Role of Catalytic Activity of Alkali Metals during Char Gasification of New Organic Products

Albert Bach
2013

Master of Science in Engineering Technology
Sustainable Energy Technology

Luleå University of Technology
Department of Engineering Sciences and Mathematics
Abstract

The field of the study is the research on reactivity of biomass char. For this purpose, several types of char were studied by conducting thermogravimetric Analysis (TGA) in a small scale furnace in the LTU.

On one hand, char reactivity of black liquor from pulp industry (BL) was studied, it was blended with different amounts of pyrolysis oil (PO) (PO fraction; 0%, 20%,30% and 100%). BL owes its reactivity to alkali metals and its role as a catalyst, therefore there was the aim to determine if char reactivity conserved when alkali fraction decreased. Experiments showed little difference in terms of char reactivity up to concentrations of PO of 20%. However the blend with a concentration of PO of 30% showed the formation of precipitates which resulted in the deactivation of the catalytic activity at low temperatures (900°C).

On the other hand, chars from four different types of liquefied organic waste (LOW) were studied. Thereafter, LOW char reactivity was compared to that of black liquor. The results showed LOW char reactivity was considerably higher.

Eventually the expression of char reactivity was modelled. Kinetic terms were figured out for each sample and the random pore model was appointed to explain the effect of char surface on the reaction rate.
Acknowledgments

I would like to thank Swedish Energy Agency, Nordic Energy Research Top-level Research Initiative (Nordsyngas project), Solander Science Park, and Bio4Energy, a strategic research environment appointed by the Swedish government, for supporting this work. I would like to thank, too, Chemrec AB, VTT Technical Research Centre of Finland, and Waste2Chemical GmbH for providing us the samples. Eventually, I want to express my most sincere gratitude towards Erik Furusjö and Kentaro Umeki for their invaluable help.
# Table of Contents

Abstract .......................................................................................................................................................... 1

Acknowledgments ......................................................................................................................................... 2

Table of Contents ......................................................................................................................................... 3

1.-Introduction ............................................................................................................................................... 5
  1.1.-Background ....................................................................................................................................... 5
  1.2.-Objectives ......................................................................................................................................... 7

2.-Biomass techniques .................................................................................................................................... 8
  2.1.-Biomass based fuels ................................................................................................................................. 8
    Physical procedures ................................................................................................................................... 8
    Biochemical procedures ............................................................................................................................. 9
    Chemical procedures ................................................................................................................................ 10
  2.2.-Dimethyl ether: from well to wheels ...................................................................................................... 12

3.-Experimental work .................................................................................................................................... 16
  3.1.-Materials studied .................................................................................................................................. 16
    3.1.1.-Black liquor (BL) ........................................................................................................................... 16
    3.1.2.-Pyrolysis Oil (PO) .......................................................................................................................... 17
    3.1.3 Pyrolysis oil & Black liquor blends. ................................................................................................. 19
    3.1.4.-Liquified Organic Waste (LOW) .................................................................................................. 20
  3.2 Experiments ............................................................................................................................................. 23
    3.2.1-Experimental procedure .................................................................................................................. 23
    3.2.2-Data treatment ................................................................................................................................ 25
  3.3-Equipment ............................................................................................................................................... 27

4.-Theory ....................................................................................................................................................... 29
4.1 Conversion.................................................................................................................. 29
4.2 Gasification with CO_2.................................................................................................. 30
  Kinetics .......................................................................................................................... 30
  Reaction surface model................................................................................................. 32
5.-Results and discussion .................................................................................................. 35
  5.1 Mass balance ............................................................................................................. 35
  5.1.1-Yields ..................................................................................................................... 35
  5.1.2.-Carbon left in the ashes ...................................................................................... 37
  5.2-Pyrolysis experiments ............................................................................................. 39
  5.3-Gasification experiments ......................................................................................... 42
    BL/PO mixtures............................................................................................................ 43
    LOW ............................................................................................................................. 47
  5.4-Reactivity model ...................................................................................................... 49
6- Conclusions .................................................................................................................. 53
7.-References ................................................................................................................... 55
Appendix I ........................................................................................................................ 57
1.-Introduction

1.1.-Background

The consumption of energy has grown without abeyance for the last two centuries. This has been allowed by the world tendency to grow and the availability of hydrocarbons at massive rates. Nevertheless, combustion of non-renewable fuels such as oil derivatives, coal or natural gas is now a matter of big concern.

On the one hand, releasing CO\textsubscript{2} stored millions of years ago, by the formation of fossil hydrocarbons, in scarcely a century may be seen as a menace for the carbon/carbon dioxide equilibrium established in the earth. Eventually it might have a direct repercussion in the rate of global warming. On the other hand, hydrocarbons fields are not homogeneously scattered across the planet but concentrated in a few regions. Historically and recently, the power over fossil fuels has proved to be a root of many national and international conflicts since it is a business that moves a lot of money. Finally, it is a question of price. Cheap and easy oilfields are the first to be operated ergo the first ones to be depleted. To meet a constant demand, more investments need to be done as easy oilfields become exhausted. In other words, oil price is likely to follow an escalating tendency in the next decades and at the same turn this attract voracious speculators whom create a distortion on the demand and ultimately on the price.

Unlike fossil fuels, biomass stocks are available anywhere on a local or international level, in big amounts and in a very wide range of forms. This is one of the main reasons why biomass is a centre of attention as the energy of the future.

Investigators from all over the world are well aware of this background and have been searching for alternatives. With oil alternatives being the centre of research efforts; electric car, hydrogen car and biofuels have been themes of deep research among other options. The present work is encompassed in biomass gasification as the first step to produce biofuels.

Typically gasifiers have been developed for forestall biomass. Some gasification technology like fluidized beds, have working temperatures around 800°C to 1000°C. However, to avoid the presence of tar in the syngas gasification temperature needs to be kept well above 1200°C. This have a direct repercussion on the composition of the output gas as an important fraction of CO\textsubscript{2} degrades its quality.
Since the late 80s entrained flow gasifiers have been developed. Entrained flow technology has the particularity to produce syngas almost free of tar. However, forestall biomass is not suitable for entrained flow gasifiers due to corrosion problems, besides biomass need to be pulverized or atomized as the first step for gasification. Consequently liquid forms of biomass are preferred.

Black liquor, as explained later on, is a by-product from paper industry with a high content of alkali metals, especially Na. Sodium is thought to act as a catalyst during the gasification of black liquor and it leads to lower working temperatures (1000°C). However the high fraction of inorganic mass in black liquor (25 % of dry weight) turns to reduce the fraction of the feedstock convertible into gas. Adding a determined quantity of pyrolysis oil into black liquor might be a possible solution to avoid this problem. Pyrolysis oil is a liquid fuel originated from the destructive distillation of wood.

Although different technologies exist for gasification of biomass they share the same principles. First, volatiles molecules are released as biomass degrades with temperature leaving stable char. Afterwards, remaining char reacts under oxidizing conditions, it is especially important since it controls the gasification rate.

The feasibility of adding pyrolysis oil into black liquor prior to gasification is given by several factors. Among all of them, char reactivity is crucial. The mixture should keep catalytic activity during char gasification within the same range than for pure black liquor.

Similarly, human activity produces several organic wastes which might become a feedstock for gasification. This would avoid the problem of waste treatment by finding a feasible way to upgrade them into valuable fuels. However, gasification technology would require standardized forms and its gasification conditions should not be very different from those of black liquor. Accordingly liquefied organic wastes have been a topic of research.

This project will contribute to provide gasification knowledge of biomass char for the potential feedstock mentioned.
1.2. Objectives

This study forms part of an initial phase of a broad field of activity undertaken by Chemrec in collaboration with the Lulea University of Technology (LTU) and the industry involved in the renewable energies. In particular, the present project is aimed to provide rates of char gasification under ideal laboratory conditions. Pyrolysis oil mixed with black liquor and liquefied organic waste are the samples studied.

The key objectives of the present work are;

- Char gasification rates of Pyrolysis oil and black liquor blends. Importance of catalytic activity during the char gasification.
- Char gasification rates of liquefied organic waste, comparison with black liquor rates.
- Model char reactivity.

