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Tar fouling during heat recovery in solid fuel gasification

Master's thesis in Sustainable Energy Systems

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Department of Space, Earth and Environment
Division of Energy Technology

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Abstract

Solid fuel gasification is the thermal conversion of carbon-based materials into gases. Depending on the gasification conditions the main share of products will be components that are in gas phase at ambient conditions. A minor share of the products will be either solid, derived from inorganics and char, or liquids, usually called tars described as hydrocarbon molecules with a molecular weight higher than benzene. Fouling, the unwanted accumulation of material on surfaces, is greatly enhanced by tars. This issue has been a recurring problem in gasification technologies for many years.

Because of a growing interest in a circular economy and sustainable alternatives, gasification is an interesting technology expected to develop in the future. Gasification is a thermally intensive process, so energy recovery in the process should be as high as possible. The main source of recoverable energy is the raw gas at high temperatures, which can be used for heating. However, recovering energy from the raw gas can provoke tars to condense and increase fouling. There is a trade-off between energy recovery, to increase efficiency and maintenance with a decrease in availability because of tar fouling.

The condensation of tars, required for fouling, was investigated. A method to analyse the dew point based on tar analysis was implemented. It consisted of raw gas extraction at decreasing temperatures, first high enough to avoid any tar condensation. Condensed tars were capture and the remaining total tar concentration for different temperatures was analysed to determine the amount of tars condensing at different temperatures. The experiments were implemented in a lab reactor using gasification conditions from references to mimic real conditions. The results validated the concept for the method, but further experiments would be required to collect more data, reducing errors and improving the accuracy.

Tar fouling can occur by direct condensation over surfaces or condensation as aerosols that stick to walls. Condensation alone does not guarantee to foul, aerosols contained in the raw gas could travel with the flow without sticking to surfaces. A review of aerosols and the influence of different flow conditions was made to investigate the fouling process. Even though heat transfer is enhanced by turbulence, it also might enhance fouling from tar aerosols. An experimental set up to compare fouling in laminar and turbulent flows was presented for future research.

Keywords: Gasification, Tars, Heat recovery, Fouling, Condensation, SPA analysis.

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Introduction

For the last decades, the world economy has relied on fossil feedstock to a large extent in many industries [1]. Fossil feedstock is used for energy generation, transportation fuel, various materials including plastics and more. With the urgency of solving climate change, reducing the greenhouse emissions, new alternatives for circular economies less dependant in fossil fuels are gaining traction.

Alternatives for products obtained from fossil feedstock have been available for many years. Technologies like gasification and pyrolysis, processes were material is heated to high temperatures in the absence of oxygen, can provide feedstock to replace fossil fuels. These technologies have had cycles of increased interest and technological development in the past, with a new interest growing today.

One of this cycle was during the Second World War in Germany [2]. Because of the limit supply of fossil feedstock during the war effort, Germany turned to gasification of biomass for fuel and chemicals production. Biomass was grown locally, including forest and agricultural products. The technology was developed rapidly with an increase in interest in processes such as Fischer-Tropsch catalytic conversion into liquid fuels. After the war interest in this technology decreased as cheap fossil feedstock become available again worldwide.

With the current demand for renewable solutions to tackle climate change, there is a growing interest in gasification. Multiple countries, especially in Europe, are developing sustainable alternatives for products like fuels, chemicals, and materials [3].

Biomass gasification is an alternative, especially for fuel production. Biomass is composed of carbohydrates (molecules consisting of carbon, hydrogen, and oxygen) with complex structures. These molecules can be gasified into a syngas that can be turned into hydrocarbons (molecules consisting of carbon and hydrogen only). These hydrocarbons are considered renewable as the feedstock to produce them is not fossil-based. But the process is still more expensive compared with fossil feedstock available worldwide for fuel production [4]. If the interest in fossil-free products keeps growing in the future, this technology could be one of the best alternatives.

Gasification can also be applied for other materials, such as plastics [5]. Unlike biomass, plastics mostly have a low content of oxygen, composed instead of hydrocarbons forming large molecules called polymers. Gasification for these products consists of breaking down these large polymers to obtain again the basic components, going back to the smaller hydrocarbons. Although hydrocarbons could come from renewable sources, most of the plastics industry currently uses fossil feedstock. Processes to use plastics as feedstock for new plastics have been developed previously but not implemented due to economical reasons. New interest is now growing aiming to achieve a circular use of plastics and its fossil carbon molecules, recycling the plastics through gasification.

The gasification process has had a recurrent problem. During the high-temperature process, materials are decomposed changing their molecular structure. Depending on the feedstock and technology the process will generate a range of different molecules. Some of these molecules can be undesirable, causing problems. The unwanted material is called tar, which is not clearly defined, but could be summarized as aromatic and large polyaromatic hydrocarbon molecules. One relevant issue is called fouling [6], which consists of the accumulation of unwanted material over solid surfaces that hinder the operation.

The fouling issue related to tars has been one of the major problems in biomass gasification. Frequently new gasification projects aiming to generate a useful gas discovers an unexpectedly large concentration of tars [7]. Then projects spend most of their resources solving this problem, often unsuccessfully and quietly disappear. Thus, the tar fouling problem is described as the Achilles tendon of biomass gasification projects.

Solutions for this problem have been designed, but often at a great economic cost and involving large thermal losses. This has made gasification processes more expensive and less efficient, preventing them from expanding in the market. The subject of this thesis is tar fouling in the gasification process during energy recovery, aiming to increase thermal efficiency and reduce fouling problems.

Objective

The objective of this thesis is to facilitate better operational strategies for raw gas energy recovery at high temperatures based on the understanding of the governing effects and parameters for the occurrence of tar induced fouling.

Specific aims

1. *What is the relevance of high-temperature heat recovery in the gasification process?*
   Importance of heat recovery in the industrial gasification process to increase overall efficiency.

2. *Which is the dew point where tars might start fouling?*
   Take forward an experimental method to determine tar dew point depending on raw gas temperature for the different gasification process.

3. *How are tar fouling mechanisms and how to prevent them?*
   Investigate the main drives for tar fouling in energy recovery at high temperatures, above the water dew point, proposal of an experimental setup design for fouling analysis.

Theory: Heat recovery in gasification

Gasification technology consists of the thermochemical conversion of materials, most of the times solid, into feedstock for different process. The gasification process changes the material properties, converting into a different type of gases [8]. These gases can be used for different purposes such as fuel, chemicals, and feedstock for materials.

Gasification is characterized by high temperatures. This breaks the molecular structure of the material into smaller molecules that can be solid, liquid or gas at standard conditions of temperature and pressure. Solids are often called char, composed of carbon molecules that agglomerate together. Liquids are commonly called tars, a diverse range of hydrocarbons. Gases are the smallest molecules, with a low molecular weight including CO, CO2 and CH4.

The efficiency of an industrial site depends on the use of energy, electrical and thermal. Because of large uses of thermal energy for multiple processes, the optimization of this resource on-site is often one of the main measures available to improve efficiency. Depending on the temperature levels of industrials flows, the energy from them is attractive to be recovered. Energy from a hot fluid is easier to recover and use than energy from a cold one.

In the gasification process, there are large thermal demands, required to heat the material. Depending on the technology this energy can be produced from different sources, such as combustion or electricity. After gasification, raw gases need to be cool down to handle them, so energy from this process could be recovered for the system. Depending on the temperatures required the heat recovery process might have different difficulties. Which brings the first relevant question:

First specific aim

What is the relevance of heat recovery in the gasification process?

A relevant industrial sector is the petrochemical industry, which uses multiple types of gasification processes. In 2002 the chemical industry of the US consumed 28% of energy from the manufacturing industry. A guide for petrochemical plants energy management shows improving the efficiency of this industry would decrease the carbon footprint considerably, with opportunities in the use of utilities, fired heaters, process optimization and heat exchangers as the most promising [9].

Efficiency requirements to achieve lower greenhouse gases footprint are growing worldwide. The European Union is expected to decrease 85-90% the greenhouse gases by 2050 [1], which will require improvements in existing and future technologies. Gasification technologies have a large developing potential expected in the future, so optimizing the energy recovery will help to improve the efficiency, consuming fewer resources and decreasing greenhouse gases.

Heat recovery temperature levels

At high temperatures, the main heat transfer mechanism is radiation, as in combustion boilers. Up to 400 ◦C radiation is still relevant, at lower temperatures, it is still not neglectable but accounts for less than 15% of heat transfer [10]. This heat at high temperature has multiple uses, such as superheating steam. Although it is not complicated to recover with common materials like regular steel, some precautions are needed. If the gas has corrosive components, such as chlorine, special materials might be required, while lower cold side temperatures might reduce high-temperature corrosion. But in general heat transfer at high temperatures in furnaces for radiative heat recovery is a well-known process easily implemented in the gasification process.

For lower temperatures, below 400 ◦C, gasification technologies often face a different problem. Different species contained in the raw gas can condense at a wide temperature range. If these components are sticky, surfaces start getting fouled. Fouling builds up over time and can become a major issue, decreasing the heat transfer first and possibly blocking flow circulation. Fouled equipment can be very hard to clean, demanding long and costly maintenance. If fouling builds up fast, this can provoke expensive maintenance costs and reduced greatly the availability of the plant.

One common solution for the fouling issue is to operate at temperatures above the condensation of components. This is usually below 350 ◦C for many gasification technologies [11], when most components have not reached the condensation point yet. To avoid this fouling problem, an alternative is to recover energy until species start to condense, and then cool down the gases fast applying a cooler substance that captures the undesired products (quenching and scrubbing). But this comes with a great efficiency loss because the gas is cooled down without recovering energy. Even though the same amount of energy is still available at lower temperatures, this decrease in temperature makes it hard to utilize.

The heat available for different temperatures is estimated in *Figure 1*. It is calculated from a biomass gasification reference [12], for raw gas concentrations, adjusting the thermal capacity for temperature. Until 350 ◦C more than 60% of the energy has been recovered, but from this point until 100 ◦C there is still more than 30% of energy available. If raw gases are quenched and scrubbed at these temperatures, a large amount of energy is lost.

The energy from the phase change of water below 100 ◦C is not included in the graph. After 100 ◦C more energy can be recovered, but this is below the dew point of water which will require extra considerations (explained later) for energy recovery. Many simple boilers operate above 100 ◦C to avoid this problem, so the same is considered for the gasification process.

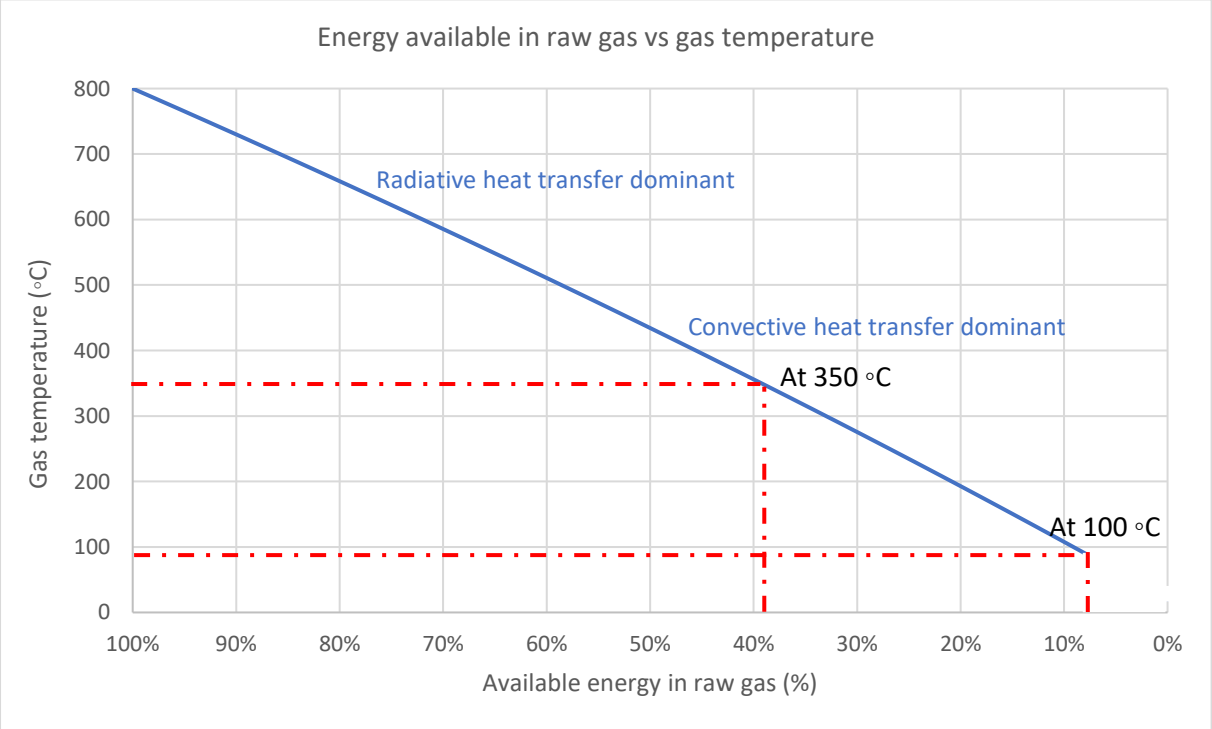


Figure 1. The energy available in raw gas vs gas temperature

The most common medium for heat exchange from gas is to water and steam, which could also be implemented for heat recovery in gasification processes. Other fluids are also used, but water is a well-known fluid, readily available, cheap and convenient [13]. Steam is not commonly used above 600 ◦C because of current material limits. Steam can be used both for cooling hot flue gases first and later to heat cold streams in the gasification process or electricity generation.

In the high-temperature range (400 – 800 ◦C) radiation is the dominant heat exchange mechanism. Heat is exchanged from hot gas in the outside of tube bundles to a fluid, usually steam, in the inside. Corrosion and material fatigue are usually the main concerns and limits for heat exchange at higher temperatures and pressures. If the hot gas contains a large number of particles high-temperature fouling might be an issue, but it is not common.

For lower temperatures (400 ◦C and below) convection is the main heat exchange mechanism. Multiple technologies for heat exchange are available, being plate heat and tube and shell the most common technologies. Suitable technologies depend on the temperatures levels, fluid properties, pollutants present, investment, maintenance costs and more. In this range, fouling is expected unless measures are implemented.

Heat transfer formulas

There are analytical calculations to estimate the heat transfer coefficient for different geometries. The tube and shell geometry are one of the most common systems for heat recovery, with plenty of experience and equipment operating in the industry. Typically, the calculations involve experimental coefficients that need to be obtained empirically, with references in the literature.

One of the most common heat exchangers is the counter flow. The hot flow enters in one end and the cold flow in the other, exchanging heat indirectly through a wall. This creates the largest temperature difference along the whole heat exchanger to improve heat transfer. For calculations, tubes from the counter-current heat exchanger are assumed to be circular and concentric [14].

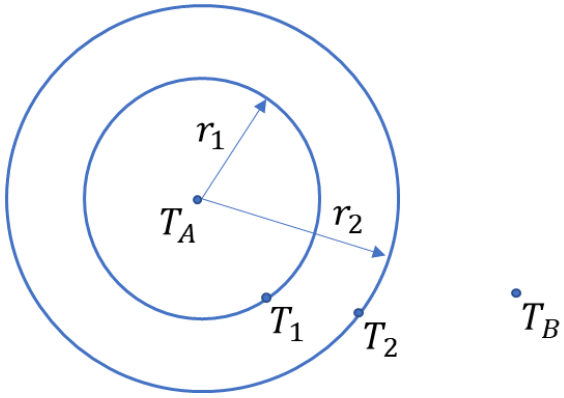


Figure 2. Temperatures concentric tubes

The heat exchange between the fluids is:

$$\dot{Q} = 2\,\pi\,r_2\,h_0\,(T_A - T_B) \tag{1}$$

$$\dot{Q}: heat\ transfer, h_0\ overall\ heat\ transfer\ coefficient, T_A: flow\ temperature\ A,$$

$$T_1: temperature\ at\ r_1, T_2: temperature\ at\ r_2, T_B: flow\ temperature\ B.$$

Where the overall heat transfer coefficient is defined as:

$$\frac{1}{h_0} = \frac{r_2}{r_1\, h_1} + \frac{r_2}{k}\ln\left(\frac{r_2}{r_1}\right) + \frac{1}{h_2} \tag{2}$$

h_1: $convective\ heat\ transfer\ coefficient\ inside$, h_2: $convective\ heat\ transfer\ coefficient\ outside$,

k: $conductive\ heat\ transfer\ coefficient$.

These equations are valid for the heat exchange in a specific segment of a tube where the flow temperatures are given. In a heat exchanger, the flow temperatures change over the length, so the temperature difference must be corrected.

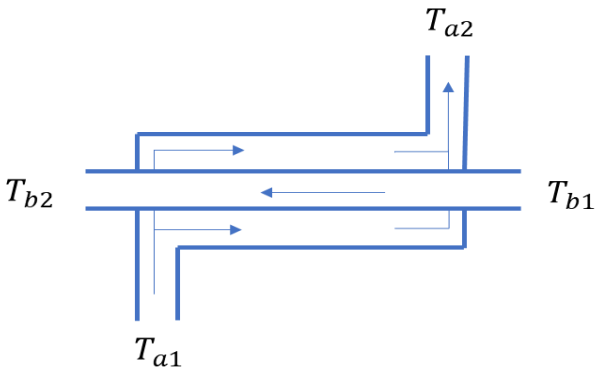


Figure 3. Countercurrent heat exchanger

The general case for the temperature change is defined for a counter-current heat exchanger, but it can also be applied for a constant wall temperature heat exchanger. This is helpful because the equation is valid even if T_{a1} and T_{a2} are constant or with a negligible difference.

$$\Delta\, T_{lm} = \frac{(T_{a1} - T_{b2}) - (T_{a2} - T_{b1})}{\ln\dfrac{(T_{a1} - T_{b2})}{(T_{a2} - T_{b1})}} \tag{3}$$

With the temperature relation for a counter-current heat exchanger, the general formula for heat exchange is defined.

$$\dot{Q} = h_0 \pi\, D\, L\, \Delta\, T_{lm} \tag{4}$$

For further information and a detailed explanation of the formulas and derivation, refer to [14].

Convective heat transfer coefficient

Depending on the flow characteristics the convective heat transfer coefficient can vary widely. This will affect the total heat transfer, as seen in equation (2). The inside and outside convective heat transfer are independent of each other, they depend instead on the properties of each flow. The first flow distinction is the condition of laminar or turbulent. Depending on this, different correlations obtain from experiments are used to calculate the convective heat transfer coefficient.

The correlations obtained from experiments give valuable information for specific situations, such as certain geometries. Depending on the geometry of interest, specific correlations should be used. It is possible to extrapolate results from a certain setup for another, but one must make a careful consideration of the experimental conditions and its applicability. The use of adimensional numbers has a major role in this analysis.

Reynolds number

The first relevant adimensional number is the Reynolds number. It permits to classify a flow as turbulent or laminar. Although this classification is not necessarily valid for every flow, it is good enough for many types.

$$Re = \frac{D\ v\ \rho}{\mu} \tag{5}$$

$$Re: Reynolds\ number, D: diameter, v: velocity, \rho: density, \mu: dynamic\ viscosity$$

The main difference between a turbulent and laminar flow for is the convective heat transfer mechanism. Laminar flow is characterized by different layers that are in contact with each other but don't necessarily mix. There is diffusion between the layers so species are transported in the radial direction to achieve equilibrium, but this process can be slow compared with the axial velocity of the flow. The main heat transport is done by conduction inside of the fluid.

For turbulent flow, there is a mixing force called eddy transport. This refers to swirls inside of the flow that forces mixing. These swirls are constantly created and destroyed in the flow, promoting a constant mixing of the fluid. These swirls are not stationary, they are constantly changing inside of the flow which would mean it is not in a steady-state. Because of the creation and dissipation rate of eddies can be similar, even though each swirl is a transient state, the average can be assumed as constant and a steady-state for many flow properties can be used.

Nusselt number (Convective heat transfer)

This number is a dimensional relation to the different heat transport mechanism. Described as the convective to conductive heat transfer of a fluid, it is to obtain from experimental data. With the fluid and flow properties, it is possible to derive the convective heat transfer coefficient.

$$Nu = \frac{h\ D}{k} \tag{6}$$

$$Nu: Nusselt\ number, h: convective\ heat\ coefficient, D: diameter, k: conductive\ heat\ coefficient$$

Because experiments are required to obtain this correlation, a distinction between laminar and turbulent flows is made. The heat transport mechanism is different for each case and the correlations of one experiment conditions are not relatable to another. Multiple correlations are depending on different authors and the main emphasis of each experiment to obtain the data. The use and accuracy of each correlation are usually explained by the authors.

For laminar conditions a proposed general correlation from [15] is:

$$Nu = 3.66 + \frac{0.0655\ Re\ Pr\ \frac{D}{L}}{1 + 0.04\left(Re\ Pr\ \frac{D}{L}\right)^{2/3}} \tag{7}$$

$$Nu: Nusselt\ number, D: tube\ diameter, L: tube\ length, Pr: Prandlt\ number$$

Where Pr is defined as a new adimensional number, the Prandtl number.

$$Pr = \frac{\mu\, C_p}{k} \tag{8}$$

This correlation is valid for short or long tubes, and as the tube becomes long compared to the diameter the correlation tends to 3,66. For turbulent conditions, a proposed general correlation is the following [15].

$$Nu = \frac{\left(\frac{f}{8}\right)(Re - 1000)\, Pr}{1 + 12.7\, \left(\frac{f}{8}\right)^{1/2} (Pr^{2/3} - 1)} \tag{9}$$

$Nu: Nusselt\ number, D: tube\ diameter, L: tube\ length, Pr: Prandlt\ number, f: friction\ factor$

Where f is the friction factor defined as [15]:

$$f = \frac{1}{(0{,}79 \ln(Re) - 1.64)^2} \tag{10}$$

This correlation is applicable for smooth tubes and Re number above 3000. Also, it is not applicable for Pr = 1 but this is a rare case for fluids. In both cases, laminar and turbulent, the flow takes some distance to develop hydrodynamically. For turbulent flows, it is usually between 10 – 15 diameters, while for laminar flows it depends on the following relation [16].

$$\frac{L}{D} = 0.05 * Re * Pr \tag{11}$$

Biot number (heat transfer inside a body)

This a dimensional number gives a ratio between the heat transfer inside a body and the heat transfer in the surface of the same body [14]. If the Biot number is much smaller than 1, a uniform temperature can be assumed. This is the case for heat exchange in many solid objects with good conductivity, such as metals. The convective heat transfer in the surface is much smaller than the conductive heat transfer inside of the body, so a constant surface temperature can be assumed. In this case, the heat transfer calculations are simplified, neglecting temperature differences inside of the body for heat transfer calculations.

$$Bi = L * \frac{h}{k} \tag{12}$$

$Bi: Biot\ number, L: characteristic\ length, h: convective\ heat\ trasnfer\ coefficient,$

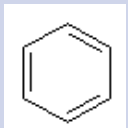
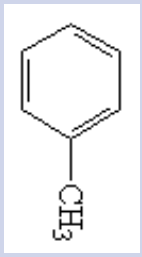
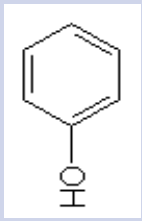
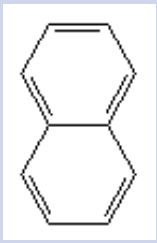
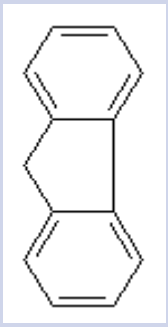
$k: thermal\ conductivyty$

Tar definition

The liquid fraction of gasification is known as tars which is a hydrocarbon, but the exact definition of tar can change between authors. The definition is ambiguous as it consists of multiple organic species. Tar is generally understood as with a wide variety of hydrocarbons obtained from the thermal destruction of organic materials. Following the definition in [6], tars are here defined as all organic species with a higher boiling point than benzene.

