

# Fuel testing procedure for pyrolysis and gasification of biomass using TGA and WoodRoll test plant (Bränsletestmetod för pyrolys och förgasning av biomassa med användande av TGA och WoodRolls testanläggning)

Marco Amovic, Pawel Donaj, Baldesca Moner, Ram Alzuheri, Rolf Ljunggren

"Catalyzing energygas development for sustainable solutions"



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Malmö, Sweden 2014

Martin Ragnar Chief Executive Officer



### Authors' foreword/Författarnas förord

This project has been managed and executed by Cortus AB. The project has been carried out in close cooperation with partners, The Dept. of Chemical Engineering and Technology at the Royal Institute of Technology (KTH) where the laboratory tests have been performed and Nordkalk, Köping, where the test plant is located. All the tests have been operated by Cortus personnel. The project started in February 2012 and was completed in November 2013.

The project had a reference group consisting of the following representatives:

Anna-Karin Jannasch Jörgen Held Klas Engvall Markus Fagervik Rolf Ljunggren Ram Alzuheri SGC (project coordinator) SGC KTH Nordkalk AB Cortus AB Cortus AB

### Summary

A characterization of six different biomass fuels (salix, sawdust, bark, vine cuttings, wood chips and a (30/70) mixture of fiber sludge and wood residuals) has been made during the project. The purpose has been to evaluate if laboratory results can be connected to a test pilot scale (500 kW syngas) in terms of reactivity of a biomass fuel.

Cortus has a patented gasification technology, WoodRoll®, where pyrolysis and gasification are separated into different steps. The gas formed during pyrolysis is supplying the gasifier with heat, while the remaining char is gasified in the gasifier with steam as oxidizing agent. Depending on the biomass fuel used, more or less volatiles will be released during the pyrolysis at a certain temperature. Pyrolysis and gasification tests have been performed at laboratory scale using Thermo Gravimetric Analysis (TGA) at The Dept. of Chemical Engineering and Technology, KTH, for a series of various biomass fuels in order to give an indication on its specific reactivity. A connection from TGA tests was performed on test plant to verify similar fuel behavior.

With respect to the heating rate and the operation temperature, the pyrolysis tests were run under the same conditions at the laboratory and at the test plant scale. The results showed a very similar behavior for each fuel type. A remaining mass of 30-50% was achieved when running the pyrolysis at 360-400 °C, where biomass with a high content of C<sub>fix</sub> was in the upper range. The energy content in the char is about 50-70 % and differs from the mass distribution as most of the carbon remains in the char after pyrolysis while the volatiles consist of a fuel of a lower calorific value.

The oxidizing agent for WoodRoll® gasification is steam. Steam gasification is an endothermic reaction and it has during the tests been shown that about 40% of the energy supplied to the gasifier is due to the endothermic reaction that is in the range of 98 - 114 kJ/molK depending on the final gas composition.

Gasification of char in the WoodRoll® gasifier is differently operated compared to TGA tests. In the test plant, there is significant more active surface area between the char and the steam. In addition, parameters, such as load and stoichiometry, need to be taken into account at the test plant gasifier, which is not considered during the TGA tests. The results could therefore only be compared from a fuel reactivity point of view. Gasification tests with three different fuels were carried out at the same conditions. The reactivity of the fuels showed the same pattern in the test plant, as indicated from the TGA results in terms of the carbon conversion.

The gas composition was found to be within the following range (dry gas analysis):  $H_2 = 54 - 60$  vol%, CO = 20 - 30 vol%,  $CO_2 = 10 - 18$  vol% and  $CH_4 = 1 - 3$  vol% for all the fuels. The results show that the stoichiometry, the load and the temperature of the gasifier, respectively, in fact has a larger impact on the result-ing gas composition than the type of biomass fuel used.



### Sammanfattning på svenska

Syftet med projektet har varit att kategorisera följande olika biobränslen utifrån deras reaktivitet: salix, sågspån, bark, vingårdsrester, träflis och en mix mellan fiberslam (30 vikt%) och grenar och toppar (GROT 70 vikt%). Målet har också varit att påvisa att laboratorietester, genom det välkända laboratorieverktyget Thermo Gravimetric Analysis (TGA) som används för att undersöka ett bränsles reaktivitet, kan kopplas till större skala.

Vid TGA mäts viktsförändringar hos ett prov som funktion av temperaturen/tiden under kontrollerade termiska förhållanden. För ett material med flera beståndsdelar, såsom ett biobränsle, kan dessa kvantifieras då de förångas eller bryts ner vid olika temperaturer. Cortus har utformat ett testprogram på TGAn för lågtemperaturpyrolys och förgasning med ånga. Cortus har en patenterad förgasningsteknologi, WoodRoll® där förgasningen delats upp i tre olika steg; torkning, pyrolys och förgasning. Teknologin har testats på laboratorienivå, där TGA använts, samt på två olika uppskalningsnivåer, 150 kW och 500 kW. Samma bränslen har testats med TGA och med 500 kW:s förgasaren och resultaten har jämförts för att undersöka om liknande beteenden kan observeras angående reaktivitet oberoende av att det är fler parametrar att ta hänsyn till i 500 kW:s förgasaren. Tidigare tester på laboratorienivå har genomförts med en äldre TGA. Försök har gjorts att transformera den gamla databanken av bränslen till den nyinstallerade TGA-utrustningen. TGA-försöken har utförts på Avdelningen för kemiteknik vid KTH i Stockholm i nära samarbete med doktorander och professorer på avdelningen. Efter att skillnaderna mellan de två TGA-utrustningarna analyserats konfigurerades ett lämpligt testprogram för den nya utrustningen, där testerna utfördes utifrån hur pyrolystesterna i pilotskala skulle utföras. En direkt jämförelse mellan det förgasningssimulerade steget vid TGA-analysen och pilotskalan är endast möjlig att göra utifrån bränslereaktivitetsperspektiv eftersom en direktöversättning till drift i pilotskaleförgasaren inte är möjlig.

WoodRoll® förgasningen arbetar vid en temperatur av 1100 °C där ånga används som oxiderande medium för att oxidera den s.k. charen (fasta fraktionen bestående av träkol), producerad i det tidigare pyrolyssteget. I pyrolyssteget separeras charen från gasfraktionen som består av gas, tjäror och en mindre del vattenånga (härifrån benämnt pyrolysgas). Pyrolysgasen används som bränsle främst i brännarna i förgasningssteget, men även i mindre utsträckning för torkning av biobränslet. Genom att ånga används som oxiderande medium vid förgasningen är förgasningsprocessen en endoterm process, d v s en process som kräver energi.

Testerna påvisar att ca 40 % av energin som tillförs förgasningsreaktorn åtgår för förgasningsprocessen p.g.a. den endoterma processen, som är i storleksordningen 98-114 kJ/mol K beroende på den producerade gasens sammansättning.

