

# Final report

## 1.1 Project details

<b>Project title</b>	Natural Gas from Wood Chips using Alternating Gasification
<b>Project identification (program abbrev. and file)</b>	12212
<b>Name of the programme which has funded the project</b>	ForskEI
<b>Project managing company/institution (name and address)</b>	Teknologisk Institut, Gregersensvej 1, 2630 Taastrup
<b>Project partners</b>	Ammongas A/S
<b>CVR</b> (central business register)	DK56976116
<b>Date for submission</b>	22 November 2017

## 1.2 Short description of project objective and results

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## **FINAL REPORT**

### **Short description of project objective and results**

#### **Engelish**

By using alternating electrical gasification, wood chips can be converted into synthesis gas, which can be used to increase methane production in a biogas plant. Alternate gasification is unique, as the gas produced is not diluted with nitrogen, and the power to operate the process comes partly from the mains, making the process flexible and quick to reduce cheap electricity. A laboratory gasifier has been established and gasification tests have been conducted under controlled conditions. Ammongas A/S performed work on rebuilding their alternate gasifier for electric heating. The work has not yet been completed and continues with own resources.

A calculation of the electricity storage potential of alternating gasification has been made and this has shown that by using electrically heated gasification, the energy content of the produced fuel can be increased by approximately 30% relative to wood, which means that the synthesis gas produced contains up to 23% "electrical energy".

Danish Technological Institute have demonstrated the concept of the electric alternating gasifier, where a low tar gas was obtained if charcoal was present in the reactor. Furthermore, it was found that heated dolomite catalyst can remove residue from the gasification gas.

#### **Dansk**

Ved brug af alternerende elektrisk forgasning, kan træflis omdannes til syntesegas, som f.eks. kan bruges til at øge metan produktionen i et biogasanlæg. Alternerende forgasning er unik, idet den fremstillede gas ikke er fortyndet med nitrogen, og energien til at drive processen kommer delvist fra elnettet, hvilket gør processen fleksibel og hurtigt kan aftage billig elektricitet. I projektet er der opbygget en laboratorieforgasser, hvor der er gennemført forgasningsforsøg under kontrollerede forhold. Ammongas A/S udført arbejde på ombygning af deres alternerende forgasser til elopvarmning. Arbejdet er endnu ikke færdiggjort og fortsætter for egne midler.

Der er blevet foretaget en beregning af el-lagrings potentialet for alternerende forgasning og denne har vist at ved brug af elektrisk opvarmet forgasning kan energiindholdet i det producerede brændsel forøges med ca. 30% i forhold til træ, hvilket vil sige at den producerede syntesegas indeholder op til 23% "elektrisk energi".

De gennemførte forsøg på Teknologisk Institut har eftervist konceptet for den elektriske alternerende forgasser, hvor en gas med lavt tjæreindhold blev opnået, når trækul var tilstede i reaktoren. Endvidere blev det eftervist at opvarmet dolomit kan fjerne resttjære fra forgasningsgassen.

### **1.3 Executive summary**

The work is based on Ammongas A/S' alternating gasifier, which is converted to electrical heating instead of the original internal combusting heating.

A thermodynamical analysis of the gasification-process using electrical energy was performed. The calculations show that by electrical heated gasification, the energy-content in the produced gas can be increased by approximately 30%, compared to the energy content in wood. This means, that the produced gasification gas will contain up to 23% more energy ( $30\%/1.3=23\%$ ), that is combustion energy that stems from the added electrical energy, that potentially could come from surplus electricity from wind-turbine production.

As a part of the project a laboratory scale alternating gasifier was established Experiment DTI, and a series of investigations were conducted. The following findings were achieved:

- Biomass, in the form of wood chips, can be gasified in an alternating electric gasifier (AEG)
- Alternation of flow direction and utilization of in-situ generated wood char as a tar-removal catalyst result in similar gas compositions of low-tar content producer gas, regardless of flow direction.
- Several wood types may be gasified, including beech and poplar, as well as combinations of wood chips and waste plastics (e.g., polyethylene).
- In-situ generated wood char plays an active role in reducing the alkane and substituted benzene species produced as a result of wood gasification. Both in-situ generated wood char and charcoal may be used as a wood char catalyst, with charcoal decreasing alkane and benzene emission to the greater extent.
- Dolomite-based stone catalysts, including un-treated and pre-calcined dolomite, can all be successfully employed as tar-removal catalysts, when operating between 1000 and 1100°C. Pre-calcined dolomite may be successfully employed at a temperature as low as 1000°C.
- Gasifier temperature ramp rate appears to play a role in gas speciation during biomass gasification, with a faster ramp rate (5°C/min) resulting in a wider variety of alkane and substituted benzenes being emitted. A slower ramp rate of 1°C/min was primarily utilized.
- Porous alumina can serve as a chemically and temperature resistant insulator for biomass gasification.

Ammongas A/S has carried out work on rebuilding the alternating pilot gasifier for electrical heating. The work is incomplete due to incompatibility between high temperature materials and the metal based gasifier unit, which has led to unwanted gas leaking. The plan is to decrease the operating temperature and use metallic components instead of high temperature ceramic materials.

Ammongas will continue the development work of the electric alternating gasifier and eventually commercialise the technology.

DTI has established new services on laboratory scale gasification, where different fuels can be tested and analysed. The service is a supplement to ongoing services on catalytic gas cleaning, heating technologies and gas analysis. It is also the plan to establish new development projects in collaboration with players in the field.

## Project objectives

The overall objective of the proposed project is the development of the alternating electric gasifier (AEG) process based on Ammongas' existing alternating gasifier technology and the pilot scale demonstration of its efficiency and reliability under real world commercial operating conditions. The existing 400 kW pilot scale plant built by Ammongas will be rebuilt in order to change the heating system from gas to electrical.

Whilst the production of liquid biofuels falls outside the scope of the proposed project, the project participants recognise that the AEG technology could play an important role in biofuel production. Hence upon successful demonstration of the AEG technology, Ammongas will commence discussions with potential endusers with respect to a future collaboration on the use of the AEG technique for the production of biobased fuels.

The project includes a work package dedicated to solving specific material selection, material testing and material characterization that can be used in the interior of the gasifier, that can withstand the temperatures up to approx. 1300°C, and that can withstand the cycling conditions when reversing the gas flow direction in the gasifier.

## 1.5 Project results and dissemination of results

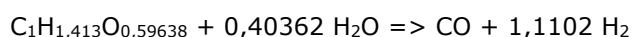
### Workpackage 0 - Feasibility study

The alternating electrical gasification technology is a energy converting technology, where electrical energy can be converted to chemical energy and thereby the electrical energy can be stored.

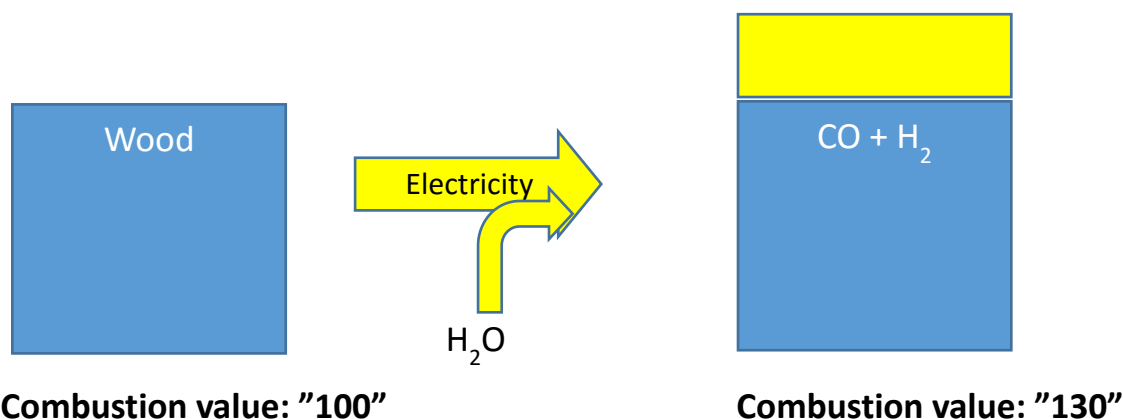
A thermodynamical analysis of the gasification-process using electrical energy has been performed. The purpose of the analysis is to determine, how much electrical energy can be added into the process, that is, how much energy can be converted from electrical energy into chemical energy per unit of biomass.

The energy of combustion of the biomass and the gasification-gas is used as a measure of the energy content in the biomass, before and after gasification.

The alternating gasification process is a steam-blown gasification process, where the wood is gasified using water in the following reaction, where  $C_1H_{1,413}O_{0,59638}$  eg. represents wood, in the correct ratios of carbon, hydrogen and oxygen:



This process is endothermic, and it requires addition of energy to run. This energy is added as electrical input in the alternating gasification process. If the heat loss to the surroundings is neglected, which is a reasonable assumption for a large scale plant with a large volume-to-surface-ratio, the energy is conserved and thereby the electrical heat input is converted to chemical energy in the produced  $H_2$ - and  $CO$ -gas-molecules. This is illustrated in the below figure:



Based on the above, calculations has been made, that show, that by electrical heated gasification, the energy-content in the produced gas can be increased by approximately 30%, compared to the energy content in wood. This means, that the produced gasification gas will contain up to 23% more energy ( $0.30/1.3=0.23$ ), that is combustion energy that stems from the added electrical energy, that potentially could come from surplus electricity from wind-turbine production.

The energy-storage potential of the electrical gasification process can be defined as  $e_p$ :

$$e_p = \frac{HHV_{\text{gasification gas}}}{HHV_{\text{wood}}}$$

Where HHV is the Higher Heating Value.

Using this definition, the  $e_p$ -values of methane, wheat-straw wood, coal and is calculated and shown in the table below:

	Wood forest residue, (FIN)	Wheat straw (DK)	Coal, antracit	Metane
Carbon content, w/w%	51,3	47,3	94,7	75
Hydrogen, content, w/w%	6,1	5,87	0,6	25
Oxygen, content, w/w%	40,85	41,49	4	0
Higher Heating value, HHV, MJ/Kg	20,54	18,94		-
Higher Heating value, HHV, KJ/mol	472,06	454,85	401,27	889,00
<b>Theoretical energy-storage potential, without heat loss, <math>e_p=HHV_{\text{syngas}}/HHV_{\text{fuel-1}}</math></b>	<b>28%</b>	<b>31%</b>	<b>31%</b>	<b>28%</b>

As seen, the energy-storage potential, or combustion energy increase of the syngas compared to the initial fuel: wood, wheat, coal or methans, is appromately 30%.

It is possible to used the electrical heated gasifier to store electrical energy. This is a potentially very interesting technique if the electrical energy comes from surplus windturbine power and has a cost close to zero. If the electricity has a higher price, the added enegy can more economically be added by simply burning the syngas and supplying the process with energy, as it is done in the original alternating gasification technology.

## **Workpackage 1 - Material selection – insulation, catalyst, high temperature materials**

### **Task 1.1: Material selection and testing of interior insulation and interior ceramic components.**

Internal insulation and ceramic components were not systematically investigated as the porous alumina insulators sold with the gasification furnaces and working tubes were (1) a very particular shape to accommodate the high temperature thermocouple in the working tubes, and (2) were found to work adequately. The original off-white porous insulation blocks and cream-colored impervious alumina rods were found to discolor with tar and soot deposition in the gasification and stone catalyst furnaces, but contin-

ued to fulfill their roles as insulators, as measured by low (relative to furnace setpoint,  $\geq 1000^{\circ}\text{C}$ ) temperature of the end-caps ( $\leq 200^{\circ}\text{C}$ ) (Figure 1).

