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METHODS FOR CLEANING OF GAS FROM GASIFICATION OF STALK

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Due to the continuous growth of energy consumption it is required that development in the energy sector is focused on renewable energy sources. Another possibility to reduce the consumption of primary energy resources is also searching for new and non-traditional fuels. Stalk and slightly contaminated biomass are representatives of these non-traditional fuels. Stalk is mostly annual plants grown primarily for subsistence. Waste parts of these plants can be utilized for production of energy. The thermal gasification is one of the possibilities to use biomass efficiently. Gasification can be understood as the thermo-chemical conversion of solid fuel into the gaseous state. The gas with low heating value is on the outlet from gasification process. The main components of produced gas are hydrogen, carbon monoxide, and methane. The final gas contains also a lot of undesirable constituents which handicap this gas for energy usage. These constituents are neutral components, that dilute gas only, and pollutants as dust, tar and compounds of sulphur and chlorine, which complicate further use of the generated gas. The research paper is focused on thermal gasification of stalk and other non-traditional fuels in Biofluid experimental device. The aim is to design methods for cleaning the raw gas from the tar compounds. The research is focused on the secondary gas cleaning methods aiming at high purity of the final gas.
Key words: gasification, biomass, straw, tar, catalytic cleaning, fluidized bed.

Metode čišćenja plina odplinjavanjem iz stabljika bilja. Zbog neprekidnog rasta potrošnje energije razvoj energetskog sektora potrebno je usmjeriti na obnovljive izvore energije. Druga mogućnost smanjenja potrošnje primarnih izvora energije također je u potrazi za novim i netradicionalnim gorivima. Stabljika i malo onečišćena biomasa su predstavnici tih netradicionalnih goriva. Stabljika je uglavnom jednogodišnja biljka koja se uzgaja prvenstveno za opstanak. Otpadni dijelovi biljaka mogu se upotrijebiti za proizvodnju energije. Toplinsko rasplinjavanje je jedna od mogućnosti učinkovitog korištenja biomase. Rasplinjavanje se može shvatiti kao termokemijska konverzija krutog goriva u plinovito stanje. Na izlazu iz procesa rasplinjavanja je plin s niskom ogrjevnom vrijednosti. Glavne komponente proizvedenog plina su vodik, ugljikov monoksid i metan. Konačan plin sadrži također mnogo nepoželjnih sastojaka koji su hendikep za energetsku iskoristivost tog plina. Ovi sastojci su neutralne komponente, koje samo razrjeđuju plin, i onečišćenja poput prašine, katrana i spojeva sumpora i klora, koja kompliciraju daljnje korištenje sintetskog plina. Znanstveni rad usmjeren je na toplinsku plinofikaciju stabljike i drugih netradicionalnihgoriva u Biofluid eksperimentalnom uređaju.Cilj je dizajnirati metode za čišćenje sirovog plina od katraniziranih spojeva. Istraživanje je usmjereno na sekundarnu metodu čišćenja plinova s ciljem dobivanja konačnog plina visoke čistoće.
Ključne riječi: plinofikacija, biomasa, slama, katran, katalitičko čišćenje, fluidizirani sloj.

INTRODUCTION

Energy from biomass has recently focused mostly on combined production of electricity and heat (heating plants and cogeneration units). This is a more effective method of fuel energy utilization. Cogeneration operation has higher efficiency and the generated energy is cheaper. With respect to difficulties concerning fuel transported over long distances, current trends favor small-scale cogeneration energy units.

Since electricity is a commodity much more valued that regular heat, facility operators try to acquire the highest share of generated electricity from the supplied fuel in energy cogeneration process.

Thermo-chemical conversion of solid biomass into gaseous fuel generates more electricity if the gaseous fuel is used in combustion engines or in combustion turbines. This type of power equipment requires a certain degree of gas purity for its smooth operations. Raw gas contains several undesired substances and compounds that have to be eliminated from the generated gas. Therefore, our research tackles methods of raw gas cleaning. Tar and dust are among the main polluting agents in the raw gas. Tar in raw gas (up to 10 [g.mn-3]) greatly exceeds limits stipulated for use of the gas in combustion engines (max. 50 [g.mn-3])[1].

This article discusses elimination of tar compounds from gas generated in thermal gasification of stalk. Primary methods of gas cleaning (i.e. technologies restricting tar compounds formation) proved insufficient due to relatively high demands on gas purity for combustion engines. Secondary methods for cleaning of generated gas (i.e. elimination of tar compounds from already generated gas) were validated as more suitable. Thanks to secondary methods, tar content in the generated gas reaches values of several orders lower than if primary methods are applied.

