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Ultrafiltration as a method of preliminary treatment of wastewater formed during gasification

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ABSTRACT

Gasification is regarded as the most promising technique considering both syngas and energy production. It is a process during which the solid fuels at proper process conditions and at presence of a gasification agent are converted into gaseous products. The finally obtained gas, however, besides desired gases, contains also a range of inorganic and organic contaminants, which need to be removed before its further processing. The use of various gas cleaning techniques is always accompanied by the formation of a highly loaded wastewater. Its proper utilization is said to be the key for gasification popularization and commercialization, especially in case of the use of solid alternative fuels and small and medium installations. In the presented study, ultrafiltration of gasification wastewater was performed as a method for preliminary stream treatment. Two polyethersulphone membranes differed in cutoff, that is, 50 and 30 kDa, were investigated at various transmembrane pressures ranging from 0.2 to 0.3 MPa. The obtained results showed that the method could be used for preparation of the stream for further treatment by means of, for example, nanofiltration or advanced oxidation, while the concentrate could be recycled to the gasification reactor.

Keywords: Gasification; Wastewater; Tars; Ultrafiltration; Fouling

1. Introduction

Gasification of solid; alternative fuels, that is, biomass; RDFs (refuse derived fuels); SRFs (solid recovered fuels), and so on, is energetically efficient and economically attractive thermal operation, which is regarded as one of the most promising method for energy production [1–3]. Gasification comprises several stages, among which one can distinguish main process zones, that is, drying, pyrolysis, reduction and oxidation. All processes are usually carried out in one reactor, called gasifier, into which a proper gasification agent is supplied. The device is operated with a fixed or a fluidized bed, in which feed and process gas streams are organized in co-current or counter-current mode [4–6]. The scheme of basic gasifiers operated with a fixed bed is presented in Fig. 1.

Mechanism of gasification process can be described by a series of thermochemical reactions, which occur during pyrolysis and combustion. An exemplary set of those reactions is given in Eqs. (1)–(5):

$$C + O_2 \leftrightarrow CO_2 \quad (1)$$

$$C + 0.5O_2 \leftrightarrow CO \quad (2)$$

$$C + 2H_2 \leftrightarrow CH_4 \quad (3)$$

$$C + H_2O \leftrightarrow CO + H_2 \quad (4)$$

$$C + CO_2 \leftrightarrow 2CO \quad (5)$$

Basic gaseous products of primary reactions can participate in further reactions, which may occur due to mechanisms presented in Eqs. (6)–(11):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (6)$$

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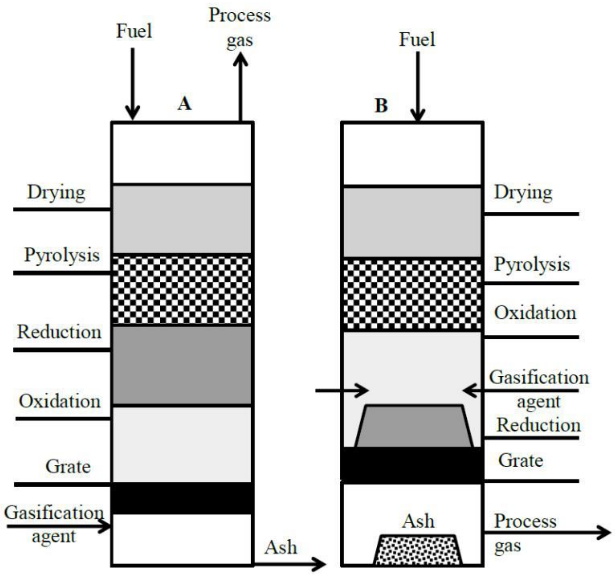

Fig. 1. Scheme of fixed bed gasifiers arranges in (A) counter-current and (B) co-current modes.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (7)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (8)$$

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2 \quad (9)$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad (10)$$

$$H_2 + 0.5O_2 \leftrightarrow H_2O \quad (11)$$

However, beside desired gases (i.e., CO, H_2, CH_4), there is always a range of contaminants, which appear in process gas, for example, tars, aliphatic and aromatic hydrocarbons, inorganic compounds, dust, and so on, which need to be removed before the further gas processing. Hence, the gas cleaning performed with the use of wet or dry method is applied. In the former method, contaminants are washed out from the gas by means of a scrubbing liquid, for example, water or oil, and simultaneous cooling of gas due to its contact with a scrubbing medium occurs. In the latter method, condensable contaminants present in gas stream appear in a form of an aqueous-tar mixture [7–10]. Regardless of gas cleaning method, highly loaded wastewater containing tars and aqueous stream contaminated with water-soluble organic and inorganic compounds is formed. Among a range of substances, which can be identified in the stream, one may find phenols, benzene, toluene, xylene and other aromatic hydrocarbons as well as ammonia and hydrogen sulphide. The overall scheme of wastewater formation at a gasification plant is shown in Fig. 2. It is said that proper management of the stream is one of the most important conditions for commercialization of gasification, especially in case of medium and small systems [11,12].

