wheat straw, on the washing time and the available space for installation. For pragmatic reasons, the following boxes are proposed.

- Box 1: Box for loading wheat straw
- Boxes 2-6: Boxes for washing
- Box 7: Box for draining
- Box 8: Box for discharging



### Time for moving a box ( $t_{Box}$ )

The time that the Bollman extractor is going to move the boxes is calculated with the following equation.

$$t_{Box} = t_s / N_{box-s} \quad (6.1)$$

$$t_{Box} = \frac{15min}{5} = 3min = 0.05h$$

- $t_s$ : Duration time of the leaching or rinsing step (h)
- $N_{box-s}$ : Boxes for the washing

### Wheat straw per box ( $WS_{Box}$ )

The amount of wheat straw per box is calculated with the following equation.

$$WS_{Box} = F_{WS} * t_{Box} \quad (6.2)$$

$$WS_{Box} = \frac{500kg}{h} * 0.05h = 25kg$$

### Volume of the box

$$V_{Box} = WS_{Box} * \frac{1}{\rho_{WS}} * D_F \quad (6.3)$$

$$V_{Box} = 25kg * \frac{m^3}{61.36kg} * 1.2 = 0.49m^3$$

- $\rho_{WS}$ : Density of wheat straw ( $kg/m^3$ ) =  $61.36 kg/m^3$  (P. S. Lam, S, 2008)
- $D_F$ : Design factor = 1.2

For pragmatic reasons the size of the dimensions of the box is  $1.2m * 1.2m * 0.4$

### Bollman extractor motor

The Bollman extractor moves 3 baskets filled with wet wheat straw so considering that each basket contains 25kg of dry wheat straw and 85/15 times this weight in water then, the Bollman extractor will move a mass of

$$m = \left( WS_{Box} * N_B * \frac{85}{15} \right) + (WS_{Box} * N_B) \quad (6.4)$$

Where  $N_B$  is the number of baskets

- $m = \left(25kgWS * 3 * \frac{85}{15}\right) + (25kgWS * 3) = 500kg$

The Bollman extractor will move a box each 3 minutes to have 500Kg of dry wheat straw per hour

- The height of the boxes is  $h = 3.2m$
- The energy that the motor is going to consume is calculated with the following equation

$$W = \frac{mgh}{t} \quad (6.5)$$

Where  $g$  is the gravity constant ( $m/s^2$ )

$t$  is time (s)

$m$  is the mass to move (kg)

$$W = \frac{500Kg * \frac{9.81m}{s^2} * 3.2m}{180s} = 87.2W$$

$$Hp = 87.2 / 746 = 0.11 \text{ hp}$$

The Bollman extractor works with a pulley so that reduce the effect of the mass in two so the motor that we will need would be 0.05hp

For the design and selection of the motor. one has to consider the weight of the boxes alone. For pragmatic purposes, it is considered a motor of 0.5hp for the Bollman extractor and the screw conveyor.

**According to the mass balance, the flow rate of fresh water for the washing step is 5667kg / h considering 2 stages. In order to have a continues to process the Bollman extractor will remove 94kg of washing water per minute and it will receive 94kg of fresh water per minute.**

### 6.1.2 Pump for the Washing Step

The Bollman extractor will require a pump for the washing water. The following considerations were assumed to select the pump.

- According to the mass balance 8500l of fresh water is needed for washing 500kg of wheat straw.
- According to the experimentation the washing last 15 min that implies that the flow of the pump for the washing ( $FP_w$ ) is

$$FP_w = \frac{513}{t_s} * \frac{1}{\rho_w} \quad (6.6)$$

$$FP_w = \frac{8500kgFW}{15min} * \frac{l}{kgFW} = \frac{566l}{min}$$

- Appendix C contains an Iwaki curve pump and base on this curve it has been chosen a pump of 5hp.

## 6.2 Leaching and Rinsing

### 6.2.1 Bollman Extractor for the Leaching and Rinsing Steps

The leaching and rinsing step is performed in a countercurrent Bollman extractor. Figure 34 presents the predesign of the Bollman extractor where the leaching takes place in right part and the rinsing step in the left part. To pre design the equipment, it was considered the following aspects which were set in previous chapters.

- The flow rate of pretreated wheat straw is 500kg/h
- The leaching and rinsing steps last 15 minutes each one

The number of boxes depends on the flow rate of wheat straw and on the leaching and rinsing time.

The following boxes are proposed.

- Box 1: Box for loading washed wheat straw
- Boxes 2-6: Boxes for leaching
- Box 7: Box for draining
- Box 8-12: Boxes for rinsing
- Box 13: Box for draining
- Box 14: Box for discharging



### Time for moving a box ( $t_{box}$ )

The time that the Bollman extractor is going to move the boxes is calculated with the equation 6.1.

$$t_{Box} = t_s / N_{box-s} \quad (6.1)$$

$$t_{Box} = \frac{15min}{5} = 3min = 0.05h$$

- $t_s$ : Duration time of the leaching or rinsing step (h)
- $N_{box-s}$ : Boxes for the leaching or rinsing step

### Wheat straw per box

The amount of wheat straw per box is calculated with the following equation.

$$WS_{Box} = F_{WS} * t_{Box} \quad (6.2)$$

$$WS_{Box} = \frac{500kg}{h} * 0.05h = 25kg$$

### Volume of the box

$$V_{Box} = WS_{Box} * \frac{1}{\rho_{WS}} * D_F \quad (6.3)$$

$$V_{Box} = 25kg * \frac{m^3}{61.36kg} * 1.2 = 0.49m^3$$

- $\rho_{ws}$ : Density of wheat straw ( $kg/m^3$ ) = 61.36  $kg/m^3$  (P. S. Lam, S, 2008)
- $D_F$ : Design factor = 1.2

For pragmatic reasons the size of the dimensions of the box is 1.2m \* 1.2m \* 0.4

### Bollman extractor motor

The Bollman extractor moves 6 baskets filled with wet wheat straw so considering that each basket contains 25kg of dry wheat straw and 85/15 times this weight in water then, the Bollman extractor will move a mass of

$$m = \left( WS_{Box} * N_B * \frac{85}{15} \right) + (WS_{Box} * N_B) \quad (6.4)$$

Where  $N_B$  is the number of baskets

- $m = \left( 25kgWS * 6 * \frac{85}{15} \right) + (25kgWS * 6) = 1000kg$

The Bollman extractor will move a box each 3 minutes to have 500Kg of dry wheat straw per hour

- The height of the boxes is  $h = 4.7\text{m}$
- The energy that the motor is going to consume is calculated with the following equation

$$W = \frac{mgh}{t} \quad (6.5)$$

Where  $g$  is the gravity constant ( $\text{m/s}^2$ )

$t$  is time (s)

$m$  is the mass to move (kg)

$$W = \frac{1000\text{Kg} * \frac{9.81\text{m}}{\text{s}^2} * 4.7\text{m}}{180\text{s}} = 256.15\text{W}$$

$$\text{Hp} = 256.15 / 746 = 0.34 \text{ hp}$$

The Bollman extractor works with a pulley so that reduce the effect of the mass in two so the motor would be of 0.15hp

For the design and selection of the motor. one has to consider the weight of the boxes alone. For pragmatic purposes, I will consider a motor of 1hp for the Bollman extractor and the screw conveyor.

**According to the mass balance, the flow rate of fresh water for the rinsing step is 2700kg / h considering 5 stages. In order to have a continues to process the Bollman extractor will remove 45kg of rinsing water per minute and it will receive 45kg of fresh water per minute.**

## 6.2.2 Pumps for the Leaching and Rinsing Steps

The Bollman extractor will be required 2 pumps one of them for the aqueous condensates and the other for the rinsing water.

### *Aqueous condensates*

The following considerations were assumed to select the pump for the AC

- According to the mass balance 5200l of aqueous condensates are needed for leaching 500Kg of wheat straw.
- According to the experimentation the leaching process last 15 min that implies that the flow of the pump for the aqueous condensates ( $FP_{AC}$ ) is

$$FP_{AC} = \frac{517}{t_s} * \frac{1}{\rho_w} \quad (6.7)$$

- $FP_{AC} = \frac{5200\text{kgAC}}{15\text{min}} * \frac{l}{\text{kgFW}} = \frac{346l}{\text{min}}$

- Appendix C contains an Iwaki curve pump and base on this curve it has been chosen a pump of 5hp.

## Water for rinsing

The following considerations were assumed to select the pump for the rinsing water

- According to the mass balance 13500l of water is needed for rinsing 500Kg of wheat straw.
- According to the experimentation, the rinsing step last 15 min that implies that the flow of the pump for the rinsing water ( $FP_{RW}$ ) is

$$FP_{RW} = \frac{S19}{t_s} * \frac{1}{\rho_w} \quad (6.8)$$

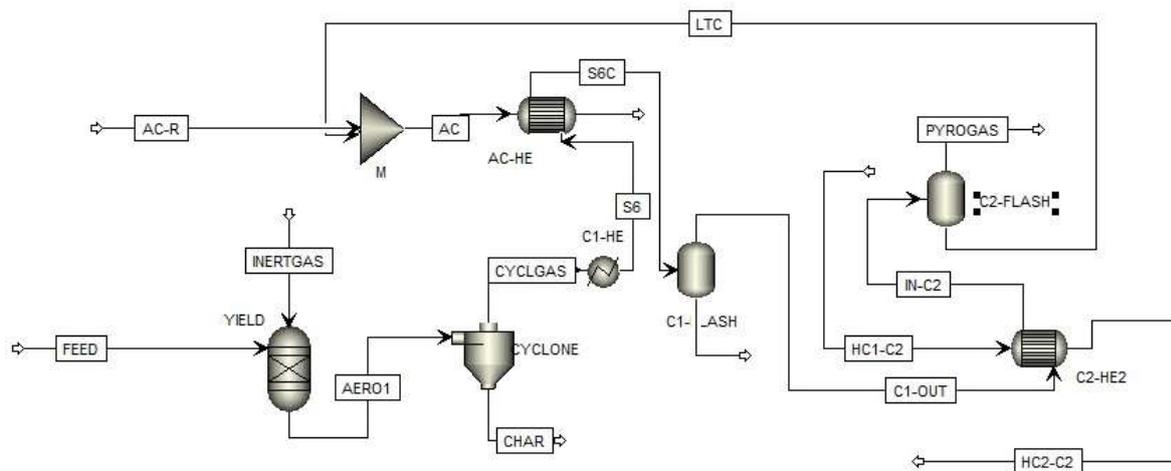
$$FP_{AC} = \frac{13500kgAC}{15min} * \frac{l}{kgFW} = \frac{900l}{min}$$

- Appendix D contains an Iwaki curve pump and base on this curve it has been chosen a pump of 10hp.