COMPARISON OF GAS GENERATED FROM WOODS AND STALK

To compare are on next figure shown content of tar compounds in gas produced from fluidized bed gasifier. As fuel were usingdifferent type of wood and plants.

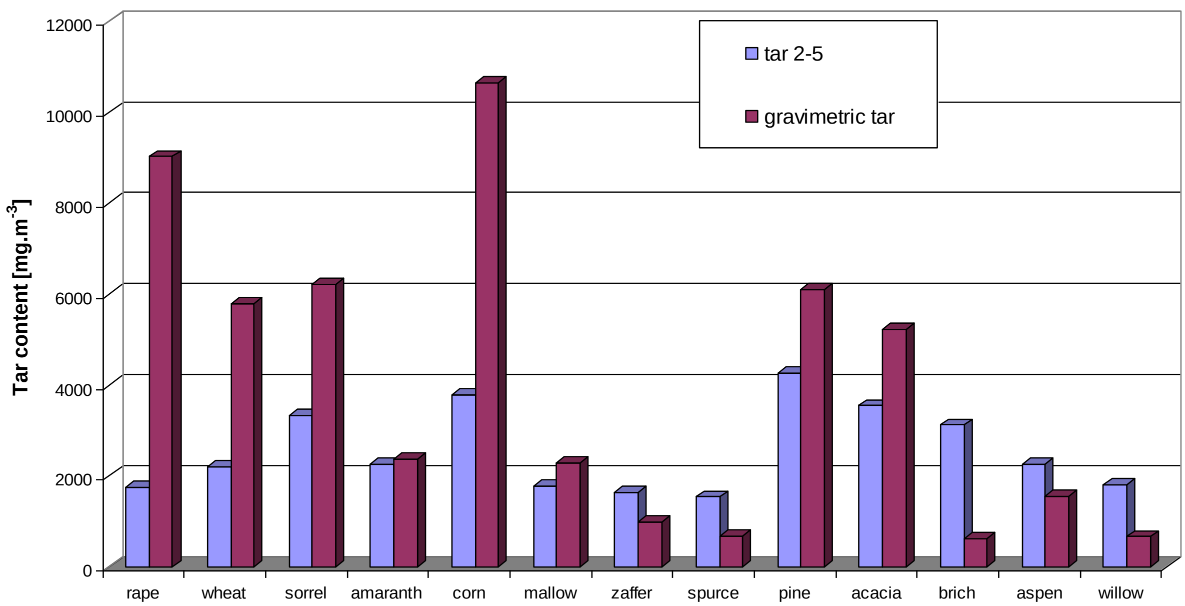

Figure 1. Comparison of tar content for stalk and woods [2]
Slika 1. Usporedba sadržaja katrana za stabljike biljaka i drveća[2]

WHAT ARE STALKS?

Stalks or straw areusually purposefully grown annual plants. In this case, stalk is different indication of straw. The most known stalks are wheat, corn, rape, rye, barley, this stalks are primary used for food production.In energy production are usually used waste parts of these plants. Seeds or grain form these plantsare mostly used for food purposes. In agriculture are parts of stalk used for feeding of livestock. Others group of stalks include amaranth, sorrel, lucerne etc. Crops belonging to this group are mostly grown specifically for energetic usage.

EXPERIMENTAL GASIFICATION DEVICE

Testing of stalk gasification was performed at a BIOFLUID 100 experimental device located in Energy Institute laboratories. Biofluid 100 is an atmospheric gasification reactor with a fluidized bed.

Types of undesired substances in gas generated from stalk are similar to substances in gas generated from wood chips and wood scobs. Concerning dust particle content, concentration might be slightly higher compared to woods as this depends on quality of fuel handling. High amount of dust particle contaminates the fuel during harvest, chipping process and transport. Biofluid 100 is equipped with cyclone that separates the dust.