Pyrolysen sker inom temperaturintervallet 360 – 400 °C beroende på biomassans initiala fukthalt samt dess reaktivitet. Då förgasningsprocessen är indirekt uppvärmd förorenas den producerade gasen inte med komponenter, som exempelvis koldioxid, som normalt bildas vid förbränning. Vidare så är gasen i stort sett fri från kväve, vilket gör gasen väl lämpad för nedströms syntesprocesser efter erforderlig gasrening. I Figur 1 jämförs återstående massprocent av char efter pyrolyssteget från försöken i TGAn med försöken i pyrolysreaktorn i Köping (60 kW tillförd effekt).



Figur 1. Jämförelse återstående massa träkol vid pyrolys för TGA samt testanläggning.

Resultaten visar en stark koppling mellan testanläggningen och TGAn där 30 – 50 vikt % av det inkommande torra biobränslet kvarstår i charen. Resultatet för homogena bränslen som bark, träflis (eng. Wood Chips) och Salix ligger väldigt nära varandra. För heterogena material som vinrankor (eng. wine cuttings) och mix är skillnaderna något större. Detta beror med stor sannolikhet på att proverna i TGAförsöken inte är helt representativa eftersom provmängden är väldigt liten.

Pyrolysgasen består av en mängd olika komponenter, som det är i stort sett omöjligt att mäta eller bestämma ingående substanser av. Därför har sammansättningen av C, H och O i pyrolysgasen beräknats med hänsyn till sammansättningen på den ursprungliga biomassan och den utgående charen, samt massfördelningen mellan char och biomassa.

En jämförelse mellan förgasningssekvensen i TGA-försöken och försöken i testanläggningens förgasare (500 kW) med avseende på bränslereaktivitet vid förgasning har utförts. Resultaten visas i Figur 2.





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Figur 2. Jämförelse mellan bränslereaktivitet på TGA resp. utbränningsgrad på testförgasaren.

Resultatet visar på ett tydligt samband mellan bränslets reaktivitet från testerna i TGAn och utbränningsgraden (omvandlingsfaktor C) uppmätta vid försöken i 500kW förgasaren. De biobränslen som visar på lägsta reaktiviteten i TGAn har även uppvisat lägsta utbränningsgraden vid försöken i testanläggningen. Slutsatsen är att de jämförande pyrolys- och förgasningstesterna visar på att TGA-metodiken fungerar utmärkt som verktyg för att förutsäga förutsättningarna för pyrolys och förgasning av ett bränsle i större skala. All data har knutits till teorin bakom WoodRoll® teknologin, som tidigare utformats, avseende värme och massbalansen och stora delar av teorin har kunnat verifieras.

Gassammansättningen (torrgas) skilde sig väldigt lite åt mellan de olika bränslena och höll sig inom följande intervall:  $H_2 = 54 - 60$  %, CO = 20 - 30 %,  $CO_2 = 10 - 18$  % och  $CH_4 = 1 - 3$  %. Resultaten visade att stökiometrin, lasten samt drifttemperaturen vid förgasningen var av större vikt för den slutgiltiga gassammansättningen än det inkommande bränslets sammansättning.

Föroreningarna i den producerade gasen analyserades och resultaten visar på mycket låga koncentrationer/nivåer av svavelväte (H<sub>2</sub>S) och tjäror i gasen. Analysresultaten avseende N-komponenter, som ammoniak (NH<sub>3</sub>) och vätecyanid (HCN), visar på en viss förekomst i den producerade gasen. Dessa N-komponenter är troligtvis till viss del bildade från kväve-inertieringen av förgasningsreaktorn, som är en del av säkerhetskravet vid driften av densamma. Mätningar utförda nedströms ett kondenseringssteg visar på en sänkning av både HCN och NH<sub>3</sub> med 90-95%, vilket beror på inlösning i det kondenserade vattnet.

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#### 1. Background

Renewable energy sources for industrial needs are one of the cornerstones to meet the growing global demand for energy and simultaneously fulfill the requirements of replacing fossil raw materials in order to reduce the global carbon dioxide (CO<sub>2</sub>) emissions and hence, the global warming. In the future, the renewable raw material needs to come from different waste streams, as a growing proportion of the cultivated areas are occupied by different energy crops. Due to economic and political initiatives, aimed at reducing the climate change, the renewable energy segment will be the fastest growing market among all energy sources. Gasification of biomass has been identified by the United Nations (UN), International Energy Agency (IEA), etc. as one of the most important technologies in order to tackle this growth.

As a R&D company of renewable energy, Cortus AB provides innovative bio-energy solutions for power, transport and process industries, based on the patented gasification technology WoodRoll®. Since 2006, the company has developed, designed and constructed a process for gasification of biomass fuels. The WoodRoll® gasification process is divided into three main process steps; drying, pyrolysis and gasification. WoodRoll® intends to be a feedstock flexible technology where a variety of waste biomass streams are supposed to be used as fuels in the process. Cortus has a test plant with a capacity of 500 kW syngas on Nordkalks industrial area in Köping. To be noted that syngas is in this report referring to the produced raw gas from the gasifier even though it contains some pollutants, condensate etc. On the user side, Nordkalk is the leading producer of high quality limestone-based products in Northern Europe. Nordkalk is today to a large extent supplied by fossil fuels, such as coal, oil and natural gas. The development of cost effective and environmental friendly energy technology, such as for example the WoodRoll® technology, is of great interest for such an energy intensive industry.

The Dept. of Chemical Engineering and Technology at KTH is since many years an internationally leading group in thermochemical conversion of biomass fuels. Cortus has since 2007 been cooperating with KTH, considering further development of WoodRoll®. Among others, experimental work has been carried out at their laboratories. More than one hundred TGA tests (Thermo Gravimetric Analysis) with more than 25 different fuels have been performed by Cortus personnel since the start-up of the company. The TGA methodology is used for characterization of thermal and thermochemical properties of various carbonaceous fuels/biomass fuels. Generated data can then be used to predict the behavior of a fuel in for example a pyrolysis and a gasification process. This in turn allows for examples actors within the pyrolysis, gasification and combustion field to compare the properties of a new material with the present ones within a relatively short period of time.

This project has been a collaboration between Cortus, KTH and Nordkalk as laboratory tests have been performed at KTH, while the Cortus test plant is located on Nordkalk's site in Köping.

#### 1.1 Aim and purpose

The aim of this project has been to verify experimental results obtained with TGA of commercially available biomass fuels at laboratory scale with results obtained in



a 500kW test pilot gasification plant using the same fuel. The underlying objective has been to create recipes for utilization of different biomass fuels in the WoodRoll process. In addition, the project results provide crucial in-depth process knowledge and experience on the WoodRoll process, which facilitates the future up-scaling of the technology.

The following fuels were tested in the program:

- Salix
- Saw dust
- Mixture of fiber sludge and wood residues (30 mass% fiber sludge, 70 mass% wood residues, abbreviated in Swedish as GROT)
- Bark
- Wood chips
- Vine cuttings

The milestones of the project were:

- 1. To characterize the different biomass fuels in the TGA with respect to low temperature pyrolysis and gasification. The test program will primarily be adapted for WoodRoll®, but the outcome may also be translated to other pyrolysis and gasification processes for the fuels tested.
- 2. To operate, at identical conditions, the pyrolysis and gasification in Cortus test plant with each of the fuels and to compare with the results achieved with TGA.
- 3. To perform analysis of gases (pyrolysis gas, syngas and flue gas), liquids (condensate) and solids (biomass, char, ash) during the tests in the test plant to refine and further enhance the understanding of the mass and energy balance for WoodRoll®.
- 4. To develop a mass and energy balance model for the WoodRoll® process in Köping based on data obtained with the test plant.

