DOI: 10.2428/ecea.2016.23(3)22 ECOL CHEM ENG A. 2016;23(3):313-320

Anna KWIECIŃSKA[1]*, Tomasz ILUK[1]
and Sławomir STELMACH[1]

# MEMBRANE PROCESSES IN THE UTILIZATION OF WASTEWATER GENERATED DURING WASTE GASIFICATION

## WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI WÓD POPROCESOWYCH ZE ZGAZOWANIA ODPADÓW

**Abstract:** Gasification, regardless of the fuel type, is always accompanied with the generation of highly loaded wastewater. Those streams are formed during cooling and cleaning of process gas and comprise of tars, condensed water vapor and a range of organic and inorganic compounds. Nowadays, there are no treatment systems of those wastewater, especially dedicated to small and medium size gasification plants, operated with alternative fuels, *ie* biomass and wastes, what is the main limitation in the technology popularization and industrial commercialization. On the other hand, conventional methods proposed for the treatment characterize with the narrow spectrum of action dedicated, mainly to the removal of tar substances. In the presented paper the possibility of utilization of waste gasification wastewater by means of membrane processes is proposed. The technology was based on the two stage treatment system enabling the separation of tars by spontaneous sedimentation/floatation and low pressure drive aqueous phase filtration. Polymeric, ultrafiltration membranes of various cut off were investigated due to the contaminants removal effectiveness and capacity. It was shown, that the use of membrane processes assures the concentration of soluble organic contaminants to the rate enabling their recycle to the gasifier. The filtrate obtained during the process characterized with much decreased load of contaminants and after the proper polishing could be directly deposited to the environment.

**Keywords:** wastewater, tars, gasification, alternative fuels, SRFs

## Introduction

The process of gasification of alternative fuels, *ie* wastes formed to SRFs (solid recovered fuels) or biomass, is energetically efficient and economically attractive thermal operation, which is regarded as one of the most promising method for energy production [1–4]. The process comprises of several stages, which usually occur in one

[1] Institute for Chemical Processing of Coal, 41–803 Zabrze, ul. Zamkowa 1, Poland, phone: +48 32 621 65 38.

* Corresponding author: akwiecinska@ichpw.pl

reactor, called gasifier, organized in co-current or counter-current flow, which is schematically presented in Fig. 1.

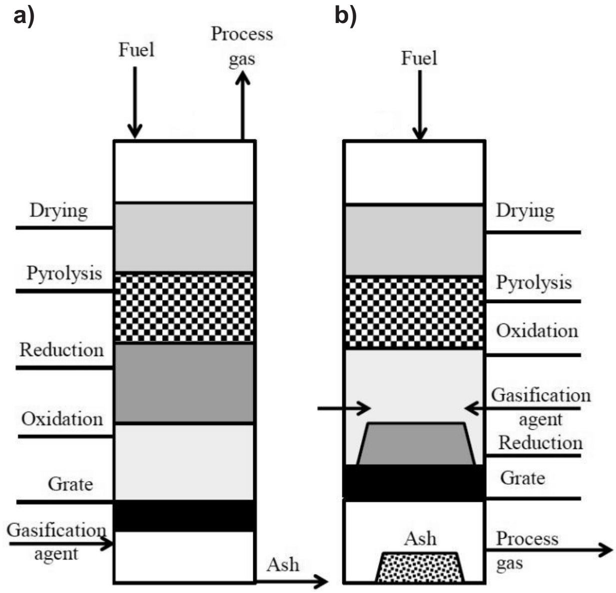


Fig. 1. Fixed bed reactor for alternative fuel (SRF) gasification: a) counter-current mode, b) co-current mode

The mechanism of gasification process can be defined as a series of thermochemical reactions, which occur during pyrolysis and combustion. As a results of those reactions and at the use of a proper gasification agent (air, oxygen, water vapor, hydrogen, carbon dioxide, etc.) and increased temperature (above 800$^o$C) the conversion of solid substrates to combustible gaseous products, which is a mixture of carbon oxide and dioxide, hydrogen, methane and water vapor, takes place [5–7].