In general, these organic species are composed of aromatic cycles, cyclic structures based on carbon bonded between them forming cycles and completing their bonds with hydrogen. Other species might be present, such as oxygen or nitrogen. When oxygen with hydrogen is present the molecules are often referred to as alcohols or phenols. If two or more aromatic cycles are present, they are called polyaromatic hydrocarbons (PAH).

Table 1. Common tar types

Specie	Benzene	Toluene	Phenol	Naphthalene	Fluorene
Elementary composition	C_6H_6	C7H8	C6H6O	$C_{10}H_8$	$C_{13}H_{10}$
Molecular weight (g/mol)	78.11	92.14	94.11	128.17	166.22
Structure					

For more tar species, an extended description is available in [17].

Different authors define tars depending on the interest of the investigation. Often, they are only measured in the total amount of tar, although the species involved can be very different. The classification used here is based on the dew point. The Energy Research Centre of the Netherland (ECN) classification system is used, with different classes to group tars with similar characteristics.

Tar classification

This classification is based on the physical properties of tars downstream of the gasification process [18]. Condensation behaviour was the first characteristics relevant for fouling tar classification. Heterogenous components such as oxygen or nitrogen changed the solubility of tars in water, so it was also included in the classification system.

Table 2. ECN classification system [18]

CLASSIFICATION	NAME	REPRESENTATIVE SPECIES	DESCRIPTION
CLASS 1	GC-undetectable	Unknown.	Unidentified too heavy species, produced in low concentrations with high dew point.
CLASS 2	Heterocyclic aromatics	Phenol, quinoline.	Heterocyclic components, including oxygen and nitrogen. High water solubility due to polarity.
CLASS 3	Aromatics (1 ring)	Benzene, toluene.	Aromatic hydrocarbons. Low dew point and low water solubility.
CLASS 4	Light PAH (2-3 ring)	Naphthalene, fluorene.	Light polyaromatic hydrocarbons. Considerable concentration in raw gas, relevant dew point.
CLASS 5	Heavy PAH (3-8 ring)	Pyrene, coronene.	Heavy polyaromatic hydrocarbons. Low concentrations and high dew points.

Relevant temperatures

Boiling point

The boiling point of a pure liquid is the temperature for a given pressure for phase change into a gas. The boiling point for pure liquids depends only on the temperature and pressure, for mixes depends also on the amount of each specie. For a pure gas condensing the same concept applies, for a given temperature and pressure it will condense into a liquid.

In many real situations, there are mixtures of different components. This is the case for example of humidity in the air. Although the boiling point of water is much higher than the ambient temperature, there are H_2O molecules in the air. This is due to partial pressure equilibrium for air and water, where the dew point sets the condensation temperature for the dilute phase to condense into a liquid.

Dew point

Dew point is defined as the temperature when a diluted phase starts to change phase, forming a liquid. The dew point for given concentrations is at a given temperature, which means at that point the phase change starts until a new equilibrium is reached between the partial pressure of both components.

For a heat exchanger, the dew point temperature will mean the start of the condensation for certain concentrations (or partial pressures). When the concentration of the dilute species decreases, changing phase into liquid, and a new equilibrium between partial pressures will be obtained. If the temperature keeps decreasing, equilibrium will be again reached at lower concentrations.

The onset of condensation is at a given temperature, and it is not going to stop until the condensing species reaches a new equilibrium. This does not mean the condensation rate will remain constant at different temperatures, only that condensation will happen at a wide range of temperatures.

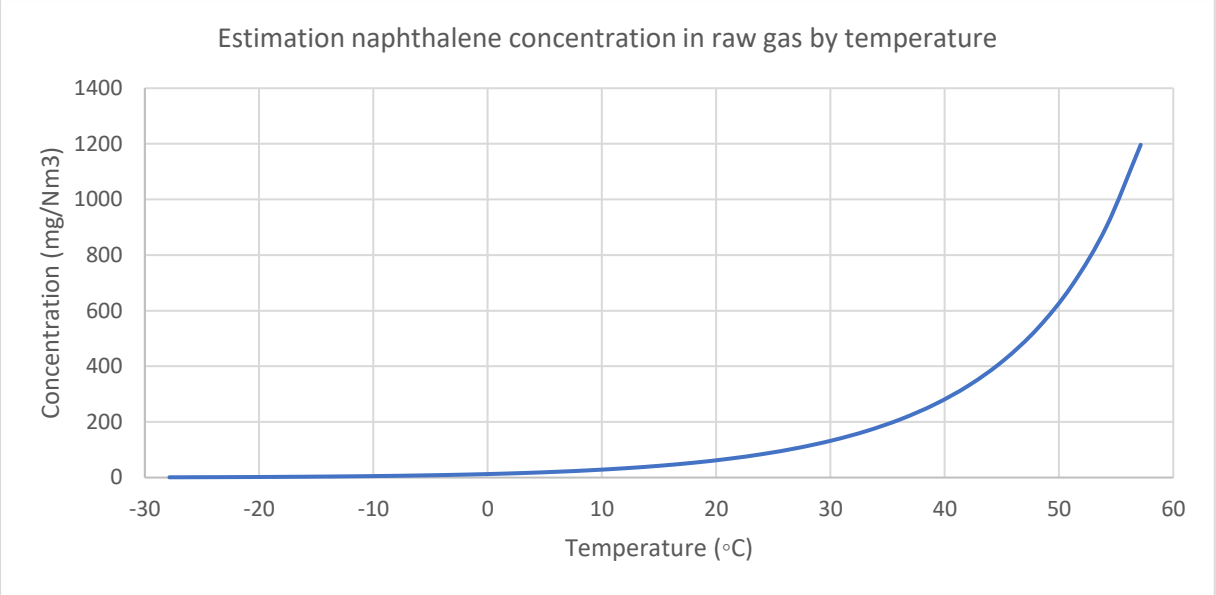


Figure 4.Estimation naphthalene concentration in raw gas by temperature

In *Figure 4* a model for the concentration of naphthalene, a common tar, is calculated for different temperatures in raw gas from a gasification process [19]. The boiling point of naphthalene is 218 ◦C, but at 50 ◦C there is still a large amount of naphthalene diluted in the raw gas. This illustrates the difference between the boiling point and dew point.

At higher temperatures, the gas can dilute more naphthalene. High naphthalene concentration at high temperatures, close to the boiling point, is uncommon because the naphthalene production from gasification is usually lower for most processes. This concept is relevant for energy recovery because tars contained in raw gas will have a dew point depending on the concentration. For a given tar concentration, once the dew point is reached tars will condense until equilibrium for that temperature, but for lower temperatures condensation of tars will continue. Heavy tar species might condense only at high temperatures ranges, decreasing considerably their concentration at lower temperatures. The opposite is true for light species, at high temperatures will not condense, only to start at lower temperatures.

A special case to consider is the water content and condensation. Depending on the gasification process, the raw gas might consist of a large share of H_2O. At temperatures above the boiling point (100 ◦C) all H_2O will be in gas phase. Once the temperature drops below the boiling point, water will start condensing, until equilibrium is reached with some water remaining in gas phase. After the boiling point of water, there will be a large decrease in water vapour pressure in the raw gas. This will be compensated by the remaining gases which will increase their partial pressure. For permanent gases, this increase in partial pressure might not be relevant, but for tars species, it will. Because condensation depends on both temperature and partial pressure, when water condenses, many tars species will increase the partial pressure. This could provoke them to condense fast until reaching a new equilibrium. This effect is only relevant for H_2O, as other common permanent gases such as CO, CO_2, CH_4 and N_2 have a much lower boiling point.

Tar dew point calculator

A model to evaluate the tar dew point was built by ECN, which is available at [17]. The model is based on ideal gas behaviour, from Raoult´s Law. This is an ideal assumption that the partial pressure of each component is equal to the vapour pressure of the pure liquid component multiplied by its concentration in moles. The main assumption of this ideal law is that partial pressure of similar species

has the same behaviour as different species. Raoult´s law should be a reasonable approximation for mixtures of similar compounds [20].

Because tars from raw gas are expected to have a large variation, Raoult´s law might not be applicable. A validation method was used for the model to check this assumption. The validation consisted on extracting raw gas from a lab gasifier to analyse the real dew point [21]. The system developed by Mitchel Instruments consisted of an optical sensor that measured the light intensity over a mirror where raw gas was flowing. The gas sample was slowly cooled until the optical sensor measured a difference due to species condensing on the glass surface. This point was defined as the dew point of the raw gas extracted. The model was validated in the 100 – 170 ◦C with a reported error of ±3 ◦C. For higher temperatures the error increases, for lower temperatures validation was not done but the error is expected to be the same or lower.

The tar dew point calculator was used to estimate the dew point of experimental samples. Introducing the concentration of each specie in milligrams per normal metric cubic returns an estimated dew point. The model has an input of 34 species if one of them is unknown, the box is left blank. Thanks to the possibility of importing and exporting concentrations using a text file, the dew point estimations were easily implemented.

A general impression of tar classes and dew points was estimated using the model in [18] as shown in the following graph. This gives a first impression of the dew point depending on the different classes and their concentration.

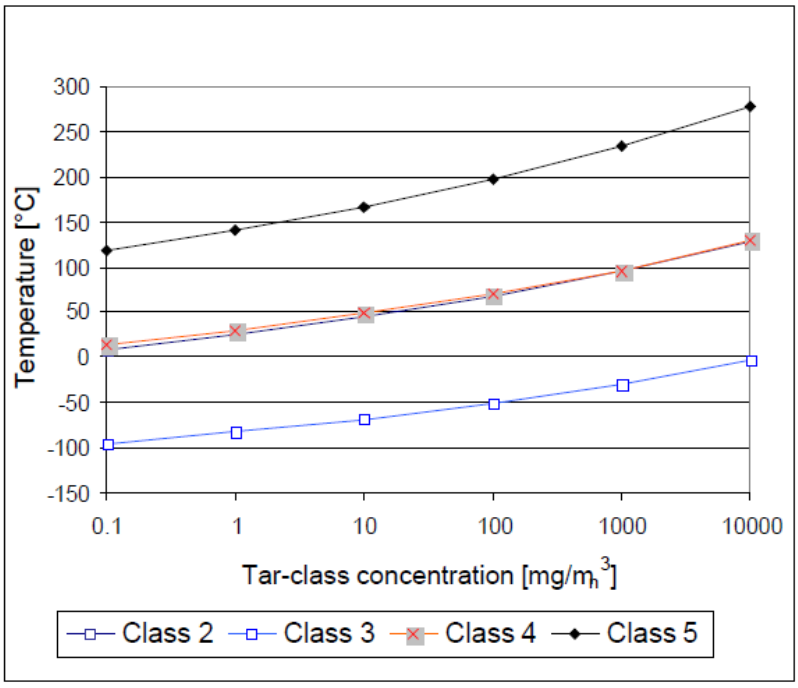


Figure 5. Tar dew point at atmospheric pressure vs tar concentration for different tar classes [18]

Tar treatment measures

Tar fouling represents a major problem for many gasification processes, but there are measures to prevent or reduce this problem. Measures to deal with tars are generally classified in two types. Primary measures which focus on reducing the amount of tars generated in the gasification process, and secondary measures that deal with tars once in the raw gas. Most processes use both types of measures to guarantee the low tar levels required.

Primary measures

Primary measures are focused on the operating conditions of gasification process. Multiple gasification parameters affect the tar production and distribution of species. The most relevant are usually temperature and catalysts, although there are many others [18]. Gasification at high temperatures, above 700 ◦C, will decompose the material, breaking bonds and reducing the size of molecules. This will promote the number of small size molecules, but will also drive the formation of larger polyaromatic hydrocarbons by polymerization. Higher temperatures will shift the concentration from average medium molecular sizes to a large amount of low molecular sizes and small amounts of large molecular sizes.

High-temperature gasification processes usually create a wide range of molecules, as the size reduction and polymerization operate over a wide range of molecular sizes. Catalytic materials can reduce further the size of the molecule and polymerization, with the possibility to choose the catalytic type to promote certain reactions. Catalytic materials for tar reduction can be applied to avoid the formation of large molecules, reducing the quantity of large tars.

One of the most popular gasification technologies is based in fluidized beds. A reactor with a fine solid material called bed is fluidized from the bottom with different gases. The solid bed material starts to behave as a liquid because of the gas going through it. This fluidized bed reactor is maintained at high temperatures for gasification. The main advantages of this technology are the high heat transfer from the bed material and the possibility to add catalyst materials directly into the bed. These primary measures help greatly to decrease the tar concentration during gasification at high temperatures [22].

Secondary measures

Secondary measures focus on reducing the fouling caused by tars that have already been generated during gasification. These measures are implemented at lower temperatures, most times after recovering heat from the raw gas before fouling starts. There are multiple proposals for tar capture and cleaning, often using two different systems to reduce the tar concentration [23].

One control system that works with two different systems and seems to have good results is the Olga system [24]. First, it condenses heavy tars at 350 ◦C, captures and recycles them into the gasifier. A second step scrubs the gas until 20 ◦C with oil, to later regenerate the scrubbing oil and again recirculates these light tars into the gasifier. Other technology in operation currently is Enerkem, a biorefinery from Canada with multiple projects around the world [25]. Raw gases are scrubbed with a liquid, this time water, condensing tars and capturing them. Both technologies reduce the temperature of the raw gas before fouling starts, losing the high-temperature energy decreasing the process efficiency.

GoBiGas project

The current work is inspired in the Gobigas, biomass gasification for methane project [4]. Using a dual fluidized bed, biomass was gasified to obtain gas, which was transformed via catalytic reactions into methane for the natural gas grid network in Gothenburg. The raw gas was cooled to 160 ◦C, in the fouling range, using tube heat exchangers. Without any measures, after a few hours, the heat exchanger had accumulated a large amount of fouling, and the process had to be stopped for cleaning. This problem was solved using primary measures, with the downside that decreased the operational flexibility of the process, which needed to be operated with very controlled settings.

This problem was the motivation to investigate fouling and dew point temperature of tars. Finding an acceptable temperature where fouling is not too serious, good thermal efficiency could be achieved without jeopardizing the operation. Secondary measures would still be needed to deal with the tars after heat recovery at low temperatures, but the efficiency of the plant could be preserved. The alternative would be scrubbing directly from above the start of the fouling temperature.

Laboratory experiments

To investigate the dew point temperature of a process such as Gobigas, the original idea was to replicate gasification conditions in a laboratory reactor to assess fouling at different temperatures. For tars to foul, they need to condense and stick to a surface. This can be either done with wall condensation directly or indirectly with aerosol formation until they hit surfaces and stick.

But replicating these conditions in a lab reactor was not possible. One relevant parameter which could not be replicated was the turbulence, which affects the temperature profile distribution and mixing of the gas. With high turbulence, the flow has a similar temperature profile between the walls and bulk. In the lab reactor, the raw gas was not enough to replicate turbulent conditions, being in the laminar range instead. This would mean the temperature distribution profile would be different in the lab reactor from an industrial reactor. This would mean the fouling conditions created in the laboratory could not be representative of a real process.

Instead, an experimental analysis only of the dew point was made, explained in the next chapter. The dew point of raw gas containing tars can be used as a reference were tar fouling could begin after condensation starts, although it is not guaranteed it will happen.

Method: Dew point experimental analysis

To understand the tar fouling in a gasification process, the first step is to identify the dew point of tars in the flow. When tars have change phase from gas to liquid, depending on the partial pressure and temperature, the tars may start adhering to surfaces as liquids. Before condensation, no fouling should occur.

Different gasification conditions will have different amounts of tars and permanent gases, which will determine the dew point. For the design of a heat exchange process, it is of interest to know when this species will condense and possibly start fouling the equipment. Before tars have condensed it can be assumed no fouling will occur. Even though tars have condensed it is not sure they will start fouling on surfaces immediately as condensation could be as aerosols that might remain in the flow instead of adhering to walls.

Knowing the dew point, depending on the species concentrations and temperatures, is a relevant parameter for heat exchange design. Special attention should be put into possible fouling that depends on the tar concentration and temperatures, which could affect greatly the operation and availability of a process. This motivates the second relevant question:

Second specific aim

Which is the dew point where tars might start fouling?

The experiments are aimed to identify the dew point when tars start condensing in the raw gas for different gasification conditions. From this temperature on fouling is expected, before this point tars should stay in gaseous state and no major fouling should occur.

Procedure

1. Production of raw gas with tars from a gasification process in a bubbling fluidized bed reactor.
2. Determination of baseline tars from raw gas at high temperatures.
3. Gas cooling using indirect heat transfer. Condensation of tars depending on the gas temperature. Tar retention over tube surface and special material.
4. Analysis of total tars for each temperature. Calculate the difference in tar concentration from baseline to determine condensed tars depending on the gas temperature.

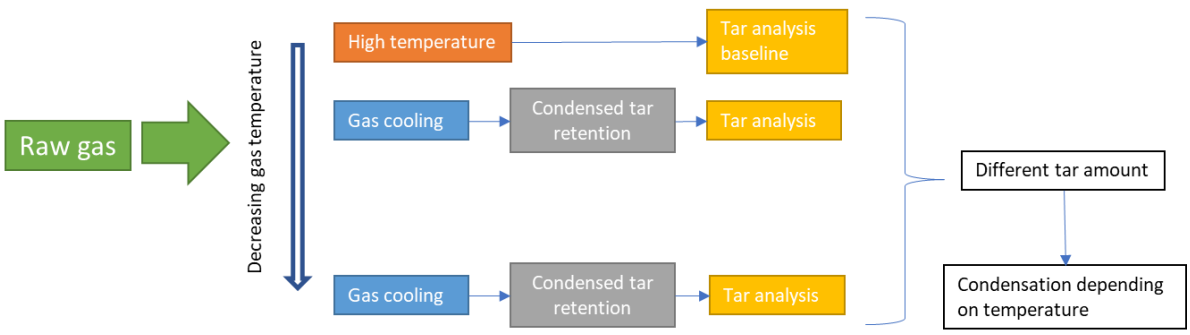


Figure 6. Diagram procedure experimental dew point analysis

Laboratory equipment

Fluidized bed reactor

The gasification process was done in a laboratory-scale bubbling fluidized bed. It consisted of a vertical steel tube heated externally with electric resistances and fluidized from the bottom with different gas mixtures. The bed material could be changed depending on the gasification conditions. The whole system operated at ambient pressure, the gases generated leave at the top of the reactor and raw gas samples could be extracted at different heights.

Gases entered through a wind box in the bottom, which created a pressure drop to distribute evenly the gases along the bed. The fluidization conditions depend on the amount and type of gases. The equipment is designed to operate as a bubbling fluidized bed. This requires a minimum fluidization velocity to operate and a maximum fluidization velocity to avoid carrying away particles, as in a circulating fluidized bed.

The external heating of the reactor allowed the process to operate at a constant temperature. Many gasification reactions are endothermic, with an energy requirement for the process to operate at

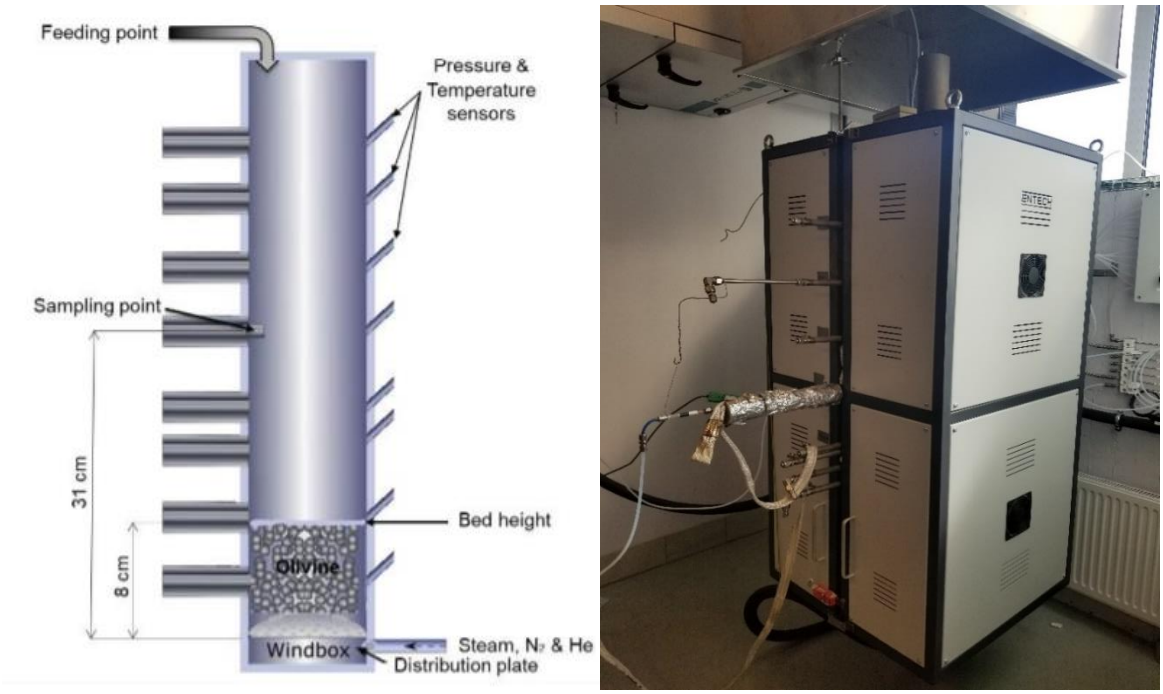


Figure 7. Left bench reactor used for gasification tests [44], picture of the reactor

steady state. The temperature of the reactor is measured continuously at different points along the vertical axis.