For each biomass fuel tested, similarities and differences (physical and chemical) were analyzed and the effect of those on the WoodRoll® process. That would generate a further development of heat and mass balance for WoodRoll® connecting it to different biomass fuels. In addition, Cortus will use the results of this project for a better understanding of the design and the construction of future WoodRoll® facilities.

#### 2. Experimental

Cortus has previously performed tests, with a developed fuel testing model, in an old TGA. More than 25 different types of biomass fuels were tested. During the initial phase of this project, a new TGA equipment was introduced at KTH and the initial purpose was therefore to transform earlier TGA results to the new equipment before transforming the method to the test plant. The method is shown in Figure 3 below.



Figure 3. Testing model showing transformation of data from old TGA to new TGA connecting it to the pilot plant.

The conditions and the comparisons of the results obtained at the laboratory and at the test plant, respectively, are shown in Table 1 below.

	TGA		Tes	t plant
	Heating rate [K/min]	Holding tem- perature [min]	Heating rate [K/min]	Holding tem- perature [min]
Drying	No purpose, fuel pre-dried		15-20	15-20
Pyrolysis	15-20	15	15-20	20
<b>Gasification</b>	Non comparable conditions		Non comparat	ole conditions

Table 1. Test conditions at new TGA and test plant.

### 2.1 TGA (Thermo Gravimetric Analysis)

Cortus has since the start-up of the company carried out fuel characterization by TGA at The Dept. of Chemical Engineering and Technology at KTH. TGA involves analysis of weight as a function of temperature change and time and has in this project been used for the analysis of various types of biomass fuels. The results have been connected throughout the project to a heat and mass balance made by Cortus. During the fuel characterization; the drying, the pyrolysis - and the gasification process, respectively, have been performed in similar way (in terms of residence times, heating rates and temperatures), as assumed in a full scale plant, as illustrated in Table 1.



The TGA testing procedure consists of; pre-drying of the biomass, the TGA-process and combustion of the remaining material, illustrated in Figure 4.



Figure 4. TGA Testing procedure.

Each experiment from pre-drying (4 hours) to testing (3-5 hours) and finally ash analysis (4 hours) takes around 17 hours, including waiting time for cooling.

#### 2.1.1 Pre-testing

The biomass fuel was crushed to a particle size of 1-5 mm and thereafter weighted and placed inside the drying furnace at 110°C for 4 hours in order to remove all the moisture. The main purpose of the drying step was to determine the humidity of the biomass, having a representative sample of 200-220 mg (for TGA) of dry biomass.

#### 2.1.2 TGA, STA 449 F3 Jupiter

The thermo balance equipment used is a simultaneous TG-DTA/DSC apparatus from NETZSCH (STA 449 F3 Jupiter) coupled to a steam generator. Different furnaces can be used depending on the measurement requirements. For gasification, the steam furnace is needed. A photo of the TGA equipment is shown in Figure 5.





Figure 5. TGA, STA 449 F3 Jupiter.

There were some limitations with the equipment:

- Maximum weight of 250 mg/sample.
- Diffusion limitation at higher temperatures due to crucible design.
- Steam flow limitation.

#### 2.1.3 Post testing

The post testing was performed in a high temperature furnace and was in turn used to verify the volatile matter remaining downstream the gasification process. Biomass fuels were ranked depending on the amount of volatile matter remaining after gasification at 850°C. Low reactive biomass fuels will have a higher amount of remains of volatile matter. When operating gasification conditions at 1100°C in TGA, there were no traces of volatile matter left.

The furnace was heated to 1100°C and after this temperature had been reached, it was kept at this temperature to allow complete combustion.

In using the high temperature furnace it is not only the weight loss that is of interest from analysis point of view but also the ash formation. Depending on which fuel is analyzed, the ash composition may vary with respect to the grain size, the color and the composition, respectively.

#### 2.1.4 Experiment procedure

In order to increase the accuracy of the experiments, a blank test was carried out in order to correct the buoyancy effect of the sample weight signal prior to every single experiment<sup>1</sup>. The blank tests were carried out with an empty crucible under the same experimental conditions (heating rate, crucible, atmosphere, temperature program etc.) as the experiments including a biomass sample.

Three aspects were essentially studied for the fuel: *drying*, *pyrolysis* and *gasification* by means of TGA. The actual sequence of each feature was programmed manually before the test began. A temperature program with specified heating rates, inert atmosphere flows, steam ratios and residence times, respectively, was prepared before each test with Proteus, the software of STA 449 F3 Jupiter. Each fuel was tested at three different pyrolysis and two different gasification temperatures, respectively. This allowed the investigation of the char yield and the gasification rate as a function of the temperature. Table 2 shows the temperature program with the heating rates used for the gasification experiment run at 850°C.



		Temperature [°C]	Heating rate [°C/min]	Duration [min]
ള	Starting point	25		
ryir	Dynamic step 7	105	15	
	Isothermal step $ ightarrow$	105		30
	Dynamic step 7	360	15	17
.s	Isothermal step $ ightarrow$	360		10
olysi	Dynamic step 7	380	4	5
yro	Isothermal step $ ightarrow$	380		10
	Dynamic step 7	400	4	5
	Isothermal step $ ightarrow$	400		10
ation	Dynamic step 7	850	20	
asifica	Isothermal step $ ightarrow$	850		40
Ga	Emergency stop	1200		

#### Table 2. TGA-procedure from drying to gasification.

#### 2.1.4.1 Drying

Biomass contains two types of water; free water and bound water. Free water is stored in the pores due to capillary forces while bound water is built in the biomass structure by intra-molecular forces<sup>2</sup>. To ensure that all the free water has been removed from the mass, the first step is a drying step. The measurement is done according to Swedish standard, SS 187170, verifying a dry biomass before the temperature is increased.

#### 2.1.4.2 Pyrolysis

After the drying was completed, the temperature was raised to the first pyrolysis temperature. The heating rate was set to the constant value of 15°C/min. There was an isothermal step for each one of the three pyrolysis temperatures to ensure complete volatization of all the species expected to be volatized at these temperatures.

Depending on the type of biomass fuel, more or less volatile matter will be driven off from the dry biomass at every isothermal temperature. Less volatile matter indicates more char remaining and vice versa. Tests made by Cortus using the old TGA, showed less volatile matter being driven off, compared to the new TGA at the same temperatures. Based on that experience with previously obtained test results, the temperature range during pyrolysis was decreased to 360-380-400°C from 400-440-480°C as carried out in earlier tests. Figure 6 illustrates this scenario.



Figure 6. Relation between char yield/amount of pyrolysis gas and time/temperature.

#### 2.1.4.3 Gasification stage

After the pyrolysis was completed with stabilized values, the temperature was raised to the desired gasification temperature. When the desired temperature was reached, gasification with steam as oxidizing agent initiated. The time for the gasification process was set to about 15- 40 minutes depending on the operation temperature applied.