## 6.2.3 Heat Exchanger

As it was mentioned before, the pretreatment process recirculates a hot stream from the pyrolysis process S6 to heat aqueous condensate. The temperature of the stream S6 is 89 °C and its flow rate is 527 kg/h. The hot stream heats 5200Kg of recirculated aqueous condensates (AC-R) and 60 kg of fresh aqueous condensates (LTC) from 50°C to 60 °C because it was assumed that process *parts of an ongoing state* where AC is at 60 °C and decrease its temperature approximately 10 °C after 15 min which is the leaching time as it was observed in the experimentation.

This heat exchanger (HE-AC) was included in Gomes Fonseca's Aspen simulation. Figure 35 represents schematically this change and Table 24 displays the results.



**Figure 35: HE-AC in Fonseca's Aspen simulation**

**Table 24 heat exchanger results.**

<b>Heat exchanger results</b>	
Calculated heat duty	53.0026 kW
Required exchanger area	6.051 sqm
Actual exchange area	6.051 sqm
Percent over (under) design	0.00
Average U (Dirty)	0.85 kW/sqm-K
Average U (Clean)	
UA	4422.77 Kcal/hr-K
LMTD (Corrected)	10.34 C
LMTD correction factor	1

For the heat exchanger, it was proposed an AQ1L Alfa Laval heat exchanger because its maximum area is 10.9sqm and the required are for this heat exchanger is 6sqm. Appendix E contains the AQ1L Alfa Laval heat exchanger design.

### 6.3 Dewatering by Centrifugation

After the process of washing, leaching and rinsing the wheat straw will contain 85/15 its weight in water so it should be dried. According to Li Wang (Ling Wang, 2015) dewatering by mechanical means can reduce moisture from an initial 80% wet basis immediately after leaching to as low as 50% wet basis thus it can be assumed that a wheat straw wet basis after the centrifugation has 50% of moisture.

For pragmatic purposes, we are going to consider a Ferrum vertical scraper centrifuge. The wheat straw flow rate is 500Kg/h and it absorbs 85/15 its weight so the volume to centrifuge is:

$$V_C = S12 * \left(\frac{85}{15}\right) * D_F \quad (6.9)$$

$$V_C = 500 * \left(\frac{85}{15}\right) * 1.2 = 3400l$$

The time of centrifugation should be around 15min

Table 25 contains the main characteristics of the Ferrum centrifuge

**Table 25: Ferrum centrifuge**

<b>VBC-W</b>	<b>1600/800</b>	<b>1600/1000</b>	<b>Unit</b>
Basket diameter	1600	1600	[mm]
Basket height	800	986	[mm]
Filter surface	4,02	4.96	[m2]
Useful volume (100%)	820	1011	[dm3]
Max. load	1025	1263	[kg]
Max. rotor speed: grease / oil circulation lubrication	750 / 950	750 / 950	[min-1]
Max. G force: grease / oil circulation lubrication	503 / 807	503 / 807	[g]
Centrifuge weight (without load)	6200	6400	[kg]
Basket weight (1.4404)	1390	1520	[kg]
Motor power for main drive	37.0	<b>37.0</b>	[kW]
Motor power for feed/wash disk (option)	3.0 / 5.5 *	3.0 / 5.5 *	[kW]
* depending on product			
<b>Dimensions</b>			
L	2650	2650	[mm]
W	2000	2000	[mm]
H (closed, scraper knife vertical movement)	3000	3200	[mm]

Source ([Ferrum,2017](#))

## 6.4 Evaporation

After the centrifugation wheat straw will continue being wet so it is necessary to remove the remaining water by evaporation. The evaporation of water this water was simulated in Aspen Plus, considering 487kg of water at 25 °C. Table 26 contains the results.

**Table 26: Evaporation results**

Outlet temperature	100	°C
Heat duty	356	kW

### 6.4.1 Wheat Straw Heat Consumption

It should be also consider the heat needed to heat the wheat straw from 25 to 100 °C

- The heat capacity of dry wheat straw is 1.7 J/gK (0.4063 cal/gC) ([A Maarten,2009](#))
- $Q = (500.000g) (0.4063 \text{ cal/gC}) * 75 = 15.236.250 \text{ cal} = 17kW$

## 6.5 Another Option to Dry (Sun drying)

The energy consumption by the evaporation step is considerable, thus replacing the evaporation by sun drying can make the process reliable. The sun drying technique is wildly used for drying grains and fruit; this technique uses cribs to store and dry. The design of the cribs should allow air to circulate past tars so that the wheat straw will dry out. One option is a round steel cage. It is proposed a similar drying to evaporate water from a wheat straw. Figure 36 presents a steel cage used to dry corn.



**Figure 36: Cage for sun drying.** Source ([Denis DeBruler, 2014](#))

## 6.6 Energy Consumed by the Pretreatment Process

One important factor of the pretreatment process is the energy consumption, to estimate the energy consumed by the pretreatment the main equipment were redesigned. Table 27 contains the energy results. This energy will be compared in Chapter 6 with the extra energy produced by the increasing of organic condensate; this will be a preliminary insight into if the process is worth it or not.

**Table 27: Energy consumed by the pretreatment**

Service	kW
Bollman extractor for the washing step	0.74
Bollman extractor for the leaching and rinsing steps	0.74
Screw conveyer x 4	2.96
Pump for the washing step	3.72
Pump for the leaching step	3.72
Pump for the rinsing step	7.45
Centrifuge	37
Evaporator	357,06
Total	414.39

## 7 CHARACTERIZATION OF PRETREATMENT PRODUCTS AND BY-PRODUCTS.

In this section, the laboratory staff of KIT has performed some laboratory analysis in order to characterize the pretreated and untreated wheat straw as well as to characterized their products from the pyrolysis. Table 28 contains the ICP Analysis from pretreated and untreated wheat straw.

### 7.1 Wheat Straw

**Table 28: ICP Analysis of pretreated wheat straw and untreated wheat straw**

Probe-	Al	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Ni	Si	Sr	Zn	Total
% Mass	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Pretreated WS sample 1	<.02	0.27	<.01	0.0087	<.01	0.0076	<.5	0.036	<.002	<.02	1.99	0.00076	0.078	2.94
Pretreated WS sample 2	<.02	0.3	<.01	<.01	<.01	0.012	<.5	0.025	<.002	<.02	1.87	0.0008	0.004	2.21
Pretreated WS sample 3	<.02	0.3	<.01	0.0185	<.01	0.065	<.5	0.026	<.002	<.02	1.98	0.00081	<.002	2.39
Untreated 1 WS sample 1	<.02	0.39	<.01	<.01	<.01	0.011	1.01	0.061	0.0021	<.02	2.14	0.00072	<.002	3.61
Untreated WS sample 2	<.02	0.37	<.01	<.01	<.01	0.0091	1.01	0.059	0.0021	<.02	2.02	0.00063	<.002	3.47
Untreated sample 3	<.02	0.38	<.01	0.0057	<.01	0.0275	0.965	0.059	0.0023	<.02	2.06	0.00069	<.002	3.5

The total ash content of an untreated wheat straw sample is around 6.5% and the ICP analysis reports around 3.5% of this ashes. However, the interesting point here is ICP analysis provides detail of which elements were removed since a normal determination of ash content is just an oxidation of all elements and detail is not provided. As it can be seen in the table that the pretreatment has removed more than 50% the amount of K and more than 60% the amount of Mg and 25% the amount of calcium.

On the other and, according to Oudenhoven the pretreatment should remove most of the K and Na and partially Mg and Ca. However, the pretreatment of Oudenhoven is different than the pretreatment performed in this thesis. For example, he used (hot) de-ionized water to wash and synthetic aqueous condensate at 90°C to leach. While in this thesis, it was used water from the tap which had a conductivity around 660 mS/cm and real aqueous condensates at 60°C. As it can be seen in table 30 the initial amount of ashes was 6.5% and in table 29 the amount of ashes is 4.6% that means that the pretreatment has removed around 30% the number of ashes in wheat straw.

**Table 29: Pretreated wheat straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
WS Moisture(%)	3.5	3.5	3	3.33	-	0.24
Ash Content	4.7	4.6	4.6	4.6	-	0.05
Elemental Analysis Moisture content (%)	8.4	8.4	8.5	8.43	-	0.05
C (%)	43.4	43.5	43.3	43.40	47.58	0.08
H (%)	6.2	6.2	6.2	6.20	8.20	0.00
N (%)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

\*as determined

\*\* dry basis

**Table 30: Untreated wheat straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
WS Moisture(%)	8.9	8.9	8.8	8.87	-	0.05
Ash Content	6.5	6.5	6.5	6.50	-	0.00
Elemental Analysis Moisture content (%)	8.7	8.6	8.6	8.63	-	0.05
C (%)	42.2	42.5	42.2	42.30	46.41	0.14
H (%)	6.1	6.2	6.2	6.17	3,85	0.05
N (%)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

\*as determined

\*\* dry basis

## 7.2 Characterization of Waste Water from the Pretreatment Process

Tables 31 and 32 present the characteristic of the waste water. This information is important because it may determinate if the water can be used for irrigation or the kind of pretreatment for the disposal or usage of the water.