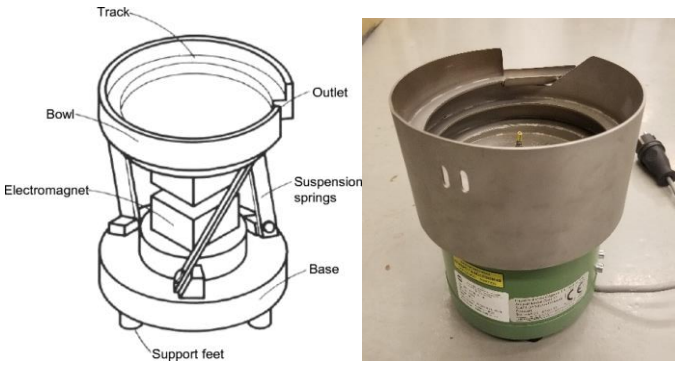
The solid material for gasification is fed from the top of the reactor. The feeding rate was a relevant aspect as it determines the quantity of gasification products generated. The dew point will depend on the concentrations of different species instantly, so the feeding should be as stable as possible.

Batch mode

The easiest solution for feeding is in batch mode, feeding by hand a sample. In this mode the gasification products will not achieve a steady state, instead the gas production will depend on the amount of solid at each moment during the gasification process. The tar species concentration would change over time, as the dew point of the gas mixture.

Continuous mode: Automatic feeding

A steady-state for the tar species partial pressure is required to analyse the dew point, which demands



a steady feeding rate. For this purpose, there is a vibratory feeding system. It consists of a vibrating system mounted on springs that makes a bowl move forward and backwards constantly. Inside the drum, there is an incline helix around the edges. With each forward movement, the solid particles move forward. With the backward movements, the particles don´t have enough time to go back to the original position before another cycle starts. This makes the material move forward constantly, even moving up against gravity. This system is used typically in manufacturing industries were different pieces need to be oriented or transported continuously with special conditions.

Several aspects determine the feeding rate. First, a voltage regulator controls the vibrating speed of the system and the particles. Higher voltages mean higher speeds. For each material there is a minimum voltage, commonly around 120 V, where the material will not move. Second, the material size and shape will influence how it moves in the bowl. Smaller particles tend to move more uniformly while larger particles are prone to get stuck. Third the amount of material in the bowl, with a full bowl the feeding rate increases. In a certain range, not too full or empty, the feeding is constant.

All these conditions make the feeding rate not constant enough for experiments. During operation, it was noted that the feeding rate changed quite significantly, even to twice the starting rate. One possible reason could be the voltage variation of the laboratory grid. The feeding rate was sensible to the voltage regulator, with a 5 V difference increasing to almost twice the feeding rate. In the electrical grid, the voltage was measured to vary up to 5 V during the day. This would need to be validated properly before implementing a solution.

Figure 8. Left diagram of a vibratory feeder [45], right picture of the lab feeder

Continuous mode: Hand feeding

Instead, a continuous feeding by hand was implemented for more accurate feeding rate. The material was weighed and fed every 20 seconds. The feeding was done for a few minutes before any sample was taken. Steady-state conditions were assumed using a continuous gas analyser for permanent gases, feeding until achieving stable concentrations for the main gases such as CH4, N2, CO and CO2.

Gas sampling

A sample of gases was extracted from the reactor. The gas contains multiple species, including permanent gases and different tars. Different techniques can be used to measure the amount of each component.

The volume extracted for the measurements is an important parameter for the experiments as it will be used to calculate the concentration of species. Because of the nature of most tar analysis, the concentration of each species in the gas is measured indirectly. Tars are captured and diluted in liquid

to analyse each component separately. For permanent gases, this is not as relevant, as the concentration of each one is calculated directly from a gas sample.

Two alternatives for gas samples were available. First using a vacuum pump and second a syringe connected to a hydraulic system.

Vacuum pump

The flow extraction from the vacuum pump could be adjusted with a valve, regulating the pressure drop that affects the total flow rate. The sampling line connected to the reactor had a total volume of 80 ml, so for each measurement to be accurate, the flow had to be running before taking a sample. Increasing the sampling volume decrease any error from the sampling process, but it was limited to the amount of flow the tar method could capture and possible infiltrations of ambient air from the top of the reactor.

The main problem with the vacuum pump was the inaccuracy for the flow extracted. The total volume depended on the flow rate, that was very sensible to the valve adjustment. The total volume extracted could be measured after filling the gas bag, but only after measuring the gas composition in them, which extracted part of the gas volume and reduced the accuracy. Because the solution to measure the volume extracted in the gas bag was not accurate, a different solution was used.

Syringe robot

The second alternative was a syringe connected to a hydraulic system, powered with compress air. The syringe was retracted automatically with a constant speed regulated with the hydraulic system. The sampling volume was constant, syringe volume of 100 ml, and it was possible to adjust the sampling time from a few seconds to more than a minute. This system was very accurate and stable during sampling.

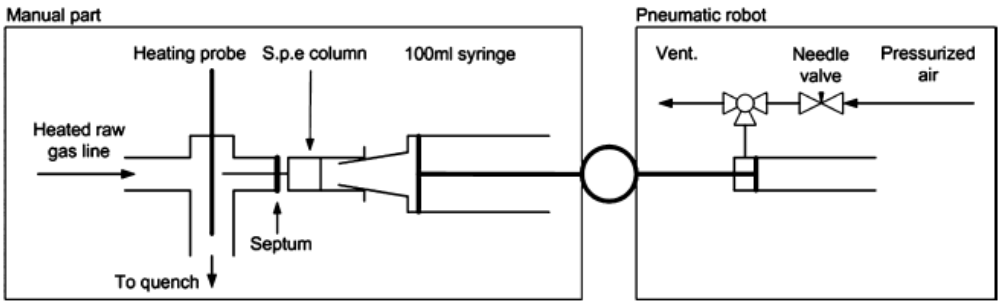


Figure 9. Left SPA sample point, spe column, and manual part of the extraction device. Right pneumatic robot for consistent sample extraction [26].

The sample volume was small, limited to the syringe volume. It was possible to take multiple samples, emptying the gas sample in a gas bag multiple times to increase the sample volume. The error from the sampling line volume decreased implementing a continuous gas extraction close to the flow extraction for tar measurement.

Helium tracing

During the gasification process, a small flow of helium is added to the fluidization gases in the wind box. The added helium is used to calculate the total dry gas flow and the carbon yield of the fuel. This calculation is based on the amount of helium injected in the reactor (0,05 lt/min), the sampling time and the amount of helium extracted in the sampling.

Tar Measurement

Gas Chromatography Columns

Different methods are available for tar measurement. Most of them involve using a Gas Chromatography (GC), where tars are diluted in liquid for analysis. In the GC, components are separated and can be analyzed independently over time with different instruments.

The principle of a GC is the process of separation of a mixture passing through columns [27]. A liquid containing the components to analyse is injected in the entrance of the column. This is evaporated and carried by another gas called carrier. Depending on the chemical and physical properties of different species will be the speed and time to go through the column. The species will interact with the solid phase of the column, inhibiting the motion via adsorption and desorption. The strength of the adsorption will depend on the specie, with stronger adsorption retaining the specie for a longer time.

Calibrating the GC previously it is possible to know the time for each species to go through the columns or retention time. A detector at the end of the column measures the amount of each component.

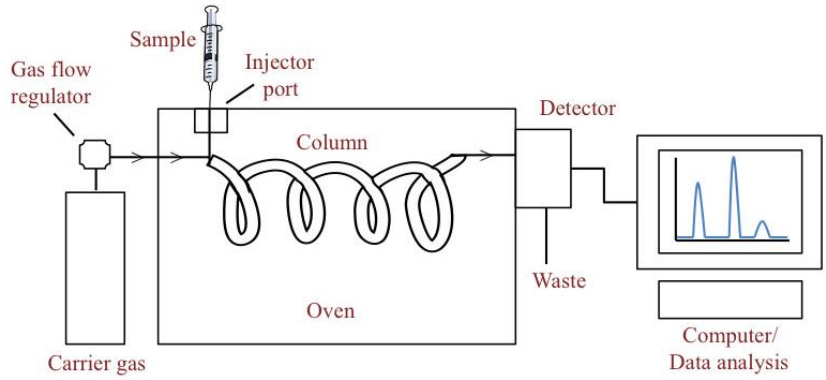


Figure 10. Diagram of gas chromatography [28]

The column temperature affects the rate of different species passing through the column. Heating the columns will make the components go faster. This is used to allow adequate separation of components decreasing the total time of analysis. Early components are analysed at lower temperatures as they move fast through the columns. For late components that would take longer to go through the column, the system is heated increasing the travel speed and reducing the total analysis time. When the heating mechanism is activated, the columns start operating as distillation columns, relating the time from the analysis to the boiling point of species. Those species with a higher boiling point will stay longer in the column until their boiling point is reached, species with a lower boiling point will go out faster.

Flame Ionization Detector

At the end of the columns, a gas detector is used to analyse the gases. Each specie will be drag by the carrier gas at different speeds, so the system can detect the amount of each specie depending on the time. A Flame Ionization Detector (FID) is used to quantify the amount of each specie by oxidizing the hydrocarbons and measuring the number of ions generated. This technology is very accurate for aliphatic hydrocarbons, but losses accuracy for aromatic and heterocyclic hydrocarbons. Even if the GC can be very accurate, it requires careful calibration for each specie of interest to identify them. The GC should be calibrated depending on a possible range of components to analyse.

SPA method

This method uses a solid-phase adsorption material to capture tars. This material is inside of a syringe, where gas flow is forced through. Tars are adsorbed in the solid phase to be later eluted, dissolving them in a liquid.

The measured flow should be isokinetic, a heterogeneous distribution of gas components, to ensure the sample taken has the same concentration as the gas. If the sample is from a large flow, it should not have aerosols or droplets, which could over or underrepresent the concentration of certain species. For tars, this is avoided sampling gases that are above the tar dew point, usually between 300 – 400 ◦C.

Multiple tests for SPA method were reported in [26]. Collection of the gas sample was found to be the most important error, while not proper treatment and storage have an effect sub representing the more volatile tar components.

The main advantage of this method is its simplicity. Samples can be obtained easily, without the need for any other chemicals as in other methods. The syringe containing the SPA must be stored in cold conditions before eluting to decrease the loss of volatile tars. It is recommended to decrease as much as possible the time between sampling and elution to avoid tar desorption, especially lightweight hydrocarbons. For storage before elution, the syringe containing the SPA should be sealed and kept cold, at -20 ◦C.

Tar protocol

This protocol consists of a standard method for the measurement of organic compounds from the gasification process. The Protocol developed works accurately over a large range of concentrations and conditions, from 1 mg/Nm3 to 100 g/Nm3 [29].

The gas is first cleaned from particulate matter in a heated filter, taking the gas sample with isokinetic conditions. Then it is quenched over several impinger bottles, where tars are trapped, using a solvent such as isopropanol. Only one bottle is not enough to capture all tars, so more need to be in place.

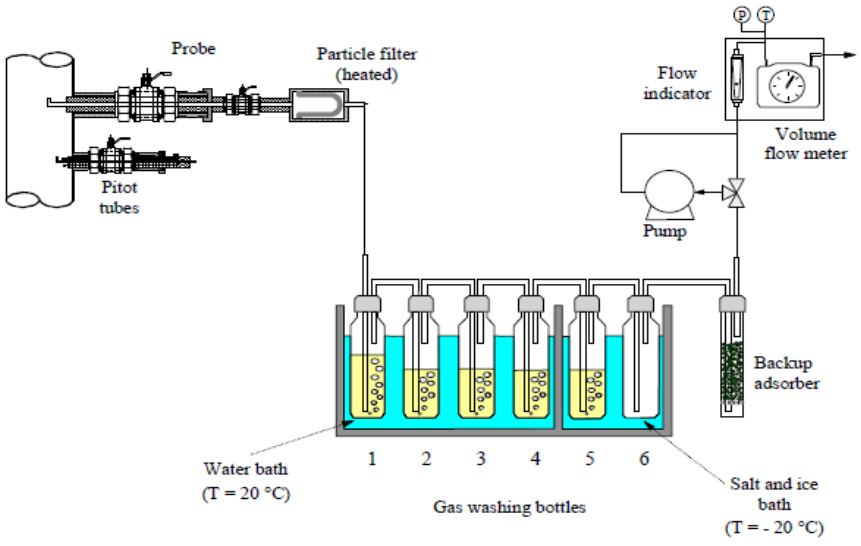


Figure 11. Module 3 of the sampling train: impinger bottles and VOC collector [29]

The tar content is measured using two methods, concentration of gravimetric tars from evaporation residue at standard conditions and individual components using GC. The guideline is expected to help

as a comparison method for different gasification technologies, mainly focused on biomass technologies.

The Tar Protocol is designed to be a reference for tar measurements. Several alternative measurements are usually prefered instead, as they are easier to use. Most of these alternatives cover a range of the Tar Protocol spectrum, but not the whole range. This is the case for SPA, which covers the range from indene to coronene. The Tar Protocol should be used when appropriate, otherwise simpler methods as SPA are easier to apply on-site.

Permanent gases

The gases from the reactor are measured using a micro gas chromatograph (μGC). The equipment used was developed to measure permanent gases and benzene in the GoBiGas project. It consists of μGC with 3 columns to separate the gases and a Thermal Conductivity Detector (TCD) calibrated for low molecular weight components, ranging from H2 to C3Hx.

The Thermal Conductivity Detector uses the thermal conductivity of different gases to identify them. The gases are eluted in a gas carrier and separated in the columns. The thermal conductivity of the gas and eluate is measured with an electrically heated resistance, which changes its resistivity depending on the temperature. This resistivity change can be calibrated to determine the type and concentration of gas. Each gas separated previously in the columns and can be measured independently.

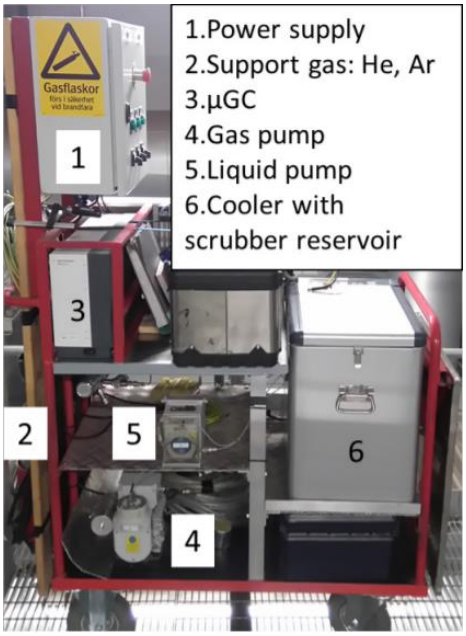


Figure 12. Mobile μGC used for measurements at GoBiGas [30]

Summary of Gas Analysis

The method used for gas and tars analysis was (μGC) for permanent gases and SPA for tar species. Permanent gases are measured in gas state, directly from a gasbag. Tar species were captured with SPA, cooled after sampling, and later eluted for GC analysis. This method was preferred as it was readily available in the laboratory with plenty of experience using it in the Chalmers laboratory.

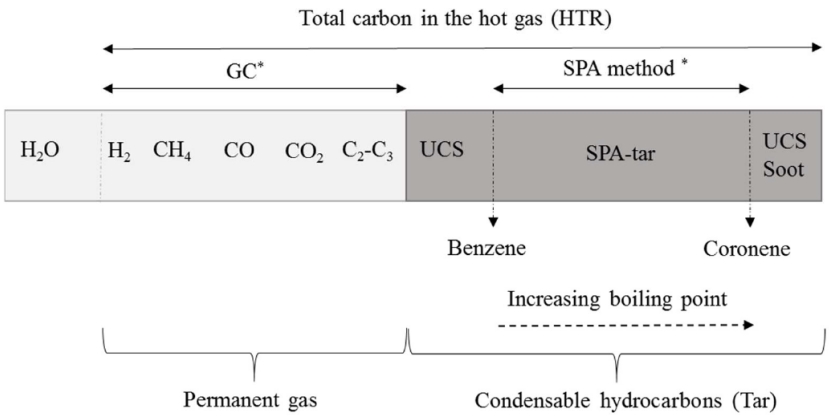


Figure 13. raw gas spectrum and measurements methods [22]

Gas cooling during sampling

The gas sample extracted from the reactor was cooled at different temperatures. The sampling probe consisted of a steel tube that was going directly into the reactor in one end and into a suction system in the other. The gas going through the sample probe was cooled down to the wall temperature.

The probe was heated with an electric resistance and cover in insulation to decrease heat losses. Adjusting the electric heating it was possible to set different wall temperatures, setting the gas temperature. The gas temperature is one of the main aspects of the experiments, so careful attention was put on the heat exchange between the wall and gas for the experiments.

Gas properties

The gas sample had a large temperature variation, from the reactor to the sampling device. The gas properties change with temperature, which affects the heat transfer calculations. It is possible to assume average values for the properties, but the temperature range was too large, so it was adjusted for different ranges.

Density

The gas density was adjusted using the Ideal Gas Law

$$P_i * V = n_i * R * T$$

$$P_i: partial\ pressure\ specie\ i, V: volume, n_i: mole\ specie\ i, R: universal\ gas\ constant,$$

$$T: temperature$$

For gases at high temperatures and low pressures, the assumption is valid [31]. This is the case for the experiments, where large molecules like tars are a minor fraction, and the permanent gases, the major fraction, do not react with each other in the sampling probe. For other conditions such as low temperatures or higher pressures, these assumptions are not valid and the Real Gas Law or other should be used instead.

Dynamic viscosity

The dynamic viscosity of gases is dependent on temperature. This property changes considerably depending on the gas temperature at the reactor and the end of the sampling probe. A polynomial regression of the major gases present was adjusted for the temperature range from [32]. The total dynamic viscosity was the average weight of each one by mass.

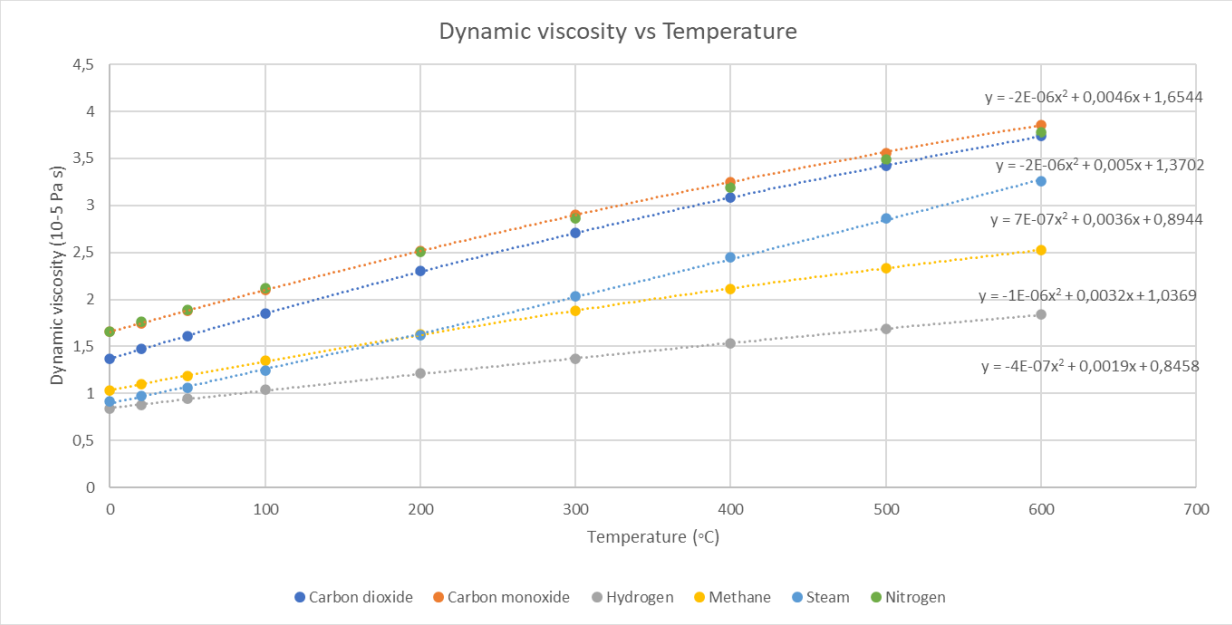


Figure 14. Dynamic viscosity vs temperature

Thermal conductivity

The thermal conductivity is also dependant on temperature, from [33]. For this property, a linear regression was a better fit, instead of the polynomial used previously. The thermal conductivity is related to the mean free path and the mean velocity of the particles. Thermal conductivity of small particles, like hydrogen, is much higher than other larger particles. Although thermal conductivity should be obtained experimentally, an approximation is made using the average of each specie.

Specific heat capacity

The gas sample extraction is assumed to have constant pressure. The pressure should be slighter lower than atmospheric and any pressure loss in the pipe is neglected as it would be very small compared to ambient pressure. The isobaric specific heat for gases is used then for the calculations [34], which again is dependent on temperature.

Heat transfer set up

The sampling probe temperature was set with an electric heater. The temperature of the wall was measured continuously and adjusted manually, with a potentiometer for the electric resistance providing the heat. Each time after adjusting the electric heating, some minutes were left for the temperature to stabilize at the desired level.

The thermal inertia of the steel tube was big enough to maintain a constant temperature through the sampling. The gas flow and heat delivered to the tube was too low to significantly affect the probe temperature. During sampling at different temperatures, no significant change of the probe temperature was noted. In case the sampling flow was increased, the heat transfer from the gases to the sampling probe would increase, possibly making a significant difference in the wall temperature.