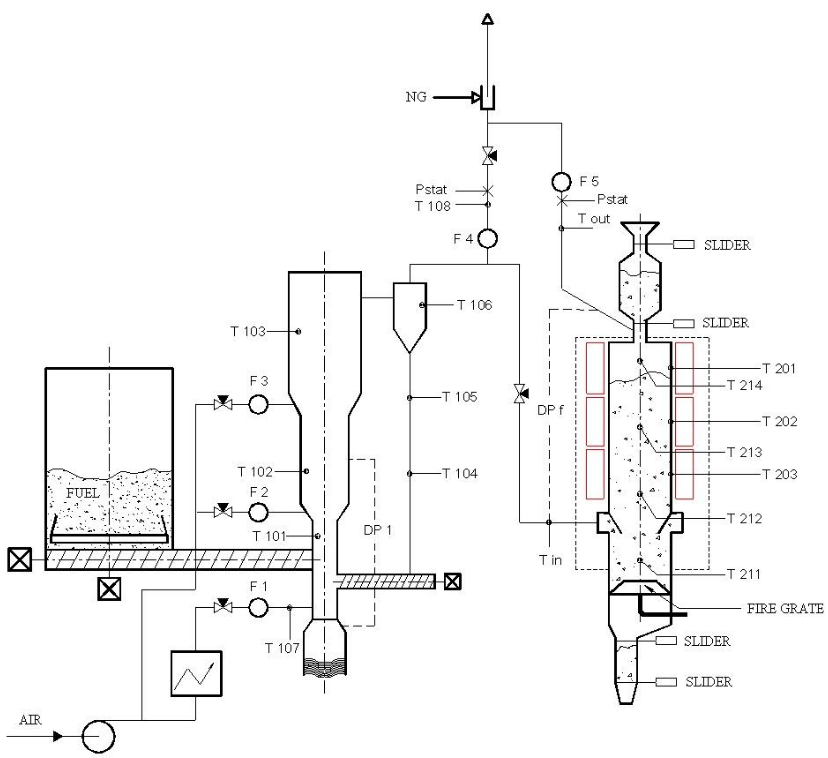

Figure 2. Scheme of experimental equipment BIOFLUID 100
Slika 2. Shema eksperimentalne opreme BIOFLUID 100

Amount of tar compound content to unit of generated gas is crucial for raw gas cleaning. Concentrations of tar in gas generated from various types of fuel (woods, stalk, see Fig. 1) are given in a previous chart. Several types of woods generate even more tar than stalk in the gasification process. Tar concentration therefore depends on particular type of stalk and woods. Yet, we have to bear in mind that tar compound content greatly depends on conditions in the gasification reactor.

TESTED FUELS

Several types of biofuels in the form of chopped straw and pellets were tested in experiments with fluid gasification of stalk. Tested biofuels mostly included waste from agricultural production (wheat straw, rape, lucern, meadow mixture) and purpose-grown energy crops (sorrel). Our objective was to maintain stable operation of the gasifier and sample gas and tar. We also tested gasification of non-traditional fuels (chipboard, digestate) and tar samples were taken, too. Following chart (Fig. 3) shows differences between individual fuels during the testing.

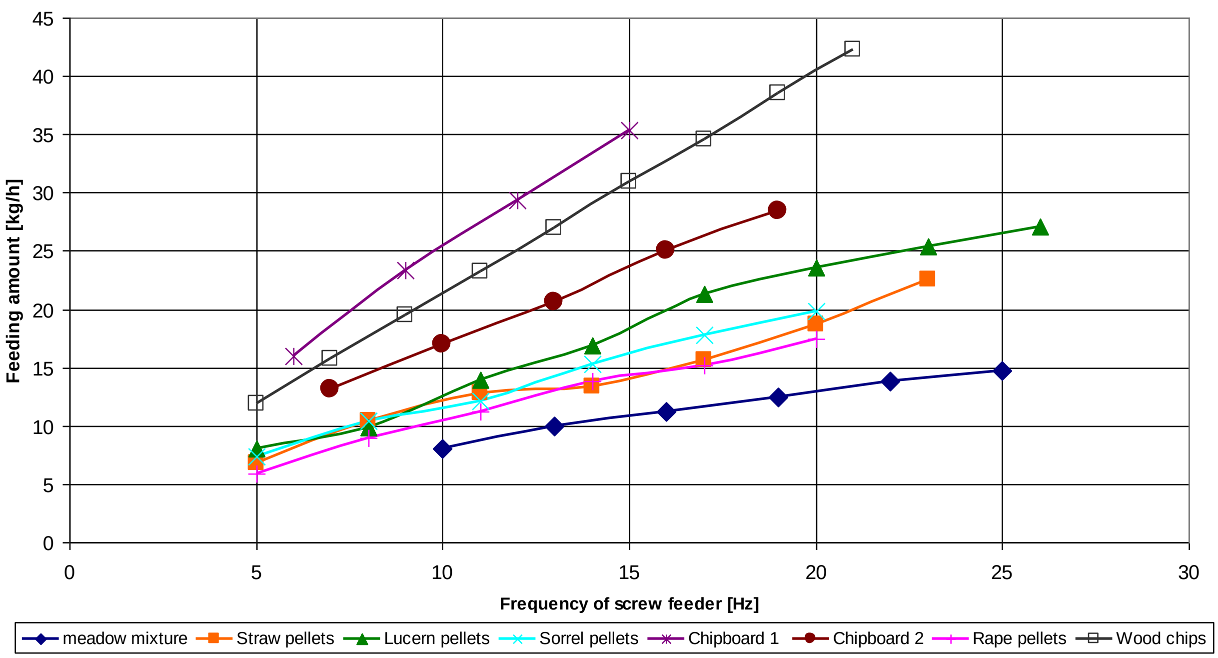

Figure 3. Results of testing of various fuels used in experimental gasification
Slika 3. Rezultati testiranja različitih goriva korištenih u eksperimentu rasplinjavanja

