Journal of Civil & Environmental Engineering

Kwiecińska et al., J Civil Environ Eng 2016, 6:4
DOI: 10.4172/2165-784X.1000241

Research Article Open Access

The Application of Ultrafiltration for Preliminary Treatment of Liquid Waste Streams Generated in Gasification Process

Anna Kwiecińska*, Tomasz Iluk, Mateusz Kochel and Mateusz Szul

Institute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland

Abstract

Gasification is regarded as one of the most promising technology for generation of energy using renewable and alternative fuels. Nevertheless, in order to obtain process gas of desired quality, a range of processes for removal of pollutants present in a raw gas stream needs to be performed. One of the most problematic side stream formed during gas cleaning operations is highly loaded wastewater. It is a mixture of organic and inorganic contaminants, which usually appears as a tar-aqueous condensate. It is assumed that the amount of wastewater corresponds to ca. 30-50% of the amount of fuel introduced to gasification. In the presented study membrane ultrafiltration process was proposed as the method of preliminary treatment of wastewater formed during gasification of alternative fuels. Three types of polyethersulphone membranes, which differed in cut off, were used. The goal of the process was to separate raw wastewater into a condensate enriched with organic compounds, which could be reused to the gasification process as a fuel remoistening agent, and a permeate, which had to be undergone to further treatment. The impact of undesired phenomena accompanying membrane filtration i.e., fouling and concentration polarization was determined. The process capacity and efficiency of contaminants removal was evaluated.

Keywords: Fouling; Gasification; Membrane techniques; Ultrafiltration; Wastewater

Introduction

Gasification of solid fuels is one of the most promising technologies of renewable and alternative fuels utilization to both, energy generation and chemical synthesis. It is a thermochemical operation, during which solid substrate, at proper process conditions and with the use of a selected gasification agent, are converted into gaseous products. The mechanism of the process is based on a set of chemical reduction-oxidation reactions, which occur in one reactor, called gasifier, in which one can distinguish particular operational zones, i.e., drying, pyrolysis, oxidation and gasification [1-3]. The scheme of fixed bed gasifiers organized in counter current and co current mode, including theoretical appearance of particular process zones is shown in Figure 1. A process gas, which is formed during gasification, mostly comprises of simple, desired gases, among which carbon monoxide, hydrogen and methane can be found. The composition of the process gas and the share of particular compounds strongly depend on a number of parameters, including type of gasified fuels, applied process conditions and gasification agent used. Nevertheless, the yield of conversion of a fuel into desired gases is never complete, hence a range of other compounds, which need to be removed from the process gas before its further utilization, can be found. The most common contaminants appearing in the process gas are ca. tars (high molecular weight aromatic compounds), phenols, alcohols, aldehydes, organic acids, ammonia, hydrogen sulphides, and many others [4,5]. In order to remove undesired compounds from the process gas, a series of various unit operations, which are arranged into wet or dry gas cleaning systems, are performed. In wet gas cleaning method, contaminants present in a process gas are washed out from the stream using a scrubbing medium, which is usually water or oil. In this case, a simultaneous cooling of the gas, which also leads to condensation of low boiling point compounds, takes place. On the other hand, dry gas cleaning relies on a complete condensation of gas contaminating compounds; hence, a proper cooling of the stream is of the highest importance. Regardless of the applied gas cleaning method, the operation is always accompanied with the formation of liquid side stream, which is highly loaded wastewater [6-8]. In the wet cleaning, the amount of wastewater depends mainly on the character of the scrubbing medium applied, its capacity toward removed contaminants and refreshing frequency. On the other hand, when dry cleaning is applied, the amount of wastewater corresponds to the amount of condensable organic compounds present in the gas as well as to the amount of water vapor, condensation of which is accompanied with the additional washing out of remaining water soluble, low molecular weight organics as well as inorganic substances, i.e., ammonia and hydrogen sulphides. It is assumed, that the amount of wastewater formed during gas dry cleaning corresponds to ca. 30-50% of the amount of fuel introduced to gasification [9-11].