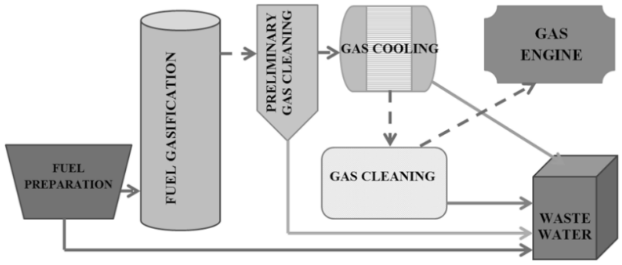

Fig. 2. Spots of wastewater formation at gasification plant.

In the presented study, the technique for the preliminary treatment of gasification wastewater obtained during dry cleaning of gas (i.e., tar-water condensate) by means of low pressure driven membrane filtration is discussed. The selection of membrane processes resulted of their universal character and relatively simple operation and management of membrane installations. Membrane systems are already widely applied to water and wastewater treatment and are operated as independent treatment systems or as a part of a technological treatment series. Among available membrane techniques, one can distinguish between low and high pressure driven membrane techniques. First group comprises micro and ultrafiltration membranes, which are applied for removal of high molecular weight compounds or are arranged in integrated/hybrid systems, together with coagulation, biological processes (membrane bioreactors, MBR), photocatalytic oxidation, and so on. Second group covers nanofiltration and reverse osmosis, which are usually applied for technological grade water production (e.g., for water softening of demineralization) and enable separation of compounds already at ionic level. Regardless of a membrane type, membrane separation is always accompanied by two unfavourable phenomena affecting its efficient performance, that is, fouling and concentration polarization. Membrane fouling results of deposition of contaminants present in treated stream on a membrane surface or inside membrane pores. Moreover, it may occur in reversible or irreversible mode, and in the latter case, initial capacity of a process cannot be recovered. However, proper process arrangement and application of suitable operating conditions can prevent an occurrence or limit a severeness of membrane fouling. Concentration polarization relies on a formation of highly concentrated thin layer of separated compounds next to a membrane surface and affects both membrane selectivity and process capacity. Nevertheless, its impact on a process may also be limited by application of proper operational conditions. Due to a wide range of available membranes and membrane modules, they need to be properly selected considering the treated medium properties. Taking into account both range and character of contaminants present in gasification wastewater (a complex mixture of organic and inorganic compounds), application of membrane processes seems to be the appropriate choice for the treatment operation [13,14].

In the discussed studies, gasification wastewater treatment system based on spontaneous tars separation and low pressure driven membrane filtration was applied. Polyethersulphone ultrafiltration membranes of cutoff 50 and 30 kDa operated at various transmembrane pressures ranging from 0.2 to 0.3 MPa were used.

2. Materials and methods

Membrane filtration of gasification wastewater was carried out in laboratory installation by KOCH Membrane Systems, model KMS Cell CF1. The device is equipped with the feed tank of volume 0.5 dm^3 and two membrane cells arranged in a series of common separation area of 56 cm^2. The construction of the device enables to run the process in the cross flow mode and at constant temperature (the discussed filtrations were carried out at temperature 20°C–21°C). The scheme of the installation is shown in Fig. 3.

In the study, polyethersulphone ultrafiltration membranes of cutoff 50 and 30 kDa of trademarks MQ and MK, respectively, by Synder Filtration, were used. The filtration of gasification condensate was preceded by both membrane conditioning and characterization with deionized water at transmembrane pressure range of 0.1–0.3 MPa as well as by the removal of tars from the treated medium by means of spontaneously occurring sedimentation and floatation of the fraction. Next, the filtration of aqueous phase of the condensate was carried out at transmembrane pressures range equal to 0.2–0.3 MPa, increased by 0.1 MPa by the process. Processes performed at 0.2 MPa pressure at particular membranes are marked as MQ1 and MK1, while processes shown as MQ2/MK2 are those carried out at 0.3 MPa pressure. All filtrations were run until 80% of the initial feed volume was recovered in the form of permeate. After the process, deionized water flux was again measured, in order to determine the impact of fouling on process capacity and possible interactions between membrane materials and contaminants present in treated wastewater.