The gasification temperature was set to 1100°C as in the real process and 850°C as performed on the old TGA. Due to the instrument limitations of the old TGA, the experiments with the latter were performed at lower gasification temperatures than when using the new TGA equipment. To still enable an accurate (relevant) comparison between the data, the experimental results obtained at the lower gasification temperatures were thereafter correlated to 1100°C using the Arrhenius equation. Once gasification was finished, the TGA was turned off and the fuel was left to spontaneously cool down to room temperature.

#### 2.2 Test plant

The WoodRoll® pilot test plant, consisting of a dryer/pyrolysis reactor and a gasifier, is located in the city of Köping, Sweden. The drying and pyrolysis processes were carried out in the same reactor after that some small modifications, specific for each process, had been carried out. The capacity of the plant is about 200 kg/h of wet biomass for obtaining about 50 kg/h of charcoal and for producing 150-160 Nm<sup>3</sup>/h syngas corresponding to about 500 kW of thermal power.

The test plant in Köping is operated as a 3-shift continuous process (5 days a week; Mon-Fri), handling several 100 kg of biomass material per hour with a need of complying to:

- Health, Safety and Environmental Risk Assessments
- ATEX studies
- Permissions for handling of chemicals and flammables
- Emergency plan
- Environmental permit



- Logistic plan for handling of the different biomasses/chars
- Work environment act
- Operational instructions and training
- Maintenance documents

The start-up of the plant takes over a week as the plant is operated time to time, in discontinuous operation. All the commissioning, including signal testing, simulation of failures, alarm boundaries, needs to be carried out prior to every start-up of the plant. For each fuel, the test procedure includes the steps shown in Figure 7 below.





#### 2.2.1 Biomass pretreatment

The requirement of biomass fuel to the process is a biomass free from impurities such as stones and metals with a particle size below 30 mm. One more specification from supplier of the dryer was a material with less than 60 % humidity as it else could be hard to reach humidity below 5 % in the output dried biomass (without rerunning the material). In this project, the following biomass pretreatment has been performed:

- Mixing of fuel (fiber sludge, wood residual) was performed by an external company in Köping.
- Separation of biomass and inerts (stones and metals) from vine cuttings was done by Cortus personnel in Sundsvall in order to test a separation process based on the density separation method<sup>3</sup>.
- Size reduction of biomass (vine cuttings, bark, salix and wood chips) was crushed at the external site to a maximum size of 30 mm.

#### 2.2.2 Drying

Drying of biomass is the first stage of the process. Depending on the biomass type and shape, drying was performed at different temperatures with the target to dry the material down to about 5 % humidity. Humidity samples of the output dry biomass were continuously taken in order to supervise the process.

The dryer is indirectly heated in a rotary drum with heat exchanging tubes. The heating medium used in the dryer is hot flue gases which are generated from propane combustion in a separate combustion chamber. Humidity, which is derived from the biomass, is led away with preheated vent air. The humid vent air out from

the dryer (containing some particles) is combusted in a flare. Dried biomass is stored in containers equipped with dehumidifiers before being pyrolyzed. The dryer/pyrolysis reactor is shown in Figure 8.



Figure 8. The dryer/pyrolysis reactor.

#### 2.2.3 Pyrolysis

The pyrolysis is performed in the same indirectly heated rotating drum. Adjustments such as removal of vent air, airlocks in the input and output feed, several control/safety and operational issues are performed before being able to switch to pyrolysis process.

Dry biomass was gradually heated for 20 minutes to pyrolysis temperature and kept for another 20 minutes. Temperatures during the pyrolysis were constantly held at around 360 – 400 °C, showing about 35 % of the mass in the char material. The reactor is air-tight and runs at a slight overpressure in order to ensure an inert atmosphere free of oxidizers. Airlocks for input biofuel and output char are a part of the system.

Produced pyrolysis gas is kept at high temperature as it contains a lot of tars aside of the gas fraction. Combustion of pyrolysis gas is also made in a torch located next to the reactor. Also, a set up was built on site together with KTH for high temperature filtering and pyrolysis tar cracking. Pyrolysis gas was cracked through a catalytic reactor reducing the tar content as well as cracking higher hydrocarbons to lower. This increases the hydrogen and methane content in the gas, making it easier to handle.

Output char is grinded on another site in order to make it to a very fine powder that is required for gasification.

The test facility is equipped with Siemens S7 control system and the plant is operated from a central control room. All the data is logged for later evaluation. In Figure 9 the HMI for drying and pyrolysis can be seen.





Figure 9. HMI of the drying/pyrolysis process.

#### 2.2.4 Grinding

The char requires a size of about 100 µm before being gasified. By grinding the char more reactive area is achieved lowering the necessary residence time inside the gasifier for reaction. There was no grinder on site and as there is risk for dust explosion during grinding of the charcoal, the material was sent to Höganäs AB (together with personnel from Cortus) and their demonstrational lab, which in turn performed the grinding. The grinding setup used is shown in Figure 10 below.



Figure 10. Grinding setup.

The grinding was performed in a BAC200 grinder (normally used for grinding of metal powder) where the output material was control sieved to assure proper output size.



#### 2.2.5 Gasification and gas cleaning

The gasifier is designed for entrained gasification of char powder and steam and is illustrated in Figure 11. An intermediate storage of grinded char is located on the top of the gasifier from which the dosing of char is made to comply with optimal load and stoichiometry from the conversion point of view. The heat is supplied by radiant heat burners where propane is combusted. Char and steam are injected to the gasifier that is operating at ambient pressure and a temperature of 1100°C. Furthermore, superheated steam is mixed with char through an injector in to the gasifier for optimum reaction conditions.

The syngas is indirectly cooled to about 400°C before the ash is separated in a cyclone while the gas is analyzed before being combusted in the flare.



Figure 11. Gasifier 500 kW.

#### 2.2.6 Analysis

Parameters analyzed during the process are shown in table 3 below.

	Solid	Liquid	Gas
Drying	Elementary analysis bio-	-	-
	mass, D-lab and Belab		
	Humidity by moisture bal-		
	<u>ance, on site</u>		
	Ash determination		
	<u>SS187187, on site</u>		
Pyroly-	Elementary analysis char,	Gravimetrical and	<u>GC, on site</u>
sis	D-lab and Belab	calculated method	
	Ash determination		Flue gas anal-
	<u>SS187187, on site</u>		<u>ysis, on site</u>
Gasifi-	Elementary analysis ash, D-	SPA, lab KTH	<u>GC, on site</u>
cation	lab and Belab		
	Ash determination	Condensate from	Pollutants, lab
	<u>SS187187, on site</u>	syngas, AK lab	SP
			Flue gas anal-
			<u>ysis, on site</u>

Table 3. Analysed components shown.

#### 2.2.6.1 Analysis of solid

Three solid streams were treated throughout the process; raw biomass, char and ash. An elementary and an ultimate analysis was made of each biomass, char produced from it and its related ash obtained in the gasification process. The elementary analysis was performed by the laboratories D-lab<sup>4</sup> and Belab<sup>5</sup>, two laboratories that are focusing on chemical analysis of solid fuels.