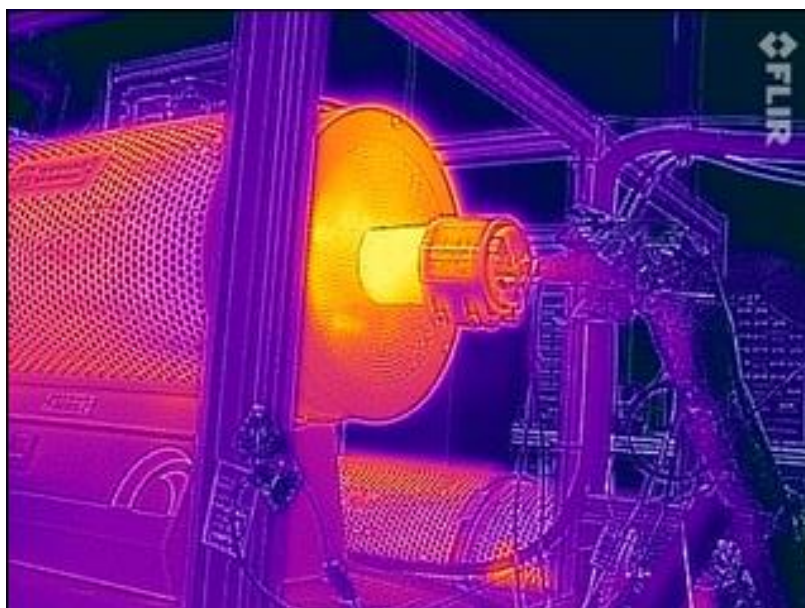


Figure 1, IR photograph showing relatively low temperature of end-caps, suggesting internal insulation was fulfilling its role of maintaining the central hot zone ( $1100^{\circ}\text{C}$ ).

The ceramic insulators were exposed to a maximum of  $1120^{\circ}\text{C}$ , and a temperature differential of up to  $900^{\circ}\text{C}$ . Under these conditions, and in a harsh reducing atmosphere ( $\text{H}_2/\text{CO}$ ), the structural integrity of the insulation blocks was maintained, without flaking or loss of material, although cracks did appear in the porous alumina blocks (Figure 2).

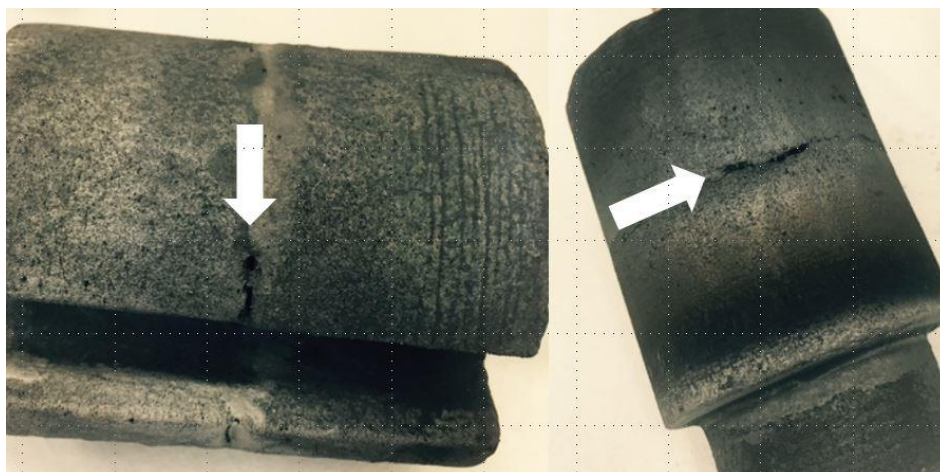


Figure 2, Discoloration and cracks formed in porous alumina insulation blocks following repeated exposure to high temperatures in the gasification furnace.

#### Task 1.2: Optimization and material selection of catalyst

Stone catalysts, all varieties of dolomite, were investigated, primarily at  $1050^{\circ}\text{C}$ , with a low density calcined dolomite (do-lime,  $\text{Ca-MgO}$ ) catalyst additionally investigated between  $1000$  and  $1100^{\circ}\text{C}$ . The dolomite employed in the production of high and low density calcined dolomite (do-lime) was mined Belgium. The do-limes were produced (Sinterco plant, Marche-les-Dames) in a normal shaft kiln fired with anthracite ( $1800-$

1900°C, 36 hrs). The low, suitable for refractory brick manufacture, and high (> 3.08 g/cm<sup>3</sup>) density fractions were separated on a Berry table.

Dolomite and do-lime were broken into 10-25 mm pieces, and ~ 400-500 g were packed into a small inner diameter tube and placed in the hot zone (middle 15 cm) of the stone catalyst furnace. The furnace was ramped to 1050°C at 5°C/min before wood gasification (poplar, 1°C/min, 1050°C) was started. All stone catalysts functioned adequately, with similar release temperatures (relative to the gasification furnace) of major and minor gas species, as shown for H<sub>2</sub> and benzene in Figure 3. Interestingly, dolomite (CaMgCO<sub>3</sub>) released a higher amount of CO<sub>2</sub> even after two use cycles (heated twice to > 1000°C).

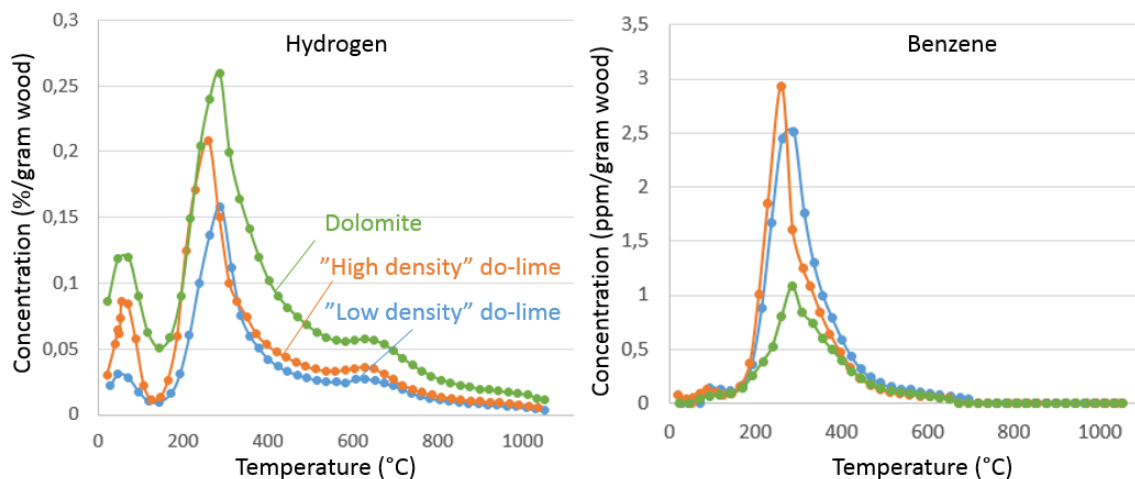


Figure 3, Poplar wood (1°C/min, 1050°C)//poplar wood char (1100°C)//stone catalyst (low and high density do-lime, dolomite) (1050°C).

Following two uses as a tar-removal catalyst (5°C/min, 1050°C) with exposure to air at room temperature in between, the stones' appearance changed from primarily grey to higher inclusions of white stones. The white stone could be crushed to powder in a ball-mill and was analyzed by powder X-ray diffraction (pXRD), revealing a composition of primarily CaO-MgO (the starting do-lime material) and a minor amount of Ca(OH)<sub>2</sub>. The hydroxide was presumably formed from reaction with water either during gasification or during cool down, and not likely at room temperature in air, as the stone catalyst was maintained under dry N<sub>2</sub> at room temperature between gasification experiments. Raw/untreated dolomite is suggested as an adequate stone catalyst at 1050°C for both tar and sulphur removal, without the need for pretreatment (calcination), although calcined dolomite was easier to handle as it is a harder (less easily pulverized) stone.

For low density do-lime, the temperature of the stone catalyst furnace was investigated between 1000 and 1100°C, for poplar gasification (1°C/min, 1050°C) inline with a poplar wood char (1100°C). As shown for H<sub>2</sub> and benzene in Figure 4, there was no systematic trend with stone catalyst furnace temperature, all temperatures ≥ 1000°C serving equally well for low-tar producer gas generation. This suggested a do-lime catalyst at 1000°C was sufficient without requiring the expenditure of extra energy to reach higher temperatures in this AEG setup.

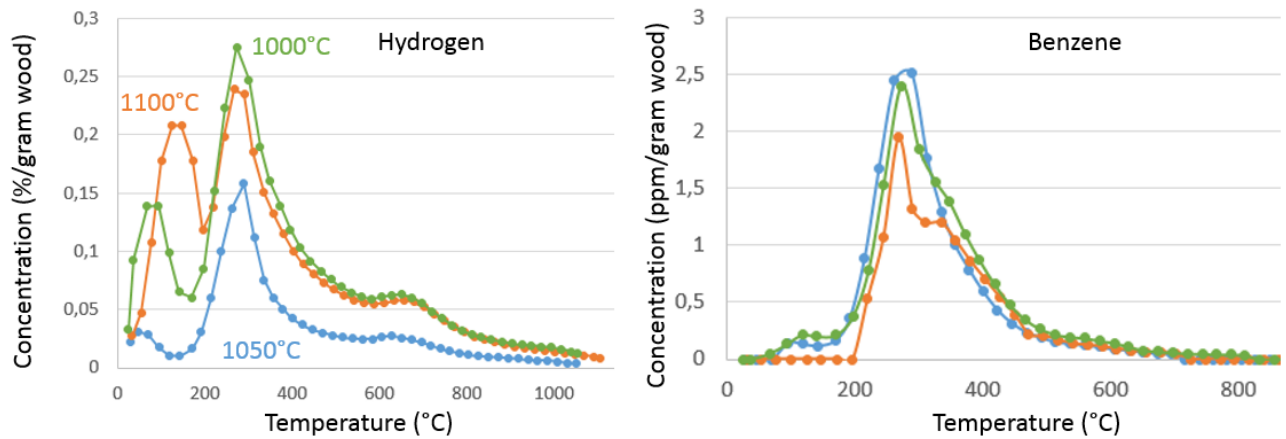


Figure 4, Poplar wood (1°C/min, 1050°C)//poplar wood char (1100°C)//low density dolime, variable temperature: 1000, 1050 and 1100°C.