To achieve the above objectives experimental work will be carried out at small scale using the equipment for ThermoGravimetric Analysis (TGA) experiments owned by the division of Energy of the Luleå University of Technology.

Gasification of new feedstock research is carried out with bio dimethyl ether (DME) production in mind from syngas as the last resort.
2.-Biomass techniques

As biomass is regarded any plant derived material interesting from an energetic point of view. Biomass originates from the reaction between CO$_2$ in the air, water and sunlight carried out by plants during photosynthesis. This reaction stores the energy from solar radiation by creating bonds between atoms of Oxygen, Hydrogen and Carbon to form lignin, cellulose and hemicellulose molecules. These structures represent almost the totality of plants dry weight. Animal remains are considered biomass too, yet they ultimately owe their stored chemical energy to plants. Biomass energy stored in its bonds is released when these bonds are broken by oxidation with O$_2$ while freeing H$_2$O and CO$_2$. Nevertheless, this CO$_2$ is regarded as carbon neutral emissions as it will be absorbed again by photosynthesis within the life cycle of the vegetal kingdom.

2.1.-Biomass based fuels

During the 19$^{th}$ and specially the 20$^{th}$ century fossil fuels replaced biomass from many energy-demanding activities and relegated it to a household warming way. However, since the 70s there has been an ever increasing effort to develop new techniques to use biomass in a more intensive way and nowadays biomass is thought to account for 10 to 14% of world’s primary energy consume [1].

The options of biomass sources are several; agricultural residues, paper mill black liquor, forestry industry, farming manure, alimentary industry residues, etc. However, for practice issues, biomass is to be transformed into a form that reduces storage, transport and combustion difficulties and costs. There are many different techniques to convert raw biomass into valuable fuels. This chapter presents a brief classification of some commercial forms in which biomass is processed and exploited.

Physical procedures

Physical procedures are quick and low cost techniques to obtain a final fuel when it is not specifically required in a fluid state.

There are several forms of biomass derivate fuels which only need to be dried so to be used as the final fuel, examples of this are; wood logs or animal dung. Others types need further treatment such as wood pellets. Pellets are commonly made out of sawdust and residual products from forestry industry. They are produced by the conglomeration of the previously pulverized biomass
into small cylinders, thus allowing a smooth supply to the combustion chamber. In the areas of the world where crops are considerable pellets are often made out of grasses.

Food industry waste products such as olive bones or nut shells may be a significant source of energy. They are usually crushed into small particles down to 3mm, and dried down to a 15 % of water content. The combustion of these forms of biomass has been long in practise to heat up large buildings such as chicken farms or warehouses.

**Biochemical procedures**

Combustible compounds appear by letting microorganism discompose the organic material in absence of oxygen.

Mankind has taken profit of this microorganism function and has developed industrial facilities to force it to happen in a large scale. As biochemical procedures two groups can be distinguished; those aimed to achieve alcohol based biofuels and those which produce methane based gas.

Alcohol based biofuels; Methanol, buthanol and mainly ethanol are aimed to fuel sparkling ignition engines as a substitute for petrol. In 2012 world’s total output of ethanol was around 85 M of m³ [2] (1.94·10^{18} J/year) which represented almost 1% of total world’s oil consumption; 88 M of oil barrels per day [3] (196·10^{18} J/year).

Ethanol is produced during the anaerobic fermentation of sugars by the Saccharomyces cerevisiae yeast species. For industrial production of ethanol corn, sugar beets and sugarcane are the preferred crops. Agricultural and forestall residues high in cellulose contain are used too. Brazil and the USA are the biggest producers of ethanol; Brazil’s ethanol derives from sugarcane plantations and it is part of an extensive integrated plan to produce refined sugar, ethanol and additionally electric power and heat. Meanwhile US ethanol is based on extensive corn crops.

Bioethanol production is a multistep process and there are several variations. Basic process starts by milling the crops, enzymatic digestion is the next stage to dissociate sugars into simple monosaccharaides (glucose). Fermentation takes place, in an agitated batch reactor and the residence time is set to 45 hours. After fermentation, sludge and other solids are removed by centrifugation while the liquid fraction is purified by ethanol distillation to reduce water contain down to 5%, pure ethanol is achieved by molecular sieve dehydration although it is no common for fuel purposes. Automobile fuel retailers usually offers ethanol blended with petrol with
different ethanol fractions. Pure ethanol can be found too in petrol stations for ethanol or flexible-fuel vehicles.

The second group of biological procedures encloses those based on biomass bacterial decomposition in anaerobic conditions to produce biogas. The total energy output from this group is much smaller than that from alcohol fuels and it responds to the need to deal with organic waste products rather than the goal to produce energy in a large scale. Farm manures, residual crops, landfills wastes, sludge from water treatment plants and waste from food processing factories are some examples of the feedstock in practice. Since the specific value (price/mass) of these materials is very low biogas plants are generally placed besides the feedstock source. These plants are specially designed to deal with the available feedstock or sometimes with a combination of them.

After raw feedstock has been homogenised and water contain adjusted biomass is pumped into the digester. Typically full anaerobic digestion undergoes four stages; Hydrolysis to break biomass molecules into monossacharides, aminoacids and fatty acids. Acidogenesis transforms the products from hydrolysis into short chain volatile acids, ketones, alcohols, hydrogen, and CO₂. Acetogenesis produces acetic acid and hydrogen from the products above and remaining glucoses and finally methanogenesis produces methane from acetic acid and hydrogen. These four stages occur simultaneously and are controlled by the populations of acidogenic, acetogenic and methanogenic bacteria. The product obtained from the digester is a mixture of CH₄ and CO₂, since the reaction develops in a aqueous solution moisture is also present in the final gas.

Due to the low quality of this biogas, it is commonly burnt in situ in a gas engine to produce electric power and heat for internal purposes.

**Chemical procedures**

Chemical procedures for biomass based fuels embrace gasification of biomass and vegetal oil refinement.

As biomass gasification it is understood those processes where biomass is transformed into a mixture of light combustible gases, called syngas. Gasification of biomass involves drying and devolatilization, oxidation of volatiles and char, and finally char gasification by an oxidizing agent.
Coal, peat and other organic materials which are not considered biomass can be gasified too in similar conditions.

Several types of gasifier have been developed; they can either be classified according to operation criteria or according to the mechanism to supply energy to the gasification.

<table>
<thead>
<tr>
<th>Operation criteria</th>
<th>Fixed bed</th>
<th>Fluidized bed</th>
<th>Entrained flow (Gas free of tar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concurrent</td>
<td>Biomass an oxidizing gas flow in opposite directions: gas outlet at the hottest zone. Smaller presence of tar in the syngas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Countercurrent</td>
<td>Biomass and oxidizing gas flow in the same directions: gas outlet at pyrolysis zone. High content of tar in the output gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bubbling fluidized bed</td>
<td>better gasification rates than fixed beds and the possibility to scale up to bigger sizes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Circulating fluidized bed</td>
<td>Higher particle residence time allowed by a greater particle recirculation than for bubbling fluidized bed system, better conversion efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-slaging</td>
<td>Ashes does not melt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slagging</td>
<td>Ashes melt, condensate on the walls and flow down</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Classification of gasifiers according to operation criteria

<table>
<thead>
<tr>
<th>Heat input mechanism</th>
<th>Autothermal (direct): Heat is generated inside the gasification chamber by partial oxidation of the fuel (Oxigen needed)</th>
<th>Air as oxidizing gas</th>
<th>Nitrogen lows the heating value and the possibilities of the output gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Allothermal (indirect): Additional input of heat to the gasification chamber</td>
<td>O₂ as oxidizing gas</td>
<td>Higher quality of the syngas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>External</td>
<td>Heat is provided from other sources than biomass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Internal</td>
<td>Char or syngas is recirculated for heat requirements</td>
</tr>
</tbody>
</table>

Table 2: Classification of gasifiers according to mechanism of heat supply
Fluidized bed gasifiers are usual designs of gasifier since they easily allow any size from pilot to fully commercial plants. The name is given by the floating motion of fuel particles on the flow of oxidizing gas. Circulating fluidized bed gasifiers are especially interesting given their high conversion rates. Both bubbling and circulating bed chambers have been designed for coal full combustion in thermic power plants as an alternative to pulverized burners and this reduces the price for this technology. However, tar presence in the syngas limits fluidized bed applications. Entrained flow gasifiers are the choice when syngas free of tar is needed.