EXPERIMENTAL STALK GASIFICATION

Similar to gas samples comparison, relevant comparison of tar samples from individual fuels requires as identical operational conditions during gasification process as possible (especially temperature in primary section of the gasifier). Tar compound concentrated in generated gas are especially influenced by gasification temperature [3]. Tar analysis is focused on higher hydrocarbons whose ability to decompose into simpler compounds decreases in low gasification temperatures. Tar concentrations in generated gas are then significantly higher.[4]

First testing with stalk gasification was aimed to verify whether stalk may be thermally gasified using Biofluid technology. Even at this point, several fuels proved unsuitable. These fuels included straw, meadow mixture and lucern. These fuels restricted smooth running of the reactor and sampling. Concerning long-run operation of the gasifier, remaining stalk did not perform any better.

EXPERIMENTAL VERIFICATION OF CLEANING PROCESS

When trying to verify methods of cleaning of tar from generated gas, we encountered problems with maintaining the gasification process. In other words, it is a bit irrelevant to research cleaning of gas generated from stalk if the gasification process itself is not stable. However, despite the difficulties with gasification, we managed to verify the technology of cleaning of generated gas.

We also experimentally verified a secondary method of gas cleaning using natural catalyst, i.e. dolomite. Dolomite is a cheap, widely used catalyst with effects proven in previous measurements. Gas was cleaned in hot catalytic filter (HCF) which is attached to the gasification reactor outlet. Hot catalytic filter comprises sliding bed of grainy material which allows for continuous partially regeneration of filter filling during experiment. HCF is heated with electric furnaces so that temperature for catalytic cleaning temperature is achieved.

Following chart (Fig. 4) shows evaluation of tar compound content in gas sampled from rape pellets gasification. Generated gas was always sampled at the same time before and beyond the HCF. Tar component is more concentrated prior to HCF than in samples taken beyond HCF, as expected. However, efficiency of gas cleaning is relatively low. Residual concentrations of tar after cleaning are still high. This is caused by insufficient heating of HCF where the temperature in filter axis reaches around 700-720 °C. Dolomite functions properly as a catalyst with temperatures above 800 °C (870 °C ideally) [3].

Improper function of catalyst may be further caused by negative impact of compounds contained in stalk and/or chipboard on catalyst. Some of the compounds may behave like catalyst poison. Catalyst poisons are substances that strongly absorb on the catalyst surface and thus prevent decomposed components from entering active catalyst centres [5]. Concerning dolomite catalyst, this option is rather hypothetical as dolomite is less susceptible to deactivation than metal catalysts. Moreover, dolomite filling is partially regenerated in catalytic filter, which minimizes impact of poison and fouling of the catalyst.

The tar compounds are summarized to the three basic group of tar. First is faction BTX. In this group are substances like benzene, toluene, styrene, m+p+o xylene, ethyl-benzene and others. Second group summarized oxygen substances (phenol, methyl-phenol, PCDF etc.). Last group include substances based on PAH.