## Workpackage 2 Construction of laboratory gasifier and lab-tests

### Task 2.1: Basic engineering, design of gasifier, PI-diagram

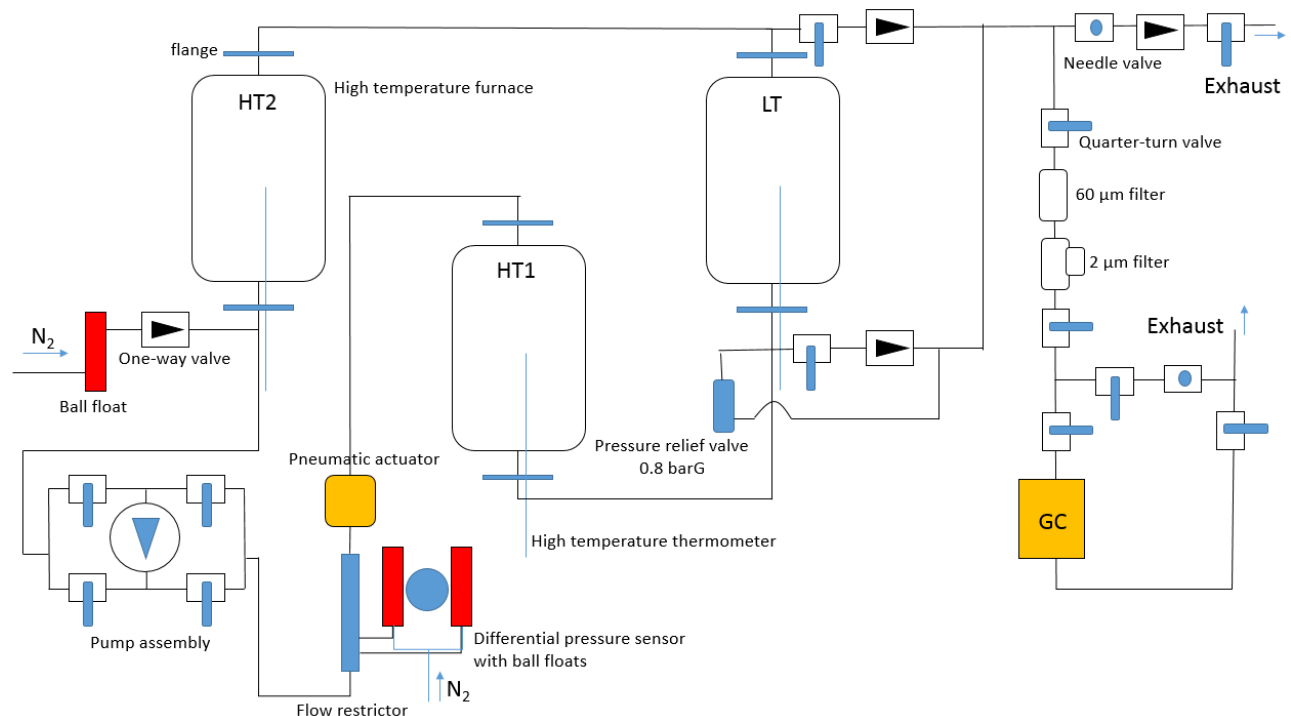


Figure 5, Flow diagram of AEG setup

### Task 2.2: Safety & Task 2.3: Construction of laboratory scale gasifier

The laboratory-scale Alternating Electric Gasifier, here referred to as the AEG setup, was assembled at the DTI facility in Taastrup. The AEG setup consisted of two gasification furnaces, and a stone catalyst furnace, all interconnected in a thermally insulated (~200°C) loop via a differential pressure sensor ( $\Delta P$ )/pneumatic actuator and a pumping assembly, allowing alternation (forward/reverse) of the flow direction within the loop. The assembly further consists of two  $N_2$  inlets: one a part of the  $\Delta P$  sensor, and the primary inlet allowing for  $N_2$  flushing to remove air prior to gasification, and remove traces of toxic/flammable gases ( $H_2/CO$ ) following gasification. The assembly contained two exhaust gas sampling points, which were used alternatively depending on the flow direction within the loop. The exhaust gas was directed to a safe exhaust/release point, and a sub-sample was directed, via a cold tar trap and soot filters ( $\geq 2 \mu m$ ) to a gas analysis instrument, a gas chromatography (GC) equipped with a thermal conductivity-



ity detector (TCD), and flame ionization detector (FID). Finally, safety features of the AEG setup included: a pressure relief valve on the gasifier/catalyst loop, gas (CO, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>) and pressure sensors, as well as the entire assembly placed in a room with very high ventilation capacity in case of leaks.

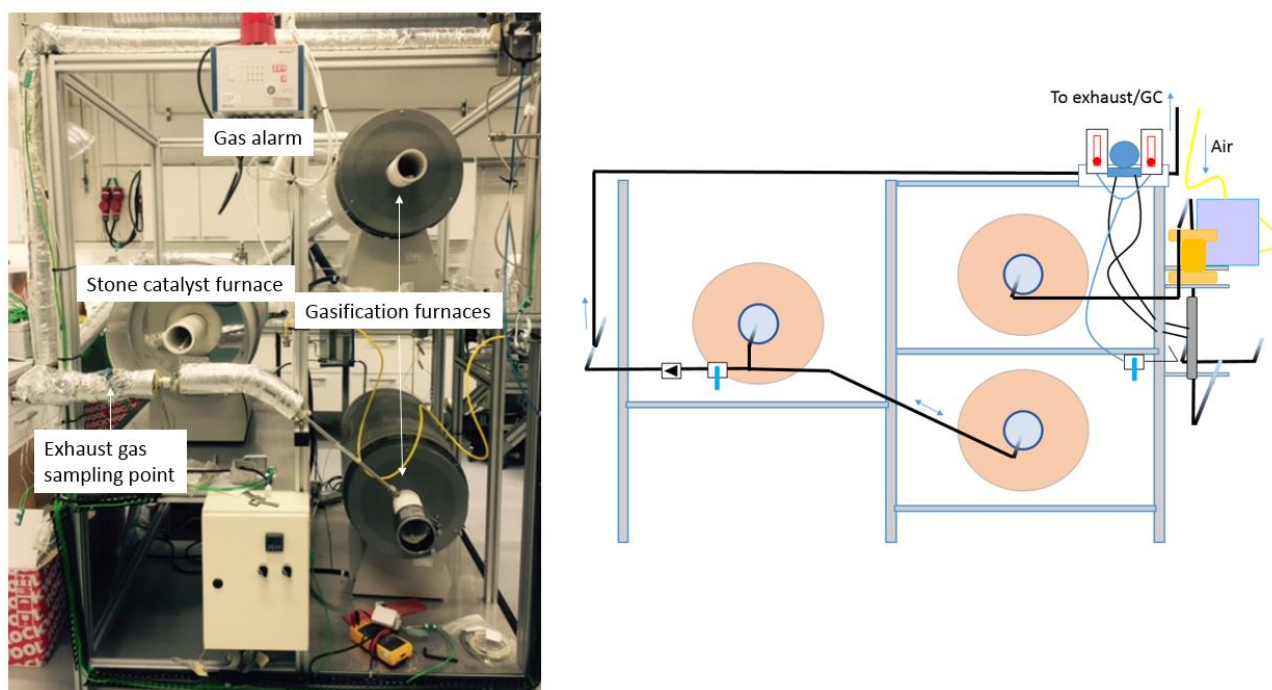


Figure 5, Photograph and schematic representation of gasification and stone catalyst furnaces, as well as differential pressure sensor/pneumatic actuator, gas sensors/alarm, and exhaust gas sampling point.

The gasification and stone catalyst furnaces were of similar construction and differed only in their temperature ranges. These were horizontal tube furnaces equipped with chemically and temperature resistance working tubes, internal insulation blocks, a high temperature thermocouple at one end of the hot zone (central 15 cm), and end-caps allowing slight pressurization (maintained  $\leq 1$  barG), sealing of the working environment (H<sub>2</sub>/CO), and connection to the pipework assembly between furnaces. These end-seals further allowed ease of opening and resealing for replenishment of the biomass tested in batches.

The biomass, in the form of wood chips, was introduced into the hot zone of the gasification furnace, and the char/ash removed, via a smaller diameter chemically and temperature inert tube. This tube was equipped with: insulation on either end of the tube to confine the biomass/char, a layer of insulation between inner and working tubes to decrease the flow of gases bypassing the biomass bed through this 5 mm gap, and a notch for easy retrieval of the inner tube with a hook assembly.

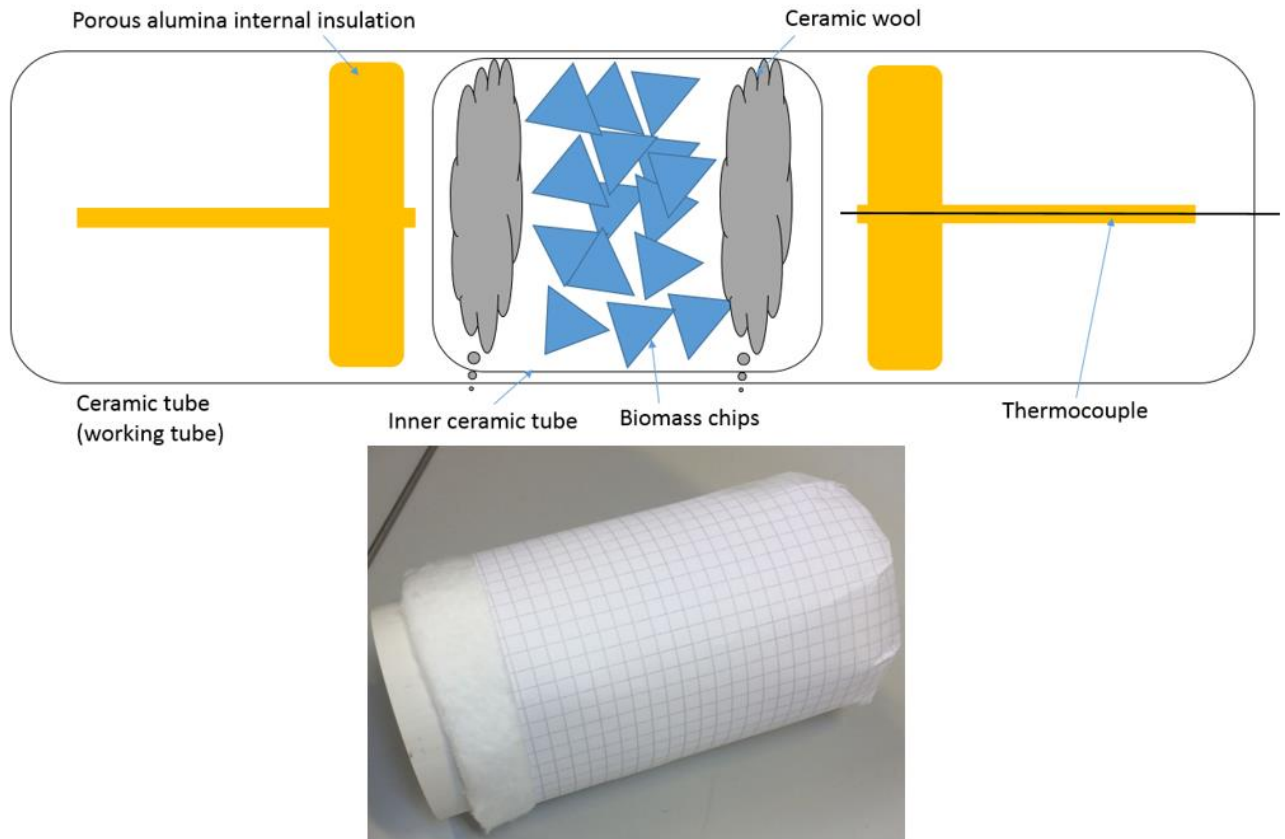


Figure 6, Configuration of working tube in gasification furnace, including inner tube used for loading/unloading biomass/char.

Construction of the AEG setup was considered complete when:

- (1) All 16 heating zones were able to reach and maintain 100°C or 150-200°C, depending on the heating zone, as recorded by the temperature data logger.
- (2) The pump assembly showed the capacity of reversing flow direction, as recorded by the  $\Delta P$  sensor over the flow restriction element.
- (3) The  $\Delta P$  sensor and pneumatic actuator were seen to be self-regulating at 10 mbar ( $\Delta P$ ).
- (4) The relief valve maintained pressure in the gasifier/stone catalyst loop at  $\leq 1$  barG when exhaust sampling points were closed.
- (5) The setup was sealed and gas-tight as seen by (a) soap bubble testing at each joint under  $N_2$ , (b) absence of detectable flammable gas ( $CH_4$  in  $N_2$ ) using a hand held gas sensor, and (c) no  $O_2$  (from air) was detected by the GC under a flow of  $N_2$ .
- (6) High temperature furnaces showed adherence to programmed ramp rates and set temperatures as measured by independent thermocouples.

#### 1. Task 2.4 Testing of laboratory scale gasifier

Experiments were carried out on the AEG setup to demonstrate the following:

- (1) Biomass, in the form of wood chips, can be gasified in an AEG assembly, this was demonstrated using several wood types, including beech, poplar and barbecue (BBQ) charcoal. Additionally, plastic was combined with wood (poplar + polyethylene) to investigate the disposal of waste plastics through gasification.
- (2) The introduction of wood char and stone catalysts inline with the gasifier produces a low tar content producer gas, this was investigated both with and with-

out the wood char catalyst bed, with varying catalysts and at varying catalyst temperatures.

- (3) Reproducibility, in the form of relatively similar gas composition results for near identical biomass loading conditions, including wood species, catalyst composition, and temperature, as well as flow direction.
- (4) Reversibility, demonstrated by similar gas composition results for near identical biomass loadings but with reversed flow directions.
- (5) Experimental conditions, including gasification ramp rate, affect the gaseous species produced, and detected, during gasification of biomass.