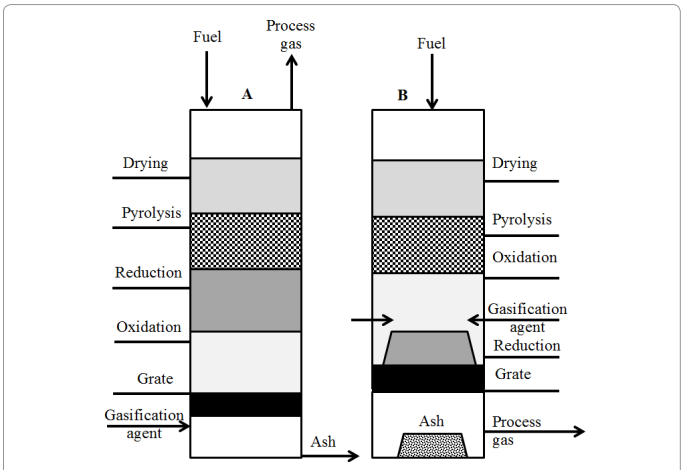

Figure 1: Schemes of fixed bed gasifiers organized in counter current (A) and concurrent (B) modes, including process zones.

Nevertheless, one should note, that the presence of organic contaminants in a process gas is the result of their insufficient retention in the gasifier as well as their partial kidnapping by the process gas, while it leaves the reactor. Hence, in order to increase the yield of conversion of the fuel into desired gas, the recirculation of those contaminants would be desired. Membrane processes are nowadays

***Corresponding author:** Anna Kwiecińska, Institute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland, Tel: 86-21-58386258; E-mail: akwiecinska@ichpw.pl

Received June 09, 2016; **Accepted** June 24, 2016; **Published** June 26, 2016

Citation: Kwiecińska A, Iluk T, Kochel M, Szul M (2016) The Application of Ultrafiltration for Preliminary Treatment of Liquid Waste Streams Generated in Gasification Process. J Civil Environ Eng 6: 241. doi:10.4172/2165-784X.1000241

regarded as one of the most efficient method of water and wastewater treatment. A number of industrial scale, membrane based treatment plants can be found worldwide. Membrane separation is based on a physical retention of compounds present in the treated stream, and depends mainly on a molecular weight of a separated substance. During a process two basic streams are formed: one, which is enriched in rejected compounds, i.e., retentate (concentrate) and second one, a purified stream, i.e., permeate (filtrate). The main parameter, which is used for membranes characterization, is so called membrane molecular weight cut off. It is defined as a lowest molecular weight of a compound, which is rejected by a membrane in 90%. For separation of compound, molecular weight of which ranges from 1 kDa up to several hundreds of kDa, processes like microfiltration and ultrafiltration are used. In order to remove substances of lower molecular weight, reaching the level of separation of multivalent ions from monovalent ones, as well as to obtain completely demineralized water, one can apply nanofiltration or reverse osmosis. Additionally, the higher molecular weight cut off of a membrane, the lower pressure required for efficient separation and satisfactory capacity of the process. Hence, microfiltration and ultrafiltration are regarded as low pressure driven membrane techniques, while nanofiltration and reverse osmosis as high pressure driven processes [12]. Regardless of a type of a membrane process applied, it is always accompanied by two phenomena, appearance of which affects process capacity. The first one is membrane fouling, which is caused by deposition of separated compounds on a membrane surface (filtration cake) and inside membrane pores. This phenomenon is characteristic for low pressure driven membrane separation. The second one is concentration polarization, which usually appears during nanofiltration and reverse osmosis, and results of the formation of a thin layer of highly concentrated solution of rejected compounds next to a membrane surface. The limitation of impact of those phenomena on a membrane separation is crucial for obtaining satisfactory capacity of the process. Hence, methods like back flushing, turbulent feed flow performance, chemical washing, as well as optimization of process parameters (proper membrane material, module construction and transmembrane pressure) are applied [13]. In the discussed study, the use of ultrafiltration as a method of preliminary treatment of aqueous phase of condensate formed during dry cleaning of gas generated during alternative fuels gasification, is discussed. A raw wastewater was a two phase mixture of tars and contaminated water. The membrane filtration was thus preceded by removal of tars and based on their spontaneous flotation enabling their efficient separation from aqueous phase. Three types of polyethersulphone ultrafiltration membranes, which differed in cut off, were used. Every process was evaluated due to both, contaminants removal efficiency and capacity.