Entrained flow gasifiers are characterized by the presence of a flame (up to 1600 °C), this creates very heterogeneous conditions along the gasification chamber with sharp gradients of temperature and strong drafts of gas. Fuel particles are atomized into the chamber along with a controlled flow of pure oxygen. Fuel is partly ignited in presence of oxygen releasing the required amount of heat and remaining particles are dragged along by gas streams. Vortex and swirl motions define the residence time of biomass particles, they are typically short (around one second). Typically, entrained flow gasifiers are run under pressurized conditions. An example of these types is the black liquor gasifier in Piteå (DP-1) owned by LTU. Entrained flow gasifiers require small biomass particles which can be atomized into the furnace, therefore liquid types of biomass are preferred to avoid mechanic work to reduce particle size.

Eventually the produced syngas (mixture of CO and H₂) is set for further refinement to increase its value. Catalytic conversion to methane, dimethyl ether or synthetic diesels is the logical path.

On the other hand, vegetal oil refinement aims to produce biodiesel for compression ignition engines.

Biodiesel is obtained by the transesterification of triglyceride molecules from vegetal oil. However, the lack of standardization in biodiesel types and the unreliability of feedstock supplies among financial issues hurdles its establishment in the commercial vehicles fleet beyond 5 % blends with petro-diesel.

### 2.2.-Dimethyl ether: from well to wheels

Well to wheels cycle is an approach that focuses on the transformation processes from feedstock (well) to transport fuel (wheel). On the field of renewable energy there are different alternatives
for this final fuel. Nevertheless, LTU and Chemrec AB have bet for Dimethyl ether (DME), as shown by the construction of a DME plant which uses syngas from black liquor gasification. It started the dimethyl ether production in 2011, being the first plant in the world of this kind and is fully comparable to a commercial plant.

The whole chain of Dimethyl ether synthesis starts with raw biomass stocks that are gasified into syngas and eventually transformed to Dimethyl ether.

First of all, let us have a glance on Syngas and dimethyl ether (DME) features;

**Syngas**

Synthesis gas, usually called syngas, is a mixture of different gases. Syngas is meant to be a mixture of H₂ and CO. Nevertheless, raw syngas composition can be further wide depending on how syngas is obtained. CO₂ Variable concentrations of H₂, CH₄, H₂O and noticeably CO₂ among others are found in raw syngas. Besides, it may content traces of particles, tars and other undesirable substances when it is obtained through biomass gasification.

Syngas is also known for its intermediate role in chemical reactions like methanol, dimethyl ether or SNG production. In this case, syngas has to be further refined in order to have the suitable concentration of CO and H₂. For such a purpose, CO₂ absorption and water-gas shift reaction are procedures extensively used.

**Dimethyl ether**

Dimethyl ether (DME) is an organic compound characterized by the simplicity of its chemical structure; CH₃OCH₃.

![Figure 1: dimethyl ether molecule](image)

Despite nowadays chief role of DME is as an aerosol propeller their excellent fuel properties are well known.

Although at atmospheric conditions it is a gas, it can be easily liquefied at reasonable pressures thus allowing it to be stored and transported without problems.
Its high cetane number makes DME an excellent fuel for Diesel engines. It can be used in current diesel engines with minor modification. These modifications basically consist in adapting the supply and the exhaust systems to the new fuel properties. Since fluid dynamics play an important role in the smooth functioning of the engine, viscosity, low heating value (LHV), density, temperature and corrosiveness of both combustible and product gases must be considered when adapting the engine to the new fuel. However, the mechanical block remains totally unchanged.

<table>
<thead>
<tr>
<th></th>
<th>DME</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point (°C)</td>
<td>-25</td>
<td>180-360</td>
</tr>
<tr>
<td>Cetane number</td>
<td>55</td>
<td>51</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>28.62</td>
<td>41.66</td>
</tr>
<tr>
<td>LHV (MJ/l)</td>
<td>18.92</td>
<td>35.66</td>
</tr>
<tr>
<td>Autoignation temperature (°C)</td>
<td>350</td>
<td>210</td>
</tr>
<tr>
<td>Density (Liquefied) (kg/m³)</td>
<td>661</td>
<td>856</td>
</tr>
<tr>
<td>Content of S (ppm)</td>
<td>0</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 3: Properties of dimethyl ether

Furthermore, the combustion of DME is reckoned to be very clean since NOₓ or Sulphur compounds are not formed.

**DME path**

First of all, raw biomass must be treated to have the correct properties at the inlet of the gasification stage. Feedstock quality is very important for the gas produced but it is even more important for the gasification reactor itself since reactor’s expectancy of life is one of the aspects which determinate the economic feasibility of the plant.

Once biomass is ready, next step is meant to achieve gas out of it. Although there are many different techniques so many different types of reactor, basically, gasification involves cracking the several polymeric molecules that form the biomass into lighter gaseous compounds; CO, H₂, CO₂, CH₄, C₂H₆, C₃H₈ and moisture. Since this reaction is endothermic, high temperature (>800 °C) is needed. As seen beforehand there are different ways to provide the reactor with thermic power to keep this temperature. In entrained flow gasifiers this energy comes from the partial oxidation
of the biomass when a controlled flow of \( O_2 \) is supplied to the biomass. However, the flow of the supplied gas must be that to avoid the full oxidation of the organic compound to \( CO_2 \). Some techniques imply pressurized reactors but high pressure is not strictly needed, though.

Eventually, last stage is meant to achieve the final desired fuel. In the production of DME methanol generation is the first step. From syngas methanol is obtained according to the catalysed reaction;

\[
CO + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}
\]

Note that 2 moles of \( \text{H}_2 \) are needed for each mole \( \text{CO} \), if syngas composition is not the suitable one a water-gas shift reaction module will be needed beforehand.

At this point methanol may be directly burned in internal combustion engines prepared for methanol. However, to achieve DME, methanol dehydratation is the next step;

\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}
\]

Bio dimethyl ether is still in an initial developing stage. Pilot plant in Piteå is unique in the world and its DME production is used to run several DME Volvo trucks.
3.-Experimental work

3.1.-Materials studied

In the present project eight different samples were studied in the laboratory, these are:

BL: Black liquor.

PO: Pyrolysis Oil.

BLPO20%: Mixture of BL and PO. BL accounts for 80% of the mass.

BLPO30%: Mixture of BL and PO. BL accounts for 70% of the mass.

LOW1: Liquefied organic waste prepared from pig manure.

LOW2: Liquefied organic waste prepared from mead and bones meal.

LOW3: Liquefied organic waste prepared from biogas digestate.

LOW4: Liquefied organic waste prepared from mead and bones meal.

3.1.1.-Black liquor (BL)

Black liquor is a by-product of the paper industry. It is obtained in large quantities. To have an order of the magnitude a mill consuming 30 kg/s of wood will get around 23 kg/s of black liquor (after drying). Smurfit Kappa Kraftliner (the pulp mill from where the samples were extracted) generates around 2000 tons of BL per day.

It appears after the process to separate cellulose from wood in a chemical reaction aimed to break cellulose fibres free of the lignin structure. Black liquor consists of dissolved lignin, other organic compounds found in wood, traces of wood inorganic compounds, important quantities of spent cooked chemical (NaOH, Na₂CO₃, Na₂S, Na₂SO₄), and a lot of water [4].

Black liquor comes out of digester tank being an aqueous solution with a solid fraction of 15%. Given the size of black liquor generation, the recovery of chemical is of paramount importance in economic matters for the paper mill. Recovering process of spent chemicals implies the combustion of black liquor in big Tomlinson recovery boilers. The ashes left after BL combustion corresponds to the alkali chemicals. After the suitable treatment, they are recirculated into the
Kraft process, this strongly requires the full combustion of black liquor (no traces of organic mass in the ashes). In the recovery boiler, the calorific value of black liquor is used to produce heat and electric power. However, for combustion dynamics, water content must be previously lowered down to 30%. Dried black liquor (25-30% of moisture) will be simply regarded as BL and this is the form in which it arrived to the laboratory for experiments.