### *Reproducibility*

Two replicate samples of BBQ charcoal chips were loaded in series with a low-density calcined dolomite (do-lime) catalyst (1050°C). The gasification furnace was ramped at 5°C/min to 1100°C. Produced gases, under a purge of N<sub>2</sub> (~ 200 mL/min), were constrained in identical flow directions without active pumping, and sampled by GC once every 23 minutes. Produced gases showed very similar output with time/temperature (H<sub>2</sub> and benzene, shown in Figure 7), demonstrating reproducibility of replicate experiments.

Concentrations of individual gases were calculated from GC-TCD and GC-FID peak areas, and the application of the appropriate correction factors for the determination of concentration, established from calibration curves run on standards (H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>) of known concentration. Calibration was repeated every 3 months for the duration of the project. Temperature, as reported in graphs throughout this report, was measured using a high temperature thermocouple placed within the hot zone (central 15 cm) of each furnace.

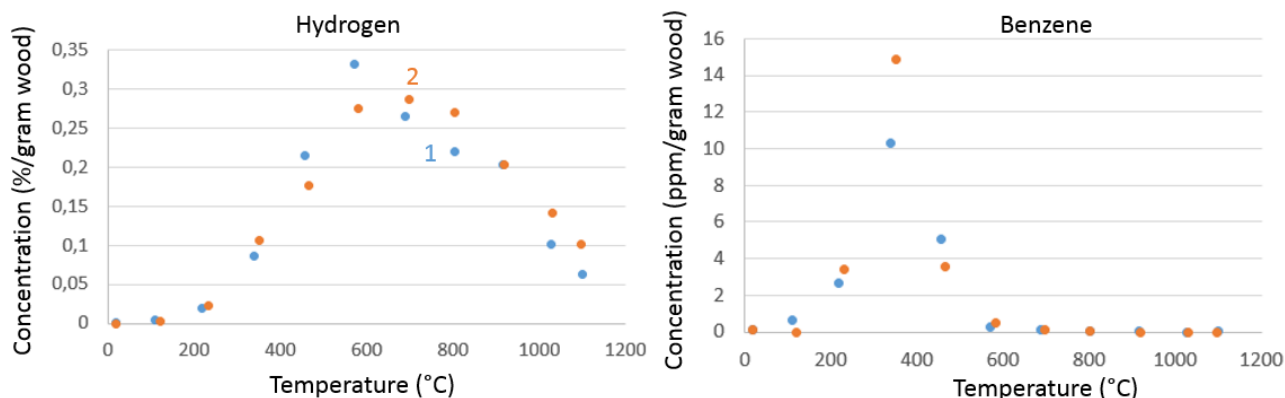


Figure 7, BBQ charcoal (5°C/min, 1100°C)/low density do-lime (1050°C), replicates 1 & 2.

### *Dependence on experimental variables*

Detected gas composition did not show any variability with gasification furnace set-points (1050 vs. 1100°C), primarily as the majority of gas emissions were complete by 800°C when the gasification furnace was ramped at 1°C/min. The influence of ramp rate was investigated at 1 and 5°C/min. Differences in detected gases with increasing gasification temperature are shown for beech wood up to the time of initially reaching 1050°C (shown for H<sub>2</sub> and benzene, shown in Figure 8).

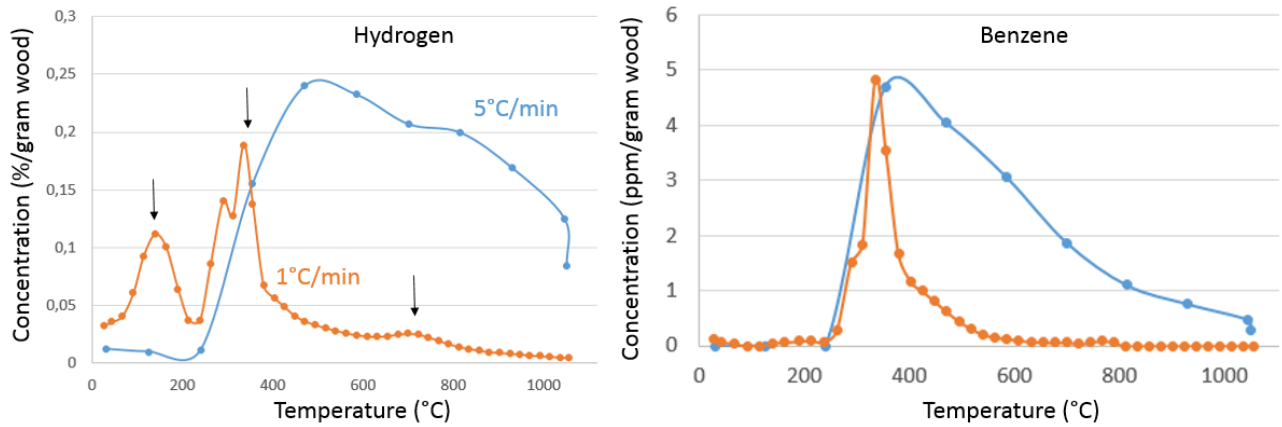


Figure 8, Beech wood (1050°C)// beech wood char bed (1100°C)// low density do-lime (1000°C), variable gasification furnace ramp rates: 1 vs. 5°C/min.

The temperature of maximum H<sub>2</sub> release is slightly lower at a lower ramp rate (1°C/min). This is consistent with a slight decrease in the temperature of major mass loss seen by thermo-gravimetric analysis (TGA) at variable ramp rates (2, 5, and 10°C/min) for beech wood under N<sub>2</sub> (Figure 9).

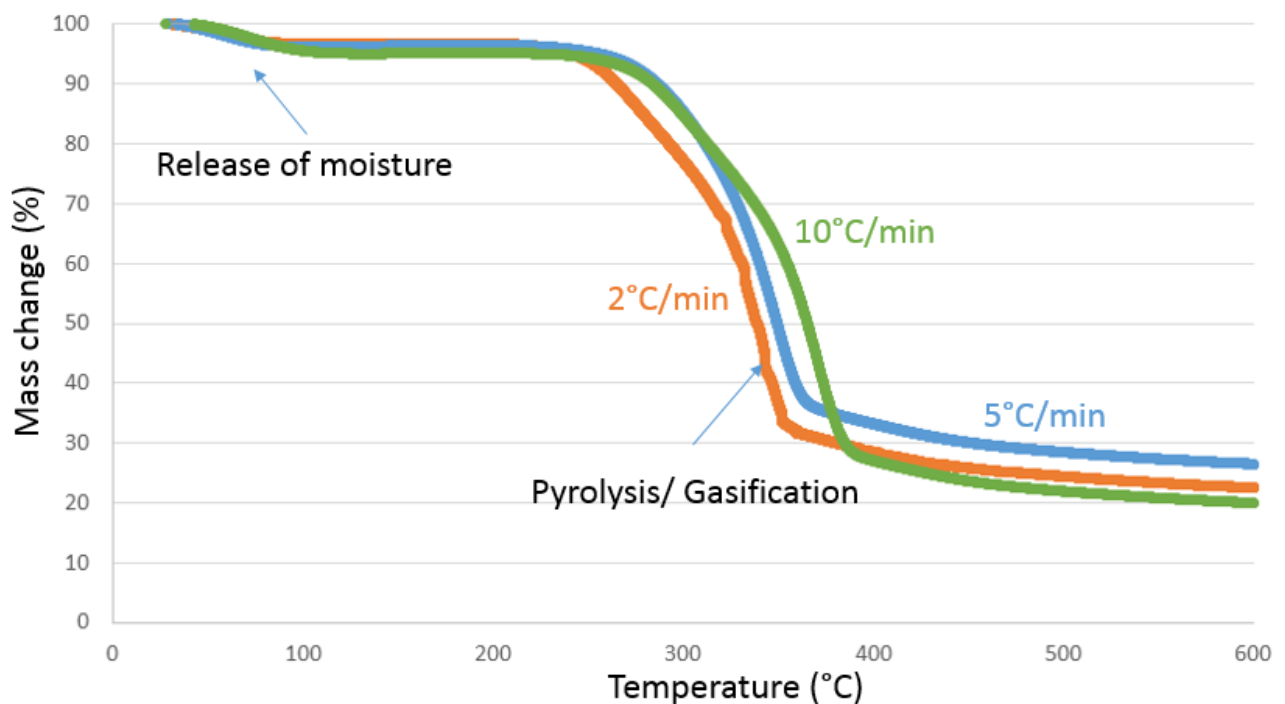


Figure 9, TGA in N<sub>2</sub> for beech wood, variable temperature ramp rate (2, 5 & 10°C/min).

Experiments were primarily pursued at 1°C/min ramp rate as it was felt to give more interesting information, such as three H<sub>2</sub> release phenomena as temperature was increased (Figure 8), which were not evident at higher gasification furnace ramp rates. Additionally, ramping at lower rates allowed collection of more data points over the gasification run. Finally, when wood (Figure 10) and wood char (Figure 11) were heated at the higher ramp rate (5°C/min), a greater diversity of higher hydrocarbons (C<sub>x</sub>H<sub>y</sub>, x = 2-5) were observed, which suggested a higher purity syngas/producer gas may be generated when the gasification furnace were ramped at a slower rate (1°C/min).

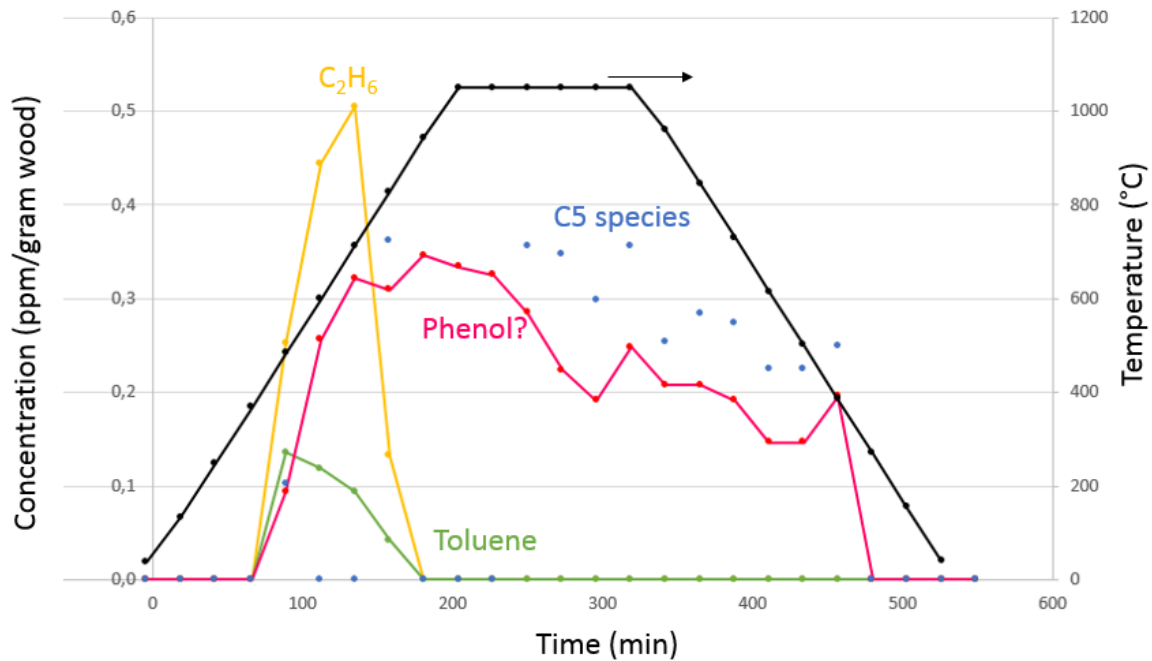


Figure 10, Beech wood (5°C/min, 1050°C/2 hrs)// low density do-lime (1000°C), variety of higher hydrocarbons (C2 and C5) and aromatics (toluene and a substituted benzene, most likely phenol) released under rapid ramp rate conditions (5°C/min).