**Table 31: ICP Analysis of the water used for washing and rinsing**

	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Sr	Zn	Total
Mass	%	%	%	%	%	%	%	%	%	%	%	%	%
Rinsing water after 5 stages sample 1	0.001	0.01525	0.001	0.01115	0.0023	0.001	0.00105	0.001	0.0125	0.0104	0.001	0.001	0.059
Rinsing water after 5 stages sample 2	0.001	0.0154	0.001	0.01125	0.0023	0.001	0.00105	0.001	0.00575	0.0029	0.001	0.001	0.045
Washing water after 1 stage sample 1	0.00345	0.0113	0.001	0.01955	0.00205	0.001	0.0014	0.001	0.001	0.00325	0.001	0.001	0.047
Washing water after 1 stage Sample 2	0.001	0.01115	0.001	0.01955	0.002	0.001	0.00715	0.001	0.001	0.00315	0.001	0.001	0.050
LD3"	0.001	0.0215	0.001	0.062	0.0041	0.001	0.0014	0.0018	0.0115	0.011	0.001	0.001	0.118

As it can be seen in the previous table the rinsing water after 5 stages contains around 0.01115% of K and 0.0015% of Na. While the washing water after one stage contains 0.01955% of K and 0.00715% Na , almost twice more K than the rinsing water and almost 7 times more Na than the rinsing water. According to Oudenhoven, that is what it was expected since water can easily dissolve most of the K and Na. While, during the leaching the deposited salts react with the acid and produces soluble compound and the cations bound to the biomass are ion, exchanged so that is why it can be observed in the table that the rinsing water contains more Ca and Mg than the washing water ([S.R.G. Oudenhoven, 2016](#)).

**Table 32: Waste water CSB and TOC from the pretreatment process**

	Washing water after 1 stage sample 1	Washing water after 1 stage sample 2	Rinsing water after 5 stages sample 1	Rinsing water after 5 stages sample 2
CSB (mg/L)	1325	1390	49750	52400
TOC (mg/L)	403	364	17400	17350

The washing water contains dissolve minerals as it was shown in table C and this water can be used as irrigation water in order to compensate the nutrients taken from the soil (S.R.G. Oudenhoven, 2016). The rinsing water contains also mineral that can be usual for the soil. However , it also contains a high amount of CBS and TOC compering to the washing water and its used as irrigation water should be fulfill the regulations of each country. There are different methods to treat this water with high levels of TOC and CSB, one of them could be bleaching with Sodium hypochlorite or another powerful oxidant until acceptable parameters and then use the water for irrigation. Without a doubt, the treatment of the rinsing water requires further investigation.

### 7.3 Characterization of Organic Condensate from the Pyrolysis Experiments

Table 33 and 34 present the characteristic of the organic condensate from the pyrolysis process using a pretreated and untreated wheat straw. Hs is the energy content in the organic condensate; this value will be considered in the next chapter. It can be also seen that the OC from a pretreated sample has lower energy content than the OC from an untreated wheat straw. This could be due to the moisture content in OC from a pretreated wheat straw is bigger than in untreated wheat straw.

**Table 33: Organic condensate from pretreated wheat Straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
H <sub>2</sub> O (%)	3.5	7.8	6.5	5.93	-	1.80
Hs (J/g)	22104	19889	20727	20906.67	19342.03	913.15
C (%)	53,4	48.8	50.9	51.03	54,21	1.88
H (%)	6.5	6.6	6.5	6.53	6,54	0.05
N (%)	<1.3	<1.0	<1.0	<1.1	<1.1	<1.1

\*as determined

\*\* dry basis

**Table 34: Organic condensate from untreated wheat Straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
H <sub>2</sub> O (%)	2.9	2.5	2.7	2.70	-	0.16
Hs (J/g)	27362	28652	28756	28256.67	26604	634.05
C (%)	62.2	64.8	65.5	64.17	65.67	1.42
H (%)	7.2	7.4	7.3	7.30	6.49	0.08
N (%)	<1.0	<1.0	<1.2	<1.1	<1.1	<1.1

\*as determined

\*\* dry basis

## 7.4 Characterization of Char from the Pyrolysis Experiments

Table 35 and 36 present the characteristic of the char from the pyrolysis process using a pretreated and untreated wheat straw. Hs is the energy content in the char; these values will be considered in the next chapter. As it can be seen the energy content in the char from an untreated wheat straw is higher than the char from a pretreated wheat straw this could be due to the ash content and water content in the char for a pretreated wheat straw is bigger than from untreated wheat straw.

**Table 35: Char from pretreated wheat straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
H <sub>2</sub> O (%)	5.4	5.3	4.2	4.97	-	0.54
Ash Content (%)	35.6	36.8	35.3	35.90	37.77	0.65
Hs (J/g)	18480	18145	19781	18802.00	18204	705.64
C (%)	50.5	50.2	52.8	51.17	53.84	1.16
H (%)	2.5	2.4	2.5	2.47	2.20	0.05
N (%)	<1.6	<1.0	<1.0	<1.0	<1.0	

\*as determined

\*\* dry basis

**Table 36: Char from untreated wheat straw**

	Sample 1*	Sample 2*	Sample 3*	Average*	Average**	$\sigma^*$
H <sub>2</sub> O (%)	4.6	4.7	4.6	4.63	-	0.05
Ash Content (%)	30.5	33.4	31	31.63	33.16	1.27
Hs (J/g)	21889	20980	20997	21288.67	20656	424.56
C (%)	56.5	58.8	57.1	57.47	60.26	0.97
H (%)	2.5	2.5	2.8	2.60	1.68	0.14
N (%)	<1.6	<1.0	<1.0	<1.0	<1.0	-

\*as determined

\*\* dry basis

## 7.5 Characterization of AC from the Pyrolysis Experiments

Table 37 and 38 presents some information about the aqueous condensates from a pretreated wheat straw and from an untreated wheat straw.

**Table 37: AC from pretreated wheat straw**

	Sample 1	Sample 2	Sample 3
H <sub>2</sub> O (%)	34.4	47.1	29.8
CSB (mg/l)	887000	704500	981000
TOC (mg/l)	321500	249500	358000

**Table 38: AC from untreated wheat straw-**

	Sample 1	Sample 2	Sample 3
H <sub>2</sub> O (%)	74.7	70.5	73.6
CSB (mg/l)	355000	409000	361500
TOC (mg/l)	127500	149500	125500

It can be observed a remarkable gap between the water content in AC from an untreated WS and from a pretreated WS. this could be for two reasons. The average moisture in the pretreated wheat straw is around 3.3% and in the untreated wheat straw is 8,9%. In addition, it was installed an extra condensate tramp working at -20 °C in the pyrolysis experiments using an untreated wheat straw

## 8 FEASIBILITY OF THE PRETREATMENT PROCESS

As it was mention in Chapter 6 the comparison between the energy consumption of the pretreatment process with the energy content in the extra organic condensate produced by the removal of ashes is a preliminary insight into if the process is worth it or not. There is a remarkable difference between the organic condensate yields from a pretreated and untreated wheat straw which could be a good signal of the feasibility of the project. However, the energy content between them is also remarkable (see Tables 39 and 40).

**Table 39: Organic condensate and char yields using a pretreated and untreated wheat straw**

	Pretreated wheat straw		Untreated wheat straw	
	Yields (%) (Y)	HS MJ/kg	Yields (%)	HS MJ/kg
Organic condensate	42	20.9	16	28.2
har	11	18.8	20	21.2

Base on this information, and using the following equations, it can be calculated the energy content in organic condensate ( $E_{c_o}$ ), in char ( $E_{c_c}$ ), and total energy content (EC) from a pretreated wheat straw and untreated wheat straw.

$$E_{c_o} = (Y_o * HVV_o)/100 \quad (8.1)$$

$$E_{c_c} = (Y_c * HVV_c)/100 \quad (8.2)$$

$$EC = E_{c_o} + E_{c_c} \quad (8.3)$$

Where

- $Y_o$ : Yield of organic condensate (%)
- $Y_c$ : Yield of char (%)
- $HSo$ : higher heating value of organic condensate (MJ/Kg)
- $HSc$ : higher heating value of char (MJ/Kg)

Then, It can be calculated the extra ( $E_e$ ) by subtracting the energy produced by pretreated wheat straw ( $E_p$ ) and untreated wheat straw ( $E_u$ ).

$$E_e = E_p - E_u \quad (8.4)$$

Finally, the extra energy can be related and compared with the energy consumed for the pretreatment process considering that the flow rate is 500Kg/h. Table 34 contains the results of the energy produced using a pretreated wheat straw and an untreated wheat straw.

**Table 40: Energy produced using a pretreated wheat straw and an untreated wheat straw**

	Pretreated wheat straw	Untreated wheat straw
Energy per Kg (MJ)	10.846	8.752
Energy per 500Kg (MJ)	5423	4376
Energy per 500Kg (kW)	1506	1215

Calculating the extra energy (Ee)

$$Ee = 1506kW - 1215kW = 291kW$$

In Chapter 6 was estimated the energy consumption by the pretreatment process (414kW). This energy is bigger than the extra energy produced by the removal of ashes thus it may be concluded that the pretreatment is not worth it. However, it was proposed a drying by the sun which can turn the situation around dramatically because the estimated energy consumption by the pretreatment process would be 57kW so that means that the final extra energy would be 234kW which represents an increase of 19.25% of the total energy produced by wheat straw.

On the other hand, it should consider if it is possible to use the waste washing water for irrigation. There are many rules, standards, exceptions, etc. In addition, these can vary from a country to another ([European Commission, Brussels 2008](#)) so a detailed research is needed. On the other hand, it is quite possible that the rinsing waters should be treated so it is also needed a detailed research. Section 8.5 describes these waste water.

## 9 CONCLUSIONS

It has removed around 30% to 40% of the ash content in the wheat straw by a pretreatment process which led to a remarkable increase in the organic condensate. In order to know if the pretreatment process is feasible, it was estimated the energy consumption of the pretreatment process and compared it with the energy content in the extra organic condensate. Unfortunately, the pretreatment is not feasible because the estimated energy of the pretreatment is 414kW while the energy content in the extra organic condensate can produce 291kW. However, it was proposed to replace the evaporation of the pretreatment process by a sun drying which turns the situation around dramatically because the energy consumed by the pretreatment would be 57 kW. In other words, this is an increase of 19.25% of the total energy produced by wheat straw. This may justify the pretreatment process from an energetic point of view. Nevertheless, the implementation of sun-drying should be evaluated since weather conditions could be not favorable the whole year in all countries or regions.

On the other hand, the waste water produced by the pretreatment process has high levels of TOC and CSB so a pretreatment of water to reduce these levels to acceptable levels and then used the water for irrigation should be considered.

