Wet scrubber for cleaning of syngas from biomass gasification

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Abstract—This paper deals with gas wet scrubbing which cleans the impurities in the gas so that the gas may be used in combustion engines. Gas is contaminated and has high temperature (500-800°C) as it leaves atmospheric fluid gasifier. Research focuses mostly on tar elimination and dust removal.

Keywords— biomass, gasification, gas cleaning, wet scrubber

I. INTRODUCTION

Gasification is a very old technology, historic records about its use date back to first half of the 19th century. Mass use of this technology began during World War II when automobiles combusted wood gas. Renewed interest in the technology continued at the turn of 1980s and in the early 1990s. Current research in the area of gasification is fuelled by need to replace fossil fuels with renewable energy sources due to expected unavailability of the fossil fuels in the future and increased impact of greenhouse effect.

Gas generated by gasification contains several impurities which impede its direct use. There are several methods to modify actual gas quality so that it complies with requirements for final gas quality. Primary methods, which positively affect gasification process itself, and secondary methods, which clean the produced gas, are researched. Both of these methods have their pros and cons. Unless their principles, boundary conditions, particulars and restrictions of use are sufficiently described, the methods cannot be compared.

This paper deals with gas wet scrubbing which cleans the impurities in the gas so that the gas may be used in combustion engines. Gas is contaminated and has high temperature (500-800°C) as it leaves atmospheric fluid gasifier. Research focuses mostly on tar elimination and dust removal.

Core of our work lies in research of tar elimination, which is a mixture of higher hydrocarbons and their compounds. Water and organic liquid may be both applied in tar elimination from gas. Boiling point (volatility), availability, and price of organic liquid are major criteria for selection of a proper material. In past, scrubbing oil was often applied for the purposes of extensive research in the area of coal gasification and production of town gas. Biodiesel and/or rapeseed oil methyl ester (RME) are alternatively widely used nowadays. Both liquids were assessed; however, since RME comes from renewable sources of energy and seems to be more environmentally friendly, most of the paper deals with RME technologies.

Scrubbing of gas generated by biomass gasification (or a different organic material) has its own specifics. Gas contains very fine little wettable dust (ash, unburned residues, and soot), tar (mixture of higher hydrocarbons and their compounds) and water vapour. Tar condensates in a wide temperature range from ca. 180 to 300°C and in temperatures below zero. As the tar condensates, it creates adhesive liquid coating on cool surfaces which, together with dust, forms deposits that are very difficult to remove. If the temperature drops below condensation point, fine tar mist is formed; this mist cannot be removed from gas by common separators. Condensation temperature and tar in gas are bound by phase equilibrium.

Different mechanisms apply when water and organic liquid are used in gas scrubbing since the tar has different solubility. This concerns condensation and subsequent capture of aerosol droplets in water applications, and absorption and diffusion in organic liquid applications. Both these mechanisms are described in the paper, and comparison of tar concentrations for various temperatures of scrubbing liquid before and after the gas scrubbing is given. Temperature range for both liquids during experiments overlaps only partially (water: 0-40°C, RME: 30-85°C). Temperature range was selected so that both types of liquid may be later practically applied. In case of scrubbing using organic liquid, the process will be conducted below water condensation point so that amount of waste water polluted with PAH and its derivates is minimized.

In addition to studying efficiency of the scrubbing, we also analysed other properties of scrubbing liquids and important technology aspects. This includes particular transport and thermodynamic properties (heat capacity, viscosity, and vapour tension), disposal and regeneration of waste liquid, risks of liquid treatment, its availability, and price.

II. GAS IMPURITIES

Potential of gas generated by biomass gasification for subsequent production of electrical energy is restricted by difficulties related to purification of this gas. Gas impurities cause several operating problems to facilities. Corrosion, fouling of supply routes and tarring of engines and turbines work areas may lead to severe accidents. Impurities may be
classified as:
- Dust (solid particulate matter)
- Alkali compounds
- Nitrogen compounds
- Tar
- Light hydrocarbons (methane, ethane)
- Heavy hydrocarbons

Chlorine, fluorine, and silicon may also be dangerous for certain pieces of equipment. Silicon is monitored in combustion engines especially as it has negative impact on quality of lubrication oil.