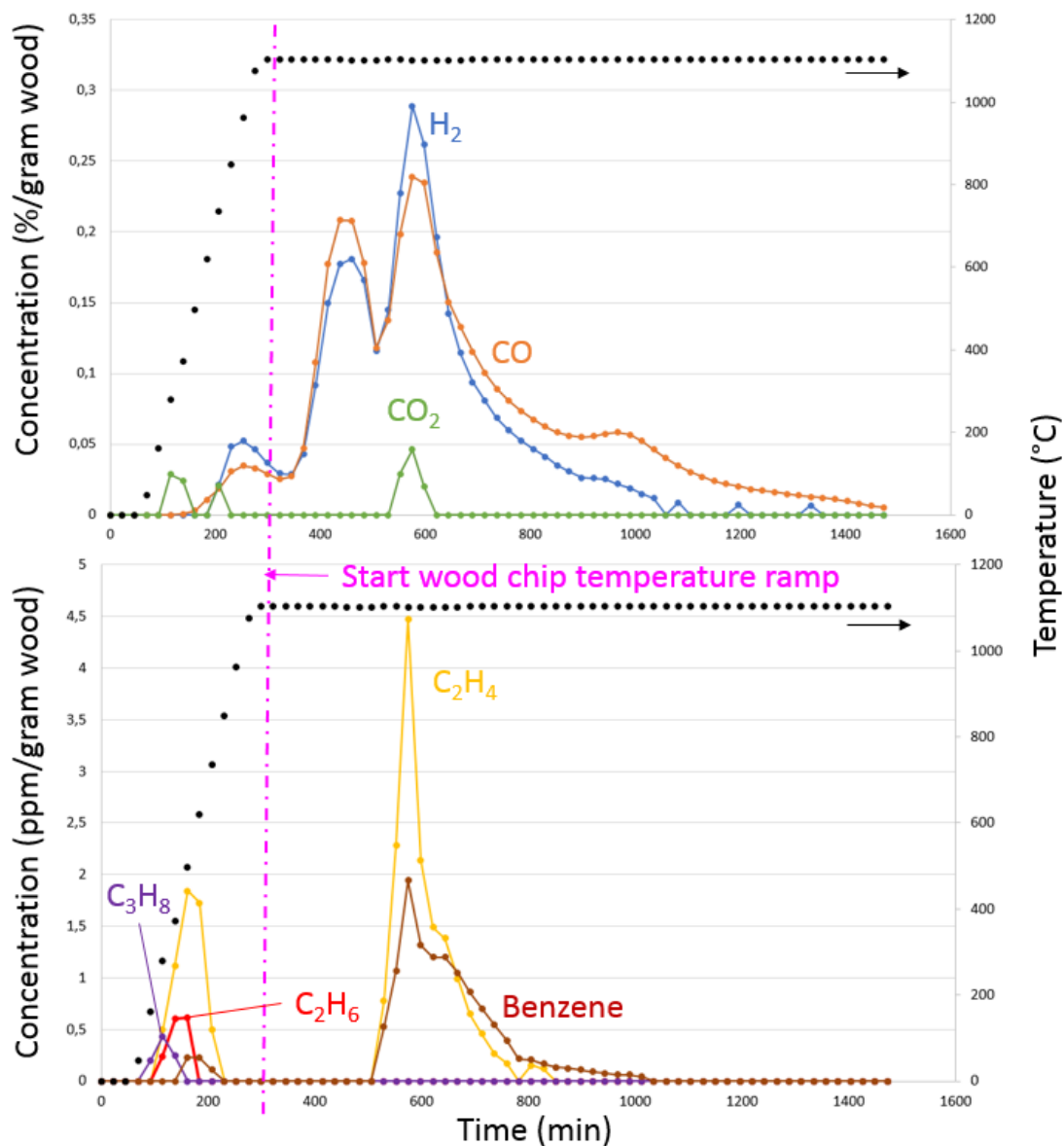


Figure 11, Poplar wood (1°C/min, 1100°C)//poplar wood char (5°C/min, 1100°C)//Low density do-lime (1100°C), variety of gaseous species detected for variable ramp rates: initial release peaks (time ≤ 300 min) during fast ramp (5°C/min) of poplar wood char, and later release peaks (time > 300 min) during slow ramp (1°C/min) of poplar wood.

Between the (re)heating of the wood char bed and wood gasification, between 400 to 900 mL of non-N<sub>2</sub> gases were released per gram of wood chip mass placed in the gasification furnace, with 30-50% of wood mass lost during gasification and subsequent use as a wood char bed. This represented 2000-4000 J/gram of wood and 2000-5000 J/gram of wood in heat of combustion energy from H<sub>2</sub> and CO, respectively, evolved primarily from wood (poplar) gasification during the require to raise the gasifier temperature from 20 to 1050°C.

An analysis of the volumes of gases produced during gasification and their heats of combustion was carried out for poplar wood (1°C/min, 1050°C), in line with poplar wood char (5°C/min, 1100°C) and dolomite stone (5°C/min, 1050°C) catalysts. This analysis is presented here as representative of the other gasification experiments carried out throughout this project.

Estimation of total gas flow was enabled through monitoring of the N<sub>2</sub> GC-TCD signal throughout the duration of the gasification experiment, where the duration was taken to be from when the wood-containing furnace started to ramp in temperature (as measured by the internal high temperature thermocouple) until the end of the gasification experiment (1°C/min, 1050°C/2hrs, 5°C/min, 25°C). Following completion of the gasification, signified by the disappearance of H<sub>2</sub> signal from the TCD (i.e., only N<sub>2</sub> detected), the N<sub>2</sub> flow rate was measured (240 mL/min). As the N<sub>2</sub> signal varied over the course of the wood gasification but the flow rate was known to be constant, the variability of the signal served as a means of calculating the dilution factor of the N<sub>2</sub> and so the total flow rate of other gases produced.

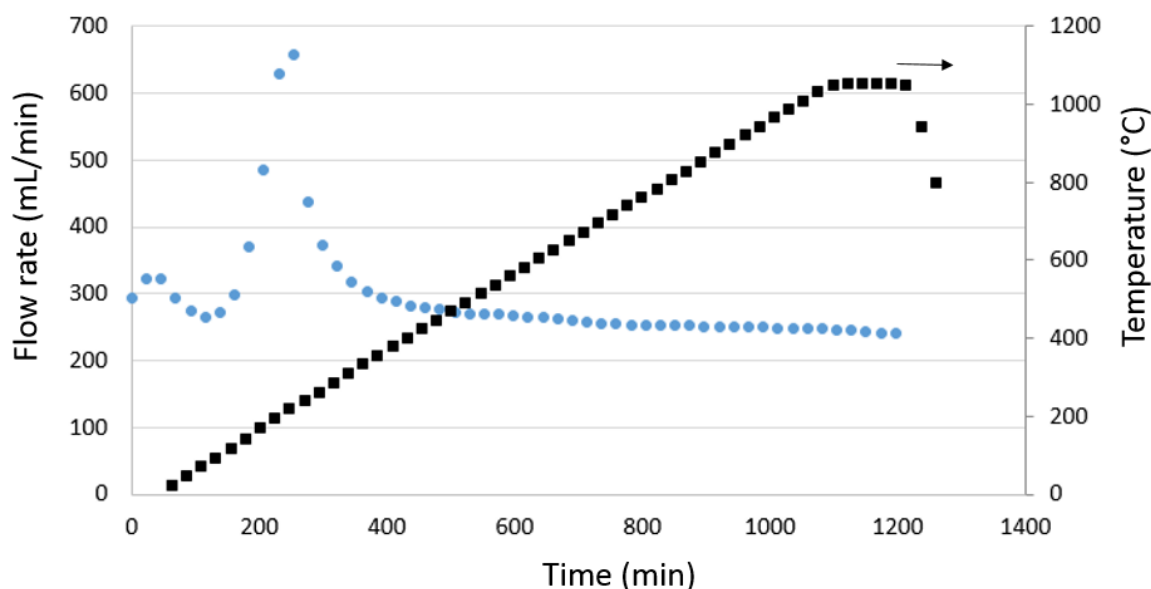


Figure 12, Poplar wood (1°C/min, 1050°C)//poplar wood char (5°C/min, 1100°C)//Dolomite (5°C/min, 1050°C), calculated total gas flow rate (including N<sub>2</sub>) over the course of wood gasification.

Assuming the gas composition and flow rates remained constant over the time periods between GC measurements (23 min), the total non-N<sub>2</sub> gases evolved summed to 609 mL/gram wood (110.76 gram poplar). The quantity included steam, which was not detected by the GC. The flow of each detected gas species was calculated from their concentrations and total gas flow rate (including N<sub>2</sub>). The total volume and volume percentage (summed over the volume of detected gases, 561.8 mL/gram wood) of gases are shown in Table 1.

Table 1. Total (summed in 23 min intervals) volumes and heats of combustion of gases evolved from the gasification of poplar wood (1°C/min, 1050°C)//poplar wood char (5°C/min, 1100°C)//dolomite (5°C/min, 1050°C)

<b>Gas</b>	<b>Volume (mL/gram wood)</b>	<b>Vol%</b>	<b>Heat of combustion (kJ/gram wood)<sup>a</sup></b>
H <sub>2</sub>	292.6	52	3.0
CO	255.6	45.5	3.08
CH <sub>4</sub> (FID)	4.64	0.8	0.1
C <sub>2</sub> H <sub>4</sub>	0.03	0.005	0.002
CO <sub>2</sub>	8.81	1.6	
Benzene	0.08	0.01	0.01
Phenol	0.009	0.002	

<sup>a</sup> Heat of combustion taken from [http://www.engineeringtoolbox.com/heating-values-fuel-gases-d\\_823.html](http://www.engineeringtoolbox.com/heating-values-fuel-gases-d_823.html)

The total volume of selected gases (H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and benzene) were employed to calculate the heats of combustion of gases evolved. The total heat of combustion from the evolved detectable gases was 6.2 kJ/gram wood. The higher heat value (HHV) of hybrid poplar and charcoal are 19.38 kJ/gram<sup>1</sup> and 29.6 kJ/gram<sup>2</sup>, respectively. Taking into account the volume of gas detected (561.8 mL/g from 51.71 g of wood not recovered as char), and mass of wood char recovered (59.05 g), 19% of the heat of combustion of the original wood batch remained unaccounted for, most probably present as undetected gases and liquid tars present within the gasification furnace.

#### *Tar removal catalysts*

The role of the wood char tar-removal catalyst was investigated by examining the gases produced from two systems with beech wood (5°C/min, 1050°C) and low density dolomite (1000°C), one with a wood char bed (1100°C) and one without. The presence of the wood char was seen to increase the output of H<sub>2</sub> and CO, while decreasing that of hydrocarbons (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) and aromatics (benzene, substituted benzene: probably phenol) (this is shown for CO and phenol in Figure 13).

<sup>1</sup> Sannigrahi, P., Ragauskas, A.J., and Tuskan, G.A., Polar as feedstock for biofuels: A review of compositional characteristics, *Biofuels, Bioproducts & Biorefining*, 4, 209-226 (2010).

Ultimate analysis of hybrid poplar: 48.45% C, 5.85% H, 43.69% O, 0.47% N, and 0.01% S (wt%, dry basis).