The gas obtained during the gasification process, except of the gaseous products, contains also a range of contaminants, which need to be removed in case, when further gas processing, *eg* in chemical synthesis or cogeneration, is predicted. Two gas cleaning methods are used for this purpose *ie* wet and dry systems. In the former method, the contaminants are usually washed out from the gas by means of water or oil absorption in scrubbers and the simultaneous cooling of gas due to its contact with the scrubbing medium occurs. In the latter method, the condensable contaminants present in gas stream appear in the form of aqueous-tar mixture, while solids (dusts and ashes) are usually removed on filters [8–10].

Regardless of gas cleaning method, the highly loaded wastewater containing tars and aqueous stream contaminated with water soluble organic compounds is formed (Fig. 2). The proper management of the stream is said to be one of the most important condition for popularization of biomass gasification, especially in case of medium and small systems. Nowadays, only large installations equipped with technologically complete

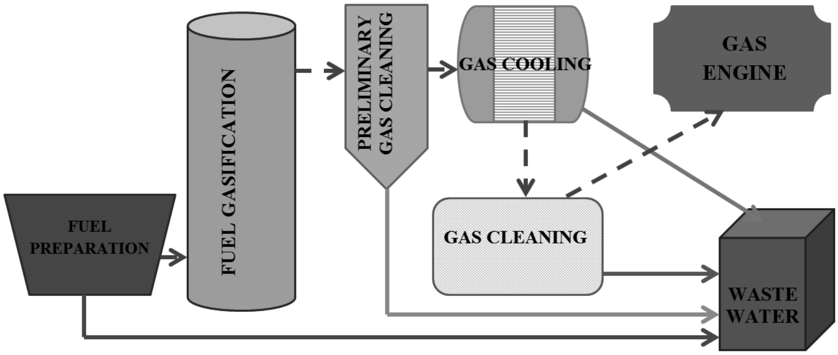


Fig. 2. Places of formation of wastewater streams generated during gasification process

wastewater treatment plants are found to be commercially available, and the lack of the method for proper utilization of smaller amount of wastewater is one of the main reason [11, 12].

In the paper, the technique for the treatment of biomass gasification wastewater obtained during the dry cleaning of gas (*ie* tar-water condensate) is discussed. The system was based on the membrane separation, and different types of membranes were used.

## Methods

The process of membrane filtration was carried out in the 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. The scheme and the photography of the installation is shown in Fig. 3.

In the study two types of membranes differ in membrane material and molecular weight cut off, *ie* polyvinylidene microfiltration membrane of pore size 0.3 μm

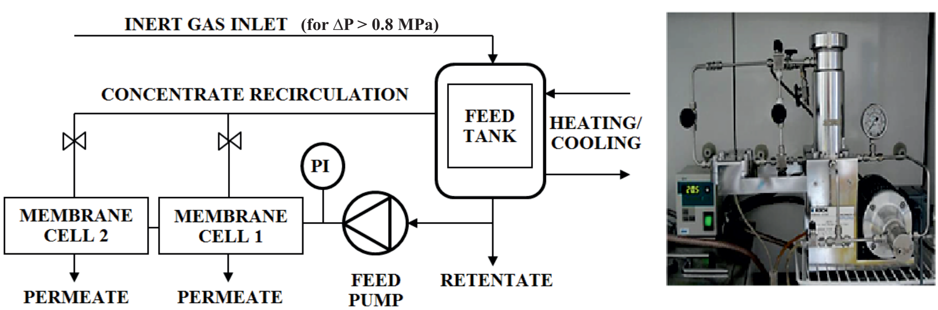


Fig. 3. The scheme and the photography of laboratory installation for membrane filtration KMS Cell CF1

(MF-PVDF-0.3) and polysulphone of cut off 30 kDa (UF-PS-30) were used. The filtration of gasification condensate was preceded by both, membrane conditioning and characterization with deionized water at transmembrane pressure of 0.1 MPa as well as with removal of tars from the treated medium by means of spontaneously occurring sedimentation and floatation of the fraction. Next, the filtration of the aqueous phase of the condensate was carried out at transmembrane pressures range equal to 0.1–0.3 MPa, increased by 0.05 MPa by the process. The difference in process pressures resulted of the dependences observed during the membrane conditioning. Both process were carried out until 80% of the feed volume was recovered in the form of permeate. After the process, the stream of deionized water was again measured, in order to evaluate the character of fouling of the membrane and possible interactions between membrane materials and contaminants present in the treated wastewater.