## 10 SUMMARY

The presence of alkali and alkaline earth metals (AAEMs) in biomass and cellulose affect the pyrolysis outcome since in combination with other elements such as silica and sulfur, and facilitated by the presence of chlorine, are responsible for many undesirable complex reactions which reduce the bio-oil yield ([Jenkins, 1996](#)).

In this thesis, a pretreatment of biomass to reduce the number of ashes was further studied and it was pre designed the pretreatment process. This process is divided into 5 parts: (1) Washing with water, (2) leaching with aqueous condensates which are produced in the pyrolysis process (3) rinsing leached biomass, (4) dewatering by centrifugation and (5) evaporation. By applying this process around 30% to 40% of the total amount of ashes was removed resulting in an organic condensate increased.

Using the pre-design of the pretreatment process its energy consumption was estimated and compared with the energy content in the extra organic condensate produced by the removal of ashes in order to have a preliminary insight into if the process is feasible or not.

## REFERENCES

- UN,2017a [online document]. [Accessed May 2017]. Available at <http://www.un.org/en/development/desa/news/population/2015-report.html>
- UN, 2017b Sustainable development [online document]. [Accessed 10 May 2017]. Available at <https://sustainabledevelopment.un.org/sdg7>
- UN,2017c. Progress of goal 7 [online document]. [Accessed May 2017]. <https://sustainabledevelopment.un.org/sdg7>
- UN,2017d Climate change [online document]. [Accessed May 2017]. <http://www.un.org/sustainabledevelopment/climatechange/>
- UN, 2017e the Paris agreement [online document]. [Accessed May 2017]. <http://bigpicture.unfccc.int/#content-the-paris-agreemen>
- Neste oil 2017, Renewable products [online document]. [Accessed May 2017]. <https://www.neste.com/fi/en/renewable-products>
- Neste oil 2017, Renewable feedstock [online document]. [Accessed March2017]. <http://biofuels2050.eu/resource-efficient/renewable-feedstock>
- European bio fuels 2017, Advance biofuels [online document]. [Accessed 10 May 2017]. <http://www.biofuelstp.eu/advancedbiofuels.htm>
- Gizem Barisik, Asli Isci, Naciye Kutlu, Simel Bagder Elmaci and Bulent Akay 2016, Optimization of organic acid pretreatment of wheat straw. *Biotechnology Progress*. *Biotechnology Progress Volume 32, Issue 6, pages 1487–1493*
- BP Statistical Review of World Energy, June 2016 [online document]. [Accessed 10 May 2017]. Available at <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf>
- Kersten SRA, van Swaaij WPM, Lefferts L, Seshan K. Options for Catalysis in the Thermochemical Conversion of Biomass into Fuels. *Catalysis for Renewables*. Wiley-VCH Verlag GmbH & Co. KGaA; ISBN: 9783527621118, 2007: 119-45.
- Christine Lagarde, 2013 A New Global Economy for a New Generation [online document]. [Accessed 10 May 2017]. <http://www.imf.org/external/np/speeches/2013/012313.htm>
- Ashok Pandey, Dr. Thallada Bhaskar, Dr. Michael Stöcker, Dr. Rajeev K Sukumaran, 2015. Recent advances in thermochemical conversion of biomass. *Feedstock Suitability for Thermochemical Processes Pages 31–74*
- Donal.L Klass, 1998, Biomass for Renewable Energy, Biomass for Renewable Energy, Fuels, and Chemicals pp 29–50

- Zhongyang Luo and Jingsong Zhou, 2017. Handbook of Climate Change Mitigation and Adaptation. Thermal Conversion of Biomass. Springer International Publishing pp 1813-1854
- Prabir Basu, 2010. Biomass Gasification and Pyrolysis Practical Design and Theory. Elsevier pp 17-23
- S.R.G. Oudenhoven, 2016. Improving the selectivity of pyrolysis by pyrolytic acid leaching of biomass: the role of AAEMS, anhydrosugar production and process design & evaluation, doctoral thesis. University of Twente
- R. M. Rowell, J. S. Han, and J. S. Rowell, 2014. Characterization and Factors Effecting Fiber Properties, Nat. Polym. an Agrofibers Compos., pp. 115–134.
- B. Jenkins, L. Baxter, T. Miles, and T. Miles, ‘Combustion properties of biomass’, Fuel Process. Technol., vol. 54, no. 1–3, pp. 17–46, 1998.
- A.V. Bridgwater, 1994 Catalysis in thermal biomass conversion Volume 116, Issues 1–2, Pages 5-47
- Cornelius Pfitzer, Nicolaus Dahmen, Nicole Troger, Friedhelm Weirich, Jorg Sauer, Armin Gunther, and Matthias Muller-Hagedorn, 2016. Fast Pyrolysis of Wheat Straw in the Bioliq Pilot Plant. Energy Fuels 30 (10), pp 8047–8054
- A. Funke, A. Niebel, D. Richter, M.M. Abbas, A.-K. Müller, S. Radloff, M. Paneru, J. Maier, N. Dahmen, J. Sauer, 2015. Fast pyrolysis char – Assessment of alternative uses within the biologic concept
- Gomes Fonseca, Frederico, 2015. Moisture content as a design and operational parameter for fast pyrolysis. Master thesis, Karlsruhe, Germany
- Song Hu, Long Jianga, Yi Wanga, Sheng Sua, Lushi Suna, Boyang Xub, Limo Hea, Jun Xianga, 2015. Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures Bioresource Technology Volume 192, pp 23-30
- Di Blasi, C., Galgano A., Branca, C., 2009. Influences of the chemical state of alkaline compounds and the nature of alkali metal on wood pyrolysis. Ind. Eng. Chem. Res. 48 (7), 3359–3369
- Mourant, D., Wang, Z., He, M., Wang, X.S., Garcia-Perez, M., Ling, K., Li, C.-Z., 2011. Mallee wood fast pyrolysis: effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. Fuel 90 (9), 2915–2922.
- R. Fahmi, A.V. Bridgwater, L.I. Darvel, J.M. Jones, N. Yates, Thain, I.S. Donnison, 2007. The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses. Fuel 86 1560–1569
- Scott W. Banks, Daniel J. Nowakowski, Anthony V. Bridgwater, 2016. Impact of Potassium and Phosphorus in Biomass on the Properties of Fast Pyrolysis Bio-oil. Bioenergy Research

Group, European Bioenergy Research Institute, Aston University, Birmingham B4 7ET, United Kingdom. *Energy Fuels*, 2016, 30 (10), pp 8009–8018

- S.R.G. Oudenhoven, A.G.J. van der Ham, H. van den Berg, R.J.M. Westerhof, S.R.A. Kersten, 2016, Using pyrolytic acid leaching as a pretreatment step in a biomass fast pyrolysis plant: Process design and economic evaluation. *Biomass and Bioenergy* 95 (2016) 388-404
- Harwood, Laurence M.; Moody, Christopher J. (13 Jun 1989). *Experimental organic chemistry: Principles and Practice* (Illustrated ed.). Wiley-Blackwell. pp. 122–125. ISBN 0-632-02017-2.
- Yifat Tishler, Aviva Samach, Ilana Rogachev, Rivka Elbaum, Avraham A. Levy, 2015 Analysis of Wheat Straw Biodiversity for Use as a Feedstock for Biofuel Production *BioEnergy Research* December 2015, Volume 8, Issue 4, pp 1831–1839
- Talebnia F, Karakashev D, Angelidaki I, 2010. Production of bioethanol from wheat straw: an overview on pretreatment, hydrolysis, and fermentation. *Bioresource Technology* Volume 101, Issue 13 4744–4753
- J. M. Suttie, 2000. Hay and straw conservation for small-scale farming and pastoral conditions.
- FAO, 2017 [online document]. [Accessed May 2017]. Available at <http://www.fao.org/docrep/006/y4011e/y4011e04.htm>
- Alfani, F., Gallifuoco, A., Saporosi, A., Spera, A., Cantarella, M., 2000. Comparison of SHF and SSF processes for the bioconversion of steam-exploded wheat straw. *Journal of Industrial Microbiology & Biotechnology* 25, 184–192.
- Ballesteros, I., Negro, M.J., Oliva, J.M., Cabanas, A., Manzanares, P., Ballesteros, M., 2006. Ethanol production from steam-explosion pretreated wheat straw. *Applied Biochemistry and Biotechnology* 130, 496–508.
- F. Talebnia, D. Karakashev, I. Angelidaki, 2010. Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis, and fermentation *Bioresource Technology*, 101, pp. 4744-4753
- T. Mani, P. Murugan, J. Abedi, and N. Mahinpey, 2010. Pyrolysis of wheat straw in a thermogravimetric analyzer: effect of particle size and heating rate on devolatilization and estimation of global kinetics, *Chemical Engineering Research and Design*, vol. 88, no. 8, pp. 952–958
- Jennifer Ruth Dodson, 2011. Wheat straw ash and its use as a silica source. Ph.D. University of York Chemistry
- Capital energy, 2017. [online document]. [Accessed May 2017]. Available at <http://capitalenergy.biz/?p=14295>