<table>
<thead>
<tr>
<th>Black liquor properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet basis</td>
</tr>
<tr>
<td>Water content (%)</td>
</tr>
<tr>
<td>Ash content (%)</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
</tr>
</tbody>
</table>

*Table 4: Black liquor properties*

Elemental composition in dry basis is shown in table 5.

<table>
<thead>
<tr>
<th>Element</th>
<th>W. fraction (dry basis) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O*</td>
<td>35.8</td>
</tr>
<tr>
<td>C</td>
<td>30.6</td>
</tr>
<tr>
<td>Na</td>
<td>21.6</td>
</tr>
<tr>
<td>S</td>
<td>5.1</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
</tr>
<tr>
<td>K</td>
<td>3.24</td>
</tr>
<tr>
<td>Cl</td>
<td>0.16</td>
</tr>
<tr>
<td>N</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*Table 5: Elementary analysis of black liquor*

* Oxygen fraction is calculated as $100- (C+Na+s+ H+K+Cl+N)$

3.1.2.-Pyrolysis Oil (PO)

Pyrolysis oil is a liquid fuel obtained from pyrolysis of biomass stocks, mainly wood and agricultural residues. Pyrolysis oil is extracted by condensing the light volatile vapours originated after the destructive distillation of the biomass.

Pyrolysis oil itself is regarded as a biofuel. However, it is of a bad quality;

- It is not flammable on its own
It is not chemically stable
It is corrosive
Low heating value

Therefore the role of Pyrolysis oil is not to become a fuel for internal combustions engines but to be an easy form to transport and store forestry products, this would reduce the relative high costs of wood transportations compared to its value.

The chemical composition of pyrolysis oil strongly differs from one sample to another. These differences are given by feedstock features and by the conditions in which pyrolysis reaction takes place. Notwithstanding, for any pyrolysis oil its basis is a microemulsion of organic acids, (carboxylic, hydroxide, and sulfonic groups), aldehydes and ketones, water, and a mixture of organic compounds derived from lignin cracking called pyrolytic lignin. Complete chemical compositions are not known but Clark and Hallet assumed the following conformation [4] which is shown in table 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acids</td>
<td>-10</td>
</tr>
<tr>
<td>Aldehydes/ketones</td>
<td>-20</td>
</tr>
<tr>
<td>Water</td>
<td>-25</td>
</tr>
<tr>
<td>Pyrolytic lignin</td>
<td>-45</td>
</tr>
</tbody>
</table>

Table 6: assumed composition of pyrolysis oil

Pyrolysis oils are not thermodynamically stable and therefore its chemical composition and its physical properties may change through storage time. Temperature speed up the ageing of PO, thence storage temperature must be below 40. Besides, char residual particles contained in the oil act like a catalyst for ageing reactions, therefore oils totally free from chars are preferred.

The sample of pyrolysis oil used in experiments was brewed in VVT (Finland). The feedstock used was tree stumps. The analysis showed the following results

Its elemental composition is listed below in table 7;

<table>
<thead>
<tr>
<th>Element</th>
<th>Weigh fraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O*</td>
<td>52.5</td>
</tr>
</tbody>
</table>
Table 7: elementary analysis of pyrolysis oil

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>39.7</td>
</tr>
<tr>
<td>H</td>
<td>7.7</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*Oxygen fraction is calculated as 100 - (C+Na+s+ H+K+Cl+N)*

Viscosity of pyrolysis oil, shown in table 8, strongly depends on temperature;

<table>
<thead>
<tr>
<th>Property</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity v (mm²/s) (20 °C)</td>
<td>40.92</td>
</tr>
<tr>
<td>Kinematic Viscosity v (mm²/s) (40 °C)</td>
<td>13.29</td>
</tr>
<tr>
<td>Kinematic Viscosity v (mm²/s) (80 °C)</td>
<td>3.16</td>
</tr>
<tr>
<td>Density (15 °C) (kg/m³)</td>
<td>1190</td>
</tr>
<tr>
<td>PH</td>
<td>2.4</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Table 8: Properties of pyrolysis oil

3.1.3 Pyrolysis oil & Black liquor blends.

Pyrolysis oil and black liquor mixtures experiments were a milestone in the project. The goal of PO/BL mixtures gasification was to study the feasibility of a new feedstock for Chemrec; Pyrolysis oil. A hypothesis of pyrolysis oil reactivity being enhanced by Black liquor was suggested. It was based on the high content of Alkali metals contained in black liquor cooking chemicals (NaOH, Na₂CO₃, Na₂S, Na₂SO₄ and K₂CO₃) acting as a catalyst for pyrolysis oil. To study this role some mixtures with different concentrations of PO and BL were prepared. In these mixtures black liquor was the core of the blending with a concentration of Pyrolysis oil of 20% and 30%.

Blending was carried out by mixing the appropriate quantities of black liquor and pyrolysis oil in a heated beaker. The content was continuously stirred with an electric whisker for 10 minutes.

An interesting fact to consider is than Lignin molecules in black liquor precipitate when pH drops below 11. Consequently the maximum fraction of PO that BL can dissolve without lignin precipitation is around 20%. This was the reason to choose the composition of the blends. For that
sample where pyrolysis oil accounted for 20 % of the weight lignin was not reported to precipitate while when it accounted for 30% precipitation was clear.

3.1.4.-Liquified Organic Waste (LOW)

Liquefied Organic Waste may apply to any waste material with an important fraction of organic mass once being liquefied. The scope of this definition is very wide and it includes infinites different substances. In the present project four different materials fulfilling this definition have been studied. They have been labelled LOW1, LOW2 LOW3 and LOW4

Gasification reactors should not directly handle raw feedstock materials. An homogenized and liquefied form of the feedstock is preferred since fluids can be easily handled in any automatized feeding system. A primary transformation is needed to obtain the so-called Liquefied Organic Waste (LOW) out of the primary feedstock;

The process that raw feedstock have undergone to obtain the four samples studied can be summarized in some steps;

-Enrichment: Involving $\text{K}_2\text{CO}_3$ addition and removal of water, $\text{CO}_2$ and $\text{NH}_3$

-Cooking at 190$^\circ$C. Further water and $\text{NH}_3$ are removed.

-3 stages of centrifugation aimed to remove solid particles and $\text{NH}_3$

LOW brewing removed most of the ammonia, solid particles and a large percentage of water from the initial feedstock. The amount of K is high for all LOW as a result of $\text{K}_2\text{CO}_3$ addition.

LOW samples were not prepared at LTU but by the German company Waste2Chemicals and later sent to LTU.

LOW1:

LOW 1 is brewed from swine manure. Pig manure is a waste product from pig farming obtained in large amounts. Despite biogas plants have been widely established in Denmark, Germany or Holland to valorise porcine manure in most of the countries the majority of it is still spread on the fields, massive pig manure dumping is a menace to water streams and aquifers so to tap water.

The composition of pig manure is basically water, large organic molecules, ammonium ($\text{NH}_3$) and salts. High contain of water increases storage and transport costs.
LOW2: LOW 2 is brewed from meat and bones meal.

Meat and bones meal (MBM) is a solid and grown product of the rendering industry. It is often used as a cheap complement to feed non ruminant animals. The importance of MBM as a source of energy is quickly increasing prompted by concerns about MBM feeding to cattle being responsible for the spread of Bovine spongiform encephalopathy (Mad cows disease).

LOW3: LOW 3 is brewed from Digestate. It is the residue left after anaerobic fermentation by microorganism. Digestate samples can be very different depending on the degraded feedstock type. Currently digestate is spread on fields as a fertilizer but gasification would increase its utility

An analysis of LOW 3 was carried out, it is shown in table 10.

<table>
<thead>
<tr>
<th>Table 9: Pig manure composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>% manure</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Organic</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>P₂O₅</td>
</tr>
<tr>
<td>K₂O</td>
</tr>
</tbody>
</table>

LOW3

<table>
<thead>
<tr>
<th>% wet basis</th>
<th>% dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry content</td>
<td>17.30</td>
</tr>
<tr>
<td>Ashes</td>
<td>12.70</td>
</tr>
<tr>
<td>HHV (MJ/Kg)</td>
<td>1.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
</tr>
<tr>
<td>O **</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>H*</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>S</td>
</tr>
</tbody>
</table>
LOW 4:

LOW 4 feedstock is the same than for LOW 2; Meat and Bones meal (MBM). However LOW 4 preparation includes one last stage, this is the addition of Ca(OH)$_2$ and water.