The feed and the filtrates obtained during the process were characterized due to the value of pH, specific conductivity, chemical oxygen demand, ammonia nitrogen and dry mass content. pH and specific conductivity were measured with the use of dedicated probes, chemical oxygen demand and ammonia 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.

## Results and discussion

In Fig. 4, the capacities of clean membranes expressed as the volumetric deionized water flux at 0.1 MPa transmembrane pressure are compared.

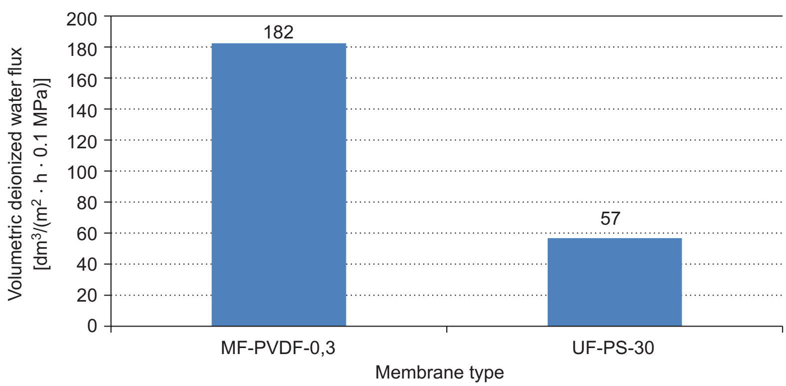


Fig. 4. The comparison of capacities determined for clean membranes

The difference in capacities between both membranes was found to be significant, and microfiltration membrane was three times more efficient than UF membrane. After the membrane characterization, the filtration of SRFs gasification wastewater was made. The processes were carried out at the transmembrane pressure range of 0.1–0.3 MPa. The results of the filtration are shown in Figs. 5 and 6.

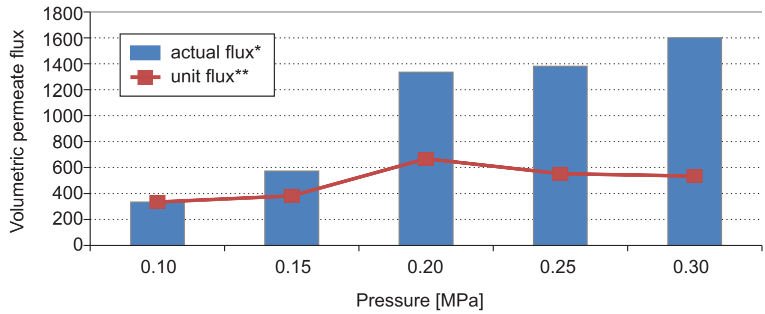


Fig. 5. The capacity of MF-PVDF-0.3 membrane obtained during SRF gasification wastewater filtration * [$dm^3/(m^2 \cdot h)$]; ** [$dm^3/(m^2 \cdot h \cdot 0.1$ M Pa)]

It was observed, for MF-PVDF-0.3 membrane, that the flux constantly increased with the pressure increase, however values obtained for 0.20 and 0.25 MPa pressure were comparable. Nevertheless, where the actual fluxes were recalculated into unit fluxes, *ie* at 0.1 MPa transmembrane pressure, it was observed, that the flux was increasing only up to 0.2 MPa pressure and then it started to decrease. It indicated that the pressure 0.2 MPa was the critical pressure for MF-PVDF-0.3 membrane, *ie* the one above which the improvement of membrane capacity was negligible.