- Atkinson, C.J., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil* 337, pp 1-18.
- Antal, M.J., Grønli, M. (2003) The art, science, and technology of charcoal production. *Industrial and Engineering Chemistry Research*. 42, (8), pp 1619-1640.
- Bridgwater, A.V., Peacocke, G.V.C. (2000). Fast Pyrolysis Processes for Biomass. *Renewable and Sustainable Energy Reviews*. 4, pp 1-73.
- K.L. Chin, P.S. H'ng, M.T. Paridah, K. Szymona, 2015. Reducing ash related operation problems of fast growing timber species and oil palm biomass for combustion applications using leaching techniques. *Energy* Volume 90, Part 1, pp 622–630
- Zhang T, Kumar R, Wyman CE, 2013. Sugar yields from dilute oxalic acid pretreatment of maple wood compared to those with other dilute acids and hot water. *Carbohydr Polym*. Pp 334-344.
- IKTF KIT, 2017 [online document]. [Accessed May 2017]. Available at <https://www.ikft.kit.edu/english/index.php>
- B. M. Jenkins and J. M. Ebeling, 'Thermochemical properties of biomass fuels', *Calif. Agric.*, no. June, pp. 14–16, 1985.
- P. S. Lam, S. Sokhansanj, X. Bi, S. Mani, C. J. Lim, A. R. Womac, M. Hoque, J. Peng, T. Jaya Shankar, L. J. Naimi, and S. Nayaran, 'Physical characterization of wet and dry wheat straw and switchgrass – bulk and specific density', in *ASABE Annual Internation Meeting*, 2008, vol. 0300, no. 07, p. 23.
- F. Trippe, M. Fröhling, F. Schultmann, R. Stahl, and E. Henrich, 'Techno-economic assessment of gasification as a process step within biomass-to-liquid (BtL) fuel and chemicals production', *Fuel Process. Technol.*, vol. 92, no. 11, pp. 2169–2184, 2011.
- Ferrum,2017 [online document]. [Accessed May 2017]. Available at [https://www.ferrum.net/en/gbz/products/vertical-centrifuges/vbc.php#tab\\_67c707baa04ede6fbfbba07c011c2f12\\_3](https://www.ferrum.net/en/gbz/products/vertical-centrifuges/vbc.php#tab_67c707baa04ede6fbfbba07c011c2f12_3)
- Iwaki [online document]. [Accessed May 2017]. Available at <http://www.iwakiamerica.com/products/Magdrive.htm>
- Alfa Laval,2017 [online document]. [Accessed May 2017]. Available at [www.alfalaval.com/globalassets/documents/products/heat-transfer/plate-heat-exchangers/gasketed-plate-and-frame-heat-exchangers/aq11-ahri-certified-plate-heat-exchanger.pdf](http://www.alfalaval.com/globalassets/documents/products/heat-transfer/plate-heat-exchangers/gasketed-plate-and-frame-heat-exchangers/aq11-ahri-certified-plate-heat-exchanger.pdf)
- A Maarten J Kootstra, Hendrik H Beeftink, Elinor L Scott and Johan PM Sanders, 2009. Optimization of the dilute maleic acid pretreatment of wheat straw *Biotechnology for Biofuels* 2009, 2:31 doi:10.1186/1754-6834-2-31

- Li wang 2013, Mechanical Dewatering of Leached Wheat Straw. Master thesis. University of California,
- Inc 2017. [online document]. [Accessed August 2017]. Available at <https://www.inc.com/encyclopedia/return-on-investment-roi.html>
- P. S. Lam, S. Sokhansanj, X. Bi, S. Mani, C. J. Lim, A. R. Womac, M. Hoque, J. Peng, T. JayaShankar, L. J. Naimi, and S. Nayaran, 'Physical characterization of wet and dry wheat straw and switchgrass – bulk and specific density', in ASABE Annual International Meeting, 2008, vol. 0300, no. 07, p. 23.
- Axel Funke, Marco Tomasi Morganob, Nicolaus Dahmena, Hans Leibold, 2017. Experimental comparison of two bench scale units for fast and intermediate pyrolysis, *Journal of Analytical and Applied Pyrolysis* 124 (2017) 504–514
- European Commission, Brussels 2008, Assessing legal compliance with and implementation of the waste acceptance criteria and procedures by the eu-15 [online document]. [Accessed August 2017]. Available at [https://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjBgqzP38LVAhXCJ8AKHYxbBpkQFggmMAA&url=http%3A%2F%2Fec.europa.eu%2Fenvironment%2Fwaste%2Flandfill%2Fpdf%2Freport\\_wac15.pdf&usg=AFQjCNFiINTwKeTwK6n1eYJWpydnnMVfoA](https://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjBgqzP38LVAhXCJ8AKHYxbBpkQFggmMAA&url=http%3A%2F%2Fec.europa.eu%2Fenvironment%2Fwaste%2Flandfill%2Fpdf%2Freport_wac15.pdf&usg=AFQjCNFiINTwKeTwK6n1eYJWpydnnMVfoA)
- Mr Neil Bird, Joanneum, 2003. Using a Life Cycle Assessment Approach to Estimate the Net Greenhouse Gas Emissions of Bioenergy [online document]. [Accessed August 2017]. Available at <https://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=14&cad=rja&uact=8&ved=0ahUKEwi1oePx48TVAhVKC8AKHUZvCok4ChAWCEIwAw&url=http%3A%2F%2Fwww.iea.bioenergy.com%2Fwp-content%2Fuploads%2F2013%2F10%2FUsing-a-LCA-approach-to-estimate-the-net-GHG-emissions-of-bioenergy.pdf&usg=AFQjCNEBmDsVEQTge04IBpVscAFsvWN0vw>
- S.R.G. Oudenhoven, et al., Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: Improved oil and sugar yields, *J. Anal. Appl. Pyrol.* (2015), <http://dx.doi.org/10.1016/j.jaap.2015.09.003>
- Funke, A., Richter, D., Niebel, A., Dahmen, N., Sauer, J. Fast Pyrolysis of Biomass Residues in a Twin-screw Mixing Reactor. *J. Vis. Exp.* (115), e54395, doi:10.3791/54395 (2016)