<sup>2</sup> [http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d\\_169.html](http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html)

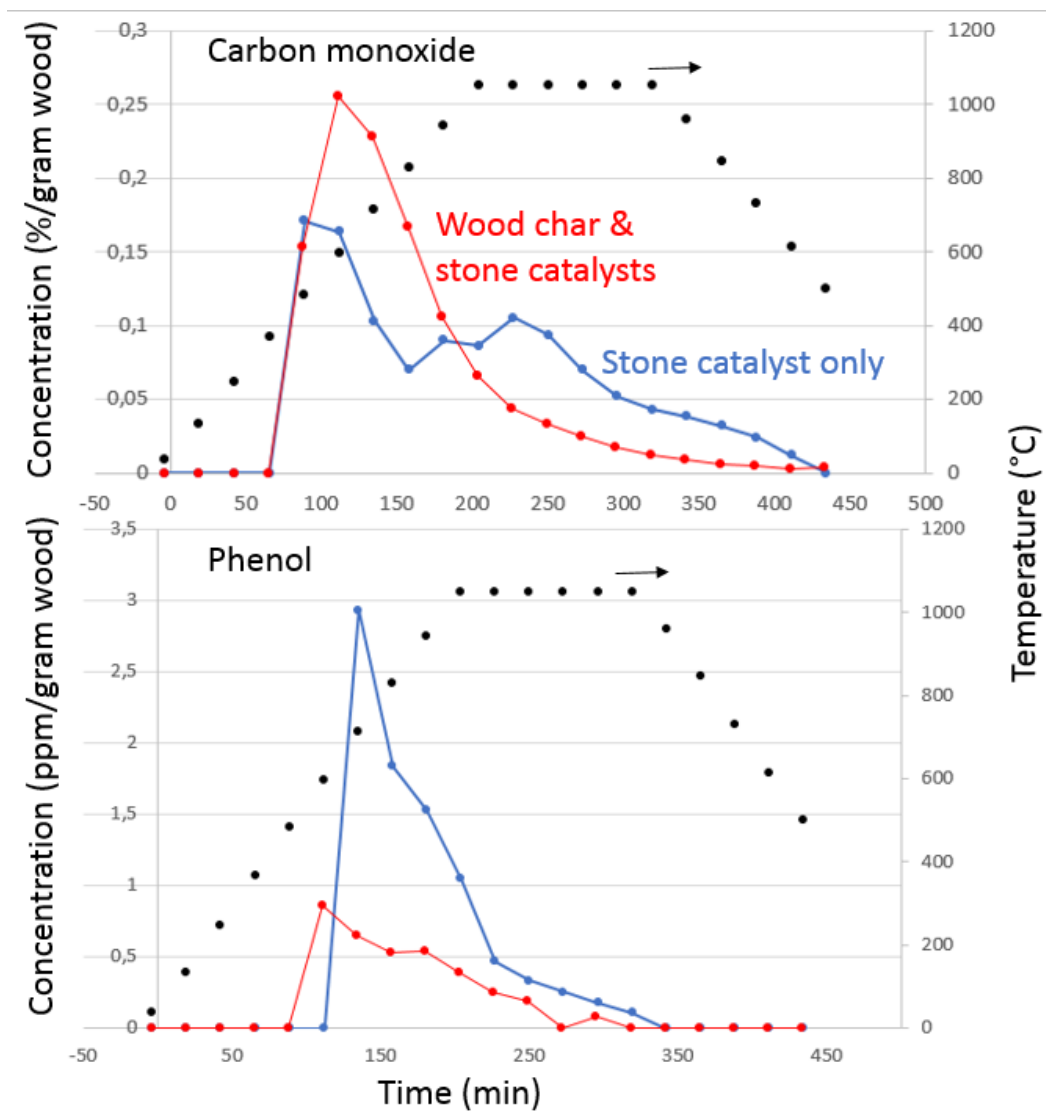


Figure 13, Beech wood (5°C/min, 1050°C)// low density do-lime (1000°C), gaseous species detected with and without beech wood char (1100°C).

The wood char beds produced by in-situ gasification were not well packed, and, therefore, had limited gas flow through the char due to the horizontal nature of the furnaces. To further demonstrate the role of the wood char catalyst, well packed BBQ charcoal chips were substituted for the wood char catalyst produced in-situ (1100°C). For the two replicate experiments of poplar wood gasification (1°C/min, 1050°C), with low density do-lime (1050°C), the BBQ charcoal increased H<sub>2</sub> and CO production, while decreasing that of benzene and phenol (Figure 14), relative to poplar wood char.



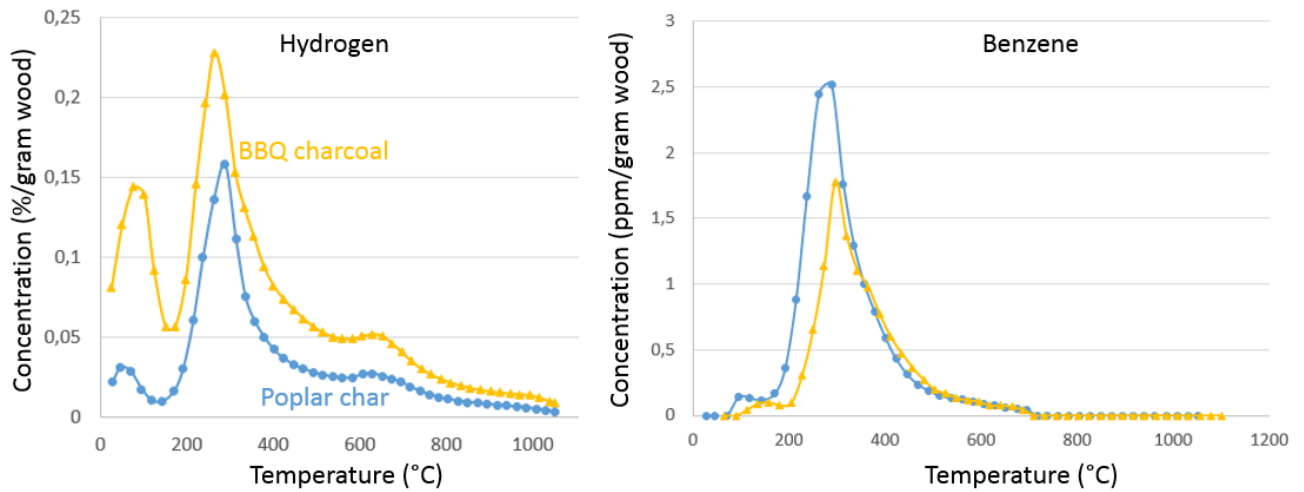


Figure 14, Poplar wood (1°C/min, 1050°C)//low density do-lime (1050°C)// poplar wood char vs. BBQ charcoal (1100°C).

#### Reversibility

The AEG setup functioned on the premise that following a gasification run, the produced wood char should be retained, and function, with heating (1100°C), as a tar removal catalyst for the subsequent gasification run in the second gasification furnace. These alternating roles of the gasification furnaces (gasifier vs. wood char catalyst furnace) were accompanied by a reversal in flow direction, as dictated by the direction of the pumping assembly. Similar results were obtained for two replicate poplar wood (1°C/min, 1050°C) runs with alternating (forward and reverse) flow directions (as shown for H<sub>2</sub> and benzene in Figure 15), demonstrating the “alternating” character of the AEG setup.

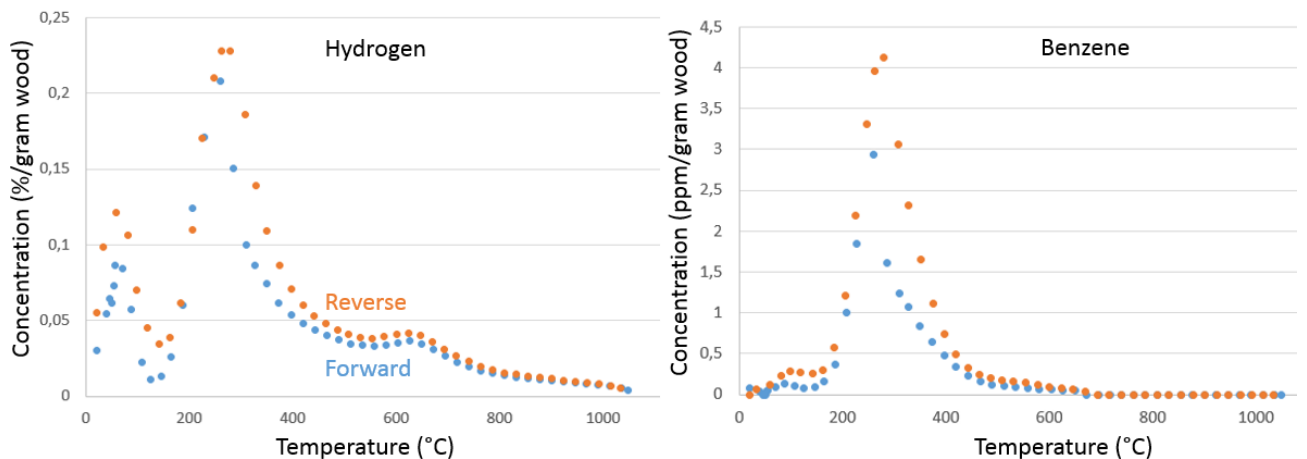


Figure 15, Poplar wood (1°C/min, 1050°C)//poplar wood char (1100°C)//high density do-lime (1050°C), variable flow direction: forward vs. reverse.

#### AEGasification

The capacity of the AEG setup to successfully gasify biomass in the form of wood chips to low-tar containing syngas/producer gas has been demonstrated for several types of biomass, including two wood types: beech and poplar. Similar experiments, where wood (1°C/min, 1050°C) and their respective wood char (beech and poplar, respectively; 1100°C) were placed inline with low density do-lime (1000°C), were carried out. Polar wood showed higher amounts of H<sub>2</sub> and CO released at a slightly lower tempera-

ture, combined with lower C<sub>2</sub>H<sub>4</sub> and benzene releases (as shown for H<sub>2</sub> and benzene in Figure 16).

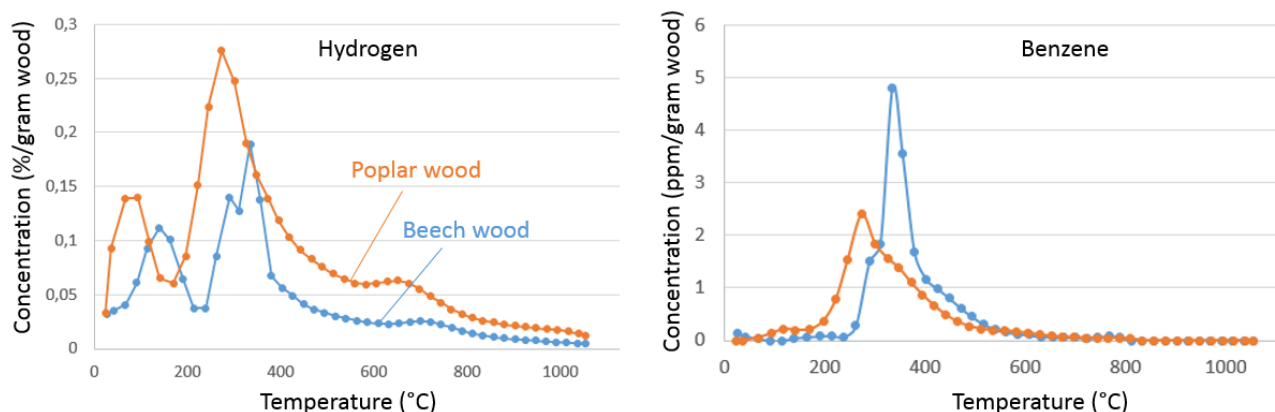


Figure 16, Wood (beech vs. poplar) (1°C/min, 1050°C)//wood char (1100°C)// low density do-lime (1000°C).

Differences between woods were consistent with their TGA in N<sub>2</sub> (2°C/min, 1100°C), where poplar was seen to release more water ( $\leq 100^\circ\text{C}$ ), and showed its major mass loss at a slightly lower temperature than beech (Figure 17). In all experiments, primary gases detected were H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>, with small releases of C<sub>2</sub>H<sub>4</sub>, benzene and a substituted benzene, probably phenol, demonstrating a low-tar producer gas was generated by biomass gasification in the absence of air or ex-situ steam. However, fine particle soot was generated, and entrained over several meters by the gas stream, requiring the placement of soot filter ( $\geq 2\mu\text{m}$ ) prior to the GC.