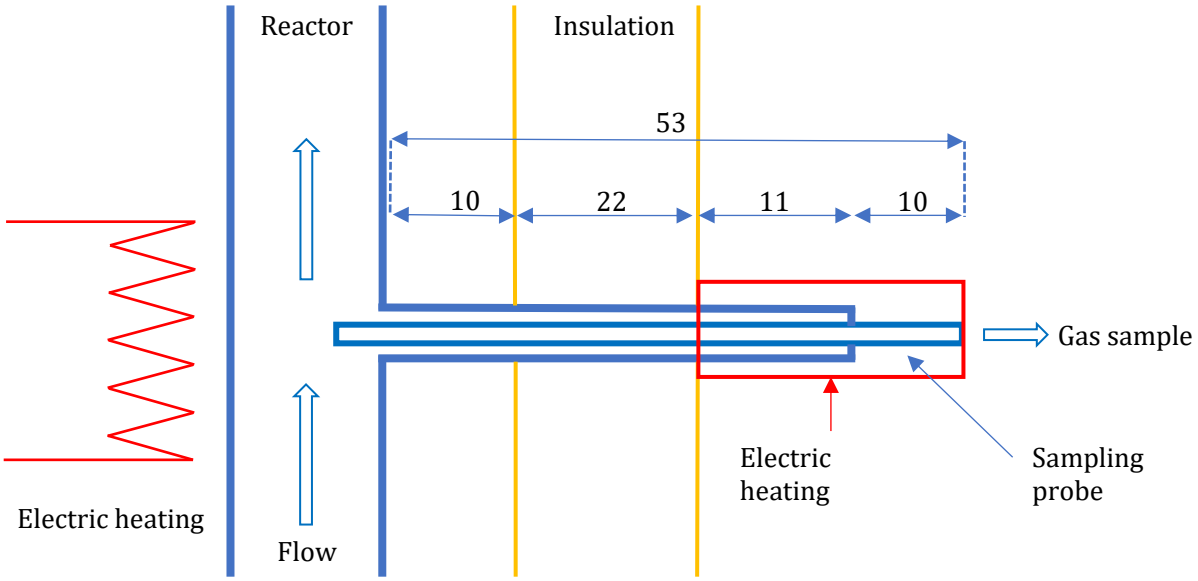


Figure 15. Experimental set up for gas extraction, all measures in centimetres

Heat exchange calculations from correlations

The heat exchange between the gases and probe wall was calculated with heat transfer correlations. The objective of the calculations was to validate if the flow had a similar temperature to the wall. The probe length could be extended if required for more heat exchange.

The geometry of the experimental set up was simplified for the calculations. Different areas were exposed to different heat transfer conditions. First, part of the probe was exposed to the reactor, were radiation heat transfer is significant. Then between the reactor and the insulation, the sample probe was covered with a tube, which was heated directly with radiation from the electric resistance. In the insulation, between the reactor and exterior, the heat dissipation through conduction was expected to be low but unknown. Finally, the last section was heated electrically and insulated.

Instead of calculating the heat transfer for each area, only the last section with the electric heating was calculated first for a steel tube of 7 mm diameter and 1,5 mm thickness. The section was assumed to have a constant wall temperature, as conduction through the steel tube should be high. The Biot number of this section was very low, validating this assumption. The temperature measured in the middle of this section was assumed to be the temperature of the whole section.

The calculations were done assuming the inlet temperature of the gases equal to the reactor at 700◦C for every case. The temperature difference from the wall and the gas flow was set to a difference of ΔT=10◦C.Two wall temperature were used, high and low to cover all the experimental range. Different gas compositions were implemented, pure nitrogen and a gas mix of gasification products including steam and different flow extraction.

The total length was calculated stepwise. The length required was the summation of the length to cool the gases every 10◦C. This corrected the gas properties every 10◦C, instead of using average gas properties for a very large temperatures difference. The gas is cooled down fast when the temperature difference is large. Almost half the total length is for the very last 50 ◦C. If the ΔT=10◦C was decreased, a much longer length would be required.

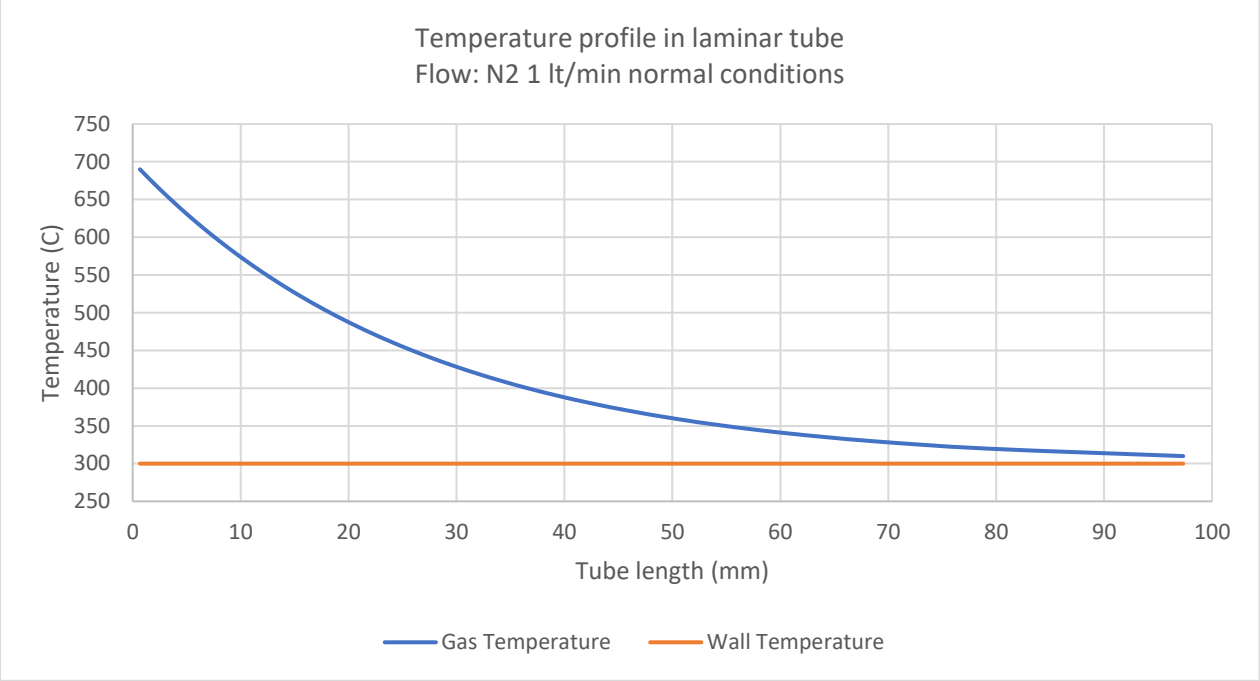


Figure 16. Length required for cooling 1 lt/min N2 to 310 ◦C from calculations

The calculations for pure nitrogen were later used to compare with experimental measurements to validate the cooling.

Table 3. Cooling length for N2 flow

Gas volume		**Flow, normal conditions**	**Wall temperature**	**Length required**
(%)		**(lt/min)**	**(◦C)**	**(mm)**
N2	100	1	300	97,3
			100	108,3
		0,2	300	19,5
			100	21,6

The calculations for a wet gas mix representing possible raw gas concentrations.

Table 4. Cooling length for reference gas flow

Gas volume		**Flow, normal conditions**	**Wall temperature**	**Length required**
(%)		**(lt/min)**	**(◦C)**	**(mm)**
H2	29,4	1	300	69,0
CO	17,6		100	76,5
CO2	14,6	0,2	300	13,8
CH4	6,4		100	15,3
H2O	32,0			

From the calculations, the largest length required for any case was 108,3 mm. The sampling probe was 560 mm long, although not all of it was at the set wall temperature. But the zone with the electric heating, which was assumed to have a constant wall temperature as explained before, was more than

200 mm. From the calculations, the sampling flow with any of the described conditions should be cooled down, at least to +10◦C the wall temperature or lower.

From the calculations, it can be concluded that the sample gas was going to cool to the same temperature as the steel tube. The temperature of the gas was constantly decreasing since it was extracted from the reactor, so once it arrived at the controlled wall temperature zone it was probably much lower than the reactor temperature. The calculations overestimated the length required to cool down the gases in the interest zone, making the gas and wall temperature likely below the ΔT=10◦C.

Heat exchange validation

To validate the gas temperature, a simple test was performed. The reactor was turned on, the wall temperature in the sampling probe was set and the gas temperature was measured while extracting a gas flow. This was done using a long thermocouple connected at the outlet of the gas extraction. The thermocouple was inserted at different lengths of the sampling probe to measure the gas temperature. At the reactor, the gas should have the reactor temperature, with decreasing temperature as it exchanges heat with the sampling probe.

The reactor was set to 700 ℃ with 500 gr of silica sand as bed material. The fluidisation gas was air at 5 lt/min. The sampling probe was heated to 300 ℃ and the sampling flow extracted was 1 lt/min.

The validation has some important errors, so the results must be evaluated carefully. The sampling flow has low thermal inertia compared to the equipment. The thermocouple was left a few minutes to achieve a steady temperature, but temperature measurement errors are expected.

The first temperature measurement error is a lower value due to heat conduction of the thermocouple to the exterior. The thermocouple is made of steel, with a good conduction coefficient. The gas will heat the thermocouple with a low convective coefficient compared to conduction. The thermal equilibrium between gas and the thermocouple will include the conduction through the steel and heat dissipation to ambient temperature. If the thermocouple had a lower conductivity or the gas flow was larger, this error would be lower. This error makes the measured gas temperature to be lower than the real gas temperature.

The second measurement error is the bending of the thermocouple inside of the sampling tube. The thermocouple is not straight, parts of it will touch the wall of the sampling tube. The heat transfer through conduction between the wall and the thermocouple will affect the temperature reading. Because the wall is cooling the flow, conductive heat exchange from the wall to the thermocouple would have a similar effect as adding more convective heat transfer surface area. Again, this error would make the measured gas temperature to be lower than the real gas temperature.

Both errors are not measured but are relevant to analyse the results.

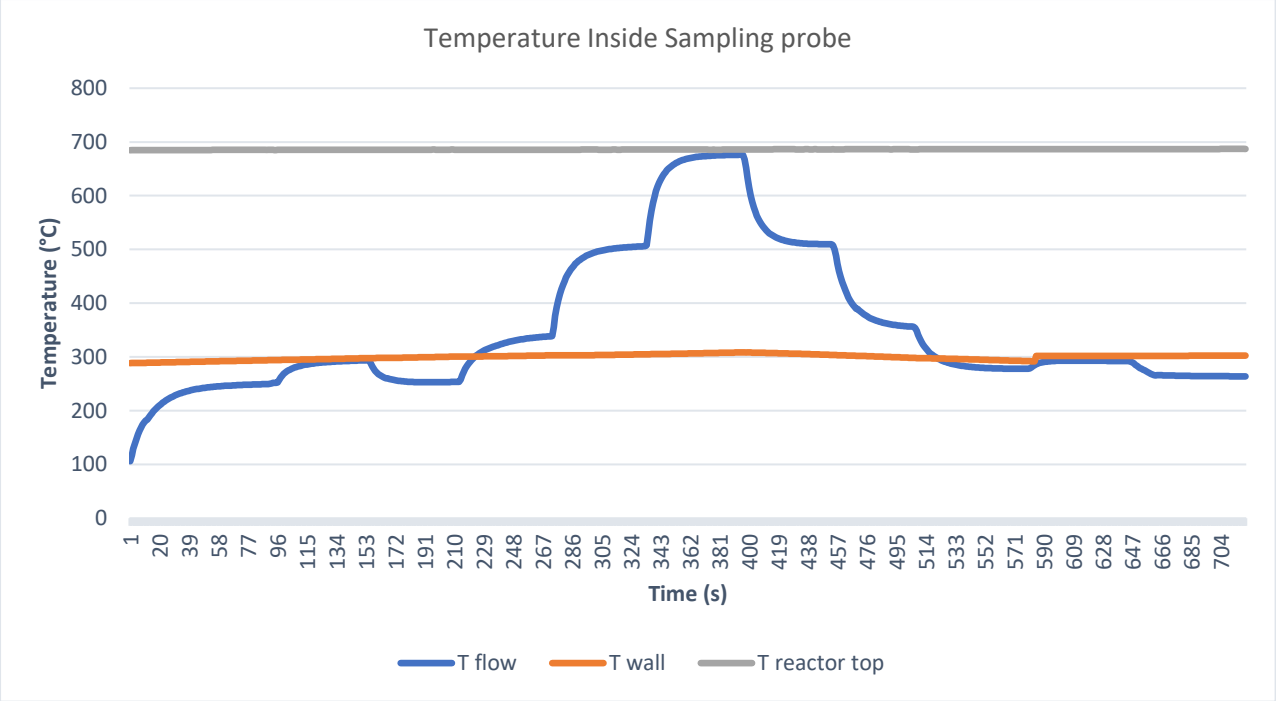


Figure 17. Transient gas temperature inside the sampling probe for different distances

In *Figure 17*, the gas temperature inside the probe is plotted over time. Once the temperature stabilized the thermocouple was inserted 10 centimetres further inside the sampling probe, until 60 cm. The measurement was made going in and out of the sampling probe.

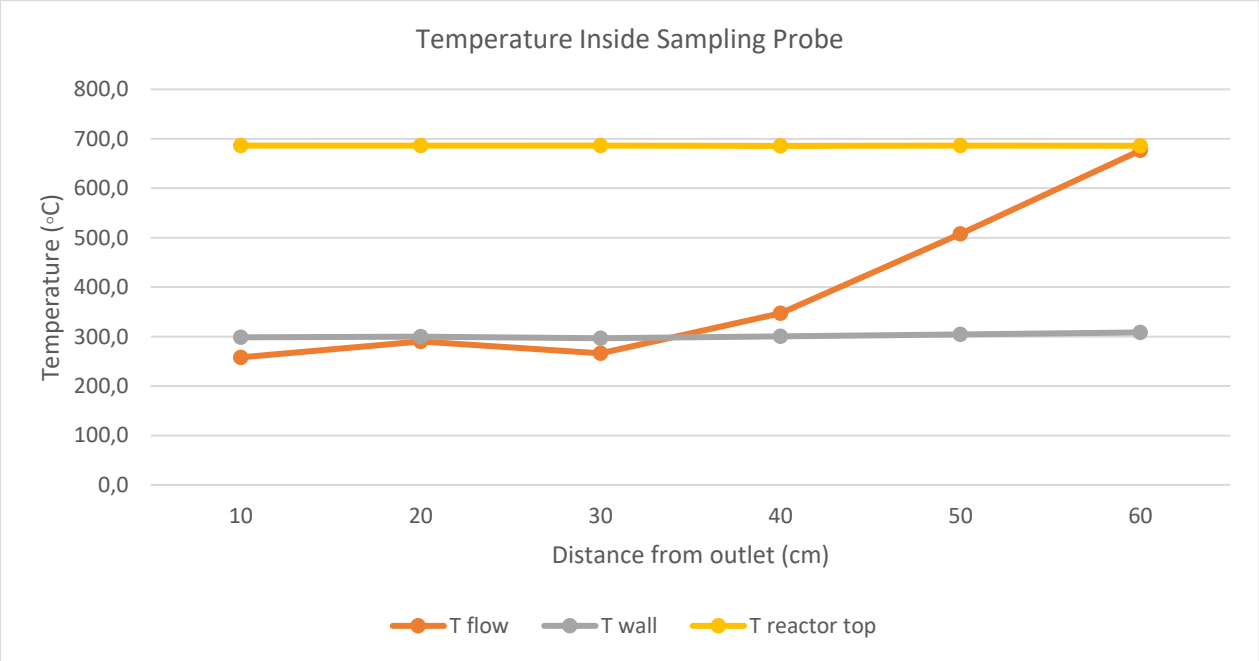


Figure 18. Average gas temperature inside the sampling probe for different distances

From the results, it is possible to conclude that the gas is cooled down in the sampling probe. It starts at 700 ℃ in the reactor as expected, and rapidly cools to the sampling wall temperature. The temperature reading is not reliable, as explained from the errors before, but it is reasonable to believe that the gas is getting cooled to the desired range set in the sampling probe.

Aerosol capture

The dew point of different gasification products depends on the tar concentration. But even if the dew point temperature is achieved, tars might take some time to condense either in surfaces or as aerosols. The kinematic of tar condensation is complex and not well understood, especially because it consists of multiple species.

The experiments were aimed to determine a safe operational temperature to avoid fouling. This is not necessarily the same as the dew point temperature, although tars are known for their sticky nature, they need to either condense in a heat exchange surface or form aerosols that later hit and stick to a surface. The possibility of tars condensing but not sticking and possible uses of this effect will be discussed in the next chapter.

To determine the safe operational temperature, a piece of equipment to promote surface condensation and aerosol adsorption was used. It consisted of extra fine glass wool, which has a very high surface area and adsorption capacity, inside of the sampling probe forcing the gases to go through it. In real industrial conditions, tars might have less surface to condense or for aerosols to stick, like smooth steel tubes in heat exchangers, but this was assumed as a worst-case scenario were tars could stick. Fouling would be expected to be lower for the same conditions in tube heat exchangers.

The filtration efficiency of glass wool was studied to prevent GC columns from being damaged with fine solid particles and letting gaseous compounds flow through [35]. The filtration efficiency was very good for PM 2,5 solid particles for the studied conditions. It was assumed this could be extended to other aerosols such as tars, which could be either liquid or solid depending on the specie and temperature.

A tube with glass wool inside was connected at the end of the gas sampling, at the same temperature as the sampling probe. The glass wool should work as a demister, capturing most aerosols formed from tar condensation depending on temperature and partial pressure. The glass wool was changed every measurement.

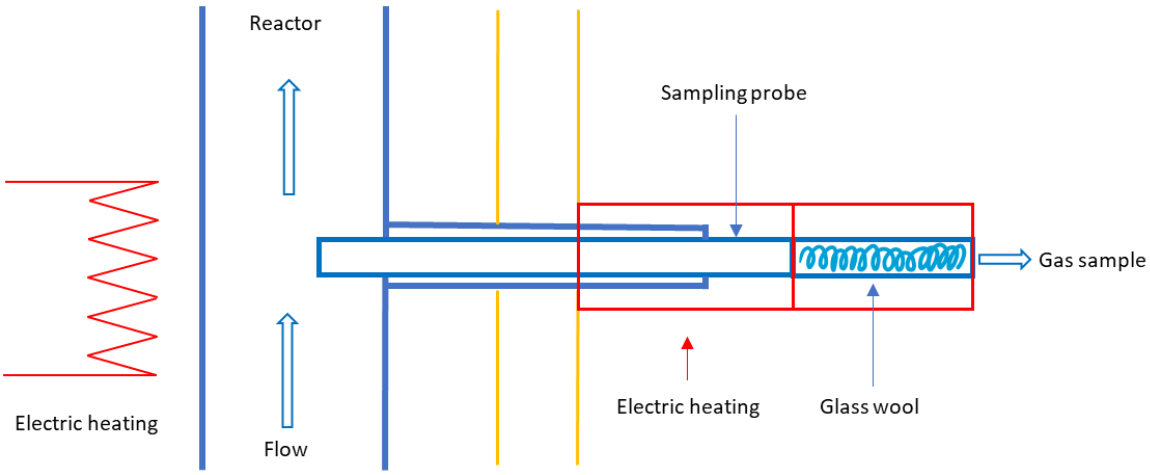


Figure 19. Diagram glass wool inside sampling tube

Results and Discussion

Biomass Experiments

Gasification Conditions

Gasification process with biomass pellets, aiming to replicate conditions from the Chalmers gasifier.

Table 5. Gasification Conditions Biomass Experiments

Condition	Unit	Amount
Bed material: Silica sand	(gr)	500
Reactor temperature	(◦C)	750
Fuel feeding rate	(gr/min)	4,5
Fluidisation gas: Steam	(gr/min)	3,4
Fluidisation gas: Nitrogen	(lt/min)	2
Steam to fuel ratio	(kg steam / kg fuel)	0,87

Each experiment was run with different wall temperature and a fresh sample of glass wool to capture aerosols. The gasification conditions for every experiment were kept constant.

Four experiments were run, with wall temperatures of 60 ◦C, 130 ◦C, 210 ◦C and 300 ◦C.

Permanent gases analysis

The feeding was done by hand every 20 seconds and gas samples were taken after a few minutes of operation, waiting for stable conditions. The permanent gases concentrations in every experiment were similar, so similar gasification conditions were assumed.

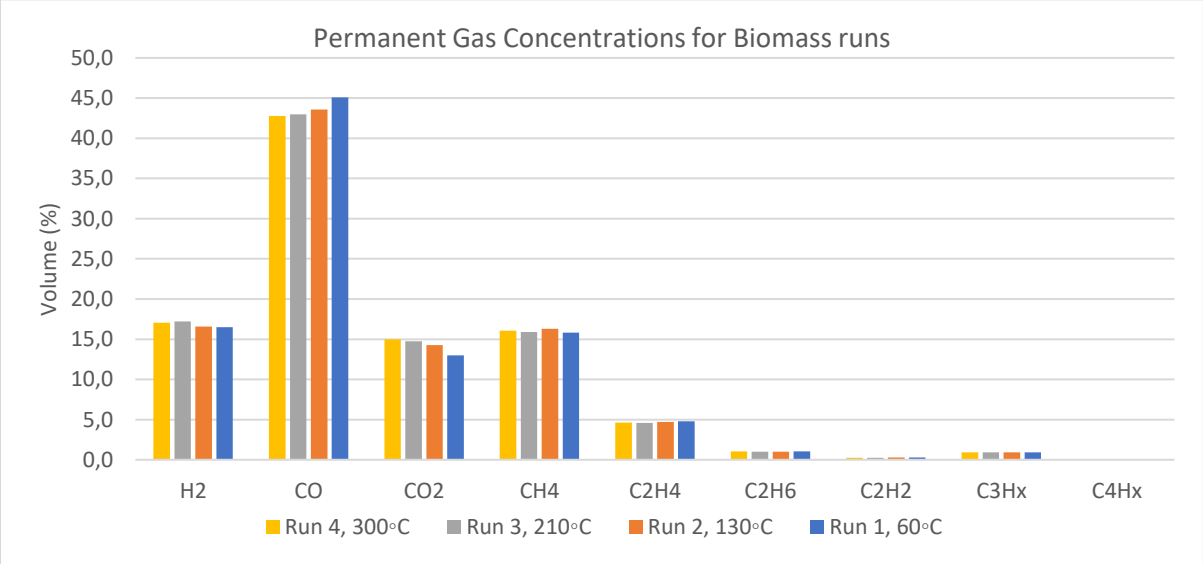


Figure 20. Permanent gases for different biomass experiments

SPA analysis

Tars were first classified according to the dew point criteria of ECN.