One may expect to have very few differences between LOW 2 and LOW 4. However the reader will have the opportunity to realise this is not accurate.

<table>
<thead>
<tr>
<th>Element</th>
<th>% wet basis</th>
<th>% dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>19.40</td>
<td>33.05</td>
</tr>
<tr>
<td>O **</td>
<td>17.79</td>
<td>30.30</td>
</tr>
<tr>
<td>C</td>
<td>14.97</td>
<td>25.50</td>
</tr>
<tr>
<td>Cl</td>
<td>0.42</td>
<td>0.72</td>
</tr>
<tr>
<td>H*</td>
<td>2.58</td>
<td>4.40</td>
</tr>
<tr>
<td>N</td>
<td>0.80</td>
<td>4.50</td>
</tr>
<tr>
<td>Na</td>
<td>0.40</td>
<td>0.68</td>
</tr>
<tr>
<td>S</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>0.31</td>
<td>0.52</td>
</tr>
<tr>
<td>Si</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>
3.2 Experiments
The temperature range was brought to the maximum allowed by the conditions. Initially the lowest temperature had been planned at 800°C and the highest at 1000°C. Notwithstanding, during the first set of experiments at 800°C no gasification was witnessed therefore the low temperature was moved to 900°C. In the other hand the equipment failed to keep a temperature of 1000°C inside its core being 940°C its maximum.

3.2.1-Experimental procedure
As explained before, biomass undergoes pyrolysis, a first step, in which the organic material degrades into lighter compounds and volatize, and a second one, gasification, where the remaining organic material, fixed carbon, reacts in a partially oxidant atmosphere. In this project both steps have been dealt separately, the reason is explained below.

Black liquor, pyrolysis oil and their mixtures swell into big spheres of char during pyrolysis, this shape creates an extra resistance for the following char gasification since mass and heat transfer limit or even control the speed. Since the aim of the project is not to study mass or heat transfer dynamics it was decided to carry out the process in two independent stages. The sample was to undergo pyrolysis followed by grinding of the char into particles down to 300μm and eventually set for gasification.
**Pyrolysis:** It was aimed to achieve char out of the raw materials after the devolatization stage. Pyrolysis was carried out at 600 °C and in an atmosphere fully composed by carbon dioxide.

Raw materials were held in alumina crucible hang from the balance. Residence time was set to four minutes. This time proved to be more than enough to achieve a flat down in the mass drop for any of the eight samples studied. Pyrolysis conditions were set to be the same for all the samples.

The crucible would be withdrawn from the core of the reactor and let it to cool down in the quenching section to prevent the char from reacting with oxygen.

Further pyrolysis experiments were conducted by using the wire-mesh basket instead of the crucible. These experiments were aimed to study the rates of pyrolysis. The contact between reactant and the reactive atmosphere is enhanced by the usage of a wire-mesh basket instead of alumina crucibles. However, it implies the reactant must be in a solid or slurry form. Consequently, the samples were evenly scattered in a clock glass and let it to dry for three days under room temperature. The result was a solid and thin layer for BL based samples and a semisolid slurry layer for LOW which could be hold in a mesh.

**Gasification**

As it is previously explained, gasification temperature ranged from 900°C to 940°C and atmosphere was entirely formed by CO₂.

The first step was to measure the initial quantity of char (usually comprised around 300 mg). Thereafter, the basket was introduced into the core of the furnace and the balance set to start storing the mass drop during the gasification of char. Weight measurements from the balance were instantly and automatically printed from the balance to an excel file in a certain frequency. The same procedure was followed for those pyrolysis experiments carried out in the platinum basket.

Replications are of paramount importance. It does not only allow the researcher to have a more representative data and an estimation of uncertainty of the results but they are also helpful to spot if there has been any mistake during the experiment by comparing the different series of data, thus rejecting any suspicious set of data.
Carbon residue in ashes

Free carbon is not soluble in water. This was used to figure out the quantity of carbon left in the ashes after gasification.

First of all the ashes were left in a desiccator cupboard for 24 h to remove all the moisture. Then, ashes were weighted. Thereafter the ashes were dissolved into distilled water at room temperature. The solution was then filtered through a 5 μm particle retention filter. Retained particles were dried and weighted, they corresponded to unreacted carbon. All weightings were carried on in a precision balance up to four decimals of gram.

![Figure 3: Weighting unreacted char](image)

3.2.2-Data treatment

Since a minimum of three replications were carried out for any experiment, next step was to average the conversion (X) vs time curves to achieve a unique curve for each experiment.

Eventually, the need to work with the derivative of the curve made the removal of the noise a fact of paramount importance. This was carried out through Butterworth filter. Butterworth filter; is an electronic filter designed to remove unwanted frequencies from the wanted signal. It was first described in 1930 by Stephen Butterworth [4]

The transfer function between the input data (array with noise) and the output signal (smoothed) is given by this expression:
\[ H(z) = \frac{b_1 + b_2 z^{-1} + \cdots + b_{n+1} z^{-n}}{1 + a_2 z^{-1} + \cdots + a_{n+1} z^{-n}} \]

Equation 1 Transfer function of the low pass filter

Note than transfer function is defined in the complex frequency domain after the Z-transform \( Z = Ae^{j\theta} \).

The smoothing was carried out by using the following matlab functions

\texttt{[b,a]=butter(n,w_n)}: Returns the coefficients \( a, b \) of the transfer function of a zero-phase lowpass filter given a value for \( n \) and \( w_n \). See appendix for \( n \) and \( w_n \) used coefficients.

\( W_n \) is the normalised cut-off frequency and it is comprised between 0 and 1, \( n \) is the order of the transfer function between the input data signal (with noise) and the output signal

\texttt{Smoothed_data= filtfilt(b,a, data)}: Returns an array of filtered data given a digital input (data to smooth) and coefficients \( a \) and \( b \)

![Example of smoothing: BL 900 C](image)

Figure 4: Reducing noise from data
3.3-Equipment

**Furnace**: The same reactor was both used for pyrolysis and gasification experiments. It consisted of a furnace aimed to thermogravimetric analysis (TGA) experiments. It allowed the user to set the exact temperature from room temperature to 940 °C.

![Reactors](image)

**Figure 5: Reactor**

Gas was supplied into the reactor from the bottom and a flowmeter was set at the inlet ducts to adjust the flow. A pump run the suction through the exhaust gas outlet. Exhaust gas is basically the return of the supply gas but it also contains syngas (CO). Besides, important amounts of tars, volatiles and suspended particles are released during pyrolysis experiments. Therefore, exhaust gas must be expelled from the laboratory to avoid dangerous environments in the laboratory.

A cold and inert flow of gas (Argon) was supplied to refrigerate the quenching section of the furnace.
**Balance**: A precision balance was placed above the furnace so that both were concentrically alienated. Two metal plates were placed under the balance to avoid hot air updrafts from disturbing the lectures.

![Balance](image)

**Crucibles**: A total of eight alumina crucibles were used for pyrolysis experiments. The volume of each one was 20ml.

**Basket**: One basket made with platinum mesh was used for gasification experiments. The basket size was 16mm in diameter and 10 mm high while the size of the mesh holes was 0.2mm.

The material of the basket proved to be an awkward issue at the commencement of the experiments since it had to stand high temperatures while remaining inert to any of the products involved in the gasification. Initially molybdenum meshes were used but they turned to fail at temperatures above 800 C as sulphur contained in BL would react with molybdenum to form molybdenum disulphide (MoS$_2$). This resulted in the destruction of the baskets. Eventually, molybdenum baskets were replaced by platinum.
4.-Theory

4.1 Conversion

During biomass gasification the weight of the reactant is expected to drop with time depicting a curve similar to an exponential decay. The reaction is deemed to have arrived to the final when the weight stabilizes.