# APPENDICES

## Appendix A: Primary Energy Consumption by Fuel

### Primary energy: Consumption by fuel\*

Million tonnes of equivalent	2014							2015						
	Oil	Natural gas	Coal	Nuclear energy	Hydro-electricity	Renewables	Total	Oil	Natural gas	Coal	Nuclear energy	Hydro-electricity	Renewables	Total
US	838.1	692.7	453.8	189.9	59.3	66.8	2300.5	851.6	713.6	396.3	189.9	57.4	71.7	2280.6
Canada	103.3	93.8	21.4	24.2	86.6	6.3	335.5	100.3	92.2	19.8	23.6	86.7	7.3	329.9
Mexico	85.2	78.1	12.8	2.2	8.6	3.0	190.0	84.3	74.9	12.8	2.6	6.8	3.5	185.0
<b>Total North America</b>	<b>1026.6</b>	<b>864.6</b>	<b>487.9</b>	<b>216.3</b>	<b>154.5</b>	<b>76.1</b>	<b>2826.0</b>	<b>1036.3</b>	<b>880.7</b>	<b>429.0</b>	<b>216.1</b>	<b>150.9</b>	<b>82.6</b>	<b>2795.5</b>
Argentina	30.9	42.4	1.5	1.3	9.3	0.8	86.3	31.6	42.8	1.4	1.6	9.6	0.9	87.8
Brazil	143.4	35.5	17.6	3.5	84.5	13.2	297.6	137.3	36.8	17.4	3.3	81.7	16.3	292.8
Chile	16.7	3.4	7.6	-	5.2	1.8	34.7	16.9	3.5	7.2	-	5.3	2.0	34.9
Colombia	14.6	9.8	6.0	-	10.1	0.3	40.9	15.5	9.5	7.0	-	10.1	0.4	42.5
Ecuador	12.0	0.6	-	-	2.6	0.1	15.3	11.7	0.6	-	-	3.0	0.1	15.4
Peru	10.2	6.5	0.9	-	5.0	0.3	22.9	10.9	6.8	0.9	-	5.3	0.4	24.1
Trinidad & Tobago	1.8	19.8	-	-	-	-	21.5	1.8	19.4	-	-	-	-	21.2
Venezuela	36.7	27.7	0.2	-	16.7	-	81.2	32.0	31.1	0.2	-	17.3	-	80.5
Other S. & Cent. America	63.6	6.9	3.0	-	20.9	3.4	97.8	65.0	6.9	3.0	-	20.7	4.3	100.0
<b>Total S. &amp; Cent. America</b>	<b>329.8</b>	<b>152.6</b>	<b>36.7</b>	<b>4.8</b>	<b>154.4</b>	<b>19.9</b>	<b>698.2</b>	<b>322.7</b>	<b>157.3</b>	<b>37.1</b>	<b>5.0</b>	<b>152.9</b>	<b>24.2</b>	<b>699.3</b>
Austria	12.5	7.1	3.0	-	9.3	2.0	33.9	12.6	7.5	3.2	-	8.3	2.4	34.1
Azerbaijan	4.4	8.5	-	-	0.3	-	13.2	4.5	8.8	-	-	0.4	-	13.7
Belarus	7.3	16.5	1.0	-	-	-	24.9	7.1	15.5	0.8	-	-	0.1	23.6
Belgium	29.8	12.4	3.3	7.6	0.1	2.7	55.9	30.5	13.6	3.2	5.9	0.1	3.2	56.5
Bulgaria	3.9	2.4	6.4	3.6	1.0	0.6	17.9	4.2	2.6	6.7	3.5	1.3	0.7	18.9
Czech Republic	9.1	6.2	15.9	6.9	0.4	1.6	40.1	9.4	6.5	15.6	6.1	0.4	1.7	39.6
Denmark	7.9	2.8	2.6	-	-	4.1	17.5	8.1	2.9	1.8	-	-	-	16.9
Finland	8.6	2.3	4.1	5.4	3.0	2.9	26.3	8.3	1.9	3.5	5.3	3.8	3.1	25.9
France	76.9	32.6	8.7	98.8	14.0	6.5	237.5	76.1	35.1	8.7	99.0	12.2	7.9	239.0
Germany	110.4	64.0	78.8	22.0	4.4	32.3	311.9	110.2	67.2	78.3	20.7	4.4	40.0	320.6
Greece	14.4	2.4	6.7	-	1.0	1.7	26.3	14.8	2.5	5.7	-	1.3	1.9	26.3
Hungary	6.5	7.5	2.2	3.5	0.1	0.6	20.5	7.0	8.0	2.2	3.6	0.1	0.7	21.5
Ireland	6.5	3.7	2.0	-	0.2	1.3	13.7	6.9	3.8	2.2	-	-	0.2	14.6
Italy	55.8	50.7	13.1	-	13.1	14.1	146.8	59.3	55.3	12.4	-	9.9	14.7	151.7
Kazakhstan	13.5	6.9	35.5	-	1.9	-	57.7	12.7	7.8	32.6	-	-	1.8	54.8
Lithuania	2.6	2.1	0.2	-	0.1	0.3	5.2	2.6	2.1	0.2	-	0.1	0.3	5.3
Netherlands	39.6	28.8	9.1	0.9	-	2.6	81.1	38.7	28.6	10.6	0.9	-	2.7	81.6
Norway	10.2	4.2	0.9	-	30.6	0.6	46.4	10.2	4.3	0.8	-	31.1	0.6	47.1
Poland	23.9	14.6	49.4	-	0.5	4.0	92.4	25.1	15.1	49.8	-	0.4	4.6	95.0
Portugal	11.1	3.7	2.7	-	3.5	3.6	24.6	11.4	3.9	3.3	-	2.0	3.5	24.1
Romania	9.0	9.5	5.8	2.6	4.2	1.5	32.5	9.1	9.3	6.1	2.6	3.7	2.2	33.1
Russian Federation	150.8	370.7	87.6	40.9	39.7	0.1	689.8	143.0	352.3	88.7	44.2	38.5	0.1	666.8
Slovakia	3.4	3.8	3.4	3.5	1.0	0.4	15.5	3.8	3.9	3.3	3.4	0.9	0.5	15.8
Spain	59.0	23.7	11.6	13.0	8.8	16.0	132.1	60.5	24.8	14.4	12.9	6.3	15.4	134.4
Sweden	14.5	0.8	2.1	14.8	14.5	5.0	51.7	14.1	0.8	2.1	12.9	16.9	6.2	53.0
Switzerland	10.6	2.4	0.1	6.3	8.5	0.6	28.4	10.7	2.6	0.2	5.3	8.5	0.7	27.9
Turkey	34.4	40.2	36.1	-	9.2	2.8	122.8	38.8	39.2	34.4	-	15.1	3.8	131.3
Turkmenistan	6.3	24.9	-	-	-	-	31.3	6.4	30.9	-	-	-	-	37.3
Ukraine	10.0	33.1	35.6	20.0	1.9	0.4	101.0	8.4	25.9	29.2	19.8	1.4	0.3	85.1
United Kingdom	69.9	60.0	29.9	14.4	1.3	13.3	188.9	71.6	61.4	23.4	15.9	1.4	17.4	191.2
Uzbekistan	2.8	43.9	1.2	-	2.3	-	50.3	2.8	45.3	1.1	-	2.5	-	51.6
Other Europe & Eurasia	32.8	13.4	22.0	2.0	21.7	2.2	94.1	33.1	13.7	23.4	1.9	21.5	2.3	96.0
<b>Total Europe &amp; Eurasia</b>	<b>858.6</b>	<b>905.8</b>	<b>481.0</b>	<b>266.2</b>	<b>196.7</b>	<b>124.1</b>	<b>2832.3</b>	<b>862.2</b>	<b>903.1</b>	<b>467.9</b>	<b>264.0</b>	<b>194.4</b>	<b>142.8</b>	<b>2834.4</b>
Iran	93.1	162.0	1.2	1.0	3.4	0.1	260.8	88.9	172.1	1.2	0.8	4.1	0.1	267.2
Israel	10.3	6.8	6.9	-	-	0.2	24.2	11.0	7.6	6.7	-	-	0.3	25.6
Kuwait	22.7	16.8	-	-	-	-	39.5	23.6	17.5	-	-	-	-	41.0
Qatar	10.0	35.7	-	-	-	-	45.7	10.9	40.6	-	-	-	-	51.5
Saudi Arabia	160.1	92.1	0.1	-	-	-	252.4	168.1	95.8	0.1	-	-	-	264.0
United Arab Emirates	37.6	59.6	1.6	-	-	0.1	99.0	40.0	62.2	1.6	-	-	0.1	103.9
Other Middle East	83.2	42.2	0.8	-	1.4	-	127.6	83.3	45.4	0.8	-	1.8	0.1	131.4
<b>Total Middle East</b>	<b>417.1</b>	<b>415.3</b>	<b>10.7</b>	<b>1.0</b>	<b>4.8</b>	<b>0.4</b>	<b>849.2</b>	<b>425.7</b>	<b>441.2</b>	<b>10.5</b>	<b>0.8</b>	<b>5.9</b>	<b>0.5</b>	<b>884.7</b>
Algeria	18.2	33.7	0.2	-	-	-	52.2	19.3	35.1	0.2	-	-	-	54.6
Egypt	38.3	43.2	0.7	-	3.0	0.3	85.5	39.2	43.0	0.7	-	3.0	0.4	86.2
South Africa	29.3	4.5	90.1	3.3	0.2	0.6	128.0	31.1	4.5	85.0	2.4	0.2	1.0	124.2
Other Africa	91.4	34.1	11.4	-	23.8	1.8	162.6	93.5	39.2	11.0	-	23.8	2.4	169.9
<b>Total Africa</b>	<b>177.2</b>	<b>115.6</b>	<b>102.4</b>	<b>3.3</b>	<b>27.0</b>	<b>2.7</b>	<b>428.2</b>	<b>183.0</b>	<b>121.9</b>	<b>96.9</b>	<b>2.4</b>	<b>27.0</b>	<b>3.8</b>	<b>435.0</b>
Australia	45.4	32.4	44.7	-	3.3	4.1	129.9	46.2	30.9	46.6	-	3.1	4.5	131.4
Bangladesh	5.7	21.5	0.9	-	0.1	-	28.3	5.5	24.1	0.8	-	0.2	0.1	30.7
China	526.8	169.6	1949.3	30.0	242.8	51.9	2970.3	559.7	177.6	1920.4	38.6	254.9	62.7	3014.0
China Hong Kong SAR	16.7	2.3	8.1	-	-	-	27.1	18.3	2.9	6.7	-	-	-	27.9
India	180.8	45.6	388.7	7.8	29.6	13.6	666.2	195.5	45.5	407.2	8.6	28.1	15.5	700.5
Indonesia	76.0	36.8	69.8	-	3.4	2.3	188.3	73.5	35.8	80.3	-	3.6	2.4	195.6
Japan	197.3	106.2	118.7	-	20.0	11.6	453.9	189.6	102.1	119.4	1.0	21.9	14.5	448.5
Malaysia	35.0	36.7	15.4	-	3.1	0.2	90.3	36.2	35.8	17.6	-	3.3	0.2	93.1
New Zealand	7.2	4.4	1.5	-	5.5	2.3	20.8	7.5	4.1	1.4	-	5.6	2.4	21.0
Pakistan	22.8	37.7	4.7	1.1	7.4	0.2	73.9	25.2	39.0	4.7	1.1	7.8	0.4	78.2
Philippines	16.1	3.2	10.6	-	2.1	2.4	34.4	18.4	3.0	11.4	-	2.2	2.7	37.7
Singapore	65.9	9.8	0.4	-	-	0.2	76.3	69.5	10.2	0.4	-	-	0.2	80.2
South Korea	107.9	43.0	84.6	35.4	0.9	1.2	273.1	113.7	39.2	84.5	37.3	0.7	1.6	276.9
Taiwan	45.4	15.5	39.0	9.6	1.0	0.9	111.4	46.0	16.5	37.8	8.3	1.0	1.0	110.7
Thailand	54.9	47.4	17.9	-	1.2	2.1	123.4	56.6	47.6	17.6	-	0.9	2.3	124.9
Vietnam	18.0	9.2	19.3	-	13.6	-	60.1	19.5	9.6	22.2	-	14.4	0.1	65.9
Other Asia Pacific	20.4	6.5	18.8	-	13.0	0.2	58.9	20.6	7.1	19.3	-	14.1	0.3	61.3
<b>Total Asia Pacific</b>	<b>1442.2</b>	<b>627.7</b>	<b>2792.5</b>	<b>83.9</b>	<b>346.9</b>	<b>93.4</b>	<b>5386.6</b>	<b>1501.4</b>	<b>631.0</b>	<b>2798.5</b>	<b>94.9</b>	<b>361.9</b>	<b>110.9</b>	<b>5498.5</b>
<b>Total World</b>	<b>4251.6</b>	<b>3081.5</b>	<b>3911.2</b>	<b>575.5</b>	<b>884.3</b>	<b>316.6</b>	<b>13020.6</b>	<b>4331.3</b>	<b>3135.2</b>	<b>3839.9</b>	<b>583.1</b>	<b>892.9</b>	<b>364.9</b>	<b>13147.3</b>
of which: OECD	2033.8	1436.8	1043.2	450.2	317.3	217.9	5499.2	2056.4	1458.9	979.2	447.6	314.6	246.3	

## Appendix B: Specifications of the aqueous condensates

Compound	wt. %	
<b><u>NONAROMATIC COMPOUNDS</u></b>		
<b>Acids</b>	<b>4,84</b>	
Acetic acid	4,165	c
Propionic acid	0,449	c
Butyric acid	0,189	#
2-Butenoic acid, (Z)-	0,013	#
2-Butenoic acid, (cis-) (NIST MQ 84)	0,025	#
<b>Nonaromatic Alcohols</b>	<b>0,94</b>	
Methanol	0,944	#
<b>Nonaromatic Aldehydes</b>	<b>0,15</b>	
Crotonaldehyde, trans	0,150	c
<b>Nonaromatic Ketones</b>	<b>5,32</b>	
Acetol (Hydroxypropanone)	2,956	c
Butanone, 2-	0,328	c
Butanone, 1-hydroxy-2-	0,430	c
Butandione, 2,3- (Diacetyl)	0,374	c
Acetoin (Hydroxy-2-butanone, 3-)	0,066	#
Propanone, acetyloxy-2-	0,106	c
3-Buten-2-one, 3-methyl- (NIST MQ 88)	0,017	#
poss: 2,3-Pentanedione (NIST MQ 87)	0,046	#
3-Penten-2-one (NIST MQ 77)	0,102	#
4-Hexen-3-one	0,006	#
poss: 3-Penten-2-one, 4-methyl-	0,011	#
Cyclopentanone	0,059	c
Cyclopentanone, 2-methyl- (NIST MQ 87)	0,017	#
Cyclopentanone, 3-methyl- (NIST MQ 90)	0,011	#
Isomere of 2-Cyclopenten-1-one, 3-methyl-	0,015	#
poss: 2-Cyclopenten-1-one, 3,4-dimethyl-	0,018	#
Isomere of 2-Cyclopenten-1-one, 3methyl-	0,017	#
Isomer of Cyclopenten-1-one, 2,3-dimethyl-2-	0,171	#
2-Cyclopenten-1-one, 3,4-dimethyl- (NIST MQ 92)	0,035	#
2-Cyclopenten-1-one, trimethyl-	0,018	#
2-Cyclohexene-1,4-dione (NIST MQ 78)	0,008	#
2-Cyclopenten-1-one, 2-hydroxy-3,4-dimethyl- (NIST MQ 80)	0,016	#
Cyclopenten-1-one, 2-	0,213	#
Cyclopenten-1-one, 2-methyl-2-	0,098	c
Cyclopenten-1-one, 3-methyl-2-	0,053	c
Cyclopenten-1-one, 2-hydroxy-2-	0,014	#

Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	0,092	c
Cyclopenten-1-one, 3-ethyl-2-hydroxy-2-	0,020	c

## HETEROCYCLIC COMPOUNDS

<b>Furans</b>	<b>0,66</b>	
Furfuryl alcohol, 2-	0,014	#
Furanone, 2(5H)-	0,074	c
Furaldehyde, 2-	0,337	c
Furaldehyde, 3-	0,040	c
Furaldehyde, 5-methyl-2-	0,033	c
Ethanone, 1-(2-furanyl)-	0,032	c
Furan-2-one, 3-methyl-, (5H)-	0,020	c
Isomer of Furaldehyde, 5-methyl-2-	0,024	#
2(5H)-Furanone, 5-methyl- (NIST MQ 84)	0,020	#
Furan-2-one, 4-methyl-(5H)- (NIST MQ 88)	0,007	#
Lactone derivative = Furanone derivative (unspecific spectrum)	0,006	#
Furan-2-one, 2,5-dihydro-3,5-dimethyl-	0,012	#
Butyrolactone, $\gamma$ -	0,042	c

<b>Pyrans</b>	<b>0,00</b>	
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## CARBOHYDRATES

<b>Sugars</b>	<b>0,00</b>	
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## AROMATIC COMPOUNDS

<b>Benzenes</b>	<b>0,00</b>	
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<b>Catechols</b>	<b>n.q.</b>	
Catechol (Benzene, 1,2-dihydroxy-)	available	n.q.
Hydroquinone (Benzene, 1,4-dihydroxy-)	available	n.q.
Benzenediol, methyl-	available	n.q.

<b>Aromatic Aldehydes</b>	<b>0,00</b>	
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<b>Aromatic Ketones</b>	<b>0,01</b>	
Acetophenone	0,008	c

<b>Lignin derived Phenols</b>	<b>0,15</b>	
Phenol	0,046	c
Cresol, o-	0,030	c
Cresol, p-	0,022	c
Cresol, m-	0,017	c
Phenol, 2,4-dimethyl-	0,005	c
Phenol, 2,6-dimethyl-	0,005	c

Phenol, 2,3-dimethyl-	0,002	c
Phenol, 2,3,6-trimethyl-	0,001	c
Phenol, 2,3,5-trimethyl-	0,001	c
Phenol, 3-ethyl-	0,004	c
Phenol, 4-ethyl-	0,016	c
Phenol, 4-vinyl-	0,005	#
Phenol, ethyl-methyl-	0,002	#
Phenol, trimethyl-	0,001	#

#### **Guaiacols (Methoxy phenols)**

**0,24**

Guaiacol	0,127	c
Guaiacol, 3-methyl-	0,007	#
Guaiacol, 4-methyl-	0,037	c
Guaiacol, 4-ethyl-	0,018	c
Guaiacol, 4-vinyl-	0,007	#
Guaiacol, 4-allyl- (Eugenol)	0,010	c
Guaiacol, 4-propenyl- cis (Isoeugenol)	0,009	c
Guaiacol, 4-propenyl-(trans) (Isoeugenol)	0,009	c
Vanillin	0,006	c
Phenylethanone, 4-hydroxy-3-methoxy- (Acetoguaiacone)	0,005	c
Guaiacyl acetone	0,005	c

#### **Syringols (Dimethoxy phenols)**

**0,03**

Syringol	0,019	c
Syringol, 4-methyl-	0,004	c
Syringol, 4-ethyl-	0,002	c
Syringol, 4-vinyl-	0,001	#
Syringol, 4-allyl-	0,003	c

### **OTHER ORGANIC COMPOUNDS**

#### **Nonaromatic Esters**

**0,09**

Propanoic acid, ethenyl ester (NIST MQ 77)	0,014	#
poss: Pentanoic acid, 4-oxo-, methyl ester	0,024	#
poss: Acetic acid, methyl ester	0,036	#
poss: 2-Butenoic acid, 2-methyl- and unknown overlapping compound	0,019	#

#### **N-Compounds**

**0,04**

Pyridine	0,006	#
Acetonitrile (NIST MQ 95)	0,025	#
Pyridine, 2-methyl- (NIST MQ 92)	0,004	#

#### **Miscellaneous**

**0,04**

poss: Decene or homologous	0,019	#
1-Tridecene	0,012	#
D-Limonene (NIST MQ 92)	0,011	#

<b>unknown compounds</b>	<b>0,07</b>	
unknown overlapping compound with Cyclopenten-1-one	0,035	#
unknown not identifiable compound (unspecific spectrum) (no NIST spectrum found)	0,013	#
overlapping not identifiable compound MW=? (no NIST spectrum found)	0,021	#

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c = calibrated compound

n.q. = not quantifiable compound

# = estimated response factor

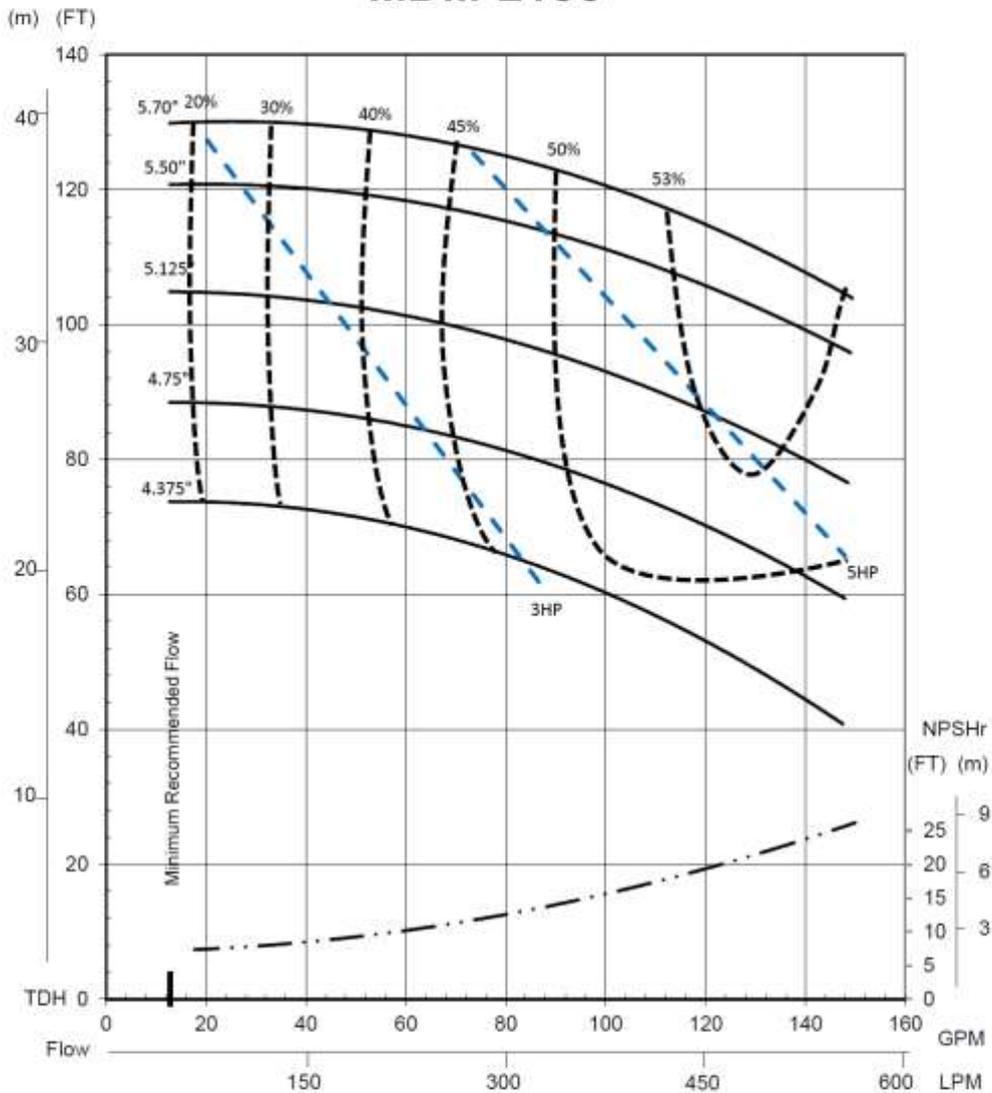
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<b>TOTAL</b>	<b>12,58</b>
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Appendix C: Iwaki Pump



### MDM-2156



Curve No. IALT-00258.A	Max. Impeller Dia. 5.70"	Suction: 2" ANSI 150LB
RPM: 3500	Min. Impeller Dia. 4.375"	Discharge: 1.5" ANSI 150LB
Date: 10/02/2013	Approved: <b>PB</b>	Ref: IP20410

Performance based on water at 70°F (21°C).