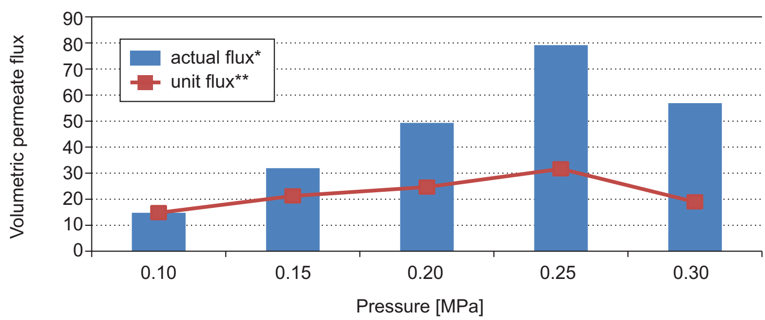


Fig. 6. The capacity of UF-PS-30 membrane obtained during SRF gasification wastewater filtration * [$dm^3/(m^2 \cdot h)$]; ** [$dm^3/(m^2 \cdot h \cdot 0.1$ MPa)]

In case of UF-PS-30 membrane the increase of the flux was observed only up to 0.25 MPa pressure, and then the decrease in the capacity was obtained. The same behavior was also noticed for the membrane unit flux. Hence, 0.25 MPa pressure was established as the critical one for UF-PS-30 membrane, and, in opposite to MF-PVDF-0.3 membrane, the pressure at which the impact and severness of fouling could be clearly marked.

In Fig. 7, the comparison of unit fluxes obtained at various transmembrane pressures for both membranes, is shown.

It was noticed, that the difference between fluxes of particular membranes obtained during wastewater filtration, where much higher than ones of deionized water. In case

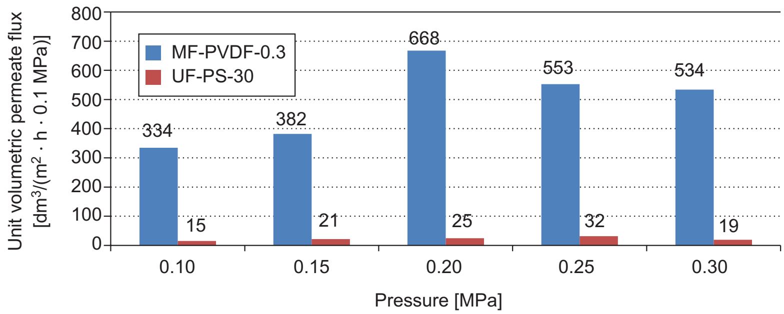


Fig. 7. The comparison of capacities obtained for both membranes used to SRFs gasification wastewater filtration

of MF-PVDF-0.3 membrane the deionized water flux was only 3 times greater than UF-PS-30 flux, while wastewater flux was ca. 20 higher for the former membrane type. Hence, it was concluded, that the process efficiency depended not only on the transmembrane pressure applied, but also on the interactions between membrane material and the treated medium. UF-PS-30 membrane was found to be more resistant than MF-PVDF-0.3 membrane.

Nevertheless, in order to confirm the impact of the wastewater properties on the membrane, after the process was finished, the volumetric deionized water flux was again measured for both membranes. The obtained results, in the form of relative permeate flux, *ie* the ratio of deionized water flux measured after the process to the deionized water flux measured for clean membrane, are shown in Fig. 8.

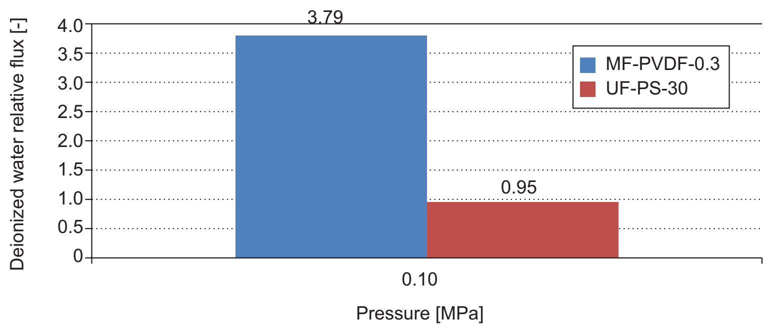


Fig. 8. The comparison of deionized water relative fluxes determined for both membranes

The comparison of relative fluxes of deionized water showed that there was a significant difference between interactions of membrane materials and treated medium. The contact of the wastewater with polyvinylidene fluoride membrane (PVDF) caused the great increase in the material hydrophilicity, hence the deionized water flux measured after the process was almost 4 times greater than the one measured before the process. On the other hand, the polysulphone membrane was found to be slightly fouled.