Since experiments are proceed with variable initial weights the measurements need to be standardized. Thence, conversion, briefed $X$, has been introduced as the variable to express the state of the reaction. So, it takes 0 as the value when the reaction has just started and 1 when it is completely finished. Conversion expression is written as;

$$X = \frac{m_{initial} - m}{m_{initial} - m_{final}}$$

Equation 2: Conversion

Thus $\frac{dx}{dt}$ represents the speed in which the reaction takes place. It is often called reaction or conversion rate and it is completely independent from the initial mass.

Conversion rate for the reactant particles can be modelled as the product of the main two phenomenon which explain the rate of the reaction.
\[
\frac{dX}{dt} = K \cdot f_{\text{surface area}}(X)
\]

Equation 3: Conversion rate

\(K\) is the kinetic constant (independent of \(X\)), it depends on the material and on the atmosphere conditions. Catalytic activity impact on the kinetic term by decreasing the energy of activation of the reaction, in consequence the constant becomes less sensitive to temperature.

Eventually, \(f_{\text{surface}}\) is a function that depends on the surface of the char pores. There are several expressions to model it.

The following chapters expose them for a particular case, reaction of char under \(\text{CO}_2\)

### 4.2 Gasification with \(\text{CO}_2\)

Char-\(\text{CO}_2\) is regarded as a good way to test reactivities of diverse types of chars. Gasification under \(\text{CO}_2\) takes longer than under steam. This is one of the reasons why it is preferred in laboratory scale since under \(\text{CO}_2\) the gasification rate is more easily controlled by the reaction mechanism rather than by mass and heat transfer dynamics. Besides, the flow of \(\text{CO}_2\) is easier to control than condensable gases such as steam. Therefore research on char gasification has based reactivities on the char-\(\text{CO}_2\) reaction

#### 4.2.1.-Kinetics

For small char particle sizes (<300 μm) and low temperatures (below 1000°C), the char-\(\text{CO}_2\) reaction is normally controlled by the chemical reaction [8,9,10].

\(\text{CO}_2\) gasification of char is an endothermic reaction therefore it requires high temperatures to take place, especially if it is not catalyzed.

If char is simplified as simple free carbon then the reaction theoretically develops according to the following mechanism [11]:

\[
\text{CO}_2 \xrightleftharpoons[k_1k_2]{k_3k_4} (O) + CO
\]

\[
C \xrightarrow[k_3k_4]{k_1k_2} (O) + CO
\]
Nevertheless, it is possible to eliminate most of these equations to arrive at a relatively simple mechanism [11].

\[
K = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO_2} + k_3 P_{CO}}
\]

Equation 5: simplified expression for the kinetic term

In expressions (5) and (7) the index of constants is picked randomly

The inhibitor role of carbon monoxide was later shown by Blackwood and Ingeme [12] as available actives carbon sites are engaged by carbon monoxide instead of Oxygen

\[
C(CO) + CO_2 \rightarrow 2CO + C
\]

\[
CO + C(CO) \rightarrow C_f + CO_2
\]

Equation 6: Carbon monoxide inhibitor

\[
K = \frac{k_1 P_{CO_2} + k_4 P_{CO_2}^2}{1 + k_2 P_{CO_2} + k_3 P_{CO}}
\]

Equation 7: kinetic term of carbon gasification under a CO₂ and CO atmosphere
4.2.2.-Reaction surface model
There are several models that describes the development of the surface during gasification; Overall reaction; shrinking core, grain, random pore, overlapped grain or percolation are some of them. In this chapter only the models used for analysis are described.

Overall reaction;

For overall reaction is understood any model than assumes that reaction takes place evenly distributed in any mass differential of the grain.

For char gasification the first order reaction model is the most reliable among all overall models. It proportionally links the conversion rate to the quantity of unreacted mass expressed by the term (1-X)

\[
\frac{dx}{dt} = K(1 - x)
\]

Equation 8: Differential equation 1st order overall reaction

\[
x = 1 - e^{-kt}
\]

Equation 9: Integrated equation 1st order overall reaction

Random pore

Random pore model (RPM) assumes that the reaction occurs in the internal surface of the porous. It was developed by Bhatia and Perlmutter [13].

RPM has repeatedly been proven to be more advantageous than any other one for modelling the gasification of both coal and biomass char [14,15,16]

RPM is based on the assumption than reacting surface does not decrease geometrically to the mass but at a slower pace at the beginning due to the pore growth phenomenon, at some cases total surface may even increase. It has the particularity to express surface as a function of porosity according to the expression below,

\[
\frac{dX}{dt} = K_{kinetics} \cdot f_{surface}(X)
\]
\[
\frac{dX}{dt} = K_{\text{kinetics}}(1 - X)(\sqrt{1 - \psi \ln(1 - X)})
\]

Equation 10: Char conversion rate. Random pore model expression

\[
\psi = \frac{4\pi L_0(1 - \varepsilon_0)}{S_0}
\]

Equation 11: Pore structural parameter

Where \(\psi\) is a structural parameter whose value is any higher than 0. Bhatia and Perlmutter assumed that pores were cylindrical [13]. \(\varepsilon_0\) is the initial porosity of the material, \(L_0\) the total length of the pores per unit of volume and \(S_0\) the total surface of the pores per unit of volume.

Species with higher \(\psi\) are those with lower initial porosity and in consequence they experience a bigger pore growth along the gasification. On the other hand, if a sample of char has got a \(\psi\) value close to zero it means it is initially very porous and it will witness little pore growth. Therefore for those chars with a \(\psi\) close to 0 the overall reaction model can successfully be applied.

Equation 10 depicts pore growth phenomenon, it has been plotted in a graph for three different values of \(\psi\); \(\psi_1 = 0.1, \psi_2 = 2, \psi_3 = 5\)

![Figure 10: random pore model shape](image-url)
Structural parameter ($\psi$) needs to be adjusted for each char. Everson and co-workers discussed in detail different ways to determine $\psi$. They proposed a manner based on the reduced time to a certain conversion; $t_x/t_{0.9}$ [17]. The same manner will be followed in this project.

According to the following expression (12), the reduced time, $t_x/t_{0.9}$, is only $\psi$ dependent given a fixed conversion [18]

$$
\frac{t_x}{t_{0.9}} = \frac{\sqrt{1 - \psi \ln(1 - X)} - 1}{\sqrt{1 - \psi \ln(1 - 0.9)} - 1}
$$

*Equation 12: Reduced time*

At the same time $\psi$, given by equation (11), depends only on the material and not on the oxidizing conditions.

Eventually $\psi$ is calculated by an optimization algorithm to minimize the sum of squared errors;

$$
\sum \left( \frac{t_{X_i}}{t_{0.9}} - \frac{\sqrt{1 - \psi \ln(1 - X_i)} - 1}{\sqrt{1 - \psi \ln(1 - 0.9)} - 1} \right)^2
$$

*Equation 13: Expression to minimize*

In other words, when the experimental points are plotted on a scatter graph with $t_x/t_{0.9}$ and $\sqrt{1 - \psi \ln(1 - X)} - 1$ for coordinates, $\psi$ is adjusted so that the points lie on a perfect 45° straight line

Once $\psi$ is known and after integrating equation (10) the expression to calculate the experimental kinetic constant is achieved;

$$
\frac{2}{\psi} \left[ \sqrt{1 - \psi \ln(1 - x)} - 1 \right] = K_{RPM} t
$$
5. Results and discussion

5.1 Mass balance

This chapter presents the time independent results. Main topics are char and ash weights as a fraction of the raw material. Carbon residue in the ashes after gasification is the other important topic of the chapter.

5.1.1 Yields

The following table expresses the weight of the sample at each stage of the transformation; it is expressed as a percentage of the initial raw mass.