A. Solid particulate matter

Solid particles in raw gas leaving the gasifier comprise inorganic fuel residues (ash), non-reacted biomass in the form of charred material (the so-called coalite), and inert material of gasifier bed. Soot is also present in the dust. Gas with high concentrations of solid particles is typical of gasifiers with bubbling and circulating fluidized bed (turbulent conditions inside the reactor). Thermal treatment of biomass may form aerosol that has negative impact on human health and causes greenhouse effect.

Together with tar, it fouls pipe walls and causes abrasion as well as fouling of equipment modifying and using the gas.

Cyclone separators, barrier filters, electrostatic separators, and wet scrubbers are used and/or tested for elimination of solid particles.

B. Alkali compounds

Biomass is low in dust. Certain components of dust may cause several operation problems, and include alkali metals, i.e., potassium (K) and sodium (Na). These are present in stalk culm plants. Salts of potassium and sodium evaporate below 700 °C; they are easily melttable and form deposits of ash on cooler surfaces of equipment (below 650 °C). Deposits concern mostly heat exchangers, combustion engines and gas turbines positioned beyond generator because unless alkali compounds are removed from the gas, they pass through the whole system, and condensate and deposit beyond the filtering devices. Another issue is a high-temperature corrosion of metal materials, which may be caused by alkali salts, especially if vanadium catalyses the corrosion (cogasification of biomass and waste).

Deposition of alkali salts is usually treated by cooling the gas and eliminating fine particles where salts condensate at temperatures below 600 °C. These technologies are highly efficient, e.g., electrostatic and bag filters, or wet scrubbers.

C. Nitrogen compounds

Most of nitrogen in the produced gas is in the form of N2, and its concentration depends on type of the gasifying medium. Nitrogen also forms compounds where ammonia (NH3) is the main nitrogen component in the raw gas from biomass gasification. NH3 is created by conversion of protein and other nitrogen-containing biomass components. Fuel rich in protein (such as animal waste) are therefore a source of high amounts of ammonia. Cyanide (HCN) is a less significant compound.

Elimination of nitrogen compounds may be performed via standard catalytic methods for NOx reduction. It is even better to use a catalyst for destruction of NH3 prior to combustion or wet scrubbing, provided gas temperatures are low enough. Nitrogen compounds may cause various operation problems in the scrubbers due to high solubility in water since their elimination from the water is very difficult (water is saturated with HCN and NH3 and is not capable of collecting them anymore).

D. Sulphure

Considering the reducing environment in the gasification reactor, sulphure in the raw gas is in the form of H2S (93-96%); carbon disulphide CS2, COS and SOx concentrations are minimum. These compounds are formed from sulphure in the fuel. In general, concentrations of these compounds in biomass are very low (hundredth and tenth of weight %) and thus H2S concentrations are commonly below limits of traceability. Yet, elimination of sulphure from the gas is highly desirable for majority of gas applications because it may cause various operation complications. Sulphure together with chlorine, fluorine, and alkali salts is corrosive for steel constructions. Sulphure is also potentially hazardous for certain types of catalysts, even in low concentrations (ppm). Technology of methanol production from syngas employs catalysts which may be deactivated (poisoned) by sulphure. Particular tar elimination catalysts are also sensitive to sulphure. Therefore it is important to thoroughly eliminate sulphure from the gas.

Wet scrubbing using additives (very costly), reactions of suitable sorbents or adsorption on metal catalysts (see chapter 6.7.3) are field-tested technologies, readily available.

E. Chlorine

Concentrations of chlorine in biofuel are rather low. Despite this fact, chlorine may cause formation of HCl and persistent organic compounds substances (PCDD, PCDF) which are created by reactions of carbon and chlorine, and catalysed by copper oxides. HCl is the most common form of chlorine in the gas.

Wet scrubber may eliminate certain chlorine compounds, especially HCl.