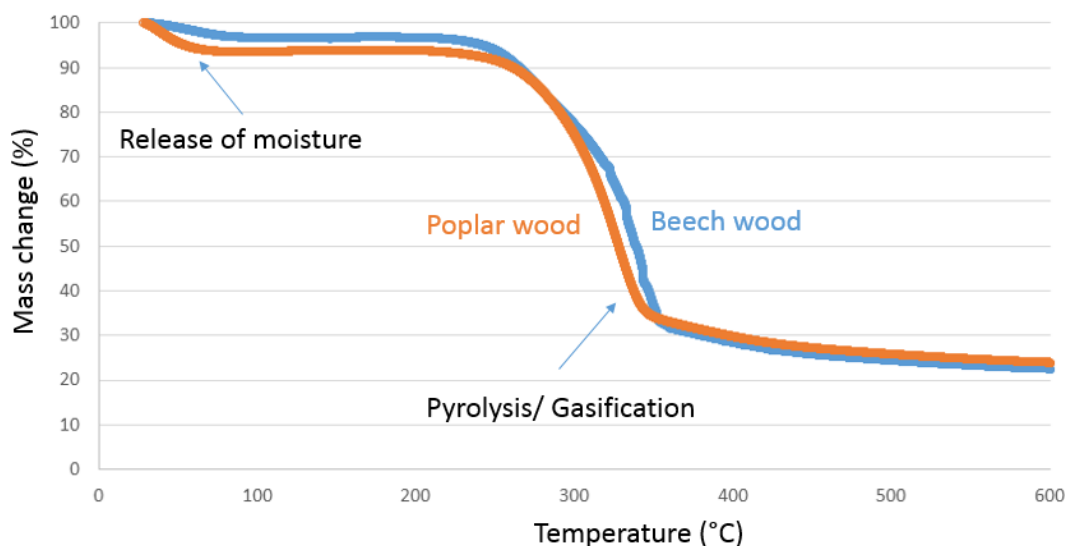


Figure 17, TGA in N<sub>2</sub> (2°C/min) for beech and poplar woods.

Further experiments included the combination of wood chips and plastics as fuel placed into the gasification oven, in order to investigate the possibility of employing the setup for the recycling of waste plastics by both decrease the volume of polymer, and producing a useful resource in the form of syngas. Virgin and waste high density polyethylene (PE) were placed in loosely packed layers with poplar wood chips, and gasified (1°C/min, 1050°C) in-line with low density do-lime (1050°C) and BBQ charcoal

(1100°C). The volume of generated gases are shown for poplar wood, as well as poplar wood combined with 11.6 wt% waste PE and 45.1 wt% virgin PE in Figure 18.

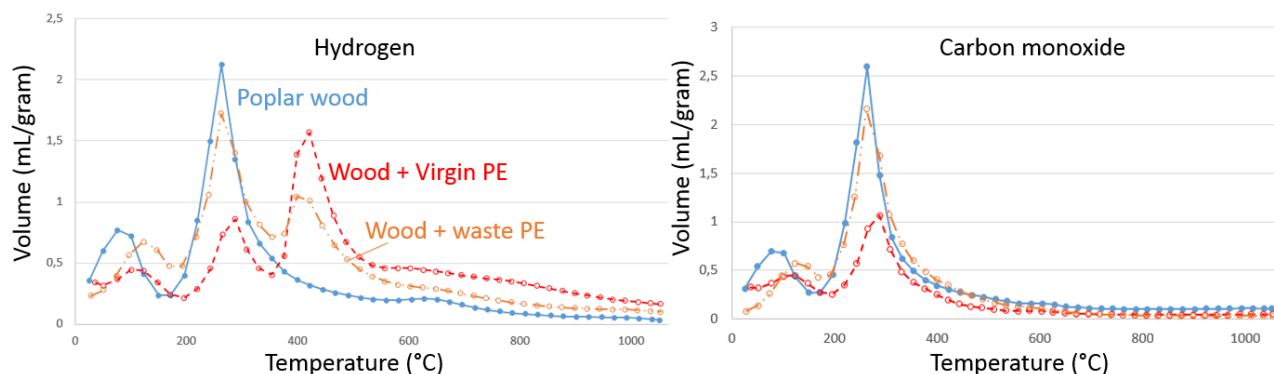


Figure 18, Poplar wood + PE (1°C/min, 1050°C)//BBQ charcoal (1100°C)//Low density do-lime (1050°C): poplar wood alone, wood + 45.1 wt% virgin PE and wood + 11.6 wt% waste PE.

The inclusion of PE with poplar wood resulted in a new H<sub>2</sub> release peak at higher temperatures, which did not coincide with an additional CO release peak. This suggested that PE decomposed at a higher temperature, releasing H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and benzene. The release of CO and CO<sub>2</sub>, originating solely from wood, were seen to decrease with the proportional inclusion of plastics. The PE within the high-temperature zone of the gasification furnace decomposed completely, leaving only wood char, which could presumably be used subsequently as a wood char bed for tar-removal. Approximately 30 wt% of the include PE was recovered in the colder zones at the ends of the horizontal tube furnace, along with the heavier (liquid) tars typically produced during wood gasification. Despite a slight increase in the production of C<sub>2</sub>H<sub>4</sub>, benzene, and a substituted benzene (presumably phenol), a relatively high purity syngas was produced with the inclusion of both waste (58 vol% H<sub>2</sub>, 39 vol% CO) and virgin PE (63 vol% H<sub>2</sub>, 30 vol% CO), with a total heat of combustion from detected gases of ~ 9 kJ/gram wood + PE. These experiments suggested the inclusion of several wt% plastic in with the wood chips had no adverse effect to the gasification process, and only a minor detrimental effect to the purity of the generated syngas. Additionally, this inclusion offers a viable means of disposing a waste plastics, while recovering a portion of the chemical resource held within, in the form of syngas.

### Workpackage 3 Rebuilding and upgrading of pilot gasifier

Here is the surveyed report on the establishment of a large pilot plant for electric gasification at Ammongas A/S.

At the time of writing, we are still unable to run the large pilot, even though we expect it is just around the corner. The reason is that the supply of the electric heat at 1400 degrees, on the other hand, presents many surprising problems, and, in fact, very few have in practice any experience that can be drawn.

We spent a lot of time choosing the right oven design and ended up looking for an additional grant for the purchase of a finished American oven, complete with power supply.

In the project we have always chosen a high ambition level, including the effort to supply the reactor with 1400 degrees of hot gas. At this temperature and the given conditions, we can not use metals but must use ceramic materials. However, this has some disadvantages as we saw when we were to start the expensive purchased American oven. Even before we had reached the operating temperature, the continuous ceramic tube broke.

We then replaced the white alumina ceramic tubes with some SiC pipes of silicon carbide (which should also be ordered in the United States but long waiting time).

At startup with these, however, we had to observe that the connection between these tubes and the reactor at one end and the catalyst at the other end was not close enough. Again, we had to stop calling potential experts, and make a new construction.

At the time of writing, we are so ready to try this out. Hope the best, but learned from the experience, we almost expect that new problems will appear.

The sealing problems between ceramic pipes and the rest of the plant is leaking when heated, due to different thermal expansion coefficient. Rubber or other elastic gaskets are not available for use at these temperatures. Instead we have to use metallic materials. This makes it much easier to establish close links, but it also means that we must turn the temperature ambitions down somewhat. Which again means that we more often have to change flow direction during the process. (it is only at temperatures above 800 degrees, that the charcoal can react with water vapor to form gas).

We can conclude that the project is really a development project. When the plant comes running, we will really have learned a lot, and found some solutions on how to design the unit.

Nothing in the introductory considerations has changed with regard to all the good possibilities for how the finished clean gas can be used and the need for green gas in our energy system has not changed so we just have to continue the work. Once that's done, we'll probably get it "sold".

### **Dissemination**

- The results were presented by DTI at DGF Gastekniske Dage 2017 den 24. maj i Billund.
- The project and developed facilities were introduced approximately 150 visitors at the DTI laboratories during the project period.

## 1.6 Utilization of project results

At DTI the developed laboratory unit will be a part of the laboratory services for high temperature chemical engineering, gasification and gas analysis. We plan to proceed with new test analysis of biomass and waste on either commercial basis and via new development projects in collaboration with the industry, utility companies and universities. We also hope to be able to continue with Ammongas A/S in the process of commercialisation of the alternating gasification technology.

Ammongas will continue the development work of the electric alternating gasifier and eventually commercialise the technology.

### New related projects

Svovlfjernelse fra biomasse, Energistyrelsen, 2015-2018

INDUCAT Induktionsopvarmet katalytisk brintproduktion, Innovationsfondens investering, 2016-2021

### Patents

The gasification process used in this project is a patentable alternating electric gasifier (AEG)<sup>1</sup>. The AEG alternates between two modes of operation. In one mode a combined catalyst and heating element is heated to its operating temperature. In the second (gasification) mode, gas is circulated between the biomass feed stock (wood chips) and an electrically heated storage system.

International Application No. PCT/EP2016/079303 on electrical heated alternating gasifier was filed on 30. November 2016 claiming priority from the Danish Application.

### Energy policy

Denmark is pioneering the large scale use of renewable energy and has an energy policy goal of producing 35% of its energy requirements for the energy and transport sectors from renewable sources in 2020 and 100% by 2050<sup>2</sup>. Fossil fuels however currently comprise a large proportion of Denmark's energy production in part because it is an important oil producer. It is a net exporter of natural gas<sup>3</sup> and the only EU-27 country that is a net exporter of oil and the only overall net energy exporter<sup>4</sup>. In order to address this dependency on fossil fuels successive Danish governments have promoted and legislated for a gradual switch to renewable energy sources. This has resulted in the proportion of Danish electricity production generated from renewable sources increasing from 18% in 2002 to 39% in 2011 (see [Table 1](#)).

As a consequence of climate and geographic factors and Denmark's long tradition of using district heating and combined heat and power (CHP), the primary sources of renewable energy in Denmark are wind and biomass (from wood, agriculture and municipal wastes). It is estimated that today biomass meets approximately 70% of renewable energy consumption in Denmark<sup>5</sup>.

Wind energy is attractive as a renewable source of energy due to its low environmental impact and low operating costs but suffers from fluctuations in availability. Hence it requires an energy storage infrastructure<sup>6</sup> to enable load levelling if Denmark is to be energy self-sufficient. One means of achieving this is to use wind energy to produce hydrogen gas by electrolysis of water<sup>7</sup> which is then stored (either as a gas or liquid for subsequent use. Hydrogen can be used as a clean zero-emission fuel for fuel cell powered electric vehicles<sup>8</sup> or to generate electricity in fast-starting gas turbines or via fuel cells. Alternatively hydrogen can be further processed to convert it to biofuels such as syngas, ethanol or methane (the latter

being particularly attractive as can be a direct replacement for natural gas<sup>9</sup>). However there are number of barriers to generating hydrogen gas using wind energy the use of hydrolysis. The technology is relatively immature and has high capital costs, there are safety issues associated with hydrogen and hydrogen storage systems, and such systems are much more expensive than existing storage systems for natural gas<sup>6</sup>.

**Table 1 - Progress in Contribution of Renewables to Danish Energy Production (1,000's toe)\***

Energy Source	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
<b>Biomass and wastes</b>	1,553	1,751	1,852	1,911	1,969	2,167	2,152	2,156	2,362	2,162
<b>Geothermal</b>	4	4	4	8	14	14	12	12	10	8
<b>Hydro</b>	3	2	2	2	2	2	2	2	2	1
<b>Solar</b>	9	9	10	10	11	12	13	14	16	20
<b>Wind</b>	419	478	566	569	525	617	596	578	671	840
<b>Total Primary</b>	28,559	28,464	31,083	31,293	29,545	27,085	26,634	23,967	23,294	21,017
<b>% of Electricity from Renewables</b>	18.39	21.61	25.5	26.27	23.97	27.04	26.7	27.49	33.11	38.81

\* Source - Eurostat

An alternative means of providing a means of load levelling and energy storage is to use the gasification of bio-mass. The as-produced syngas can be either directly converted into power by combustion or, as with hydrogen, upgraded and converted into gaseous fuels which can be stored for later use. Compared to the production of hydrogen by hydrolysis, gasification has several major advantages. Firstly, due to Denmark's long experience in using biomass for energy generation the technology is well proven, syngas can be used in the existing natural gas grid and storage infrastructure and it provides a means of safely and environmentally friendly depositing of agriculture and municipal waste.

This project supports the Danish energy policy goal of 35 % renewable energy in 2020 by establishing an efficient technology for production of combined heat and power by gasification of biomass. Gasification is an important part of the national strategy within energy production from biomass and waste. Especially R&D on gas cleaning and operation reliability of CHP technologies are of specified as important in the "Strategy for research, development and demonstration of thermal biomass gasification in Denmark", published in 2011 by the Danish energy agency and relevant partners.