#### 2.2.6.1.1 Humidity

Humidity analysis was continuously made of the input and output biomass to the dryer. The output humidity was controlled to be about 5% and a moisture balance giving the response within 10 minutes was used for the purpose.

#### 2.2.6.1.2 Char

To determine the remaining amount of unburned, fixed carbon in the output pyrolyzed material, standard SS187187 (solid fuels – determination of the amount of unburned material in solid residues from combustion) was used. The same test was performed with the input raw material in order to verify mass% remaining in the char compared to the biomass. The standard has been applied for several samples throughout the pyrolysis run and compared with measured mass of the input and output material, respectively.



Furthermore, char samples were analyzed at a laboratory for elementary analysis and subsequently balance of the species before and after thermal treatment had been made in order to complete mass balance of the system.

#### 2.2.6.1.3 Ash

In this project, the elementary analysis of ash has been carried out. Depending on the ash composition, there is a risk for slagging, sintering or corrosion at the gasification temperature which can in a long term cause problems to refractory etc.

#### 2.2.6.2 Analysis of liquids

Tars and condensate are considered as liquids.

#### 2.2.6.2.1 Tar analysis

Due to the complexity of composition and diversity in physical properties some difficulties in analysis of tars originating from cellulosic materials are generally encountered and need to be considered. Analyses of tars have been made from gasification with Solid Phase Absorption (SPA), i.e. a method for determination of light tars (molecular weight from 78 (benzene) to 300 (coronene))<sup>6</sup>. The light tar compounds correspond to the total tar amount when heat treatment is performed at temperatures above 850-900°C<sup>7</sup> which is the case for syngas that is produced at 1100°C. The pyrolysis gas (produced at 400°C), however, contains a lot of heavy tars and SPA cannot be applied.

The sample was sucked through the syringe (100 mL) over 1 minute from the tar sampling port, while the raw gas is passing through the gas cleaning line. The samples were stored in a dry-ice thermos and subsequently sent to the tars laboratory of The Dept. of Chemical Engineering and Technology at KTH. To be noted that the determination of the exact chemical composition of tars formed during pyrolysis is nearly impossible. However, for the purpose of this work, the most applicable parameters of tar to be determined were the mass fraction in the unit volume of gas, energy density and C-H-O analysis. Tars and water from pyrolysis were collected into the gas washing bottles and weighted periodically (gravimetrical method).

#### 2.2.6.2.2 Condensate analysis

The amount of steam in the raw syngas is estimated based on measurement of the weight of condensate increment over the certain time of sampling during gasification. For a complete analysis of the condensate composition, pH etc. the condensate is sent to AK-lab (i.e. a laboratory for water analysis performing chemical and microbiological analysis).

#### 2.2.6.3 Gas analysis

Different methods are applied for measurement of gases that are formed in different parts of WoodRoll® process. Continuous measurement with a gas chromatograph is performed of combustible gases formed during pyrolysis and gasification. Pollutants in combustible gas are sent and analyzed in different laboratories. Exhaust gases are measured in situ on site with equipment based on electrochemical and non-dispersive infrared (NDIR) sensors.

#### 2.2.6.3.1 Exhaust gas

Flue gas during combustion of propane (heat-exchanged with the pyrolysis reactor and the gasifier) and syngas from the flare was analyzed to adjust the burners to a proper value. Combustion of syngas and pyrolysis gas were run in an over-stoichiometric environment as the importance was to fully combust the outgoing gas rather than optimizing the combustion. The analysis was made with the instruments ABB EL 3000 and Madur (GA-40T<sup>plus</sup>) measuring O<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub> and CO, respectively.

#### 2.2.6.3.2 Combustible gas

The combustible gases formed at the pyrolysis and the gasification were measured continuously on site by a gas chromatograph (GC). The GC system used is equipped with two separation columns and is capable of measuring the gases listed in Table 4.

Column A	Column B
H <sub>2</sub>	Air (N <sub>2</sub> , O <sub>2</sub> , Ar)
N2	CH <sub>4</sub>
O <sub>2</sub>	CO <sub>2</sub>
СО	C <sub>2</sub> H <sub>4</sub>
CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
	C <sub>2</sub> H <sub>2</sub>

Table 4. Analyzed gases by GC.

A micro gas chromatograph (GC) Varian CP-4900 coupled with a TCD was used for analysis of transparent gases. It measures gas concentrations in vol%. The GC was used only during steady-state operation. Gas must be pretreated before being analyzed. The pretreatment involves capture of particles, tars, humidity (steam), ammonia (NH<sub>3</sub>) and sulfur hydride (H<sub>2</sub>S). Volume gas flow rate to the GC is in this case about 2.5 l/min.

Figure 12 shows the schematic gas sampling/tar removal system. The system consisted of a series of gas washing bottles filled with water or iso-propanol moreless to the 50 % of their volume, a pump system with inbuilt filter, a refrigerator and a GC. Tar removal and iso-propanol was only needed in the pyrolysis gas conditioning but the same set-up can be used for syngas conditioning.





Figure 12. Gas sampling/tar removal system.

#### 2.2.6.3.3 Gas pollutants

Pollutants in the syngas, such as  $NH_3$ ,  $H_2S$  and HCN were sent in bags to the Technical Institute of Sweden, SP, in Borås. The samples were taken both from the raw gas stream (at about 400°C) and after the filter, illustrated in Figure 12 above, in order to verify the difference.

#### 2.2.6.3.4 Tar analysis

Tar in the raw gas is measured by SPA method.

#### 3. Results and discussion

The result section has been divided into three different parts. The first part describes the TGA results achieved. The second part describes the tests made on the test plant. A connection between these results, connecting the results to energy and mass balance (theory) for the WoodRoll® process is finally presented in the third and last part.

#### 3.1 TGA

In order to validate previous TGA data and compare the difference, obtained with old equipment, the same test parameters were used with the new system. Vine cuttings were used as a reference fuel for calibration of the old TGA to the new TGA. The difference and settings are shown in Table 5 below.

	Old TGA	New TGA		
	Fuel difference	·		
Size	< 50 mm	< 5 mm		
Amount	10 gram	220 mg		
	System difference			
Volume furnace	500 ml 74 ml			
N <sub>2</sub>	Adjusted to volume	Adjusted to volume		
Steam	Adjusted to volume Adjusted to volume			
Heating rate	Heating rate No difference between instruments			
Residence time	idence time No difference between instruments			
Gasification tempera-	pera- < 850°C < 1100°C			
ture				

Table 5.	Fuel a	and s	vstem	difference	between	old a	and new	TGA.
rabic 0.	i uci e	unu o	yolom		Detween	ora c		ron.

#### 3.1.1 Drying

The drying was measured mainly to determine the humidity of the input fuel and not aimed at investigating the process in detail.

#### 3.1.2 Pyrolysis

In the old TGA, the pyrolysis was operated using the temperature profile 400 - 440 - 480°C. Tests in the new TGA displayed a lower mass-% of carbon residues at same temperatures as for the old TGA. Therefore a different temperature profile with the pyrolysis temperatures 360 - 380 - 400°C were selected. Mass-% was defined according to equation 1 below.

```
mass\% = (mass, dry char)/(mass, dry biomass) (1)
```

Figure 13 shows the mass-% remaining at temperatures  $360 - 400^{\circ}$ C of input biomass for the different fuels.