The feed and filtrates obtained during process were characterized due to values of pH, specific conductivity (spec. cond.), chemical oxygen demand (COD), ammonium nitrogen ($N\text{-}NH_4$) and dry mass content. pH and specific conductivity were measured with the use of dedicated probes; COD and ammonium nitrogen were indicated by means of HACH Lange methodology, while dry mass content was analyzed by means of conventional thermal method at 105°C temperature. Such a narrow range of analysis resulted of considered options of treated wastewater utilization, which were: collection in tanks and transportation to industrial wastewater treatment tank or collection in tanks/direct deposition to sewage system and further treatment in municipal wastewater treatment plant. Industrial wastewater plant set up the prizes for external wastewater accepted to the treatment on the basis of COD level, while for municipal wastewater treatment plant, the amount of ammonium nitrogen as well as the level of COD are of the highest importance.

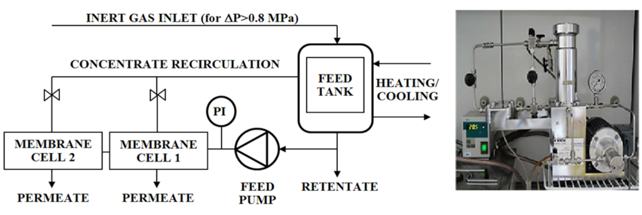

Fig. 3. The scheme of the laboratory installation for membrane filtration KMS Cell CF1.

3. Results and discussion

In Fig. 4, results of MQ and MK membranes characterization with deionized water at a transmembrane pressure range of 0.10–0.30 MPa are presented. The flux at every transmembrane pressure is a mean value of five measurements.

It was noticed that despite differences in membrane cutoff, deionized water fluxes established for both membrane types were comparable, and MK1 membrane revealed even higher fluxes than the investigated MQ membranes. However, such a phenomenon is often met during membrane characterization, and results of the difference in membrane porosity, that is, MK1 membrane, characterized with the highest porosity among all investigated membranes. It was also observed that dependence of deionized water flux on transmembrane pressure at investigated parameter range was linear, and the determination coefficient established for all membranes above 0.9.

Next, the separation of tars from obtained condensate by means of spontaneously occurring processes of sedimentation and flotation was run. It was observed that the amount of tars in the collected wastewater varied between 3% and 40% w/w, and in average, it was 21% w/w. Next, aqueous, tarless fraction of the condensate was undergone to membrane filtration. The obtained results are presented in Fig. 5.

It was observed that both filtration time as well as process capacity noted for MQ1 and MK2 membranes were comparable. Due to the very poor capacity obtained for MK1 membrane, the process was stopped after ca. 6 h, when the permeate flux decreased to 2 $dm^3\,m^{-2}\times h^{-1}$. The highest process capacity as well as the shortest filtration time were noted for MQ2 membrane. In order to establish the impact of fouling on

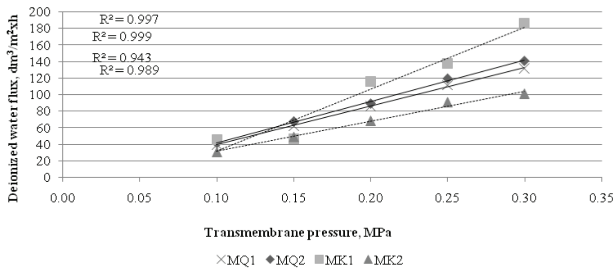

Fig. 4. Characteristics of applied ultrafiltration membranes – deionized water flux at transmembrane pressure range of 0.10–0.30 MPa.

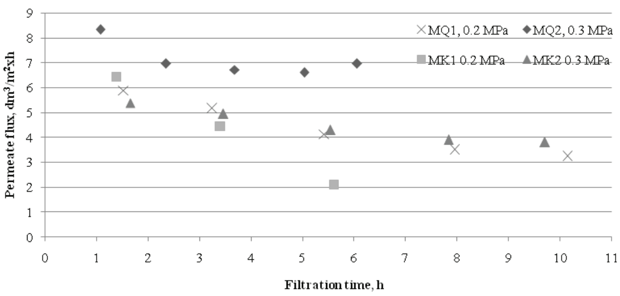

Fig. 5. The run of the gasification wastewater ultrafiltration using MQ and MK membranes at 0.2 and 0.3 MPa pressure, respectively.

the membrane capacity, the filtration of gasification wastewater was proceeded with the measurement of deionized water flux. The obtained results are shown in Fig. 6.