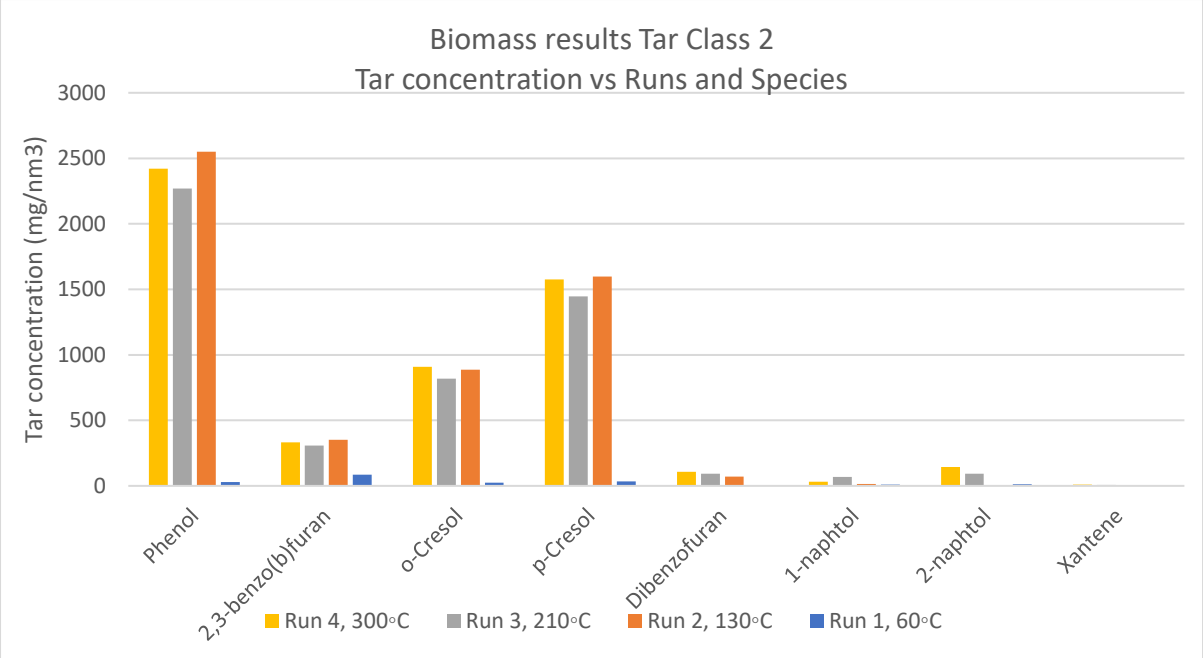


Figure 21. Biomass experiments, tar class 2 concentration heterocycles

From tars class 2 most species concentration was similar, but a significant change was obtained for temperatures below the dew point of water, at 60 Celcius. When water condenses there is a sudden decrease of the tar dew point because the partial pressure of the species increases rapidly. If there is a large concentration of steam that suddenly condenses, the partial pressure or every other gas increases. This increase of partial pressure induces tars to condense until the previous partial pressure is achieved.

Runs for temperatures lower than 100 Celcius are not included in the following graphs as the effect from water condensation hinders the comparison.

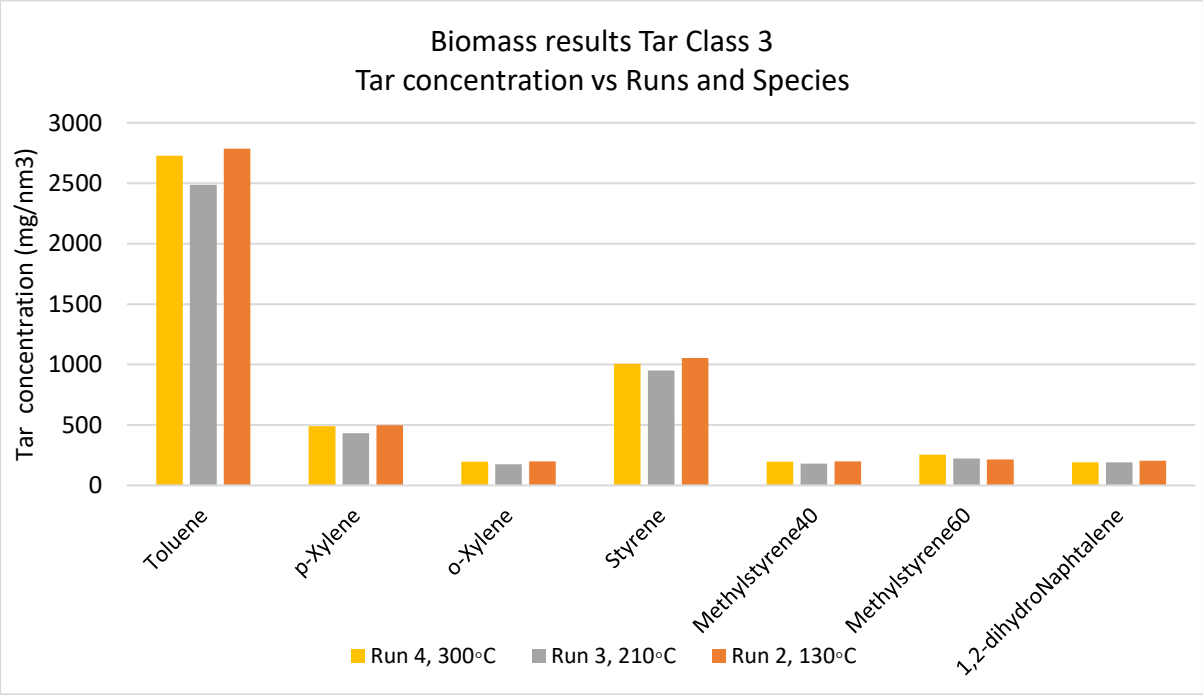


Figure 22. Biomass experiments, tar class 3 concentrations one ring aromatics

From tar class 3 most concentrations remain constant independent of the gas temperature, except for the temperature below the dew point where a smaller amount could be expected explained with the previous effect. This class of tars is not expected to condense or foul at temperatures above 100 ◦C.

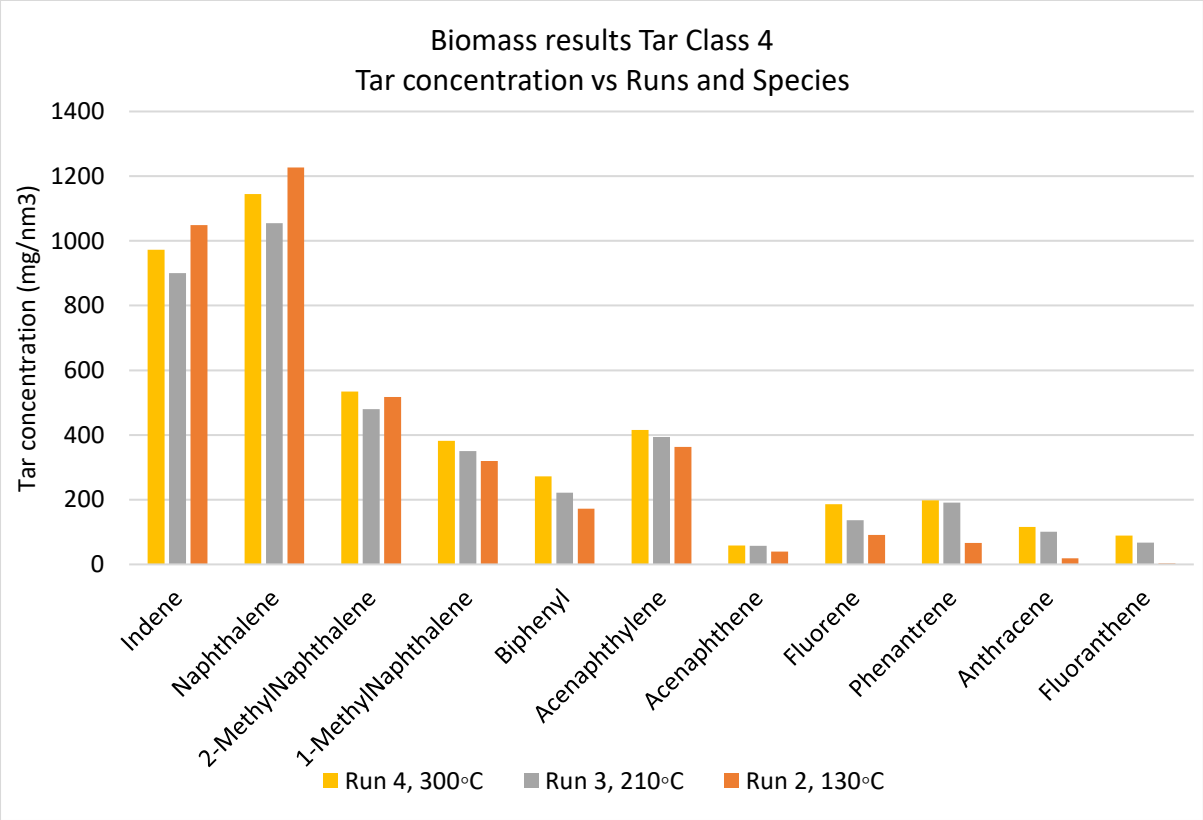


Figure 23. Biomass experiments, tar class 4 concentrations 2 and 3 aromatic rings

In tar class 4 there is a decrease in the concentration for tars with higher molecular weight. From 1-MethylNaphthelene there is a clear decreasing trend of tar concentrations for decreasing temperatures.

Possibly due to experimental uncertainties, Run 2 with a lower gas temperature has a larger concentration of most tars class 2 and 3 until naphthalene and then concentrations decrease as expected with temperature. This could be because of a larger tar generation during that test, although all conditions should have been constant. Although the trend is clear, for quantification more experiments would be required.

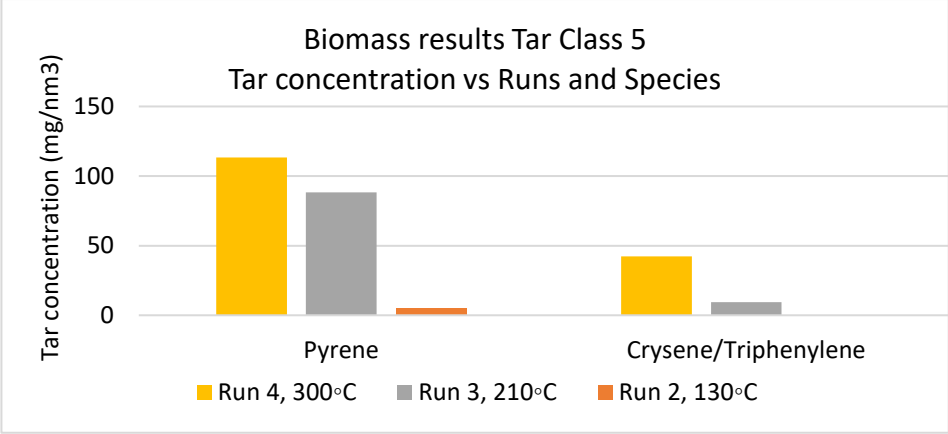


Figure 24. Biomass experiments, tar class 5 concentrations larger 3 to 8 aromatic rings

Finally, for tar class 5 the trend is clear, decreasing gas temperature reduces significantly tar concentration. Even when the concentration of this class is much lower than the previous, the temperature difference has a major effect condensing them.

From the SPA results, it is possible to conclude the main tars that will condense at temperatures above 100 ◦C are heavier ones. From class 3 to 5 the classification is related to the molecular weight, tars with more rings are heavier. The heavier the less concentration depending on the lower gas temperature. The same could be observed in class 2, even if the classification is not based on molecular weight, only the heavier tars had lower concentrations with lower gas temperatures.

While heavier tars are condensing, it does not seem to affect the condensation of lighter tars. Tar condensation, in surfaces or aerosols, is not well understood and difficult to predict as multiple species are interacting. But it seems that light tars and heavy tars do not interact during condensation above 100 ◦C.

ECN Dew Point Model

The SPA results were implemented in the online ECN model dew point model, Thersite. This model is supposed to have good accuracy for the 100 – 170 ◦C range, while for the 20 – 100 ◦C should also give good results. Above 170 ◦C the dew point calculation will have a larger error.

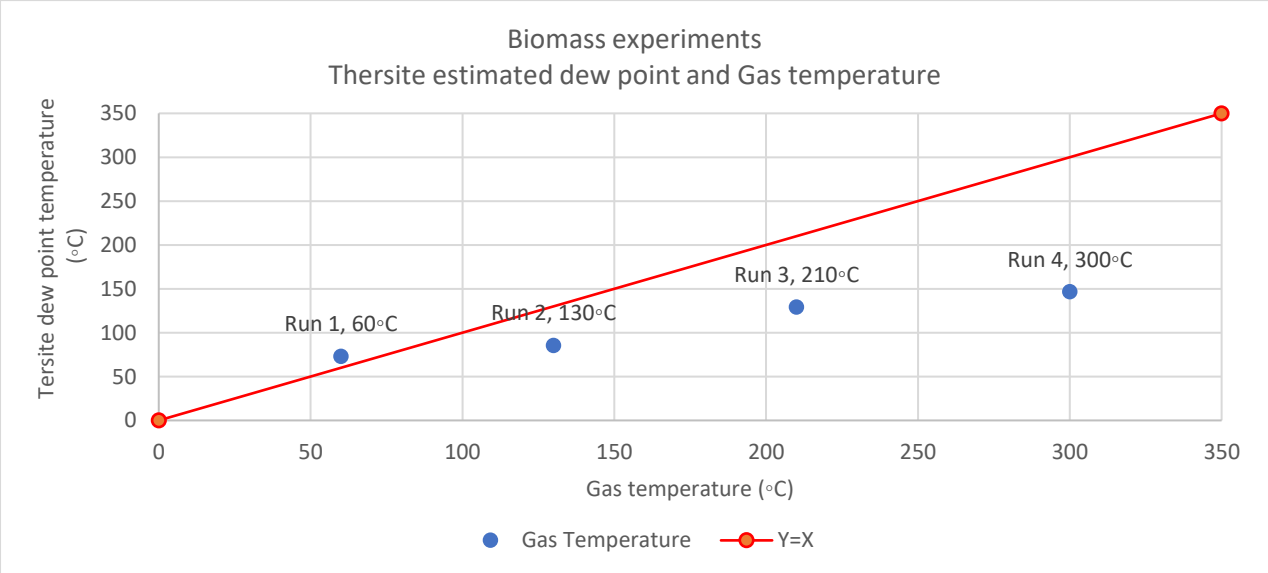


Figure 25. Thersite estimated dew point and Gas temperature

In the graph, the calculated dew point from the Thersite model should be the same as the gas temperature of the sample. The concentration of tars species from the SPA at a given temperature should be in the Y=X axis. They are not, probably due to the low number of species detected in the SPA analysis. The complete Thersite model uses 34 tar species, excluding class 1 tars that are undetectable with GC.

Table 6. Species for Thersite model and detected with SPA in the experiments. Green is detected and red is undetected

Compound	Molecular Weight	Compound	Molecular Weight
"Benzene"	78.11	"Acenaphtylene"	152.19
"Pyridine"	79.1	"Acenaphtene"	154.21
"Toluene"	92.14	"Fluorene"	166.23
"2-mePyridine"	93.13	"Phenanthrene"	178.24
"3+4-mePyridine"	93.13	"Anthracene"	178.24
"Ethylbenzene"	106.17	"Fluoranthene"	202.26
"m/p-Xylene"	106.16	"Pyrene"	202.26
"o-Xylene + Styrene"	106.17	"Benzo(a)anthracene"	228.3
"Phenol"	94.11	"Chrysene"	228.3
"o-Cresol"	108.14	"Benzo(b)fluoranthene"	252.31
"Indene"	116.16	"Benzo(k)fluoranthene"	252.31
"m/p-Cresol"	108.14	"Benzo(e)pyrene"	252.31
"Naphthalene"	128.18	"Benzo(a)pyrene"	252.31
"Quinoline"	129.16	"Perylene"	252.31
"Isoquinoline"	129.16	"Indeno(123-cd)perylene"	276.33
"2-methylnaphthalene"	142.2	"Dibenzo(a,h)anthracene"	278.35
"1-methylnaphthalene"	142.2	"Benzo(ghi)perylene"	276.33
"Biphenyl"	154.21	"Coronene"	300.35
"Ethenylnaphthalene"	154.21		

Most of the heavy tars are undetected in the SPA. Those tars are responsible for increasing the dew point, so the low dew point from the Thersite model is probably explained because of this.

It is important to show this because it highlights the difficulty of basing a dew point analysis for tars on the measured species. Depending on the gasification process there can be different tars presents. Being able to detect and measure a wide range of species, from light to heavy, would require careful calibration of many species, that is often not easy to achieve.

Models could be useful for lower temperatures, with both advantages of analysing a smaller number of light species and higher concentrations. But for higher temperature dew point calculations, other methods that don't require the identification of every specie could have better results with easier implementation.

Total SPA analysis Biomass

The tars analysis from the SPA samples is done in GC-FID equipment explained before. The identification of species will depend on the calibration of the GC, but for species that are not identified there is a quantification from the FID.

Each peak measured by the FID over time in the GC analysis is expected to be a different species, with increasing molecular weight as heavier tars should take longer, in general, to travel through the columns. Even if the species are not identified, the total amount of tars by weight can be obtained.

Light tar concentration

Between different gas temperatures, the total concentration of tar species below naphthalene is expected to remain constant, as no low molecular weight tar should condense at these temperatures.

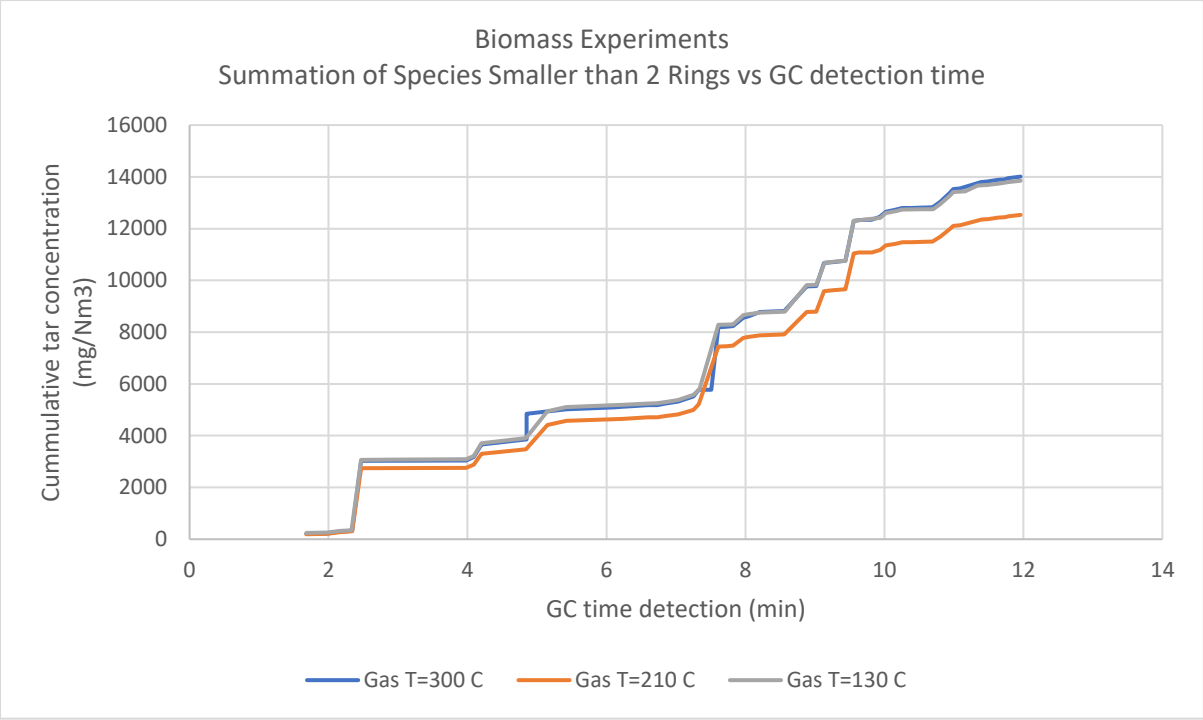


Figure 26. Biomass total concentration of species with molecular weight lower than naphthalene

The cumulative tar concentration of light tars is similar for every run. Note that this concentration should be equal, as light tars are not condensing. The constant deviation from one experiment, Gas T=210 C, can be originated from a sampling volume difference, which will be explained later. Normalizing the cumulative tar concentration against the total benzene concentration of each run gives the expected results, with very similar total light tar concentration overtime for every run.

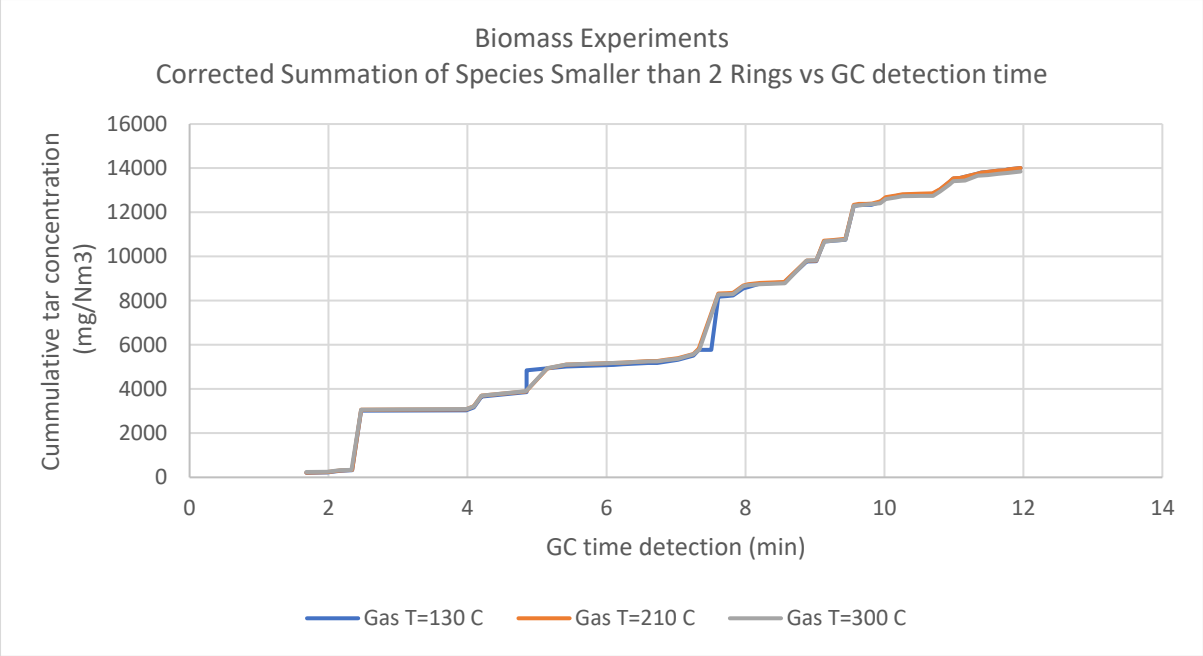


Figure 27. Biomass corrected total concentration of species with molecular weight lower than naphthalene

Heavy tar concentration

Between different gas temperatures, tar concentrations are expected to decrease as heavy tars should be condensing in this range. The light tar normalization is applied for heavy tars, correcting possible differences in experimental sampling that will be explained later.