Four different states have been quantified; Raw is the initial form exactly how it arrived to the laboratory, dry is a virtual stage resulting from excluding water according to the analysis, char is the weight left after pyrolysis and eventually ashes represents the weight left after gasification, either at 900 or 940 °C

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>Dry*</th>
<th>Char</th>
<th>Ashes 900</th>
<th>Ashes 940</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO</td>
<td>100</td>
<td>73.7</td>
<td>10.6</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>BL</td>
<td>100</td>
<td>72.8</td>
<td>45.4</td>
<td>35.2</td>
<td>29.5</td>
</tr>
<tr>
<td>BL (analysis)</td>
<td>100</td>
<td>72.8</td>
<td>45.4</td>
<td>39.5</td>
<td>39.5</td>
</tr>
<tr>
<td>BLPO(30%)</td>
<td>100</td>
<td>73.1</td>
<td>44.7</td>
<td>20.3</td>
<td>24.7</td>
</tr>
<tr>
<td>BLPO(30%) lin.expectance</td>
<td>100</td>
<td>72.8</td>
<td>34.9</td>
<td>24.7</td>
<td>20.7</td>
</tr>
<tr>
<td>BLPO(20%)</td>
<td>100</td>
<td>73.0</td>
<td>41.8</td>
<td>26.8</td>
<td>26.2</td>
</tr>
<tr>
<td>BLPO(20%) lin.expectance</td>
<td>100</td>
<td>73.0</td>
<td>38.4</td>
<td>28.2</td>
<td>23.6</td>
</tr>
<tr>
<td>LOW1</td>
<td>100</td>
<td>-</td>
<td>41.7</td>
<td>32.7</td>
<td>38.0</td>
</tr>
<tr>
<td>LOW2</td>
<td>100</td>
<td>-</td>
<td>25.8</td>
<td>18.3</td>
<td>20.6</td>
</tr>
<tr>
<td>LOW3</td>
<td>100</td>
<td>17.3</td>
<td>12.0</td>
<td>7.3</td>
<td>8.1</td>
</tr>
<tr>
<td>LOW3 analysis</td>
<td>100</td>
<td>17.3</td>
<td>12.0</td>
<td>12.7</td>
<td>12.7</td>
</tr>
<tr>
<td>LOW4</td>
<td>100</td>
<td>58.7</td>
<td>35.9</td>
<td>29.0</td>
<td>29.0</td>
</tr>
<tr>
<td>LOW4 analysis</td>
<td>100</td>
<td>58.7</td>
<td>35.9</td>
<td>33.7</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Table 12: Mass balance (values as a percentage of raw biomass)
The origin of PO, condensed gases from wood pyrolysis, is the reason for such a low yield for pyrolysis oil char and ashes since the inorganic amount is negligible.

Figure (11) and (12) show that most of the mass drop occurs during the devolatization stage. This can be attributed to the low contain of carbon (15-25 % on dry basis) and the high quantity of
water in the samples. This is exaggerated for the sample number 3 since the quantity of water is around 83%.

5.1.2.- Carbon residue in the ashes
As it has already been explained, ashes from black liquor gasification must be char free. Otherwise, the re-introduction of the alkali salts into the pulping process would be much more expensive making black liquor gasification economically unfeasible for the pulping plant. The following point compares the quantity of char residue in the ashes of BL, BLPO20%, BLPO30% and one of the liquefied organic waste samples.

<table>
<thead>
<tr>
<th></th>
<th>BL</th>
<th>BLPO20%</th>
<th>BLPO30%</th>
<th>LOW1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashes</td>
<td>0.350</td>
<td>0.077</td>
<td>0.072</td>
<td>0.210</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>0.00340</td>
<td>0.00000</td>
<td>0.00070</td>
<td>0.00000</td>
</tr>
<tr>
<td>% Carbon residue</td>
<td>0.971</td>
<td>0.000</td>
<td>0.967</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 13: Unreacted char

However figures shown in table (13) lack of precision. The main source of inaccuracies is that a subtraction between measurements must be done to figure out the quantity of ashes and carbon left. Any small inaccuracy in any of the two measurements is amplified as a result of the subtraction. These inaccuracies come mainly from moisture weight. Despite ashes and filters are totally free of moisture when extracted from the desiccator, they quickly absorb moisture back in the next few seconds. To try to limit this perturbation a definite time lapse was set to carry on weighting measurements. Nevertheless, the small size of the measurements and the variability of room humidity concern the author of the project about the reliability of these figures.

Qualitative inspection of the filters (see figure 13) revealed than the amount of carbon residue in its ashes strongly decreased when black liquor was mixed with pyrolysis oil. This is a very positive aspect of the blends and it deserves further study with better conditions and in a larger scale.
Figure 13: unreacted char on the filter

- **LOW1 unreacted char** (from 210 mg of ashes)
- **BLPO30% unreacted char** (from 77 mg of ashes)
- **BLPO20% unreacted char** (from 72 mg of ashes)
- **BL unreacted char** (from 350 mg of ashes)
5.2-Pyrolysis experiments

The results shown in this chapter are extracted from pyrolysis experiments conducted by using the mesh basket. For this purpose, the samples were dried at room conditions for three days, as explained in chapter 3.

Theoretic models have not been fitted to pyrolysis reactions. Differential analysis, figure (14), reflects pyrolysis development was limited by heat or mass transfer.
Regarding pyrolysis, no significant difference can be seen between BLPO20% and BLPO30%. However, the difference with black liquor is really important. The reason for this behaviour lies in pyrolysis oil high volatility. Pyrolysis oil as it name shows originates by the pyrolysis of wood, the compounds that volatizes during this process are later condensed to obtain pyrolysis oil. Consequently pyrolysis oil molecules are very prompt to volatize again. Unfortunately, pyrolysis oil could not be dried enough to be hold in a mesh basket but its pyrolysis time is supposed to be significantly lower than that of the rest of samples.

![Pyrolysis conversion rate](image)

*Figure 16: Pyrolysis conversion rate, liquefied organic waste*
While pyrolysis oil blended samples were showing an enhanced pyrolysis speed three out of the four liquefied organic samples showed a slower pyrolysis rate than pure black liquor.

Pyrolysis and gasification laboratory sessions were interspersed in time so already by this time it was confirmed that it did not exist any correlation between pyrolysis and gasification time.
5.3-Gasification experiments

The results shown in this chapter are extracted from gasification experiments that took place at 900 and 940°C and in a pure CO\textsubscript{2} atmosphere.

Gasification time of chars was diverse ranging from 6 minutes to scarcely 20 seconds depending on the sample and on the temperature.

The following plot can help the reader to have a first glance on the reactivity of each sample.

Despite the range of gasification temperatures was small, only 40°C, the differences between both are clear for some samples. It can be easily seen than PO is the most sensible sample to temperature.
**BL/PO mixtures**

Four types of char have been studied. These chars come from pure BL, PO/BL blends and pure PO.

The blends were defined by a pyrolysis fraction of 20% and 30%. In this chapter they will receive the name of BLPO20 and BLPO30. The main difference was that for the last, part of the lining of black liquor precipitated as a consequence of acidity. Therefore, large solid particles appeared in the sample.

Next graphs plot the conversion of car as a function of time.

---

**Figure 20: Char conversion of black liquor & pyrolysis oil**
The most reactive char is black liquor char as it is the first to fulfil the conversion, this level of reactivity is attributed to the catalytic role of Na. On the other hand pyrolysis oil is clearly the least reactive.

At 900°C it can be seen how BLPO30 conversion rate falls to a level similar to that of PO. It means that at 900°C BLPO30 is poorly catalysed. This might be explained by lignin precipitation. The formation of precipitates difficult the interaction of alkali metals with char particles and, thus reducing the affectivity of catalytic activity.

Figure 22 clearly shows the difference with the situation at 900°C.
Unlike char gasification at 900°C, at 940°C it was not witnessed any problem regarding the activity of catalyst. Blends turned to be as reactive as pure black liquor. The explanation of such a good
reactivity for the blends chars in comparison to the 900°C case lies on the fact that at 940°C, Na₂CO₃, the main alkali component completely melts, in this way it can homogeneously spread around char particles regardless of the presence of lignin precipitates. In fact, Na₂CO₃ melting point is 850°C so it should melt in both cases. Nevertheless, as char gasification is an endothermic reaction the temperature around char particles can locally drop down to 850°C thus avoiding alkali melting.

When both 900°C and 940°C results are plotted on the same graph, the difference become clearer.

![Gasification times](image)

Figure 24: Char gasification time. Black liquor & pyrolysis oil

The outlying point correspond to BLPO30, as it has already been commented, it showed poor catalytic activity due to the unsuccessful contact between char particles and alkali metals. Excluding this point the rest of the chars showed a very similar reactivity. They have constant reactivities regardless of the fraction of alkali elements as catalytic activity is thought to be in a saturated zone. According to Whitty K [19], sodium role as a catalyst witnessed saturation for ratios of sodium to carbon higher than 0.1. Indeed, chars studied in this project were well above this value.
This chapter aims to compare BL with the four samples of LOW studied.