Figure 13. Mass loss during pyrolysis 360 - 400 °C.

As seen in Figure 13, the bark and the mixture of 30 % fiber sludge, 70 % wood residues results in higher remains of char after the pyrolysis compared to other fuels tested. Bark and wood residues (main part of the mix) have more fixed carbon  $(C_{fix})^8$  than the other fuels tested, which is the main reason for a higher mass content after pyrolysis.

#### 3.1.3 Gasification

In case of the old TGA, the sample was gasified at three different temperatures (750-800-850°C). By using the Arrhenius equation, the pre-exponential factor and the energy activation, it was thereafter possible to extrapolate and predict the gasification rate at 1100°C.

For the new TGA, it is possible to perform gasification at 1100°C. Therefore, a comparison was made between gasification experiments at 1100°C and prediction obtained by the Arrhenius equation. The Arrhenius prediction showed a higher gasification rate than the experimentally obtained value which is shown in figure 14.



Figure 14. Gasification rate at 1100°C predicted with Arrhenius and experimentally tested.

The difference shown in figure 14 is most likely due to diffusion limitations between the steam and the char in the gasification experiments at 1100°C. To validate this, several tests were performed with an increased content of steam to the upper limit (maximum steam rate) possible for the TGA setup. The results display an increased gasification rate at higher steam content but still lower than the predicted. This indicates that the diffusion limitations still are present also at the upper limit of steam addition.

Results from gasification tests in the TGA at 850°C and 1100°C, respectively, are plotted in Figures 15 and 16 below.





Figure 15. Steam gasification at 850°C.



Figure 16. Steam gasification at 1100°C.

The results in Figures 15 and 16 show that it is more difficult to distinguish the reactivity of the fuel at 1100°C compared to at 850°C. The gasification rate is so high at 1100°C that other parameters, such as diffusivity, particle size and ash amount become of significant importance. Conclusively, comparison at 1100°C is of less

importance. At the lower gasification temperature, the reactivity of the fuel is more clearly illustrated, as shown in the Figure 15. The results obtained with bark and the mixture of 30 % fiber sludge, 70 % wood residues display the lowest reactivity during gasification, most probably due to the high amount of fixed carbon. Bark has also a more dense structure than wood which also has a negative impact on the reactivity.

#### 3.2 Test plant

For the lab scale, there was no need to characterize the biomass as very small amounts were handled. In case of a test in the pilot plant, parameters such as density, humidity, size, fines etc. are of importance for the operation as well as the outcome of the test.

#### 3.2.1 Biomass characterization

The characteristics of the biomass tested are shown in Table 6 below.

	Moisture content [%]	Ash [%] DS	Bulk density [kg/m3]	LHV [MJ/kg]
Bark	29	3.54	279	12.6
Saw dust	60	0.22	375	4.2
Mix	40	6.02	350	9.8
Vine cuttings	11	8.5	350	14.7
Wood Chips	50	0.4	219	8.1
Salix	20	1.9	246	13.6

Table 6. Properties of tested material (biomass as received).

#### 3.2.2 Drying

The fuels tested have a very wide range of humidity as shown in Table 7. Therefore, the temperature inside the dryer was adjusted between 100 - 130 °C at the outlet, depending on the biomass fuel processed. Continuous measurement of the output humidity was performed by operators to secure a humidity of around 5 % in the output biomass. Table 7 shows the output humidity for each fuel.

Table 7.	Output	humidity fr	om dryer.
----------	--------	-------------	-----------

	Output Humidity [%]
Bark	4.5
Saw dust	6
Mix	3.17
Vine cuttings	5.8
Wood Chips	2.5
Salix	3.5

After identifying the calibration curve for the feeding rate and the drying temperature for each fuel, no further problems were experienced in the drying process.



#### 3.2.3 Pyrolysis

The pyrolysis was carried out at a temperature interval of 360 – 380°C, except for when bark was used as the fuel when instead a very low temperature of only 335°C was used. From the elementary analysis of biomass and char, all important species for the energy and mass balance (C, H, and O) were excluded from the rest and equation 2 was created. The water in equation 2 is from the dried biomass fuel that still contains about 5 % of water. As it is impossible to measure all components present in the pyrolysis gas, the mass balance equation as shown in equation 2 was applied:

$$\left( \dot{m}_{(C,H,O)} + \dot{m}_{(rest\ product)} + \dot{m}_{(H_2O)} \right)_{raw} - \left( \dot{m}_{(C,H,O)} + \dot{m}_{(rest\ product)} \right)_{char} = (\dot{m}_{(C,H,O)} + \dot{m}_{(H_2O)})_{pg}$$
(2)

The assumption was simplified as all the water is following with the gas meanwhile all the other elements (rest product) in the biomass are assumed to follow with the char. Rest product consists mainly of ash but also S and N are included. That is not the case in reality but as it mainly is C, H and O that are of interest for energy balance this assumption can be motivated and hence, made.

The C, H, O distribution (in molar ratios based on one mole of carbon) and lower heating value over the pyrolysis reactor is shown in Table 8 below.

	Raw biomass (ash free, incl. moist af-	
Fuel	ter dryer)	LHV MJ/kg
Saw dust	$CH_{2.02}O_{0.86}H_2O_{0.12}$	16.7
Vine cuttings	CH <sub>1.62</sub> O <sub>0.67</sub> H <sub>2</sub> O <sub>0.09</sub>	16.3
Salix	CH <sub>1.54</sub> O <sub>0.68</sub> H <sub>2</sub> O <sub>0.05</sub>	17.1
Wood chips	$CH_{1.50}O_{0.66}H_2O_{0.06}$	16.9
Bark	CH <sub>1.35</sub> O <sub>0.58</sub> H <sub>2</sub> O <sub>0.04</sub>	16.9
Mix	CH <sub>1.48</sub> O <sub>0.62</sub> H <sub>2</sub> O <sub>0.04</sub>	16.5
	Char	
Saw dust (360 °C)	CH <sub>0.64</sub> O <sub>0.11</sub>	24.0
Vine cuttings (380 °C)	CH <sub>0.62</sub> O <sub>0.15</sub>	28.3
Salix (380 °C)	CH <sub>0.79</sub> O <sub>0.15</sub>	27.8
Wood chips (380 °C)	CH <sub>0.69</sub> O <sub>0.16</sub>	28.3
Bark (335 °C)	CH <sub>0.62</sub> O <sub>0.19</sub>	24.6
Mix (370 °C)	CH <sub>0.83</sub> O <sub>0.21</sub>	24.6
	Pyrolysis gas (gas, tar and water)	
Saw dust	CH <sub>4.70</sub> O <sub>2.30</sub> H <sub>2</sub> O <sub>0.34</sub>	10.0
Vine cuttings	$CH_{3.10}O_{1.40}H_2O_{0.23}$	11.8
Salix	$CH_{2.30}O_{1.20}H_2O_{0.10}$	12.6

Table 8. C, H, O distribution divided in to biomass, char and pyrolysis gas.