F. Tar

Tar is a by-product of pyrolysis (main source is a volatile combustible). Definitions of tar differ and there had not been a unified scientific view on what constitutes tar, what its composition is, and how to analyse it. Energy Research Centre of the Netherlands (ECN) has researched tar for a long time and initiated a change in studying tar, its components, properties, tar collecting, and analyses. ECN published the so-called Tar Protocol whose definition and methods are recognized both in Europe and in the world [1]. Tar designates a group of organic substances with various
structures and chemical properties with boiling point higher than boiling point of benzene (80.1 °C). [2]

Concentrations of tar in gas from biomass gasification ranges from 1 to 15 g.m⁻³ (in rare cases up to 75 g.m⁻³) depending on a type of gasifier, temperature in the gasifier bed during gasification, temperature and retention time of gas in freeboard, and fuel properties (granulometry, moisture, etc.). [3][4][5]

Tar in gas is in the form of vapours or persistent aerosols. Tar condensates in lower temperatures. Tar, condensed on cool surfaces, creates tar deposits and, together with solid particles, fouls pipe and other equipment. Initiation of tar condensation is related to concentrations of tar in the gas and its composition. If temperatures are below 400 °C, tar components may be dehydrated and start to create charred materials and coke. Not all tar components are dangerous and undesired, certain compounds may have positive impact on gas lower heating value and cause no operational difficulties. Despite this fact, tar is considered to be an underbelly of thermal treatment of biomass. Therefore, if the gas from biomass is to be further used, tar has to be removed.

III. DECREASE IN CONCENTRATIONS OF TAR FROM GAS

There are generally two types of methods to decrease tar concentrations in gas: primary and secondary methods. Secondary methods further distinguish between dry and wet procedures.

A. Primary methods

Primary methods concern procedures performed inside the reactor. This is a desired practice because it has a potential to increase a total efficiency of energy conversion; concentrations of tar in produced gas are reduced and subsequent tar disposal is eliminated. In general, two procedures are applied:

Thermal destruction – pyrolysis process takes place with temperatures above ca. 1200 °C, no catalysts needed [4]. There is no minimum temperature defined for efficient destruction which depends on type of tar produced in reactor. Gasifiers with counter-current arrangement and sliding bed create primary tar and sufficient temperature for thermal destruction is 900 °C. Partial combustion of produced gas usually increases temperature; however, this process is accompanied by decrease in lower heating value by 25-30 %. Use of plasma also increases temperature but this is more suitable for waste disposal where electrical energy necessary for plasma creation is a by-product. Both these procedures are expensive and therefore thermal destruction is not a very promising method of elimination of tar from gas produced in biomass gasification.

Catalytic destruction – various materials, such olivenite, silica sand and other minerals and metals, are added into reactor fluidized bed as catalysts to enhance cracking. Dolomite, thanks to its availability, price and properties, seems to be the most promising catalyst. Relatively high temperatures and turbulent streamings produces intensive reactions in the fluidized bed; however, catalyst is scratched and becomes deactive. On the other hand, there is insufficient contact between catalyst and tar in fixed bed reactors, and tar destruction is often incomplete.

B. Secondary methods

Secondary methods for decrease in tar concentrations are applied outside of the reactor:

Barrier filters – fixed layer of loose material, e.g. wood chips, sawdust, cork, sand. Filters remove especially dust (tar elimination is less significant). Also, there has to be a continuous renewal of filtration material so that high pressure drop due to filtration cake is avoided. Used material has to be either regenerated, combusted or disposed.

Catalysts – dolomites, zeolites, calcites, and silicates are commonly used for tar destruction as well as metal catalysts based on Ni, Mo, Co, Pt, Ru, and other metals. Majority of metal catalysts is highly sensitive to sulphure deactivation and their life is rather short. Tar elimination using dolomite achieved 95-99 % efficiency in laboratory conditions, with temperature ranging from 750 to 900 °C. Obsvious disadvantage is the need to reheat the gas (temperature of gas leaving a reactor is mostly below 800 °C) to temperatures above 900 °C. Temperature distribution also has to be even throughout the whole reactor. Catalyst may be heated internally by gas combustion (decrease in lower heating value will be smaller than decrease for thermal destruction); catalyst may be heated with external sources of heat. Both types of heating lower the efficiency of the equipment. Dolomite may be further deactivated due to carbonate forming on the catalyst surface, and it is also sensitive to scratching (due turbulences in a bed – slightly bubbling fluidized bed).