**Figure 25: Char conversion. Liquefied organic waste**

**Figure 26: Char conversion rate. Liquefied organic waste**
At 900 °C, liquefied organic waste (LOW) samples showed a better char reactivity than black liquor. Samples number one and three were those with the highest reactivity among them. LOW 1 was particularly reactive as its gasification time tuned to be only one third that of black liquor.

On the other side, sample number four is the least reactive, yet, it still lies within the same level than black liquor char.

This high reactivity is attributed to the stronger catalytic role of potassium in comparison to sodium. Results are reaffirmed at 940°C.

![Figure 27: Char conversion. Liquefied organic waste](image-url)
5.4- Reactivity model

From an academic point of view and with simulation in mind it is important to adjust the experimental data to a model.

As explained in chapter 4, char reactivity takes this expression;

\[
\frac{dX}{dt} = K_{\text{kinetic}} \cdot f_{\text{surface area}} (X)
\]

Equation 14: general expression for conversion rate

Despite the model to predict the kinetic term \( k \) has not been within the scope of the work, the kinetic values for char gasification have been figured out according to equation (14). They are a good estimator of the reactivity of each char.
<table>
<thead>
<tr>
<th>$K_{\text{RPM}}$ (s$^{-1}$)</th>
<th>BL</th>
<th>BLPO20%</th>
<th>BLPO30%</th>
<th>PO</th>
<th>LOW1</th>
<th>LOW2</th>
<th>LOW3</th>
<th>LOW4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{RPM}}$(900)</td>
<td>0.0184</td>
<td>0.0146</td>
<td>0.0129</td>
<td>0.0064</td>
<td>0.0572</td>
<td>0.0286</td>
<td>0.0433</td>
<td>0.0201</td>
</tr>
<tr>
<td>$K_{\text{RPM}}$(940)</td>
<td>0.0166</td>
<td>0.0169</td>
<td>0.0186</td>
<td>0.0089</td>
<td>0.0884</td>
<td>0.0491</td>
<td>0.042</td>
<td>0.0214</td>
</tr>
</tbody>
</table>

Table 14: Kinetic constants

On the other hand, the surface function has been modelled;

A differential method approach was followed to determine the best model. In other words, the surface function from experimental data, $\frac{dx}{dt}/k_{\text{kinetic}}$, was contrasted with different models. Among all them random pore model was deemed to be the most suitable one.

Thereafter surface function from experimental data is plotted against the random pore model

![Surface model: BL](image_url)

**Figure 29: Random pore model. Black liquor**
Hence, expression 14 turns into equation 15 when the random pore model is assumed.

\[
\frac{dx}{dt} = k_{\text{kinetic}}(1 - X)(\sqrt{1 - \psi \ln(1 - X)})
\]

Equation 15: Conversion rate modeled by random pore model

The way to adjust \( \psi \) is explained in detail in chapter 4.2. Adjusted \( \psi \) values are these;

<table>
<thead>
<tr>
<th>( \psi )</th>
<th>BL</th>
<th>BLPO20%</th>
<th>BLPO30%</th>
<th>PO</th>
<th>LOW1</th>
<th>LOW2</th>
<th>LOW3</th>
<th>LOW4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.178</td>
<td>1.020</td>
<td>0.001</td>
<td>0.001</td>
<td>1.268</td>
<td>0.669</td>
<td>0.054</td>
<td>0.596</td>
</tr>
</tbody>
</table>

Table 15: adjusted pore parameter \( \psi \)
Figure 31: Modeled reaction rate
6- Conclusions

This project was appointed to give an answer to two basic questions;

The first question was whether or not catalytic activity was present during the char gasification of blends of pyrolysis oil and black liquor.

The project can return a moderately positive answer to it; Addition of pyrolysis oil into black liquor does not mar catalytic activity during char gasification. Catalytic activity does not decrease even when the quantity of catalyst is reduced as black liquor’s quantity of sodium is far higher than that of saturation threshold. Blending only turned to be unsuitable in terms of char reactivity when the sample witnessed lignin precipitation combined with low gasification temperatures. Experiments at laboratory scale indicated that black liquor mixed with pyrolysis oil up to a fraction of 20% approximately behave the same way than pure black liquor. Therefore, blends could be used with the current black liquor gasification technology. If pyrolysis oil fraction exceeds this value then lignin precipitates and it can lead to the dysfunction of the catalyst at some conditions (low temperatures). In this direction, work should continue to determine the decay of catalyst activity as a function of temperature. Furthermore, scanning electronic microscope (SEM) analysis should be conducted for partially reacted chars to verify if catalyst deactivation is a consequence of lignin precipitation.

Additionally, positive facts beyond the question have appeared such as pyrolysis oil addition to black liquor being associated to smaller quantities of unreacted carbon in the ashes. Furthermore adding pyrolysis oil into black liquor reduces the viscosity making it more suitable for transportation trough pumping.

The second target set on the objectives was to study whether char reactivity of liquefied organic waste (LOW) was comparable to that of black liquor.

The answer is clear, LOW chars show a much larger reactivity than BL char. In particular, LOW 1 has showed the best reactivity by reducing gasification time to one third that of BL. This is attributed to the stronger role of potassium as a catalyst.
Additionally LOW sample are less viscous than BL making LOW samples easier to work with.

Only to judge by gasification rate it seems clear LOW samples studied deserves further experimental research beyond small scale thermogravimetric analysis. Besides, research on other fields of LOW as energetic balance, reliability on their sources or economic feasibility should accompany gasification research.

Time limitations in the present work made only possible experiments under CO$_2$. It has allowed us to compare many different samples at easy conditions. However, other experiments at different temperatures and different concentrations of CO$_2$ could not be fully analysed. As prospective work for the forthcoming months these undisclosed experiments will be studied. Additionally, for a reduced number of chars steam will be used as an oxidation agent to have a wider understanding of the best gasification conditions.

On the other hand, a model for char reactivity has been proposed. It consists of two factors; a kinetic term and a function dependant on char surface. The values of the kinetic constants have been figured out for each char according to the experimental data. However, owing to time and equipment limitations, extensive research on kinetic models has remained out of the scope of the project. The second term, a char surface function, was found to be best described by the random pore model. Therefore, we provided the values of structural parameter of char pores, $\psi$, for each of the char samples.
7.-References


[2] Source: F.O. Licht

http://www.eia.gov/forecasts/steo/report/us_oil.cfm


### Appendix

$w_n$ and $n$ values for buterworth filter:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$n$</th>
<th>$w_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black liquor</td>
<td>3</td>
<td>0.02</td>
</tr>
<tr>
<td>BLPO20%</td>
<td>3</td>
<td>0.012</td>
</tr>
<tr>
<td>BLPO30%</td>
<td>3</td>
<td>0.018</td>
</tr>
<tr>
<td>Pyrolysis oil</td>
<td>3</td>
<td>0.007</td>
</tr>
<tr>
<td>LOW1</td>
<td>3</td>
<td>0.04</td>
</tr>
<tr>
<td>LOW2</td>
<td>3</td>
<td>0.034</td>
</tr>
<tr>
<td>LOW3</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>LOW4</td>
<td>2</td>
<td>0.03</td>
</tr>
<tr>
<td>940°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black liquor</td>
<td>3</td>
<td>0.025</td>
</tr>
<tr>
<td>BLPO20%</td>
<td>3</td>
<td>0.022</td>
</tr>
<tr>
<td>BLPO30%</td>
<td>3</td>
<td>0.021</td>
</tr>
<tr>
<td>Pyrolysis oil</td>
<td>5</td>
<td>0.012</td>
</tr>
<tr>
<td>LOW1</td>
<td>3</td>
<td>0.06</td>
</tr>
<tr>
<td>LOW2</td>
<td>3</td>
<td>0.034</td>
</tr>
<tr>
<td>LOW3</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>LOW4</td>
<td>2</td>
<td>0.03</td>
</tr>
</tbody>
</table>