Wood chips	CH <sub>2.44</sub> O <sub>1.23</sub> H <sub>2</sub> O <sub>0.12</sub>	10.9	
Bark	$CH_{3.67}O_{1.82}H_2O_{0.23}$	8.2	
Mix	CH <sub>2.15</sub> O <sub>1.05</sub> H <sub>2</sub> O <sub>0.11</sub>	12.1	

The energy and mass distribution for the fuels is shown in Figure 17 below.



Figure 17. Mass and energy distribution of the tested fuels.

Figure 17 shows that 30 - 50 mass% of the incoming dry biomass remains in the char. The concentration of carbon is higher in the char than in the incoming biomass fuel and because of that 50 - 75% of the energy is still remaining in solid phase.

#### 3.2.4 Gasification

All the six chars produced were grinded in Höganäs without any major problems and stored in a container. During the storage time, a fire started in the container as bark self-ignited destroying all the bark and wood chips. Efforts were made to save some of the material but without any success. As a consequence, gasification could only be performed with four, instead of six, fuels in this project.



#### 3.2.4.1 Load

The gasifier is operated with four burners with a total power output of about 200 kW. The heat distribution in the gasifier during the tests at 1100°C is shown in Figure 18.



Figure 18. Energy distribution in the gasifier.

A large part of the energy is needed for the steam gasification process, an overall endothermic process, as steam is used as the only oxidizing agent.

Table 9 shows the standard heat of formation for the selected species.

Table 9. Enthalpy of formation
--------------------------------

Enthalpy of formation for differ- ent molecules					
C (s)	0	kJ/mol			
H <sub>2</sub> O (g)	-241.82	kJ/mol			
H <sub>2</sub>	0	kJ/mol			
CO	-110.53	kJ/mol			
CO <sub>2</sub>	-393.5	kJ/mol			
02	0	kJ/mol			
CH4(g)	-74.81	kJ/mol			

During steam gasification, several endothermic and some exothermic reactions occur. The most influential and important reaction is the heterogeneous charsteam reaction (3). The final energy that is needed to be supplied to the system depends on the stoichiometry and other reaction conditions such as load and temperature. Endothermic reactions:

C + H2O → H2 + CO, ∆Hr= 131.3 kJ/mol	(3)
·	• • •

$$C + CO_2 = 2CO, \Delta H_r = 172.44 \text{ kJ/mol}$$
 (4)

Exothermic reactions:

 $CO + H_2O = CO_2 + H_2, \ \Delta H_r = -41.15 \text{ kJ/mol}$ (5)

 $CO + 3H_2 = CH_4 + H_2O, \ \Delta H_r = -206.1 \text{ kJ/mol}$ (6)

$$C + 2H_2 = CH_4, \Delta H_r = -74.81 \text{ kJ/mol}$$
 (7)

Assuming that the gas is composed of aH<sub>2</sub>, bCO, cCH<sub>4</sub>, dCO<sub>2</sub>, where a, b, c and d are the molar fraction of the gas components, it is possible to calculate the standard heat of formation of the gas mixture using Hess' law. Therefore, by balancing the equation (8) below it is possible to calculate the enthalpy of reaction (from a given gas mixture composition).

$$CH_{x}O_{y} + nH_{2}O + \Delta H_{f} \rightarrow aH_{2} + bCO + cCH_{4} + dCO_{2} + eH_{2}O$$
(8)

As seen in Figure 18, about 40% of the energy supplied to the gasifier is required for the heat of reaction. The total  $\Delta H_f$  is illustrated in Figure 19 below where the chemical energy of the input char is increased over the gasifier as heat is supplied giving an increased chemical energy in the syngas.



Figure 19. Endothermic reaction with steam gasification.

Depending on the syngas composition, the reaction is more or less endothermic with a theoretical maximum (for a given stoichiometry and temperature) consisting of only CO and H<sub>2</sub> (reaction 3). The heterogeneous reaction 5 is the other dominating reaction and for every CO<sub>2</sub> formed heat is released.  $\Delta$ H<sub>f</sub> over the gasifier is in the range 98 – 114 kJ/mol K depending on the syngas composition.



#### 3.2.4.2 Gas composition

The syngas composition was continuously analyzed during the tests. The composition depends on the stoichiometry, the load and the temperature in the gasifier. By varying those parameters the equilibrium will change as shown in equation 8. The gas composition for the four different fuels is shown in Figure 20 below.



Figure 20. Gas composition of the four fuels tested.

Figure 20 shows an average gas composition for each fuel. The error bars indicated display the variations of the gas as a function of stoichiometry, load and temperature. The main variation observed in the gas for each fuel is the ratio between CO and CO<sub>2</sub>. By operating the process with over-stoichiometry, more CO<sub>2</sub> (also some more H<sub>2</sub>) will be produced, while CO but also CH<sub>4</sub> will decrease. The measurement was made on dry gas and the water content varied between 2-25 mol % in the output gas. The lower heating value of the gas is 8.5-10.8 MJ/Nm<sup>3</sup>.



Figure 21. Combustion of syngas from gasification tests at the test plant.

#### 3.2.4.3 Gas pollutants

The quality of the gas was measured at KTH (tars) and by the Technical Research Institute of Sweden, SP, (N-components +  $H_2S$ ). The pollutants present in the raw gas and cleaned gas are shown in Table 10 and 11, respectively.

Pollutant	Mix [ppm]	Vine cuttings	Sawdust [ppm]		
H <sub>2</sub> S	< 1	< 1	< 1		
NH <sub>3</sub>	560 ± 20	180 ± 10	120 ± 5		
HCN	> 30	15 ± 2	5 ± 2		
Tars					
Benzene	14 - 114 µg	103 µg	44 - 55 µg		
m/p-Xylene	0	0	0 - 5.8 µg		
Indan	0	0	0 - 2.7 µg		
Indene	0	0	0 - 4.7 µg		
1-Methylnaphthalene	0 - 1.9 µg	1.9 µg	1.7 - 2.4 µg		

Table 10. Pollutants in the raw gas shown.

The ammonia and HCN contents in the gas are related to the inerting by N<sub>2</sub> of the gasifier. This was verified by increasing the N<sub>2</sub>-flow during the test, using the mixture of 30 % fiber sludge, 70 % wood residues as a fuel, which directly resulted in a higher content of ammonia and HCN in the gas. Due to safety handling documents, it was not possible to turn off the nitrogen flow to try to determine the amount of NH<sub>3</sub> and HCN coming from nitrogen bonded in the fuel. Additionally, a test for one of the fuel for N and S- compound in the washing water (part of the gas cleaning system) has been made in order to estimate the concentration of NH<sub>3</sub>, HCN and H<sub>2</sub>S in the condensate.

Table 11. Pollutants in gas after condense	r.
--	----

	Pollutant [ppm]			
H₂S	< 1			
NH <sub>3</sub>	10			
HCN	< 10			

 $NH_3$  and HCN are very soluble in water and the main reason of the large decrease of those pollutants in the cleaned gas after the condenser is due to dissolving in the water in the water-washing bottles. Temperature after the condenser was around 25 °C and a further decrease would possibly result in even lower concentration of  $NH_3$  and HCN in the gas.