Wet scrubbers – droplets of separated matter and scrubbing liquid precipitate in the scrubber, and thus decrease tar concentrations. Formation of tar droplets has to be preceded by cooling of the gas to temperatures below 100 °C (usually from filtration temperature of ca. 250 °C - separates solid particles). Exhaust temperature of gas is required to range from 35 to 60 °C. Scrubber must comprise a cooler, fine tar mist separator, and occasionally a solid particle separator, at the same time. High concentrations of solid particles may have a negative impact on efficiency of the process of tar elimination. In addition to condensation and precipitation of particles, other physical phenomena may be used for tar elimination, e.g. diffusion, solubility, and absorption. Therefore, we should focus on properties of scrubbing liquid that not only collects the relevant particles but also cleans the gas. This issue is discussed further in the text. Disadvantage of gas scrubbing systems is their decreased efficiency, which may be influenced by applying organic liquids. High-capacity sensible heat of the gas passes into a scrubbing liquid but cannot be utilized due to low output temperature of the liquid. Unless a different liquid is used, polluted water is produced and has to be pre-treated before entering the sewage system.

IV. COMPARISON OF SCRUBBING LIQUIDS

Elimination of tar from gas using a wet scrubber technique
differs for water and for RME. Although the scrubber may remove dust from the gas, dust should be removed prior to entering the scrubber as it may cause several difficulties in operation of the equipment.

A. Scrubber using organic liquid

Several organic liquids dissolve tar compounds very easily. The two substances may be mutually miscible. Scrubber using organic liquid separates tar by absorption and the process is driven by differences in actual and equilibrium concentrations. Temperatures of scrubbing should be higher than condensation point of water contained in the gas because properly selected scrubbing liquid provides satisfactory results even for high temperatures (e.g. 70-90 °C) and the scrubbing liquid should be easily regenerated. Process of tar elimination from the gas using organic liquid may be divided into several stages:

− Direct gas-to-liquid contact cooling – gas inlet temperature should be higher than initial condensation temperature of tar so that fouling of connection pipes and equipment located prior to absorber is prevented. Certain amount of tar is to be absorbed by scrubbing liquid during a cooling phase. Tar vapors may be oversaturated and aerosol formed due to sudden temperature drop; this does not occur on large-scale basis, though. Outlet gas temperature should not be lower than water condensation point so that scrubbing liquid is not spoiled.

− Tar absorption and tar mist separation – mass transfer by diffusion, driven by concentration differences, occurs when gas gets in contact with liquid under relatively stabilized temperatures (gas may be further cooled in second stage of tar elimination). Mass flow dominates over mechanical actions in aerosol separation. Scrubber for mass transfer is preferred in a second stage of tar elimination. Efficient droplet separator should be arranged beyond the scrubber to avoid scrubbing liquid or coagulated aerosol droplets leaving the scrubber.

− Cooling and treatment of gas – temperature of gas leaving the scrubber is too high and cannot be lead directly into combustion engine; therefore the gas has to be further cooled. Gas is not saturated with tar vapours due to absorption of tar by scrubbing liquid and may be further cooled to a certain level without the risk of condensate formation. Or another stage of gas cleaning may be alternatively located beyond the scrubber, e.g. for elimination of hydrogen sulphide, hydrogen chloride or nitrogen compounds.

B. Scrubbing using water

Water absorbs PAH only to a certain degree. It saturates quickly and tar starts to form a separate liquid phase – sub-micron type of aerosol (tar mist). This dispersion has to be separated so that the gas is pure enough. Tar separation in water-scrubber consists of following steps:

− Direct gas-to-liquid contact cooling – gas inlet temperature should be higher than initial condensation temperature of tar so that fouling of connection pipes and equipment located prior to absorber is prevented. Minority of tar may be absorbed by water during the cooling stage; tar vapours may be oversaturated and aerosol formed due to sudden temperature drop; water condensates in low temperatures, too.