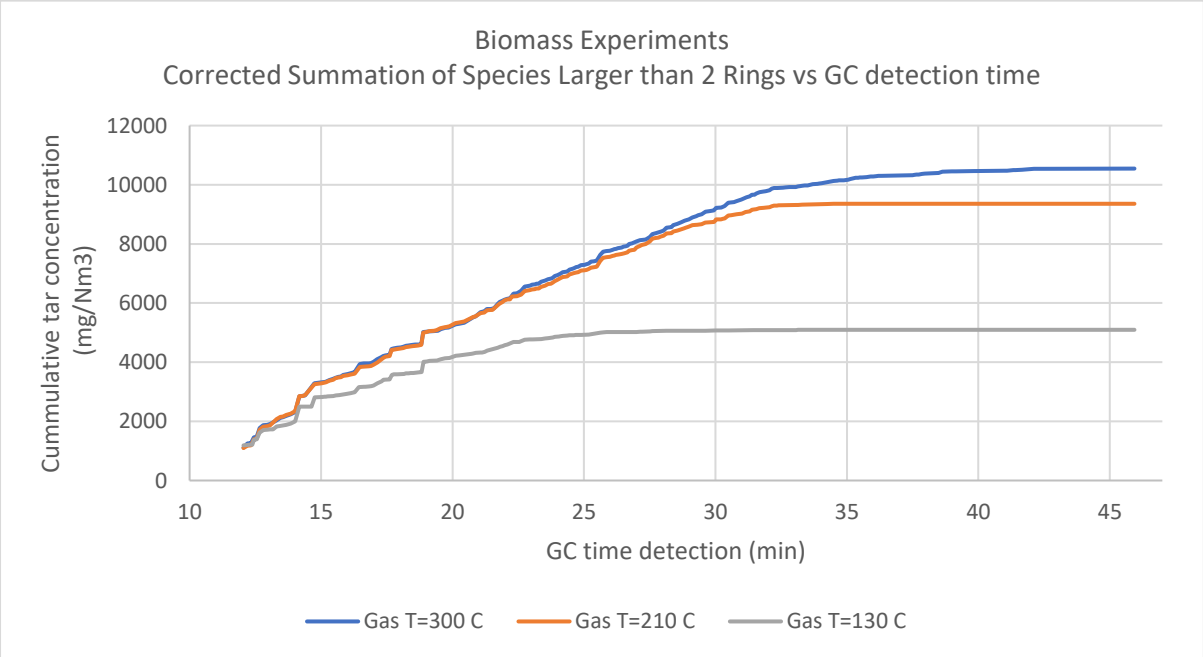


Figure 28. Biomass corrected total concentration of species with molecular weight higher than naphthalene (including)

With different gas temperatures, the cumulative tar concentrations change considerably. As expected, the lowest temperature has the lowest tar concentration, and the highest temperature the highest

tar concentration. Naphthalene, the first specie in the heavy tars, is similar for every run. But as species go through the GC over time, heavy tar concentration decreases.

Tars over GC time

The total amount of tars summated per minute was plotted against the GC sampling time in *Figure 29*. This was done adding the total tar first concentration for the first minute, then for the second and so on. For the first minutes, the total tar concentration for different runs is similar and the distribution follows the same trend, meaning that light tar concentration is similar. For late GC time, the concentration of heavy tars differs between samples, as expected from condensation.

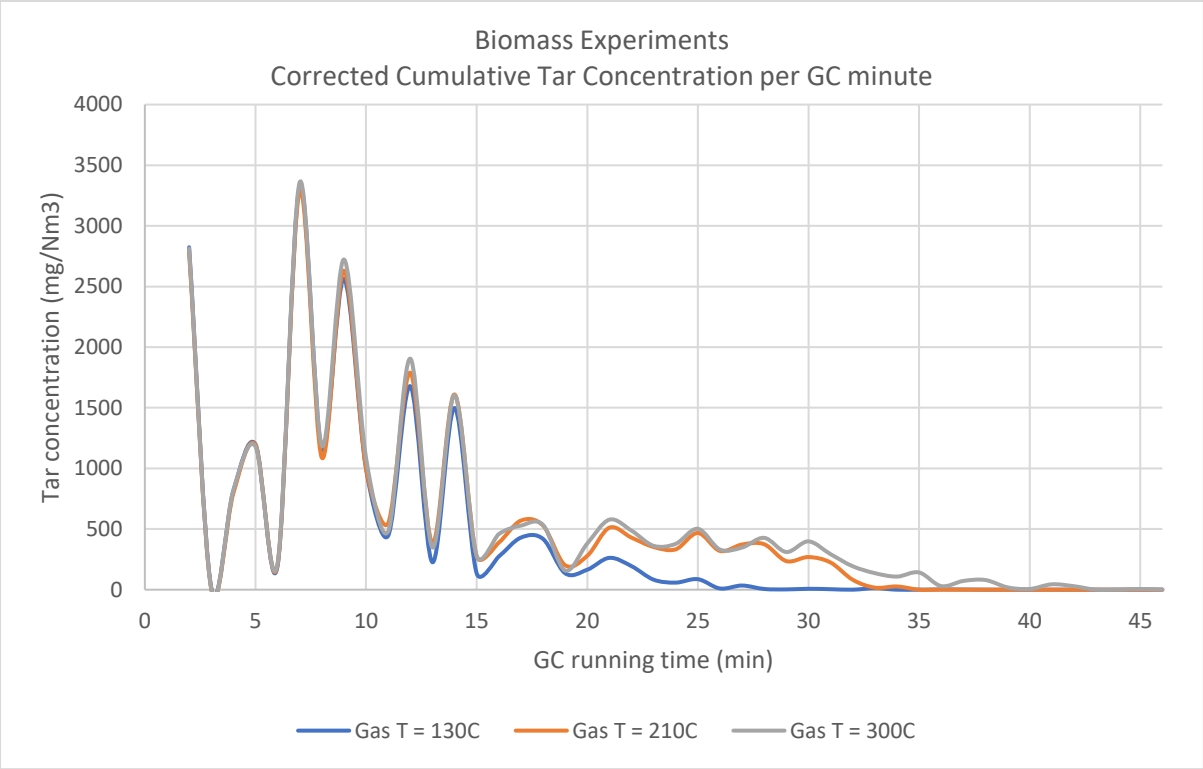


Figure 29. Biomass corrected cumulative tar concentration per GC minute

This graph illustrates the idea of heavier tars condensing at lower temperatures, while light tars are still in the gas phase without condensing. At later GC running time, only heavy tars remain, and the difference in tar concentration per minute between runs is significant. Also, there is a large difference between runs, even though similar temperatures differences between them were implemented, the low temperature run has a much higher tar concentration difference.

Tar difference between temperatures

Light tars concentration were constant but heavy tars were not. This difference is the total amount of tars that condense and might foul for different temperatures.

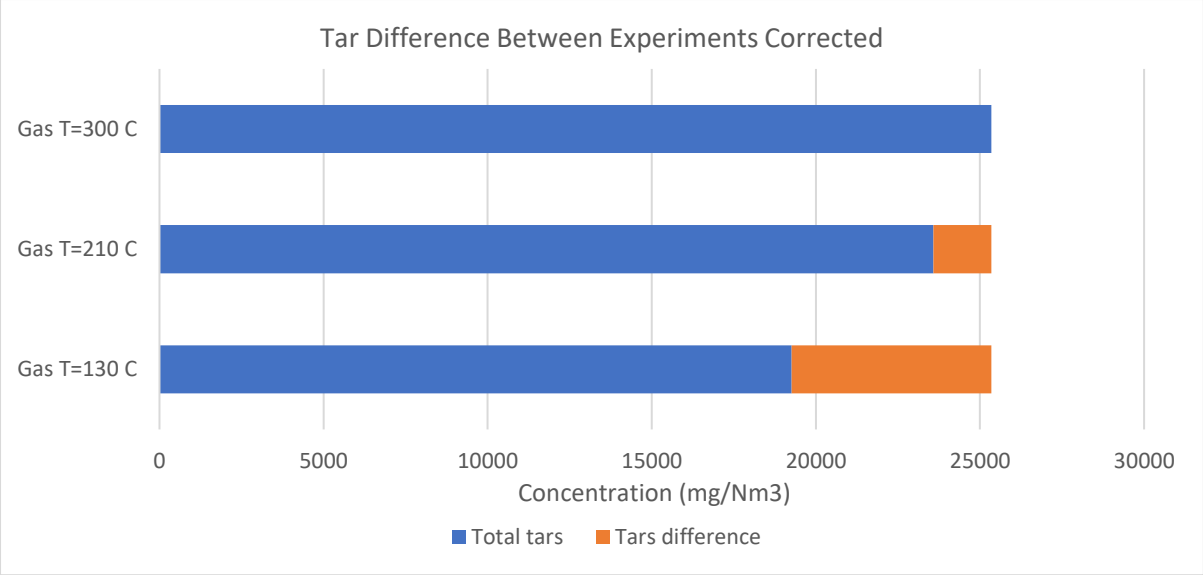


Figure 30. Corrected tar difference for gas temperatures

The share of heavy tars related to total tars decreases with lower gas temperatures. This difference could be used to determine the acceptable operational temperature of heat exchangers. Lower gas temperatures would mean that more energy can be recovered with a heat exchanger, but more tars would condense and possibly foul the equipment.

Table 7. Tar difference for temperatures

GAS TEMPERATURE	TOTAL TARS (MG/NM3)	DIFFERENCE FROM BASELINE (MG/NM3)	DIFFERENCE FROM BASELINE (%)
300 ◦C	25350	0	0
210 ◦C	23577	1773	7,0
130 ◦C	19261	6088	24,0

The concentration difference between high and low temperature is significant. If all these tars would condense and stick to surfaces in heat exchangers, the fouling would be very fast.

As a reference, a tube and shell heat exchanger have an approximate flow rate of 15 Nm3/hr per 2-inch diameter tube. The number of tars condensing for this gasification conditions between 130 ◦C and 300 ◦C would be 91,3 gr/hr. If all condense tars stick to the wall of the tube, just over 1 day this would mean fouling of 2,2 kg of tars per tube, which would probably require often cleaning.

Polyethylene Experiments

Experiments with polyethylene (PE) plastic pellets were also done to validate the decreasing heavy tar concentration with different gasification conditions.

Table 8. Gasification Conditions Polyethylene Experiments

Condition	Unit	Amount
Bed material: Silica sand	(gr)	500
Reactor temperature	(◦C)	700
Fuel feeding rate	(gr/min)	1-3
Fluidisation gas: Nitrogen	(lt/min)	2

Three experiments were conducted, with wall temperatures of 120 ◦C, 220 ◦C and 330 ◦C with and without glass wool.

These experiments were done with an automatic vibratory feeding system, explained before. The feeding system was constant for a few minutes, but not for the whole experiment. Although it was adjusted multiple times, the total fuel feeding changes widely up to 3 times the original value. This would provoke a variable tar concentration. The full analysis as in the previous case was not done because the gasification conditions were very variable, and the different tar concentration might be due to other issues more than different gas temperature.

SPA Analysis

The same ECN classification system was used. As with biomass, light tars were not condensed while heavier were.

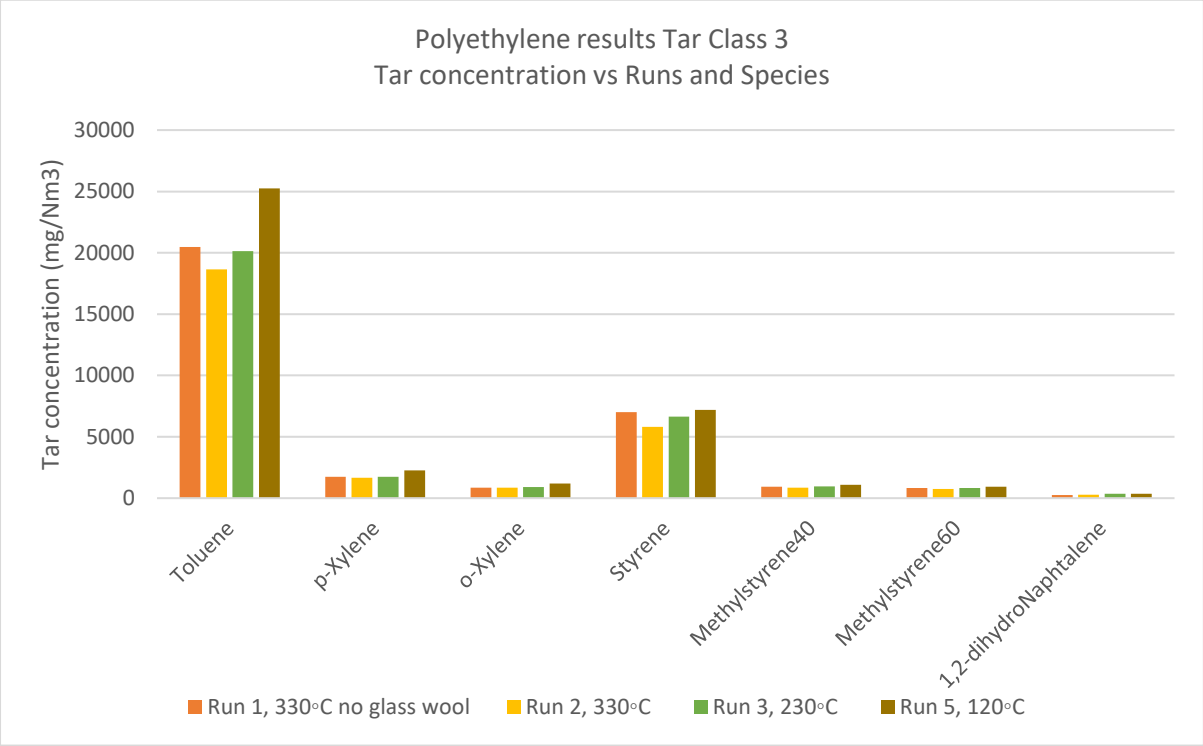


Figure 31. Polyethylene experiments, tar class 3 concentration 1 aromatic rings

Light tars did not condense with gas temperatures from 120 to 330 ◦C. The difference tar concentration is due to experimental errors, probably due to the feeding. It is important to note the

concentration difference with the previous biomass experiments. For biomass high concentration tars such as toluene had 2.500 mg/Nm3, for PE the concentration is around 20.000 mg/Nm3 and in neither case there is any significant condensation of these light tars at these temperatures.

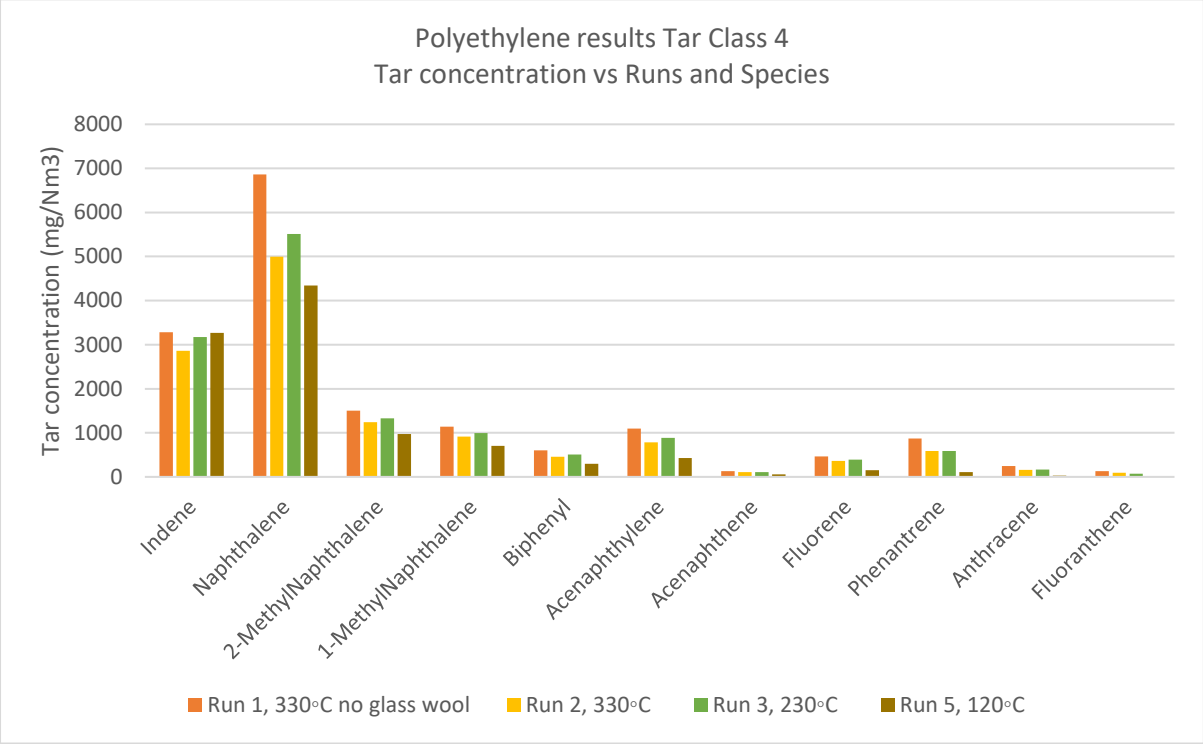


Figure 32. Polyethylene experiments, tar class 4 concentration 2 and 3 aromatic rings

For larger tars, class 4, there is a clear trend to lower concentrations with lower gas temperatures. In this case it seems naphthalene is also condensing with lower temperatures, although this was not the case for the biomass experiments.

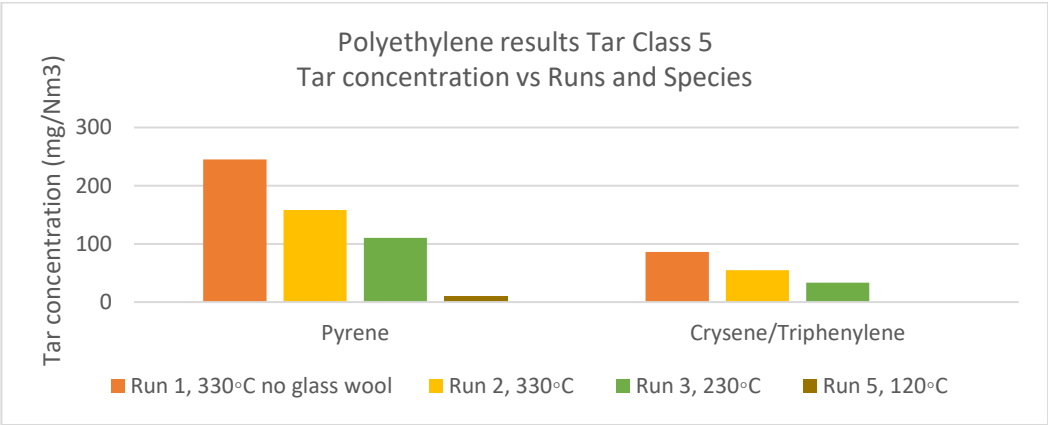


Figure 33. Polyethylene experiments, tar class 5 concentration 3 to 8 aromatic rings

For class 5, the trend is clear. These tars have a low concentration, the Y-axis is much lower than the previous graphs, and with decreasing temperature there is a decreasing tar concentration.

ECN Dew Point Model

Using the Thersite model, again the calculated dew point is much lower than the actual dew point. The lower calculation is due to many species not measured with the SPA method, especially the heavy tars. Again, the model was not appropriate because of this problem.

Total SPA analysis Polyethylene

Making the full SPA analysis, including unknown tars, the same trend from biomass experiment was observed. Light tars did not condense, even when there is a much higher concentration of them for tar class 3. For heavier tars, class 4 and 5, the concentration decreases considerably with decreasing temperature.

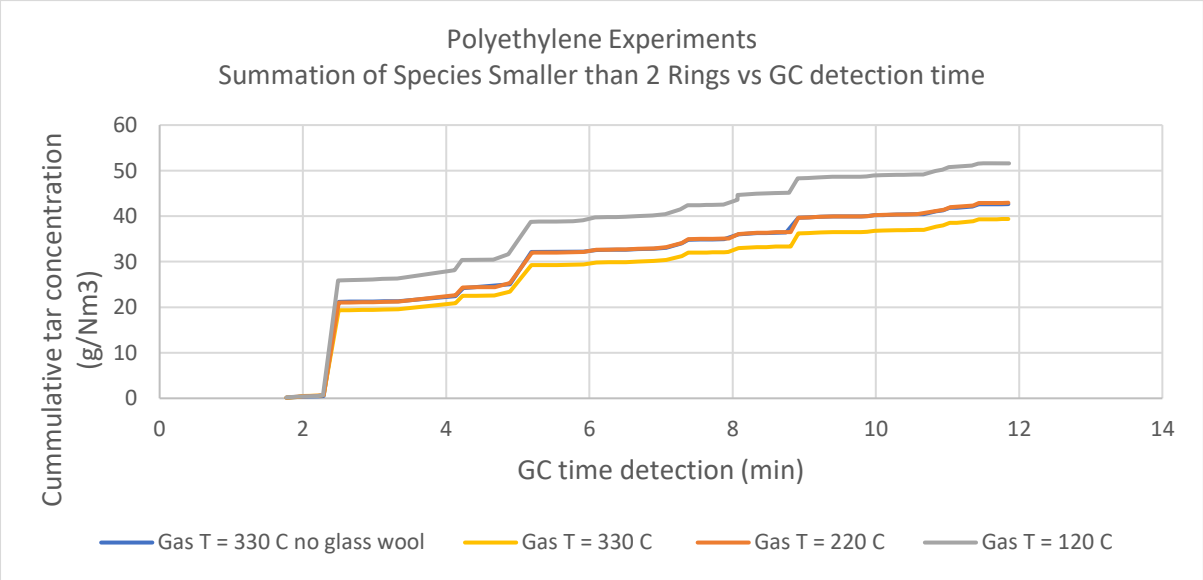


Figure 34. Polyethylene Summation of Species Smaller than 2 Rings vs GC detection time

But the correction used for the previous case with biomass did not correctly adjust the tar concentrations, so results from PE experiments were not considered. This probably because the tar concentration from different runs was different due to the uneven feeding rate.