Biomass and waste have been the major drivers in the growth in renewable energy production in the EU-27 Member States contributing 68% of the total (see [Figure 1](#)). Consequently the European Commission's Biomass action plan<sup>10</sup> encourages the member states to harness the potential of all cost-effective forms of biomass electricity generation and the use of biomass to produce second-generation biofuels.

On a European level this project is in line with the European Industrial Initiative (EII) on bioenergy where the objective is to ensure at least 14 % bioenergy in the EU energy mix by 2020 and guarantee greenhouse gas savings according to the RES directive. In the project proposed here, tar and dust problems are considered to be minimal. This opens the possibility of syngas production for liquid fuels in the thermochemical pathway of EII and the proposed project is directly in line with the proposed EII pathway for optimization of combined heat and electrical power through gasification.

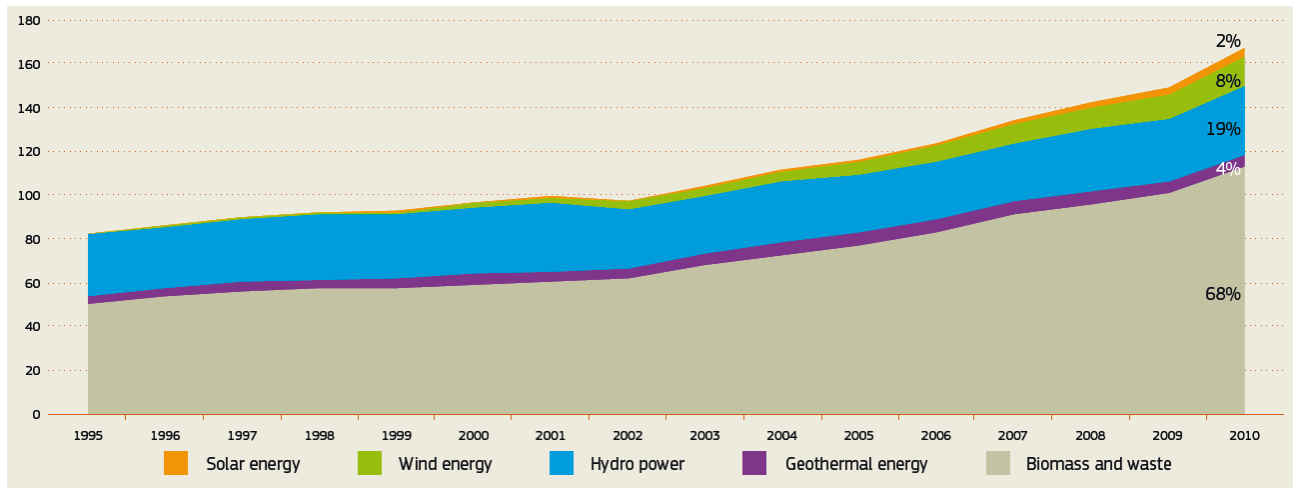


Figure 1 - Renewable Energy Production in the EU-27 Member States (Source - Eurostat<sup>3</sup>)

### Relevance to Energinet.dk's strategies

With the alternating gasification technique, an input of power and biomass can be converted to syngas, which is converted to methane in a biogas plant.

Figure 2 shows the alternating gasification process in integration with a biomass fermenter and the inputs and outputs of gas, power and syngas in the different steps. The focus of the current project is emphasized by the red box in the figure, but the entire process illustrates the flexibility and interaction between the different energy systems that the alternating gasification technique can be used for.

This combination of different energy systems, together with the use of a renewable fuel, biomass, supports the strategy by Energinet.dk, "Strategy 2014+". The alternating gasification technique is a flexible production technique; the biomass can be stored, and the gasification can be started and be operational within 1-2 hours and produce syngas, when e.g. the price of power is low, with also supports Energinet.dk's strategy for flexible power- and gas production.

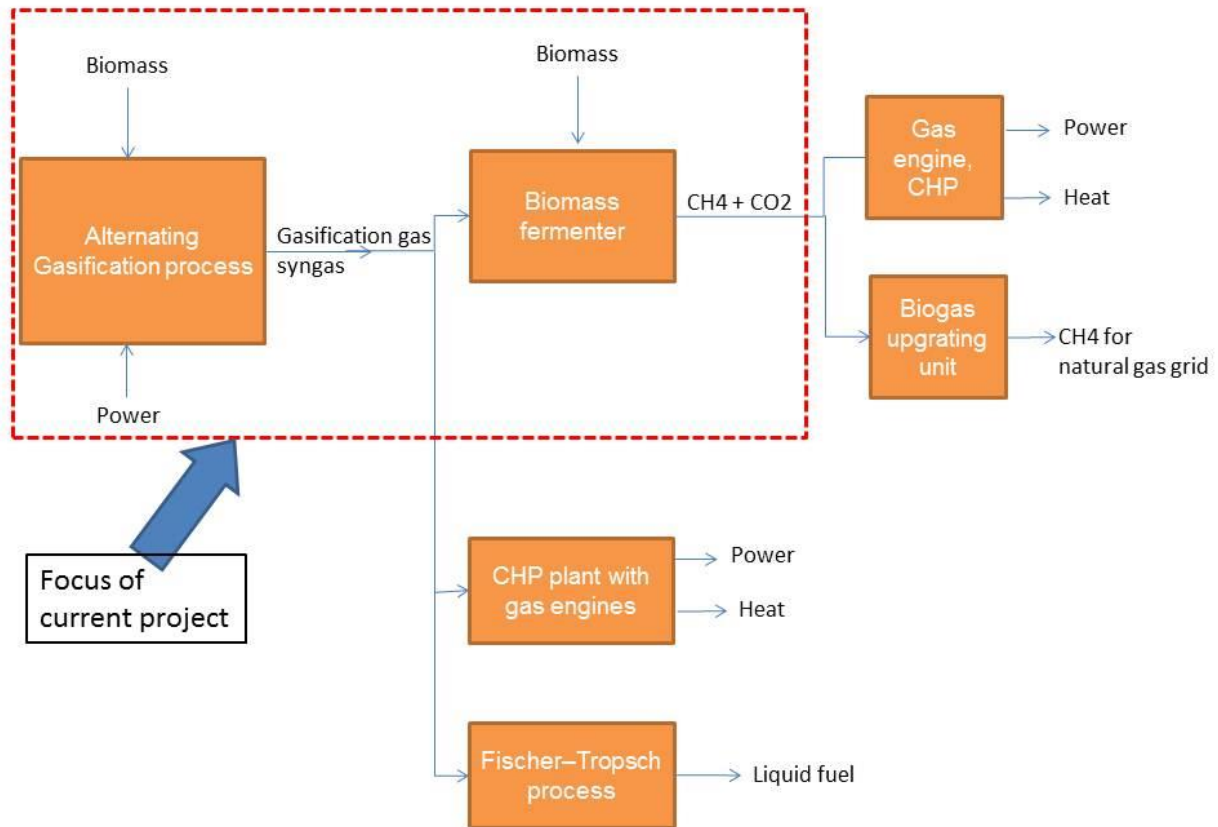


Figure 2 - Mass- and energy input and output from alternating gasification process and different post treatment possibilities

### 1.7 Project conclusion and perspective

The following findings may be applicable to the up-scaling of the AEG process:

- It is feasible to use alternating electric gasification of biomass, in the form of wood chips, inline with a wood char and dolomite-based catalyst to produce a low-tar producer gas, composed primarily of hydrogen (~ 50 vol%) and carbon monoxide (~ 45 vol%), with smaller inclusions of methane and carbon dioxide, and minor inclusions of ethylene, ethane, benzene and phenol.
- Operation of the AEG setup in alternating flow directions produced gas of similar composition, regardless of flow direction.
- Inclusion of the wood char bed is warranted to decrease the evolution of alkanes and substituted benzene compounds during wood gasification, as well as promoting the formation of hydrogen and carbon monoxide. This is probably due to the catalytic activity of wood char towards producer gas species and tar compounds, resulting in their shift and breakdown, respectively, to H<sub>2</sub> and CO.
- Wood species (beech vs. poplar) being gasified does not significantly affect the species of gas produced.
- Heating the electric gasifiers at a low heating rate (1°C/min) tended to produce fewer alkane and substituted benzene species. When heating up the wood chip gasifier at this rate, gasification is largely complete at 800°C, such that this is sufficient as the maximum setpoint temperature.
- When utilizing a pre-calcined dolomite (do-lime) stone catalyst for tar removal, a temperature of 1000°C is sufficient to produce a low-tar producer gas.



- Utilization of untreated dolomite, without pre-calcination, as a stone catalyst for tar removal is adequate, such that pre-calcination is not required.
- Porous alumina is a stable, well-performing insulator suitable for internal, chemical and temperature resistant insulation up to at least 1100°C under reducing conditions.

The laboratory-scale horizontal furnaces, a fairly pure, highly valuable (high H<sub>2</sub> and CO content) synthesis gas was produced. As such, a larger plant with more efficient vertical columns is expected to produce a very clean syngas. Further, the large-scale plant is not expected to employ N<sub>2</sub> as a purge gas, unlike the laboratory-scale experiments, such that a nitrogen-free high purity syngas would be produced. Not only the catalyst but also the produced wood char has shown a high purification efficiency, which underlines the benefit of alternating between two gasification furnace, or the large-scale vertical reactors, i.e., utilization of in-situ generated wood char as a tar-removal catalyst in subsequent gasification sequences.

Ammongas A/S has carried out work on rebuilding the alternating pilot gasifier for electrical heating. The work is incomplete due to incompatibility between high temperature materials and the metal based gasifier unit, which has led to unwanted gas leaking. The plan is to decrease the operating temperature and use metallic components instead of high temperature ceramic materials.

Ammongas will continue the development work of the electric alternating gasifier and eventually commercialise the technology.

## Annex

Links to publications, home pages etc:

<https://www.energiforskning.dk/node/7838>

[https://www.danskgasforening.dk/sites/default/files/inline-files/GTD2017\\_Jens\\_Kroman\\_Nielsen.pdf](https://www.danskgasforening.dk/sites/default/files/inline-files/GTD2017_Jens_Kroman_Nielsen.pdf)

[Test af katalysatorsystemer](#)

[Gasanalyse](#)

[Simulering af små reaktorer og brændere](#)

## References

<sup>1</sup> 'Method and Apparatus for Producing Synthesis Gas from Biomass', United States Patent US 7,951,212 B2, May 31, 2011.

<sup>2</sup> '[Energy Policy in Denmark](#)', Danish Energy Agency December 2012.

<sup>3</sup> '[Energy Markets in the European Union in 2011](#)', Eurostat 2012, 978-92-79-25489-5.

<sup>4</sup> '[Europe in Figures – Eurostat Yearbook 2012](#)', Eurostat 2012, 978-92-7922085-2.

<sup>5</sup> 'A World Leader in Bioenergy', T. Y. Toftdahl, [BE Sustainable 3](#) (2013) 6-7.

<sup>6</sup> 'Chapter 8 - Hybrid wind-hydrogen energy systems', T. Tsoutsos in 'Stand-Alone and Hybrid Wind Energy Systems - Technology, Energy Storage and Applications', J. K. Kaldellis (ed.), Woodhead Publishing (2010), 978-1-84569-962-8.

- <sup>7</sup> 'Wind energy and the hydrogen economy - review of the technology', S. A. Sherif, F. Barbir and T. N. Veziroglu, *Solar Energy* **78** (2005) 647-660.
- <sup>8</sup> 'Hydrogen Fuel Cells for Road Vehicles', P. Corbo, F. Migliardini and O. Veneri, Springer (2011), 978-0-85729-136-3.
- <sup>9</sup> 'Wind Power Stored into the Gas Grid – Wind and Biomass Energy Integration', K. Tybirk, [BE Sustainable 3](#) (2013) 23-27.
- <sup>10</sup> '[Biomass action plan](#)', COM(2005) 628 final, European Commission 2005.