The small amounts of light tars (mainly benzene) in raw gas at higher temperatures shall not be present in the gas after condensation (boiling point for all the tars present in hot gas is over 80 °C).



#### 3.2.4.4 Condensate

The condensate from gas condensation during the test with saw dust was sent for analysis as it is of interest for future design of a possible water cleaning system. Results from chemical analyses are shown in Table 12 below.

Element	mg/(kg condensate)				
Cl	124.8				
Total N	1080.0				
NH <sub>4</sub> H	1140.0				
Р	3.9				
рН	8.1				
Total suspended solids	396.0				
TOC (org C)	294.0				
Non-volatile org C	174.0				
HCN	15.0				
Са	79.2				
Fe	10.1				
К	28.1				
Mg	37.6				
Na	187.8				
AL	3.4				
As (arsenik)	0.0233				
Ва	0.2622				
Cd	0.0010				
Со	0.0037				
Cr	0.0084				
Си	1.2780				
Hg	0.0002				
Mn	0.3990				
Ni	0.0726				
Pb	0.0238				
Si	12.96				
Ti	0.0540				
Zn	0.8460				

Table 12. Pollutants present in the condensate.

#### 3.3 Correlation TGA/Test plant

The results from test using the TGA and the test plant is compared and correlated in terms of energy and mass balance. This is carried out in order to verify the TGA as a methodology for the prediction of fuel properties in relation to the use of the fuel at realistic conditions at larger scale.

#### 3.3.1 Pyrolysis

The results from tests, investigating the pyrolysis of the fuels, using TGA and the test plant pyrolysis reactor are shown in Figure 22.



Figure 22. Comparison between mass% remaining after pyrolysis in the test plant and at the new TGA.

The results are very similar comparing obtained residual char content of the TGA and the test plant. The largest difference is between the mixture of 30% fiber sludge, 70% wood residues and the vine cuttings. Those two fuels are the most heterogeneous and non-representative samples were probably used in the TGA-tests due to the small sample size.

#### 3.3.2 Gasification

The gasification was performed at totally different conditions in the TGA compared to the test plant gasifier. Factors as load and stoichiometry are of major importance in the test plant while they are not considered in the TGA where only the reactivity of the fuel is valid.

Salix, vine cuttings and the mixture of 30% fiber sludge, 70% wood residues were tested at the same conditions in the test plant, see Table 13.



	Temp [°C]	Steam [kg/h]	Fuel [kg/h]	H2 [%]	CO [%]	CO₂ [%]	CH₄ [%]
Salix	1100	56	35	56.3	30.0	11.4	2.3
Mix	1100	53	26.4	55.9	28.4	12.2	3.6
Vine cuttings	1100	53.8	30	57.0	27.6	12.4	3.0

Table 13.	Gasification	test at same	conditions i	for salix,	mix and	vine cuttings.
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Referring to the results obtained with the TGA, salix and vine cuttings were the two most reactive fuels, while the mixture of 30% fiber sludge, 70% wood residues was the fuel with the lowest reactivity. A comparison of the carbon conversion in the test plant with the reactivity measured with the TGA is shown in Figure 23.



Figure 23. Gasification reactivity comparison between test plant and TGA at 850°C.

Vine cuttings and salix have carbon conversions in the range of 96-98% while in case of 30% fiber sludge and 70% wood residues only about 85% is observed. A similar observation is found for the same fuels in the TGA gasification tests at 850°C. The obtained gasification rate for salix and vine cuttings is 1.05-1.1% of "mass loss"/minute. In case of the mixture of 30% fiber sludge, 70% wood residues and a gasification rate of 0.89% is obtained.

Conclusively, the reactivity of the fuel from TGA scale at gasification temperature of 850°C can be used to predict the behavior of gasification in a pilot plant scale at 1100°C.

#### 3.3.3 WoodRoll heat and mass balance

A general energy and mass balance over the pyrolysis reactor and the gasifier has been carried out for the test plant. It can be connected to each fuel tested where

mainly the temperature in the pyrolysis reactor has to be changed depending on the fuel that will be used to achieve sufficient amount of pyrolysis gas. Fuels with low reactivity may cause a slightly decreased efficiency in the gasifier but this can be avoided to a high extent by varying the stoichiometry and the load. The energy and mass balance is illustrated by two Sankey diagrams in Figure 24.







Figure 24. Mass and energy balance test plant WoodRoll®.

The mass and energy balance is illustrated from the pyrolysis reactor where decomposition of biomass, into char and pyrolysis gas, takes place. In the gasifier, steam is added as oxidizing agent while pyrolysis gas is heating the gasifier.

#### 4. Conclusions

Six different biomass fuels have been characterized by thermo-gravimetry analysis (TGA) in order to provide with information regarding reactivity during low temperature pyrolysis and gasification. The results from TGA have been validated with the results obtained from tests in a 500 kW plant in order to check their utility for practical applications.

The pyrolysis results obtained with TGA, showed a very close correlation with results acquired from tests performed in the test plant for the homogenous fuels (salix, woodchips, bark), whereas small differences were observed in case of the heterogeneous fuels (mixture of 30% fiber sludge, 70% wood residues and vine cuttings).

TGA gasification tests with steam at 850°C presented a better insight regarding char reactivity compared to 1100°C. Therefore results from 850°C could be translated to conversion rates of fuels obtained from the pilot tests. The reason for this is the fact that at 850°C the gasification reaction rate is relatively slow and is mainly limited by the kinetics of the gasification reaction, whereas at higher temperatures thermal and mass diffusion becomes the limiting factors of the overall reaction rate.

Conclusively, the reactivity of the fuel from TGA scale at gasification temperature of 850°C can be used to predict the behavior of gasification in a pilot plant scale at 1100°C.

In the WoodRoll process, char is used as a fuel for gasification while combustible pyrolysis gases (volatiles) are used as a source for thermal energy for the entire process. For that purpose, testing different fuels with TGA is a highly beneficial and cost-effective tool for the prediction of mass and energy balance of the gasification plant.

Char gasification with steam produces a syngas nearly free of tars and nitrogen compounds with high H<sub>2</sub> content. The syngas composition and heating value are insensitive to the fuel type. However, the char reactivity and reaction conditions have an effect on the conversion rate inside the gasifier.



#### 5. Acknowledgements

A large number of people have contributed to this project and altogether made it possible to accomplish:

Continuous operation of the process, during mornings, afternoons and nights, in test plant during several months has required a huge effort and flexibility from the whole Cortus team consisting of nine persons during the runs.

All collection, preparation and logistic of the biomass has required a lot of time and only been able to do in such a good way due to Rickard Winkler that has been available days, nights and weekends.

Thanks to the whole Nordkalk (especially Mikael Olsson) and YIT team in Köping who have helped us so many times with everything that we have needed in form of tools, media supply, transport, electricians, conference rooms etc.

VAFAB in Köping has supervised the heating of the plant during weekends on distance but also made daily visits and due to their knowledge and attitude on solving problems many trips to Köping for Cortus team members during weekends have been saved.

The Dept. of Chemical Engineering and Technology at KTH and especially Klas Engvall and his group of PhD's needs a special thank mainly for the TGA-tests at their site but also due to all good advices during the project.

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