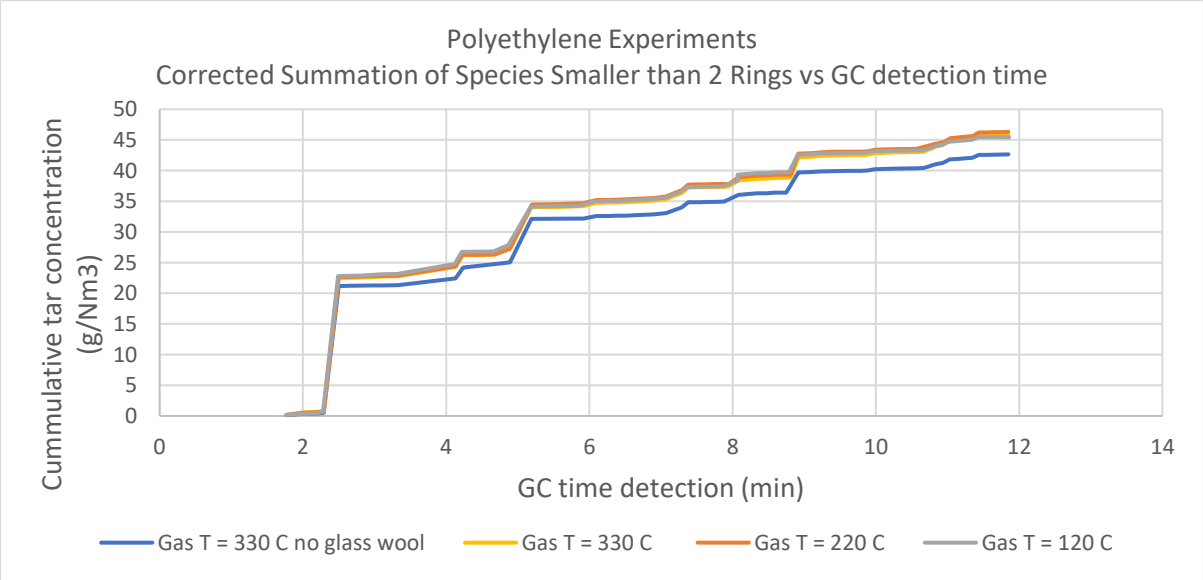


Figure 35. Polyethylene Corrected Summation of Species Smaller than 2 Rings vs GC detection time

The total concentration of tars lighter than naphthalene should be the same for every experiment after correcting, but it is not as seen in *Figure 35*. Because of experimental errors, in this case probably the uneven feeding rate, there was a difference with the lowest temperature experiment having the highest concentration. The sampling with the lowest gas temperature is likely to have had the highest feeding rate, increasing the tar generation with a total higher tar concentration.

With further experiments controlling the feeding rate, the total concentration for light tars should be the same independent of gas temperature.

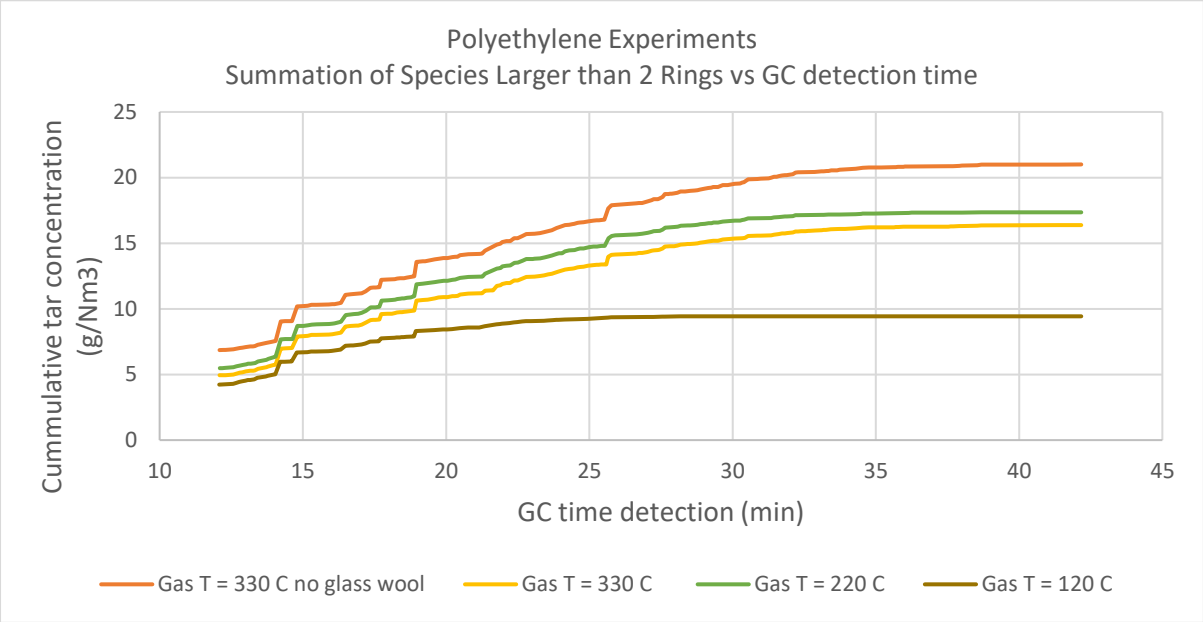


Figure 36. Polyethylene corrected total concentration of species with molecular weight higher than naphthalene (including)

For heavier tars the concentration decreases with temperature. Even for experiment with variable feeding rate, which would vary the tar concentration, the lower temperature is related to lower tar concentration of heavy tars.

Measurement errors

There are two main reasons for differences from the true value to the measured value in tar concentration analysis, referred to as errors. The first error is related to the variability of the process itself, how stable the gasification parameters are during sampling. The objective is to identify the difference in dew point for similar raw gas concentrations, so changes in the gasification conditions should be kept to a minimum. Second the error due to the sampling procedure and measurements from different equipment involved in the sampling.

First error, process variability

Many gasification processes are supposed to operate in steady-state conditions, but in reality, gasification parameters are kept within a certain range that is considered stable. The dew point is dependant on the partial pressure of each specie, which depends on the gasification conditions. The objective is to determine dew point for a stable raw gas, so if gasification conditions change the dew point calculations would not be accurate.

This problem is especially relevant in laboratory reactors, where gasification conditions are more susceptible to variation because of the small scale. For large reactors, these variations should be lower, with a more stable raw gas. Nevertheless, some variations are always expected for any process. The dew point will always have some uncertainty related to this, so results should be examined to assume acceptable raw gas conditions between samples.

If raw gas has different tar concentration, this should be observed in the distribution of light tars. For different samples, the number of light tars should remain constant. If the concentration of tars has a different distribution over GC sampling time, the raw gas was not constant. Instead, if the concentration of tars between samples has the same distribution but lower total concentration, the raw gas was probably similar, but the sampling procedure had errors.

The error due to process variability between experiments should be low, as the tar distribution of light tars is similar. This means the gasification process was similar between samples, so the raw gas had similar conditions.

Second error, equipment and procedure

The second error is related to the procedure of sampling and the errors from different steps in the tar analysis. Some of these errors can be adjusted with the rights references, others have to be assumed into the experiment uncertainty. Finally, if the difference is too large, it is probably due to large sampling errors and the sample must be discarded.

Volume sample

Because the tar concentration is measured indirectly, first taking a gas sample through the SPA, then eluting it for the GC, the total calculated tar concentration in the gas is susceptible to errors. The same amount of tars by weight would have different concentrations depending on the gas volume from the sample and the liquid volume for eluting. This error can be adjusted assuming the gasification conditions are stable and correcting the concentration with the total light tars.

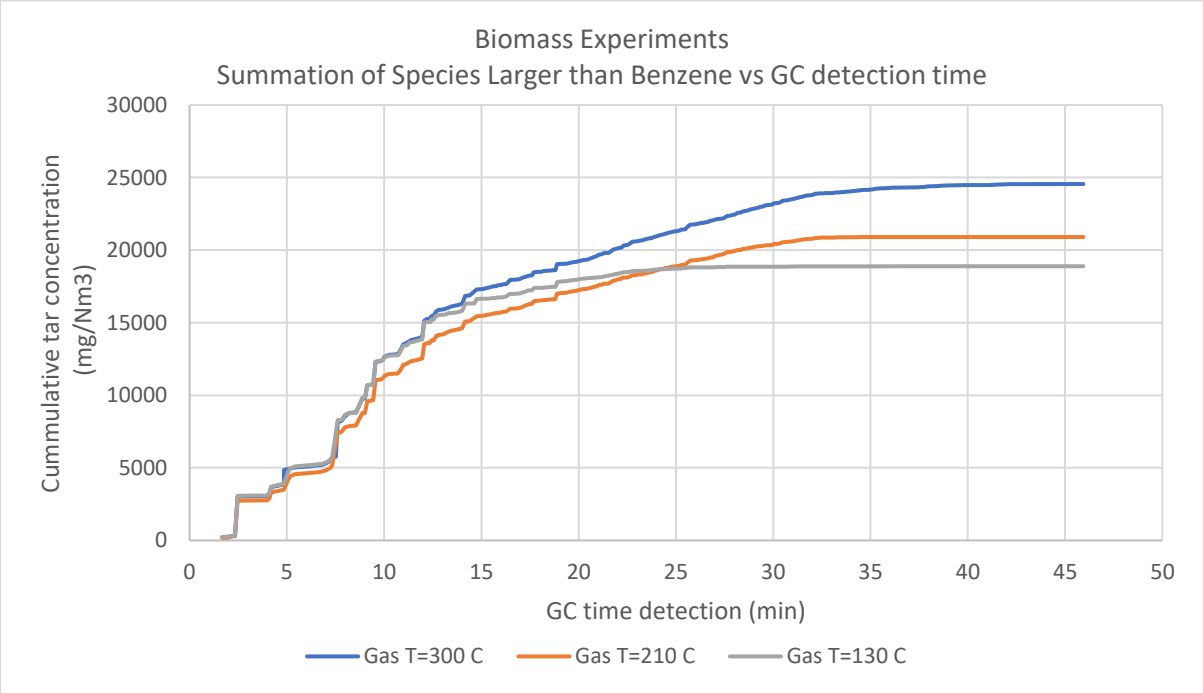


Figure 37. Total cumulative tar concentration for biomass experiments with NO correction

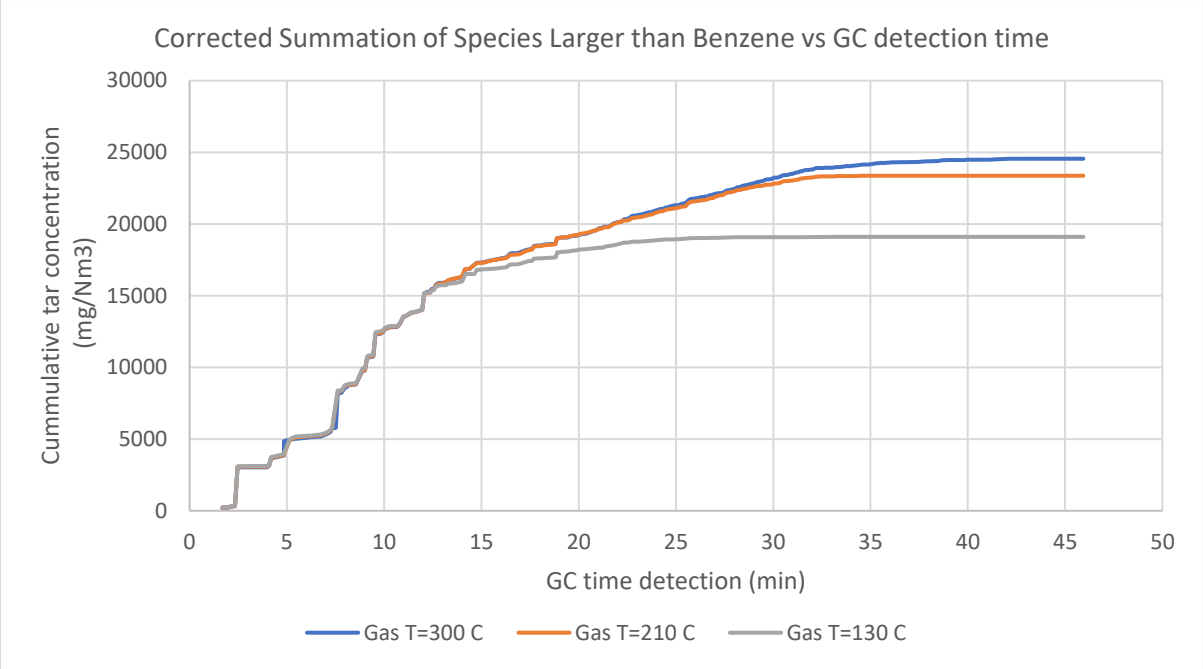


Figure 38. Total cumulative tar concentration for biomass experiments with correction

The amount of tars for run Gas T=210 C was lower than the rest from the beginning. This makes the graph of cumulative tar summation over GC time in *Figure 37* to be lower. Normalizing by the amount of benzene from the baseline run, the corrected summation of tars has an expected shape shown in *Figure 38*, with same concentrations for light tars and diverging from the baseline for high temperatures. The orange line is now close to the rest and always on top of the grey line, which is expected from the temperature levels.

Table 9. Benzene and correction ratio between runs

GAS TEMPERATURE	LIGHT TARS (MG/NM3)	RATIO (%)
GAS T=130 C	5097	1,02
GAS T=210 C	4621	0,92
GAS T=300 C	5021	baseline

This correction is valid only to adjust concentrations from sampling. The difference in concentrations due to sampling could come from the gas volume sample or the eluting liquid. If the distribution is similar, this correction could be done. But in general, it is not recommendable if the difference in concentrations is not large no correction should be implemented. With a larger number of samples, this error would decrease. In this report, the correction was implemented because the number of samples was low, only one per temperature level. This allowed using the sample from Gas T=210 C in the analysis.

Equipment errors

The next set of errors comes from the equipment operation. This error is unavoidable and should be added to the total uncertainty. The GC will have an experimental error inherent to the system, which is usually explained by the manufacturer.

The tar absorption in the SPA will also create an error as it might not be capable of absorbing every tar from the gas phase and desorbing every tar into the liquid phase for elution. Light tars, which are more volatile, might escape the SPA sample reducing the total measured estimation. But this problem is more pronounced for light tars and not too relevant for heavy tars.

Recommendations for tar condensation analysis

Dew point calculation using models that require multiple species for the calculations are difficult to implement. Measuring accurately concentrations of different species over a large range of molecular weights is not easy to achieve. Equipment capable of measuring a wide range species, like those products from the gasification process, require special attention that can be demanding.

An alternative could be to reduce the analysis scope when implementing models. For lower temperatures, close to and lower than water condensation temperature, many tars species should have already condensed to a large degree, making it possible to analyse closely a smaller range of species. A similar approach is described in [19], where a dew point model using a representative specie for each of ECN classes is used, considering different permanent gas compositions. Models for low temperatures range could be useful as there a fewer species.

For higher temperatures, above the water dew point at ambient pressures, use of models involving many different species would be hard to implement. Instead, a general approach could be used classifying total tars. Using GC, a sample could be analysed having only a few species as a reference to classify large groups, and the total amount of tars could be quantified using the whole GC analysis. Implementing the same procedure described here with glass wool, experimental runs decreasing the gas temperature would give the difference of tars condensation that could start fouling the equipment at different temperatures.

Using SPA for this purpose would simplify the operation. It would be recommendable to implement a baseline based on the Tar Protocol [29] to quantify the heavy tars that are not measured by the SPA and GC. These heavy tars could be measured with the gravimetric tar measurement, although this method could be used for every sample, it is likely more time consuming than using the SPA. Assuming the tar protocol would be more accurate, comparing a Tar Protocol measurement with SPA would give an idea of the error, valuable for the first experiments but likely not necessary later. It should not be large for the tar range of interest, class 4 and 5, so the SPA method could be used to quantify all the heavy tars that might condense at different raw gas temperatures.

The aim question: Which is the dew point where tars might start fouling? could instead be adjusted to: Which is the raw gas temperature where tar condensation exceeds a certain limit? This temperature would depend on each gasification process and could be measured with the proposed method. After defining an acceptable amount of tar condensation, and possible fouling for industrial equipment, a minimum gas temperature could be identified. With this criterion, it would be possible to optimize the design of the heat exchanger to recover heat from the raw gas until this gas temperature.

Finally, although the temperature is defined for a gasification process, it is not certain fouling will happen. For fouling condensation is the first step, next the species need to adhere to a surface. This process is complex, so an overview is done in the next chapter.

Tar fouling mechanism

The dew point of tars is an important measure to know if different species could start fouling or not. But even below the dew point for different species, they might foul in the surfaces as they could be carried away as aerosols. A flow below the dew point is a minimum requirement for species to foul but not sufficient. Depending on the flow conditions, fouling could be enhanced or decreased.

Most of the heat exchangers for gases are based on the optimization of costs, between investment and operation. The investment cost is related to the size of the heat exchanger depending on the rate of heat transfer, while operational costs to the pressure drop of fluids. A common recommendation is to have high turbulence, which enhances heat transfer. For gas flows susceptible to fouling, the recommendation of high turbulence could increase fouling. For tars that are likely to condense during heat exchange, fouling could be affected by the turbulent or laminar conditions.

Third specific aim

How are tar fouling mechanisms and how to prevent them?

Aerosol formation and fouling are both complex processes which make it difficult to model. Previously the dew point was examined, in this chapter focus in a general description of the fouling conditions. The fouling process is not well understood, especially for tars that consist of multiple species. A general description of aerosol and its distribution could help understand this problem and propose a set up for future fouling experiments.

Aerosol description

Aerosols are defined as liquid or solid particles suspended in a gas flow [36]. Clouds and mist are common examples of aerosols. In most process with aerosols, there is a size distribution and shapes. When an aerosol has similar lengths in every dimension it is called isometric, for example in a spherical particle. This is a relevant property as the radius of the particle can be used to describe the size. Aerosols are often described as particles, either liquid or solid.

The behaviour of aerosols depends on external and internal mechanisms. The internal mechanism includes coagulation, condensation, evaporation adsorption and nucleation. External include convection, diffusion and external forces.

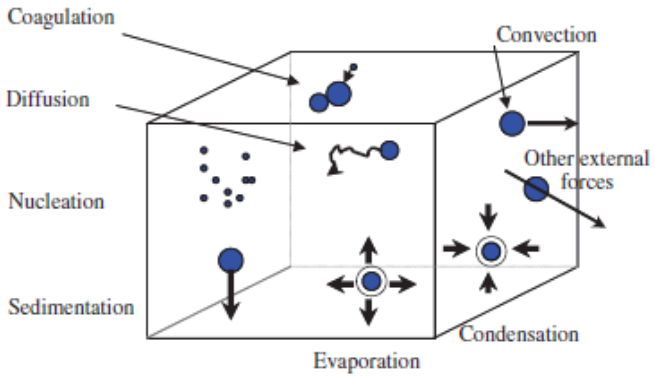


Figure 39. Internal and external mechanisms in aerosol behaviour [37]

There are multiple classifications for aerosols depending on the application. Lognormal distributions are commonly used to describe the particles based on mass, number of particles and total surface area [37]. Depending on the type of aerosols, the distribution is very different. For example, in a system with many small particles and few large particles, the total number of particles would be dominated by small particles. But the total mass of the system could be dominated by large particles, even though they are few in quantity.

This is relevant because of the different nature that tar aerosols can have. Depending on the different species with different partial pressure and dew points, the aerosol behaviour is increasingly complex and might be very dependant on the gasification conditions. Conditions such as the presence of solid particles for aerosols to adhere and grow, the attraction between different species such as polar and nonpolar and more, can affect the aerosol behaviour.

Convective heat exchange conditions

Most heat exchangers operate with turbulent conditions to enhance the convective heat transfer. Turbulence conditions are associated with Reynolds number, although there are exceptions. In a turbulent flow, there are three main regions, a laminar sublayer close to the walls, a buffer layer and the bulk turbulent region [16]. In the bulk, turbulent region eddies have a major role in mixing the flow. This makes properties distribution, such as temperature and mass, close to homogeneous in the bulk.

For heat exchangers design, multiple recommendations depend on the flow and other criteria. For turbulence, it is recommended to have a Reynolds number above 10.000 to enhance heat transfer reducing the size of the buffer layer [38]. This recommendation might change depending on the properties of the flow, the importance of pressure drop and more.

In the bulk of a turbulent flow, aerosols will be carried away by eddies, circular movements inside of a flow. How they are distributed will depend on different factors, including the aerosol properties, which is a complex process. This is especially hard for multiphase flows, as in tar condensation, because of multiple physics that need to be integrated into the simulation.

One of the main complexities from the simulations can be simplified depending on the flow characteristics. Instead of using turbulent flow, recommended for heat transfer, the flow velocity could be decreased until the laminar range. In laminar flow, the Navier Stokes equation that describes the flow is dominated by viscous forces. This simplifies the fluid mechanic equations, with possible solutions for many geometries.

Stokes number

If a flow has different phases, such as gas and liquid, the problem is described as multiphase flow. Depending on the properties of the phases, the second phase or disperse phase could be described as particles. These particles could be in any state (solid, liquid or gas) if it is in a different state from the main flow. A new adimensional number is useful to describe how the particles will interact with the flow called the Stokes number [39].

$$St = \frac{\tau_d}{\tau_T}$$

St: Stokes number; τ_d: $timescale\ of\ disperse\ phase$; τ_T: $time\ scale\ of\ flow$

Depending on this number, particles will be susceptible to the flow, following it or moving with a trajectory of its own.