− Tar mist separation – expected dispersity of tar mist reaches 0.1 to 2 μm, according to literature. Tar droplets may be separated using certain types of scrubbers or other separators, see below. Their use is limited by a potential of micron and submicron particles to be separated.

− Gas heating – gas leaves the equipment saturated with tar, it is therefore recommended to slightly increase its temperature to prevent further condensation. Final outlet temperature has to be lower than maximum allowed temperature of the gas at the engine entrance.

Gas may be cooled to low temperatures using organic liquids, e.g. scrubbing oil. Outlet tar concentrations may be much lower, too. Disadvantage of this solution is the mixing of condensing water and organic substances. Used liquid is then hard to regenerate. If water is the cooling medium, NH₃, H₂S and HCl may be absorbed from the gas, too. However, absorption process is limited by water saturation, and successful separation of these gases is conditioned by regeneration of the scrubbing liquid.

Efficient droplet separator should be positioned beyond every scrubber so that final effect of the method is not spoiled by droplets driven by scrubbing liquid and aerosol.

V. METHODOLOGY OF MEASUREMENT AT BIOFLUID 100 GASIFICATION FLUID GENERATOR

Research was performed at Biofluid 100 stand (see Fig. 1) which is equipment with stationary fluidized bed.

Fig. 1 Experimental equipment Biofluid 100

Simplified scheme of experimental equipment is presented at Fig. 2. Fuel is supplied from fuel storage tank equipped with
shovel and is introduced via dosing screw with frequency convertor into reactor. Primary supply of blower compressed air is lead into reactor under the bed, secondary and tertiary supplies are located at two high-rise levels. Produced energogas is stripped of its solid particulate matter in cyclone. Output gas is combusted in burner equipped with stabilization burner for natural gas and individual air supply. Ashes from reactor can be removed from tank located beneath bed. Power based heater for primary air supply is placed behind blower so that impact of air preheating may be monitored. In recent years, filters for research of efficiency of various methods of gas cleaning were attached to basic part of stand.

Reactor parameters:
• Capacity (in produced gas) 100 kW_t
• Fuel demand (consumption, requirement) 150 kW_t
• Wood consumption 40 kg.h⁻¹
• Air flow rate 50 m³.h⁻¹

Basic characteristics of operation at fluid generator are described in following respect:
• Operation of fluid generator – after ignition, fluid generator is operated in combustion mode so that its heating is quick. After achieving required gasification temperatures, secondary and tertiary air is supplied into generator and thus produced gas is immediately combusted and consequently heats up the generator. Air supplies are then shut off and generator is introduced into stable mode for specific and preset gasification temperature. Stable mode is achieved when amount of dosed fuel is not altered, amount of gasified air is even and temperature swings in middle section of gasification generator are stable within narrow range given by gasification temperature.

• Frequency of convertor of dosing screw so that mass flow rate is determined;
• Temperature in various parts of equipment which is measured by thermocouples; position of thermocouples is given in detail in scheme at Fig. 2. There are 3 thermocouples along generator top, 1 thermocouple in cyclone and 2 thermocouples in in semi-coke pipe, 1 thermocouple in output gas pipe and 1 thermocouple measures temperature of primary air supply.
• Pressure difference between upper and lower sections of fluid generator (fluid bed);
• Pressure difference at orifice plate so that gas flow rate is determined;
• Pressure of the generated gas at the generator outlet and at the fuel storage tank.

Other values such as temperature and air moisture, primary air flow rate and its temperature have to be recorded manually.

Aim of the research was to determine concentrations of tar eliminated from the generated gas. Tar samples were collected using a methodology of Tar Protocol [6] and evaluated by weight spectrometer of a gas chromatograph.

VI. RESULTS AND DISCUSSION

Several experiments were performed to assess theoretical requirements of gasification. Results are given in the graph below.