However, the capacity of the process must be accompanied with the efficiency of contaminants removal. In case of such open membranes the removal rate should be measured only for organic contaminants marked as COD and dry mass content. The obtained results are showed in Table 1.

Table 1

The values of parameters of process streams and removal rates of contaminants

| Parameter | Unit | Feed | MF-PVDF-0.3 permeate | UF-PS-30 permeate | MF-PVDF-0.3 removal rate | UF-PS-30 removal rate |
|---|---|---|---|---|---|---|
| pH | — | 3.51 | 7.63 | 7.61 | — | — |
| COD | [$mgO_2/dm^3$] | 67 000 | 62 000 | 42000 | 8 | 38 |
| Dry mass | [$mg/dm^3$] | 593 | 90 | 42 | 85 | 93 |

Both filtrations resulted in the production of filtrate, which needed to be undergone to further treatment. Nevertheless, the significant reduction in dry mass content, reaching 93% in case of UF-PS-30 membrane was shown. Additionally, this membrane enabled to remove almost 40% of contaminants marked as COD. Hence, if a combined system of membrane filtration and *eg* activated carbon adsorption was applied to such a wastewater purification, it was UF-PS-30 membrane, which was suggested to be used.

## Summary and conclusions

The wastewater generated during solid fuels gasification, equipped with the dry gas cooling and cleaning system, is a highly loaded tar-aqueous mixture of a wide range of contaminants. The proper management of the stream is said to be crucial for popularization and commercialization of small and medium biomass gasification system. In this paper, a study on the treatment of aqueous phase of the stream by means of membrane filtration is discussed. The feed to the membrane process was the water fraction of the tar-water condensate, from which tar fraction was removed by means of spontaneous sedimentation and flotation. Two types of membranes were used, polyvinylidene fluoride microfiltration of pore size 0.3 μm 5 and polysulphone ultrafiltration of cut off 30 kDa. It was found, that both membranes should be followed by further treatment, *eg* activated carbon adsorption, in order to enable the deposition of the treated stream to sewage system or to the environment. In case of process capacity, significant differences were found between membranes, and polyvinylidene fluoride membrane was significantly affected by the treated medium, *ie* its hydrophilicity increased. On the other hand, polysulphone membrane was slightly fouled after the process. However, considering both, the membrane capacity and the effectiveness of contaminants removal, it was concluded, that the process should be carried out with the use of UF-PS-30 membrane.

### Acknowledgements

Investigation presented in this paper is done according to the 23_2011_IP19_CoalGas contract between IChPW and KIC, the legal basis for implementation of the work is the approved research and development project 21.11.002 “Solid Recovered Fuel for renewable Combined Heat and Power production via gasification process”.

## References

[1] Kotowicz J, Sobolewski A, Iluk T. Energetic analysis of a system integrated with biomass gasification, Energy.2013;52:265-278. DOI: 10.1016/j.energy.2013.02.048.

[2] Stelmach S, Wasielewski R, Figa J. Zgazowanie biomasy – przykłady nowych technologii [Biomass gasification – examples of new technologies]. Arch Gosp Odpad Ochr Środ. 2008;7:9-20. http://www.awmep.org/index.php/index/help?journal=ago&page=article&op=download&path%5B%5D=64&path%5B%5D=51.

[3] Sobolewski A, Kotowicz J, Matuszek K, Iluk T. Reaktory zgazowania biomasy w układach CHP – przyszłość energetyki odnawialnej w Polsce [Reactors for biomass gasification in the CHP systems – future of the renewable energy in Poland]. Pol Energ. 2011;14(2):349-360. https://www.min-pan.krakow.pl/Wydawnictwa/PE142/25-sobolewski-kotowicz-i-in.pdf.