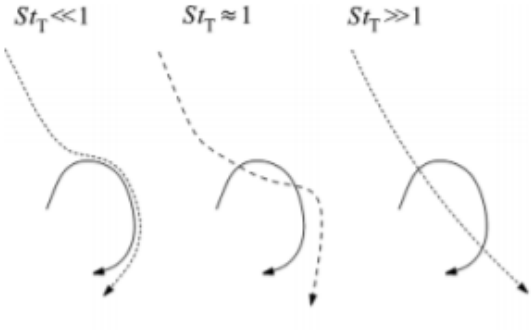


Figure 40. Effects of a turbulent eddy (solid line) on a particle trajectory (dashed line) for different Stokes number [39]

Tars that form aerosols would be particles in the permanent gas flow. Depending on their size, which is one of the most relevant aspects for the particle time scale, the aerosols will follow the flow or not. In turbulent flows, particles with small Stokes number will follow the eddies, while larger particles will have their own trajectory. In laminar flows, turbulent eddies should not be present so particles will follow the bulk of the flow. This means there is a significant difference in aerosol transport in turbulent or laminar flows, while in turbulent particles will move around transported by eddies, in laminar most particles will follow the same trajectory as the flow in a possibly stratified fashion.

For both flow types with aerosols there will be multiple forces affecting the movement, not only related to eddies. These forces will affect aerosols depending on the flow properties, pushing them to the walls or making aerosols coalesce or agglomerate. This will affect how condensed tars could hit and stick on walls during heat transfer, increasing or decreasing the fouling.

Depending on the forces acting over the particles, heat exchangers could be designed to avoid fouling instead of optimizing heat transfer for flows with tars. If tars condense into aerosols, they can be carried away in the flow instead of sticking to the heat exchange walls. Optimizing the conditions for this would prevent fouling, decrease maintenance, and increase the availability of the equipment.

The question would remain for tars condensing directly into surfaces instead of aerosols. Because this condensing mechanism is not well understood, experimental analysis is needed to understand the share of tars condensing as aerosols or directly over surfaces. If a large quantity is condensing as aerosols, laminar flow heat exchange could have a large impact on fouling.

Particle forces

Depending on the size of aerosols forces will be relevant. A review of the main forces is explained, comparing laminar and turbulent flows.

Drag force

One of the main forces over a particle is produced by drag from the flow, generated from the relative velocity between the particle and the flow.

$$F_{drag} = \frac{1}{2} * A_d * C_d * \rho_f * |U_f - U_d| * (U_f - U_d)$$

$$F_{drag}: Drag\ force, A_d: Particle\ area\ normal\ to\ the\ flow, C_d: drag\ coeffcient, U_f: flow\ velocity,$$

$$U_d: particle\ velocity$$

The drag coefficient C_d depends on the particle and flow characteristics. If the particle is small, the drag coefficient would be in the Stokes regime, where viscous forces are much larger than inertial forces. This regime is closely related to low Stokes numbers, described before.

The effect of higher Reynolds number was studied in [40]. The deposition of particles in a square channel was investigated. One of the conclusions was for higher turbulence the deposition was higher for every particle diameter. The turbulence was related to the Reynolds number, from 6.000 to 20.000. Even if no laminar simulation was run, a tendency for higher turbulence-induced a higher deposition of aerosols.

Brownian force

This force is generated from the random collisions of individual molecules to the particles. Is usually modelled with a random white-noise process. It only affects small particles, for larger particles the total force is balanced over the entire surface [39].

Aerosol nucleation would probably start in the range where Brownian forces are relevant. If most aerosols are small particles and stay the same size without growing, this force will have a major role. Brownian diffusion would make small aerosols move in the radial direction along with the heat exchanger, likely towards the walls. During this process it is possible particles will hit each other, possibly growing and reducing this force influence.

Thermophoretic force

Force due to a temperature gradient in the flow. Hot molecules in the flow move faster than colder molecules, provoking a force in the opposite direction to the temperature gradient. This force is relevant only for small particles. Inside of the heat exchanger, there should be large temperature gradients, especially if the flow is turbulent. The bulk and the wall temperature at the entrance of the heat exchanger would have the largest gradient. For laminar flows instead, the gradients would be lower as the flow is stratified with different temperature layers.

Studies about the thermophoretic effect over aerosol particles conclude that a turbulent flow would enhance the effect of particles moving and hitting colder temperatures [41]. The difference from a laminar flow and a turbulent flow would depend on the aerosol characteristic but could be a large difference.

Other forces

Many other forces should have a lower impact over aerosols. This is the case for lift forces, virtual mass forces, history forces and turbulent forces for laminar flows [42]. The total effect over aerosols requires either very good resolutions for the simulation or good models. Neither are simple to obtain due to the variable nature of tars.

Experiment proposal

Experimental analysis of fouling could give important insights from tar fouling. As the condensing and fouling process is complex, experiments would help to adjust the models. With a better understanding of the process, computational fluid dynamics tools could be used to design heat exchangers less prone to foul.

Turbulence

The implementation of these experiments would first be oriented on the difference in fouling for laminar and turbulent flows. The equipment would need to be connected to a gasification process big

enough to provide a gas flow for turbulent or laminar conditions. The main parameter for this would be the flows Reynolds number.

The flow in a tube is considered laminar below 2300 and turbulent above 4000. The region of 2300 < Re < 4000 is the transition range [38], where the flow does not have a clear regime for many fluids. This range is not accurate, a flow can have different behaviour depending on specific conditions but are used as a general condition. Turbulence condition was not possible to achieve in the Chalmers lab reactor as the flow produce were too small. It is always possible to decrease the tube diameter to increase the turbulence, but for small flows, the tube would need to be too small.

A tube of 10 mm diameter could be used to simulate the turbulence conditions. For raw gas using concentrations from Gobigas [12], which is relevant to define the dynamic viscosity and density for Reynolds number, with a temperature of 400 ◦C the required flow at normal conditions for the pump (assuming condensed water) for different Re numbers is shown in *Table 10*.

Table 10. Gas flow and Reynolds number

Pump flow (lt/min)	Reynolds number	Condition
5	513	Laminar
25	2564	Transition region
40	4103	
100	10257	Turbulent

To operate at high turbulence, recommended for heat exchangers, the flow would need to be high for a lab reactor. Instead, this equipment should be implemented in a large reactor, such as the Chalmers Dual Fluidized bed reactor.

Visual inspection

The objective of experiments would be to analyse the tar fouling process. One relevant aspect would be to understand if fouling starts building up slowly around surfaces, possibly due to surface condensation or small aerosols, or suddenly due to large aerosols sticking to the wall. For this, the process should be possible to inspect visually during operation.

The tube for heat exchange should be transparent. This could be done with different types of glasses, such as Duran [43]. Usually fouling at these temperatures is related to heavy tars, which often have dark colours. This would allow visual inspection to determine if fouling is happening and later an optical sensor could be implemented for quantification.

Heat transfer

The process will require heat exchange, cooling the raw gas to replicate real conditions. Because visual inspection is required, the most suitable flow would be air. With a large flow of air compared to the raw gas, the wall temperature of the glass tube in the equipment could achieve a constant temperature. A high-temperature fan to operate from 100 ◦C to 350 ◦C would allow fouling experiments at different temperatures. The air could be heated with electric resistance and recirculated.

Diagram experimental setup proposal

A system to decrease the raw gas temperature in a glass tube to inspect fouling is proposed. Raw gas would be extracted at temperatures above 350 ◦C to avoid condensation of tars in before the setup. After the setup, raw gases could be recirculated to the gasifier.

The air temperature of recirculation would set the wall temperature of the tube with raw gas inside. Adjusting the air temperature different raw gas temperatures could be analysed. For the thermophoretic effect, which is expected to be relevant in the aerosol distribution, increasing air temperature would help to decrease the temperature difference. This would replicate a gas heat exchanger, where both flows are changing temperatures. But this effect would be complicated to obtain in this experimental set up because of uneven temperature distribution due to the flow distribution. Instead, this set up would replicate a boiler, where water is around the fire tubes with a constant temperature set by the pressure.

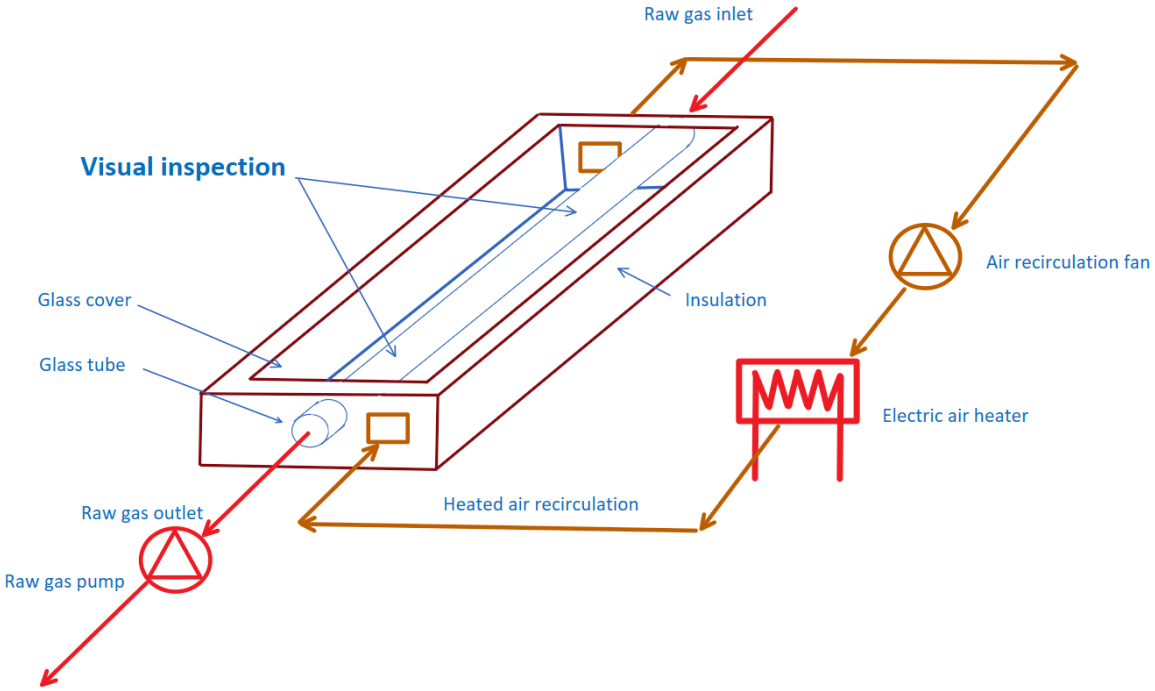


Figure 41. Experimental set up for fouling tests

The main characteristics of the set up would be:

- Changeable glass tubes to decrease or increase the diameter, changing the Reynolds number.
- Visual inspection and later possible optical measurement of fouling.
- Heated air recirculation with a large flow compared to raw gas for constant wall temperature along the tube.
- Raw gas pump with a scrubbing system, to avoid fouling. Adjustable flow to control Reynolds number and flow conditions.

Conclusion

Gasification is a technology with great potential and expected to develop in the future. Raw gases from the process can contain different components, of which tars are especially troublesome below 350 ◦C due to fouling. A solution for fouling consists of cooling fast the raw gases before fouling starts, resulting in a loss of efficiency because of the temperature drop without energy recovery. Recovering energy from raw gases below the tar dew point can provide up to 30% of high-quality energy above 100 ◦C, which would improve the thermal efficiency of gasification processes. Understanding fouling formation could decrease the accumulation of unwanted material, striving for a balance between lower maintenance and higher heat recovery.

Models for dew point prediction were not accurate because of difficulties measuring all the different tars species contained in the raw gas. Instead, an experimental method was performed in a laboratory-scale fluidised bed gasifier to measure the onset of tar condensation for raw gas at different temperatures. First, the total tar concentration for given gasification conditions was analyzed above 350 ◦C to avoid condensation. Next, the gas temperature was decreased, condensing and capturing tars, measuring the total tar difference at different temperatures. This method proved to be successful with easy implementation in the laboratory set up at Chalmers and could be applied to similar facilities. The same sampling probe for raw gas was used, adjusting externally the temperature with an electric heater to set the gas temperature with good results. Using a simple tube extension with glass wool inside was an effective way to capture condensed tars from the raw gas. For further experiments, the set up could be improved to simplify the procedure, demanding less time for multiple samples.

Experiments were performed with biomass and polyethylene. Tar concentrations in raw gas were analysed using the SPA method and GC-FID equipment. Even without knowing the exact amount of each specie, which requires a careful calibration of the GC-FID equipment, the total amount of tars was available in the FID data. Raw gas samples for biomass experiments at different temperatures, between 130 to 300 ◦C, had a difference of 24% tar concentration. This is a significant difference, which would explain the fast fouling of gasification process with raw gases at low temperatures. Because of the low number of experimental runs, the results were corrected based on the amount of the smallest tar, benzene. Experimental errors due to raw gas variability, volume sample and equipment uncertainty were adjusted with good results, showing a consistent trend of higher tar concentration at higher temperatures for the biomass experiments. For polyethylene, the samples were not consistent due to large raw gas variability related to the feeding system. Even though the correction based on benzene was useful, it could be avoided with more samples to reduce the raw gas variability, which was the main issue for the laboratory trials.

The objective of the previous method was to quantify the condensation of tars, but for fouling tars need to condense and stick on a surface. A review of the fouling mechanism related to aerosols and flow characteristics highlighted the complexity of the process. Currently, there are no conclusive solutions to assess total fouling, so test methods are needed to validate the theory and adjust the models. This could be addressed with the help of the proposed design for a piece of equipment to evaluate the fouling under varying conditions. Considering the current design of heat exchangers, based on increasing turbulence to enhance heat transfer, the proposed design could enlighten new designs based on laminar flows to decrease aerosol fouling.

Bibliography

[1] European Commission, "Energy roadmap 2050," Publications Office of the European Union, Luxembourg, 2012.

[2] A. Stranges, "A History of the Fischer-Tropsch Synthesis in Germany 1926-1945," *Studies in Surface Science and Catalysis,* vol. Volume 163, pp. 1-27, 2007.

[3] M. Materazzi and P. U. Foscolo, "The role of waste and renewable gas to decarbonize the energy sector," in *Substitute Natural Gas from Waste*, Elsevier Inc., 2019, pp. 1-17.

[4] H. Thunman, "GoBiGas demonstration - a vital step for a large-scale transition from soffil fuels to advanced biofuels and electrifuels," Department of Space, Earth and Environment, Chalmers University of Technology, 2018.

[5] W. K. John Scheirs, Feedstock Recycling and Pyrolysis of Waste Plastic: Converting Waste Plastic into Diesel and Other Fuels, Chichester, UK: Wiley, 2006.

[6] M. Israelsson, "Tar and Condensable Hydrocarbons in Indirect Gasification Systems," Department of Energy and Environment Division of Energy Technology Chalmers University of Technology, Gothenburg, 2016.

[7] National Renewable Energy Laboratory, "Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion," National Renewable Energy Laboratory, Colorado, 1998.

[8] S. Ciuta, D. Tsiamist and M. J. Castaldi, "Fundamentals of Gasification and Pyrolysis," in *Gasification of Waste Material: Technologies for Generating Energy, Gas, and Chemicals from Municipal Solid Waste, Biomass, Nonrecycled Plastics, Sludges, and Wet Solid Wastes*, Academic Press, 2018, pp. 14-34.

[9] M. Neelis, E. Worrell and E. Masanet, "Energy Efficiency Improvement and Cost Saving Opportunities for the Petrochemical industry. An ENERGY STAR® Guide for Energy and Plant Managers," Environmental Energy Technologies Division. Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, 2008.

[10] J. T. Dawid Taler, "Simplified Analysis of Radiation Exchange in Boiler Superheaters," *Heat Transfer Engineering, 30(8):1–9,* vol. 30, no. 8, pp. 1-9, 2009.

[11] D. Maggiolo, M. Seemann, H. Thunman, O. Santos, A. Larsson, S. Sasic and H. Ström, "Self-Cleaning Surfaces for Heat Recovery During Industrial Hydrocarbon-Rich Gas Cooling: An Experimental and Numerical Study," *American Institute of Chemical Engineers,* vol. 6, no. 1, pp. 317-325, 2018.

[12] H. Thunman, "Advanced biofuel production via gasification - lessons learned from 200 man-years of research activity with Chalmers research gasifier and the GoBiGas demonstration," *Energy Science & Engineering,* vol. 6, no. 1, pp. 6-34, 2018.

[13] Fluid Control Institute, "Tech Sheet #ST 103," 2003. [Online]. Available: www.fluidcontrolsinstitute.org. [Accessed 2020].

[14] P. Z. S. Spakovszky, "Thermodynamics and propulsion," 03 September 2007. [Online]. Available: https://web.mit.edu/16.unified/www/FALL/thermodynamics/notes/node131.html.

[15] R. S. Subramanian, "Heat transfer to or from a fluid flowing through a tube," Semantic Scholar, [Online]. Available: https://pdfs.semanticscholar.org/809a/b85fce9fb51afe436231072631149d15179a.pdf. [Accessed 03 2020].

[16] R. Karwa, Heat and Mass Transfer, Singapore: Springer Science+Business Media, 2017.

[17] ECN part of TNO, "Thersites," [Online]. Available: https://www.thersites.nl/structures.aspx. [Accessed 2020].

[18] J. Kiel, "Primary measures to reduce tar formation in fluidised -bed biomass gasifier," ECN Biomass, 2004.

[19] R. Harb, "Towards synthetic fuels production from biomass gasification: Tar content at low temperatures," *Biomass and Bioenergy,* 2020.

[20] D. P. Tassios, Applied Chemical Engineering Thermodynamics, Athens, Greece: © Springer-Verlag Berlin Heidelberg, 1993.

[21] S. v. Paasen, "Tar Dewpoint Analyzer for application in biomass gasification product gases," ECN Biomass, 2005.

[22] T. B. Vilches, "Operational strategies to control the gas composition in dual fluidized bed biomass gasifiers," Department of Space, Earth and Environment, CHALMERS UNIVERSITY OF TECHNOLOGY, Göteborg, 2018.

[23] M. Asadullah, "Biomass gasification gas cleaning for downstream applications: A comparative critical review," *Renewable and Sustainable Energy Reviews,* vol. 40, p. 118–132, 2014.

[24] H. Boerrigter, " “OLGA” Tar Removal Technology Proof-of-Concept (PoC) for application in integrated biomass gasification combined heat and power (CHP) systems," Dahlman Industrial Group, 2005.

[25] R. Vierhout, "Biofuels and Chemicals from Waste: The Enerkem Contribution to Sustainability and Circular Economy," European Technology and Innovation Platform Bioenergy, Brussels, 2019.

[26] M. Israelsson, "Assessment of the Solid-Phase Adsorption Method for Sampling Biomass-Derived Tar in Industrial Environments," *Energy & Fuels,* no. 27, p. 7569−7578, 2013.

[27] L. M. Blumberg, "Theory of Gas Chromatography," in *Gas Chromatography*, Elsevier, 2012.

[28] S. Aryal, "Online Microbiology Notes," 20 07 2018. [Online]. Available: https://microbenotes.com/gas-chromatography/. [Accessed 03 2020].

[29] J. Neeft, "Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases," Energy project ERK6-CT1999-20002 (Tar protocol), 1999.

[30] A. Larsson, "Development of a Methodology for Measurements at the Gobigas-Gasifier," Energiforsk, 2018.

[31] K. M. Tenny and J. S. Cooper., "Ideal Gas Behavior," The National Center for Biotechnology Information, 2020.

[32] Engineering ToolBox, "Gases - Dynamic Viscosity," 2014. [Online]. Available: Available at: https://www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html. [Accessed 02 2020].

[33] M. Harvey, L. Huber and H. Allan, Handbook of Chemistry and Physics, Boca Raton, FL: CRC-Press, 2011.

[34] Engineering ToolBox, "Specific Heat," 2005. [Online]. Available: https://www.engineeringtoolbox.com/methane-d_980.html. [Accessed 02 2020].

[35] L. Hao, "Filtration efficiency validation of glass wool during thermal desorption–gas chromatography-mass spectrometer analysis of fine atmospheric particles," *Journal of Chromatography A,* vol. 1380, p. 171–176, (2015).

[36] M. Lazaridis and I. Colbeck, "Introduction," in *Aerosol Science Technology and Applications*, John Wiley & Sons,, 2014, pp. 1-14.

[37] M. Lazaridis and I. Colbeck, "Introduction," in *Aerosol Science: Technology and Applications*, John Wiley & Sons, Ltd., 2014.

[38] HRS Heat Exchangers, "Comparison of Laminar and Turbulent Flow," 2020. [Online]. Available: https://www.hrs-heatexchangers.com/resource/comparison-laminar-turbulent-flow/. [Accessed 04 2020].

[39] B. Andersson, R. Andersson, L. Håkansson, M. Mortensen, R. Sudiyo and B. v. Wachem, Computational Fluid Dynamics for Engineers, Gothenburg: Cambridge University Press, 2018.

[40] S. Abuzeid, A. A. Busnaina and G. Ahmadi, "Wall Deposition of Aerosols Particles in a Turbulent Channel Flow," *Aerosol Science,* vol. 22, no. 1, pp. 43-62, 1991.

[41] H. Ström and S. Sasic, "The role of thermophoresis in trapping of diesel and gasoline particulate matter," *Catalysis Today,* no. 188, p. 14– 23, 2012.

[42] C. T. Crowe, J. D. Schwarzkopf, M. Sommerfeld and Y. Tsuji, Multiphase Flows with Droplets and Particles, Boca Raton: CRC Press, 2012.

[43] G. C. &. G. Division, "Borosilicate Glass - Properties of Borosilicate Glass (Pyrex/Duran)," AZO Materials, 6 2019. [Online]. Available: https://www.azom.com/article.aspx?ArticleID=4765. [Accessed 2 2020].

[44] I. C. Vela, "Valorisation of textile waste via steam gasification in a fluidized bed reactor," Division of Energy Technology, Chalmers University of Technology, Göteborg, 2019.

[45] C. Stocker, "Reinforcement learning-based design of orienting devices for vibratory bowl feeders," *The International Journal of Advanced Manufacturing Technology,* no. 105, p. 3631–3642, 2018.

[46] D. Edwards, "Transfer processes: an introduction to diffusion, convection, and radiation".

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