[Graph showing scrubber efficiency and condensation point temperature on temperature]

• Graph shows a strong dependence of scrubber efficiency on scrubbing water temperature and thus also on condensation point of tar after scrubber. If RME is used as a scrubbing liquid, this dependence is not obvious. This may be attributed to the fact that efficiency of tar absorption by RME is very high and no dependence can be observed.
• Paper deals with elimination of tar from gas generated by biomass gasification. Tar is especially dangerous due to
formation of thick condensate. Engine manufacturers do not provide limit concentrations of tar but they do require there are no condensates in the suction area. Problems related to corrosion (H₂S, HCl, and NH₄Cl) and fouling (alkali compounds, tar, dust, NH₄Cl) may arise during cooling of gas from gasifier outlet temperature (ca. 700 °C) to engine inlet temperature (10-60 °C). It is recommended to eliminate dust at high temperatures (ca. 180-300 °C, depending on tar concentration and composition) and then lead the gas into the scrubber; this procedure helps prevent formation of sticky deposits (mixtures of tar and dust).

- Sudden cooling of gas creates fine persistent aerosol: tar mist. Size of aerosol droplets ranges from 0.1 to 2 μm. If gas saturated with vapour cools slowly, small amount of droplets nuclei are formed which develop into small droplets, as the gas continues to cool. If the gas is cooled suddenly, lot of droplet nuclei are formed and later form small droplets. If the diffused droplets are very small, mist is stable. Efficient elimination of aerosol or prevention of its formation is a key factor in gas scrubbing.

- Combustion engines require gas free from mist with temperature sufficiently exceeding condensation point of the tar. Temperature of cool walls and external pressure in suction must be considered.

- There are vast differences between water scrubbing and organic liquid scrubbing.

**A. WATER**

- Solubility of most tar components in water is low (except for heterocyclic compounds). Absorption by pure water eliminates heterocyclic compounds and highest PAH, especially. Polycyclic hydrocarbons with two to three rings remain in the gas and their concentrations allow for subsequent condensation. Separate liquid phase is either driven by water or leaves with gas in the form of aerosol. Water supplied to real-life equipment is assumed to be partially saturated with tar. Tar scrubbing is therefore based on elimination of aerosol.

- Disadvantage of gas scrubbing using water is a transfer of applicable heat of the gas into low-potential production of environmentally unfriendly waste water; another disadvantage is the need to have a source of cool water or equipment for its production. During summer, facilities may utilize spray tower, sprinkled cooler or chiller. Chiller is very expensive.

- Method of scrubbing using water is relatively cheap.

**B. ORGANIC LIQUID**

- Most of the tar components are fully soluble in the organic liquid. Ability of organic liquids to collect tar is therefore high, and the equilibrium concentrations corresponding with the selected temperature are much lower than equilibrium concentrations of tar condensation. Elimination of tar using organic liquid is based above all on diffusion, and therefore it is necessary to use an efficient mass exchanger. Similar to the technology of water scrubbing, the gas must be cooled. Gas output temperature should not drop below 75-80 °C (depending on gas moisture) so that scrubbing liquid is not impaired by the condensing water, and that no condensation of water disrupts the heat and mass flows in the scrubber.

- The advantage of organic scrubbing is high efficiency and ability to reduce tar condensation point well below the scrubbing temperature. Other positive aspects include: virtually waste-free facility and the ability to use gas heat for cooling of scrubbing liquid.

- Disadvantage of scrubbing using organic liquid is especially the high cost of scrubbing liquid, which must be constantly replenished due to evaporation.

- Type of organic liquid should be selected with respect to price, in accordance with Ewell classification and vapour pressure. Considering the need to minimize the liquid loss, scrubbing liquid pressure at operating temperature should be as low as possible.

- For economic reasons, it is desirable that the tar concentrations, or concentrations of other impurities in the gas, are minimized within the scope of primary methods (as a part of optimization). This reduces consumption of scrubbing liquid and requirements for gas scrubber efficiency.

- Organic dust dispersed in the generated gas is difficult to wet with water and contains a large proportion of micron and submicron particles. Its removal in water scrubber is therefore very difficult. Alternatively, direct water cooler and electroseparator may be used. Elimination of dust using organic liquid is, from the physical point of view, relatively simple, and it is therefore possible to combine the process with tar scrubbing. It is necessary to be careful and take measures to prevent the formation of sticky deposits in the scrubber and find solution to liquid regeneration problems. Elimination of dust using textile filter seems to be a much easier solution for both tar elimination methods.

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**REFERENCES**