The post-process measurements of deionized water flux indicated that more severe fouling occurred at MK membranes, for which the recovery of initial capacity did not reach 10%. In case of MQ membranes, relative deionized water fluxes "α", determined as the ratio of deionized water flux measured after the process to deionized water flux measured before the process, were equal to 21% and 27% for 0.2 and 0.3 MPa pressure, respectively. Hence, considering the overall process capacity, the filtration should be carried out using MQ membrane at 0.3 MPa pressure. However, such the preliminary suggestion needed to be confirmed by contaminants removal effectiveness. In Table 1, parameters of process streams, that is, feed and permeates, are presented, while in Fig. 7 removal rates of particular contaminants are shown.

Parameters of permeate obtained within particular ultrafiltration were comparable; nevertheless, removal rates determined for MK membranes were slightly higher than ones established for MQ membranes. Both membranes allowed to decrease the value of specific conductivity by ca. 20%, and slightly lowered the content of ammonium nitrogen in the range of 2%–7%. Removal of organic contaminants indicated as COD reached 30% and 35%, for MQ and MK membrane, respectively, while dry mass content was decreased almost by half. Hence, it was finally decided that the preliminary treatment of gasification wastewater should be carried out at MQ membrane at transmembrane pressure of 0.3 MPa.

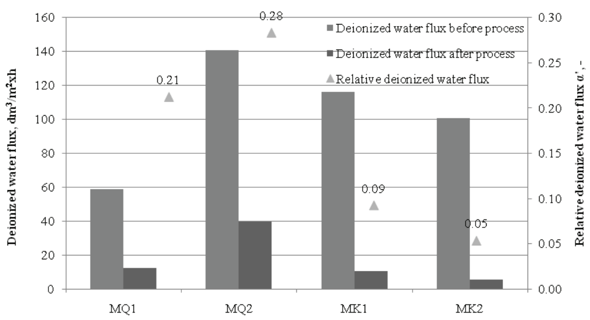

Fig. 6. Deionized water fluxes measured before and after gasification wastewater filtration and relative deionized water flux.

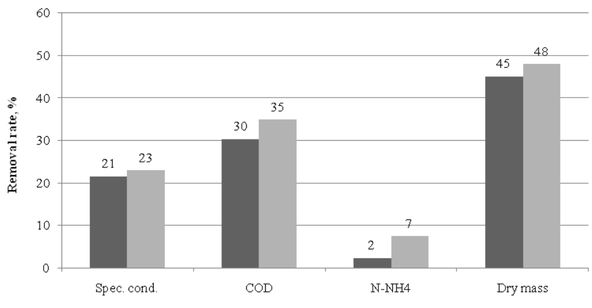

Fig. 7. Removal rates of contaminants or their indicators obtained during ultrafiltration of gasification wastewater with the use of MQ and MK membranes.

Table 1
Parameters of feed and permeates obtained during gasification wastewater ultrafiltration

Parameter	Feed	MQ permeate	MK permeate
pH	8.96	8.85	8.88
Specific conductivity, mS cm^{-1}	47.47	37.27	36.60
COD, mg dm^{-3}	36,807	25,667	24,000
N-NH_4, mg dm^{-3}	703	687	651
Dry mass, mg dm^{-3}	34,967	19,250	18,220

4. Conclusions

Gasification wastewater is highly loaded stream, which requires proper methods of treatment. Nowadays, there is no suitable, compact technique, to be applied in situ, especially in case of small and medium installations operated with alternative fuels, e.g., biomass, waste derived fuels, and so on. Hence, the development of the proper method of the stream management is crucial for the popularization and commercialization of the gasification systems.

In the discussed study, ultrafiltration of aqueous phase of tar-water condensate generated during dry cleaning of the process gas was proposed as the method for preliminary stream treatment. Tars present in the raw wastewater were removed using spontaneous separation processes, that is, sedimentation and flotation. The tarless wastewater was next undergone to membrane filtration performed with the use of polyethersulphone membranes of cutoff 50 kDa (MQ) and 30 kDa (MK) operated at transmembrane pressures of 0.2 and 0.3 MPa. The results obtained during the study revealed that both membranes removed the contaminants present in the treated wastewater at comparable level, while the higher capacity and the lower impact of fouling on the process performance was noted for MQ membrane. Hence, taking into account that the filtrate obtained during the process had to be undergone to further treatment, which in case of such quality of final stream should be carried out at industrial wastewater treatment plant, it was decided that the process should have been carried out using MQ membrane at 0.3 MPa transmembrane pressure. Moreover, savings resulting of COD load decrease as well as the application of concentrate for gasifier feed remoistening (instead of freshwater) should balance the relatively low process capacity.

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