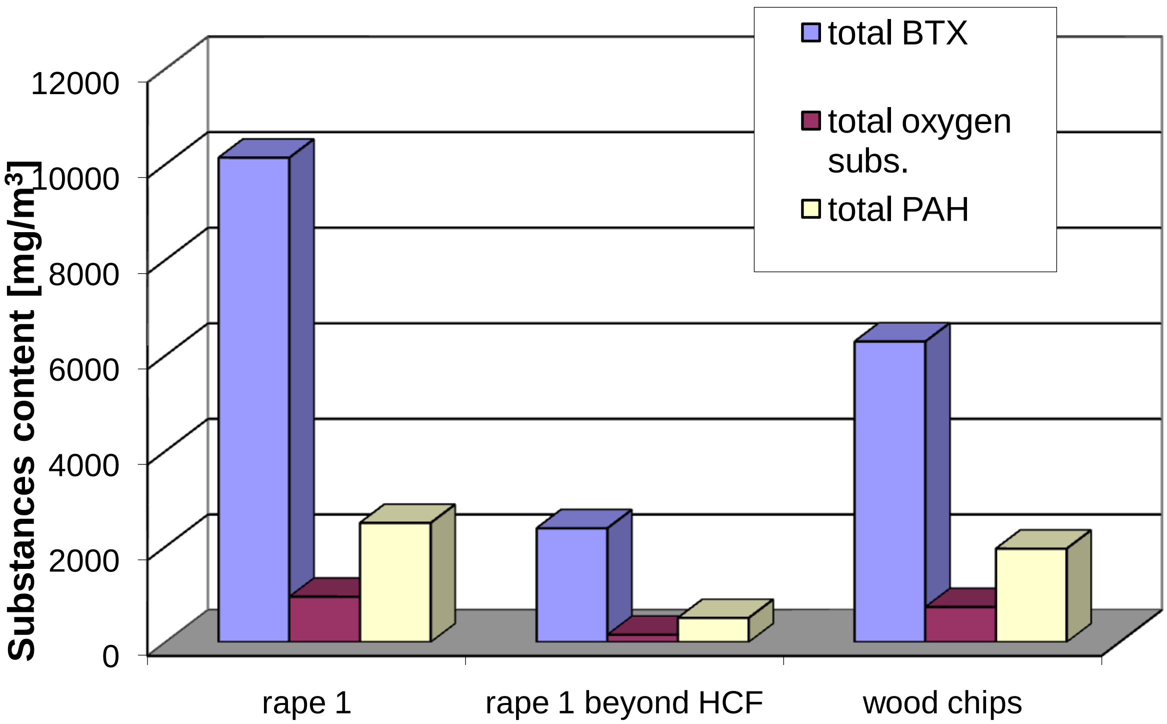

Figure 4. Tar compound content sampled before and beyond HCF during gasification of rape. To compare isthere shown content of tar in gas from gasification wood chips
Slika 4. Sadržaj katranskih spojeva u uzorcima prije i poslije HCF rasplinjavanja repice. Za usporedbu je tu prikazan sadržaj katrana u plinu iz rasplinjavanja drvne sječke

Chippings for chipboard, i.e. contaminated biomass, represent a non-traditional fuel. This material produces lot of tar compounds duringthe gasification process. It contains increased content of PAH and n-alkanes, i.e. compounds with high molecule weight, when compared to other discussed fuels. Increased content of complex molecules in the generated gas, e.g. PAH and n-alkanes, may be caused by different material composition of the chipboard.

Chipboard is not a conventional biomass since its properties have been modified by addition of binding material, adhesives, and colours. Gas generated from chipboard has relatively good energy potential but it contains large amount of harmful substances. However, gas in thermal gasification is not a final product. It is a sort of an intermediary product that is incinerated in the following technology at the shortest time after it has been generated. Thus it makes sense to measure harmful emissions after the gas is incinerated.

METAL CATALYSTS

Sulphur compounds have negative impact on most of catalysts, in general. This is a problem especially with metal catalysts. Metal catalyst poisons include compounds from Vb and Vlb groups in a periodic table (S, As, Se, Te, Pb, Sb, etc.). Compounds with unsaturated bonds also have negative impact on metal catalysts (CO, cyanide, unsaturated hydrocarbons) [5].

Cleaning properties of nickel catalysts were previously tested in laboratories of Energy Institute. Catalyst poisons of nickel catalysts include mainly compounds of sulphur, even if original biomass contains only low amount of sulphur (wood chips) [5]. Since stalk contains higher amount of sulphur than wood chips for which nickel catalysts were tested and sulphur deactivation issues arose, we refrained from using this type of catalyst. Catalyst would be deactivated shortly after the experiments started, moreover, metal catalysts are expensive and hard to obtain.

CONCLUSION

Main objective of the experiment was to test the potential of thermal gasification of stalk and verify differences between gas generated from common wood chips and gas generated from stalk. Experiments proved that certain types of stalk may be gasified. It is crucial, however, to maintain continuous and slow regulation of the screw due to risk of clogging.

Fluctuating pressure drop of fluidized bed reflects worsened stability of the gasification process itself. Fluctuation may be caused by non-homogeneity of the tested fuel. Chopped straw from stalk has generally lower power density and large share of fine fraction, which results in unstable dosing of fuel into fluidized bed of the gasification reactor.

Samples of tar compounds was taken before and beyond HCF during stalk gasification show a decrease in tar content after the cleaning process was performed. Impact of different filter temperatures upon catalyst efficiency corresponds with values measured during biomass gasification. Gas cleaning using natural catalysts brings identical results both for stalk gasification and wood biomass gasification.

Acknowledgement

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