[4] Ruiz JA, Juarez MC, Morales MP, Munoz P, Mendivil MA. Biomass gasification for electricity generation: Review of current technology barriers. Renew Sust En Rev. 2013;18:174-183. DOI: 10.1016/j.rser.2012.10.021.

[5] Pytlar TS Jr. Status of existing biomass gasification and pyrolysis facilities in North America. NAWTEC18. Proceed. 2010:1-14. DOI: 10.1115/NAWTEC18-3521.

[6] Mishra AK, Singh RN, Mishra PP. Effect of Biomass Gasification on Environment. Mesop Environ J. 2015;1(4):39-49. www.bumej.com/papers/mej_pub2015_8175538.pdf.

[7] Sulc J, Stojdl J, Richter M, Popelka J, Svobooda K, Smetana J. Biomass waste gasification – can be the two stage process suitable for tar reduction and power generation? Waste Manage. 2012;32:692-700. DOI: 10.1016/j.wasman.2011.08.015.

[8] Han J, Kim H. The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renew Sust En Rev. 2008;12:397-416. DOI: 10.1016/j.rser.2006.07.015.

[9] Hernandez JJ, Ballesteros R., Aranda G. Characterization of tars from biomass gasification: Effect of the operating conditions. Energy. 2013;50:333-342. DOI: 10.1016/j.energy.2012.12.005.

[10] Tripathi L, Dubey AK, Sandip G, Singh PL. Waste water treatment of biomass based power plant. Int Chem Tech Res. 2013;5(2):761-764. http://sphinxsai.com/2013/conf/PDFS%20ICGSEE%202013/CT=33(761-764)ICGSEE.pdf.

[11] Belgiorno V, De Feo G, Della Rocca C, Napoli RMA. Energy from gasification of solid wastes. Waste Manage. 2003;23:1-15. DOI: 10.1016/S0956-053X(02)00149-6.

[12] Chiranjeevaraoseela, VinodbabuCh, VykuntaRao M. Techniques of Tar Removal from Producer Gas – A Review Int J Innov Res Sci Eng Technol. 2015;4(2):258-266. DOI: 10.15680/IJIRSET.2015.0402055.

### WYKORZYSTANIE TECHNIK MEMBRANOWYCH W UTYLIZACJI WÓD POPROCESOWYCH ZE ZGAZOWANIA ODPADÓW

Instytut Chemicznej Przeróbki Węgla, Zabrze

**Abstrakt:** Proces zgazowania, niezależnie od typu zastosowanego paliwa, wiąże się z powstawanie wysoko obciążonych ciekłych strumieni odpadowych. Wody te formowane są podczas chłodzenia i oczyszczania gazu procesowego i stanowią mieszaninę smół, skroplonej pary wodnej oraz szeregu związków organicznych i nieorganicznych. Brak odpowiednich rozwiązań systemowych, przede wszystkim w przypadku małych i średnich instalacji powoduje, że ich popularyzacja i komercjalizacja na skalę przemysłową są znacznie ograniczone. Obecnie proponowane metody utylizacji ciekłych strumieni odpadowych charakteryzują się zawężonym spektrum działania, skupiając się na jednym z aspektów problemów jakim jest obecność substancji smolistych.

W niniejszej pracy zaproponowano możliwość zagospodarowania ciekłych strumieni odpadowych z procesu zgazowania SRF z wykorzystaniem technik membranowych. Rozwiązanie oparto o dwustopniowy system oczyszczania umożliwiający separację smół poprzez samoistnie zachodzące procesu sedymentacji i flotacji oraz niskociśnieniową filtrację membranową. W badaniach wykorzystano polimerowe membrany mikro i ultrafiltracyjnej o różnych granicznych masach molowych. Wykazano, że zastosowanie procesów membranowych umożliwia zatężenie rozpuszczonych związków organicznych w stopniu umożliwiającym ich zawrócenie do reaktora oraz powstawanie filtratu o obniżonym ładunku zanieczyszczeń, który, po odpowiednim podczyszczeniu, może zostać odprowadzony do kanalizacji lub do środowiska.

**Słowa kluczowe:** ścieki, smoły, zgazowanie, membrany, SRF