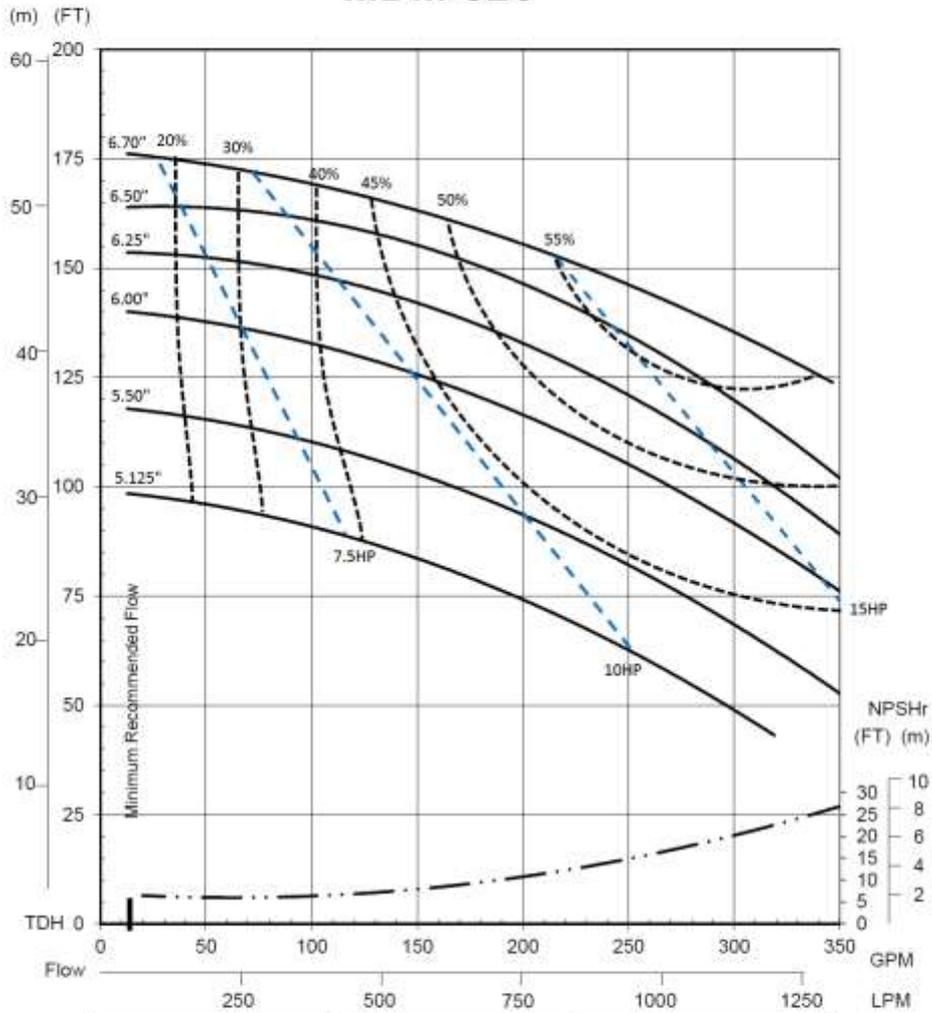
5 BOYNTON ROAD HOPPING BROOK PARK HOLLISTON, MA 01746-1446 USA  
 TEL: 508-429-1440 FAX: 508-429-1386 WEBSITE: WWW.IWAKIAMERICA.COM

Source ([Iwaki, 2017](#))

Appendix D: Iwaki Pump



MDM-326



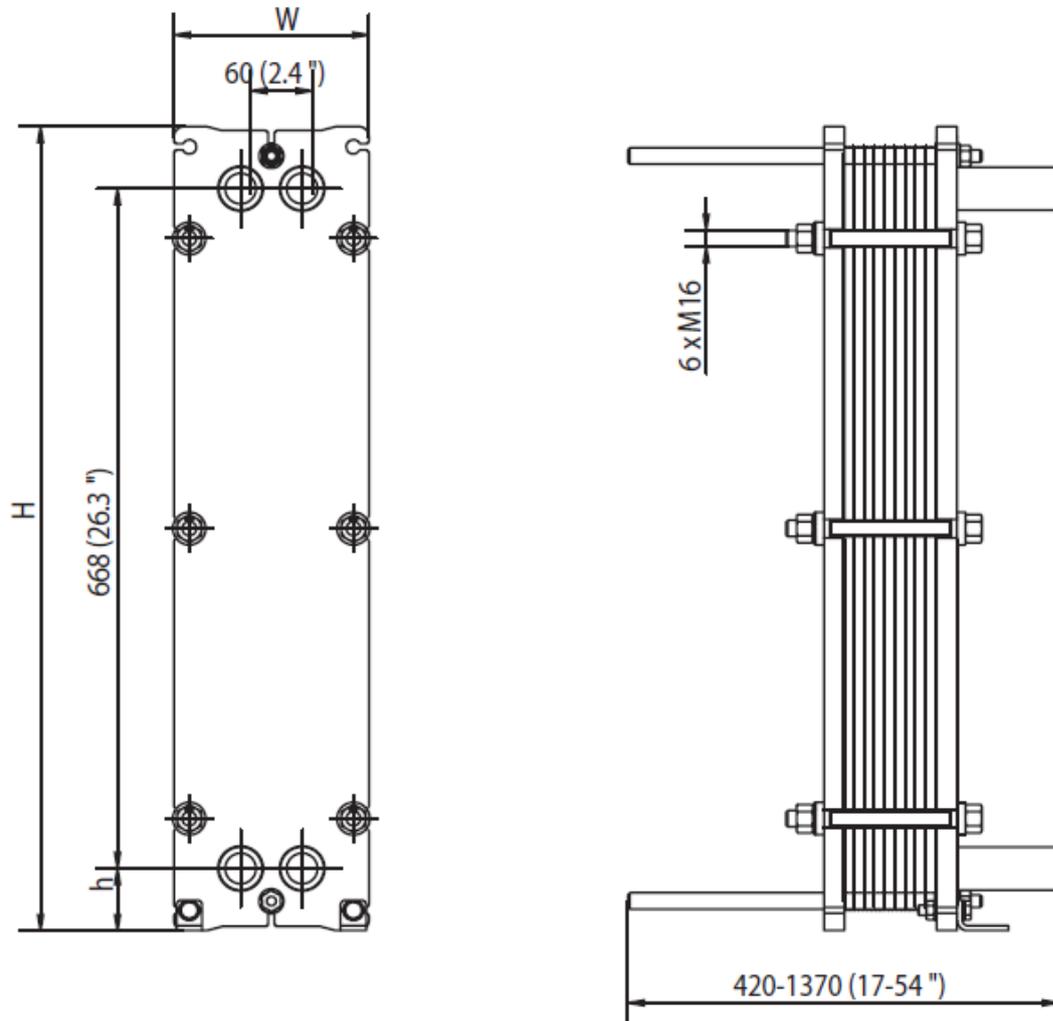
Curve No. IALT-00261.A	Max. Impeller Dia. 6.70"	Suction: 3" ANSI 150LB
RPM: 3500	Min. Impeller Dia. 5.125"	Discharge: 2" ANSI 150LB
Date: 10/02/2013	Approved: <i>FB</i>	Ref: IP20411

Performance based on water at 70°F (21°C).

5 BOYNTON ROAD HOPPING BROOK PARK HOLLISTON, MA 01746-1446 USA  
 TEL: 508-429-1440 FAX: 508-429-1386 WEBSITE: WWW.IWAKIAMERICA.COM

## Appendix E: AQ1L Alfalaval Heat Exchanger

### Dimensions



### Measurements mm (inch)

Type	H	W	h
AQ1L-FG	790 (31.1")	190 (7.5")	61 (2.4")

## Appendix F: Pyrolysis Process Mass Balance

	FEED S1	INERTGAS S2	AERO1 S3	CHAR S4	CYCLGAS S5	IN-C1 S6	HTC S7	C1-OUT S8	IN-C2 S9	LTC S10	PYROGAS S11
T (°C)	25	25	521,7	513,5	513,5	89	74	74	16,1	16,1	16,1
P (bar)	1,013	1,013	1003	1,013	1,013	1,267	1,267	1,267	1,267	1,013	1,013
H (kW)	-865,58	-0,008	-695,05	-4,553	-677,21	-803,47	-410,12	-419,39	-456,81	-215,08	-241,32
ρ (kg/cum)	1302,19	1,145	481,151	1434,11	0,542	1,747	1088,08	1,294	2,053	1000,05	1,323
N2		125	125	0,001	124,999	124,999	0,087	124,912	124,912	0,104	124,808
H2			0,275	trace	0,275	0,275	trace	0,275	0,275	trace	0,275
CO			31,004	<0,001	31,004	31,004	0,029	30,974	30,974	0,039	30,935
CH4			3,825	<0,001	3,825	3,825	0,005	3,82	3,82	0,002	3,817
CO2			73,258	0,001	73,257	73,257	0,584	72,673	72,673	0,272	72,402
C2H4			0,405	trace	0,405	0,405	0,001	0,404	0,404	<0,001	0,404
C2H6			1	trace	1	1	0,002	0,998	0,998	<0,001	0,998
C3H8			1,2	<0,001	1,2	1,2	0,002	1,198	1,198	0,001	1,197
C4H10			2,63	<0,001	2,63	2,63	0,007	2,623	2,623	0,002	2,621
C5H12			6,44	<0,001	6,44	6,44	0,024	6,416	6,416	0,007	6,409
O2			3,295	<0,001	3,295	3,295	0,006	3,289	3,289	0,008	3,281
WATER			92,227	0,001	92,226	92,226	48,322	43,904	43,904	41,429	2,475
ACACID			31,414	<0,001	31,414	31,414	21,527	9,887	9,887	9,203	0,685
PROPACID			7,695	<0,001	7,695	7,695	6,278	1,416	1,416	1,372	0,044
GLYCOL			5,805	<0,001	5,805	5,805	5,776	0,029	0,029	0,029	trace
ACETAL			5,28	<0,001	5,28	5,28	0,322	4,958	4,958	0,468	4,49
ACETOL			49,119	<0,001	49,118	49,118	44,376	4,742	4,742	4,704	0,038
FURFURAL			8,6	<0,001	8,6	8,6	6,919	1,68	1,68	1,574	0,106
PHENOL			8,175	<0,001	8,175	8,175	7,943	0,231	0,231	0,231	<0,001
GUAIACOL			13,39	<0,001	13,389	13,389	13,253	0,136	0,136	0,136	<0,001
SYRINGOL			11,73	<0,001	11,73	11,73	11,685	0,044	0,044	0,044	<0,001
LEVOGLUC			19,954	<0,001	19,954	19,954	19,954	trace			
METHANOL			0,325	trace	0,325	0,325	0,09	0,235	0,235	0,162	0,073
C2H3N			1,26	<0,001	1,26	1,26	0,25	1,01	1,01	0,349	0,661
PYRIDINE			1,26	<0,001	1,26	1,26	0,977	0,283	0,283	0,274	0,009
C											
STRAW	500										
CHAR			120,436	97,156	23,28	23,28	23,28				
ASH											
T(Kg/h)	500	125	625,002	97,159	527,841	527,841	211,699	316,137	316,137	60,41	255,728