Materials and Methods

Membrane filtration was carried out in the laboratory scale unit KMS Cell CF1 by Koch Membrane Systems. The device is equipped with the feed tank of volume 0.5 dm^3 and two membrane cells arranges in series, which enable the installation of flat membranes of separation area 28 cm^2 each. The construction of the device allows to perform processes in a cross flow mode. The permeate obtained during filtration is continuously collected outside the device, while the retentate is recirculated to the feed tank (concentrating mode). The heating/cooling system enables to keep constant temperature of a filtered feed, which in case of this study was 20.0 ± 0.5°C. The scheme of the device is shown in Figure 2. In this study, three types of polyethersulphone ultrafiltration membranes supplied by Synder, were used. Membranes of trade mark MQ, MK and SM, differed in molecular weight cut off, which was 50 kDa, 30 kDa and 20 kDa, respectively. The filtration of aqueous phase of condensate was preceded with membrane capacity

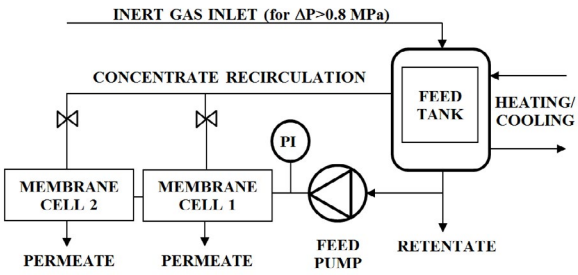

Figure 2: The scheme of laboratory installation for membrane filtration KMS Cell CF1.

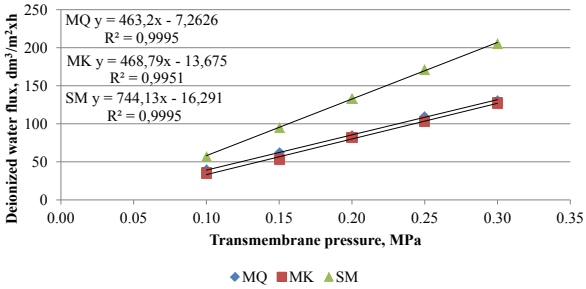

Figure 3: The deionized water flux determined for investigated membranes at trans-membrane pressure range 0.1-0.3 MPa.

characterization. For this purpose, a volumetric flux of deionized water at a transmembrane pressure range of 0.1 to 0.3 MPa was measured. Next, wastewater treatment process at a transmembrane pressure of 0.3 MPa was run and its duration corresponded to the time required for recovery of 80% of initial feed volume in the form of permeate was measured. Finally, the deionized water flux was established for membranes after wastewater treatment, in order to evaluate the impact of fouling and concentration polarization on the process capacity. All process streams, i.e., feed, condensates and permeates, were analyzed according to pH, specific conductivity, chemical oxygen demand (COD) and dry mass content. pH and specific conductivity were measured with dedicated probes, COD was analyzed using HACH Lange methodology, while dry mass content was established with the use of conventional thermal method, i.e., evaporation at 105°C.

Results and Discussion

Membrane characterization

In Figure 3, the characteristics of membranes due to their capacity in respect to deionized water flux at transmembrane pressure range 0.1 to 0.3 MPa is shown. It was found, that despite the same membrane material, it was SM membrane, i.e., the one with the lowest molecular weight cut off, which revealed the highest capacity in regard to deionized water, while fluxes measured for MQ and MK membranes were similar. However, it is a common phenomenon often met in membrane filtration, and it is caused by membrane porosity. It is generally accepted, that membrane capacity results not only of its cut off, but also of porosity, i.e., a number of pores in a unit area of a membrane. Hence, the obtained results indicated, that SM membrane characterized with the highest porosity. Nevertheless, at investigated transmembrane pressure range all membranes revealed the linear dependence between deionized water flux and the pressure. Hence, the critical value of the parameter, i.e., the transmembrane pressure above which no further increase of deionized water flux is observed, was not reached. On the basis of membrane characterization it was decided,

that the filtration of gasification wastewater would be performed at 0.3 MPa in case of all membranes.

Gasification wastewater treatment

In Figure 4, the change of permeate flux in time of ultrafiltration treatment of gasification wastewater is shown.

It was observed that despite the highest cut off, the lowest capacity and the longest duration were obtained for MQ membrane. On the other hand, it was MK membrane, which revealed the shortest duration and the highest average permeate flux. However, for this membrane, the most significant capacity loss (the ratio of final permeate flux to initial permeate flux equal to 37%) was observed (in case of MQ membrane it was 38%, and for SM it was 60% - the most stable membrane). In order to compare the overall capacity loss of all processes, relative permeate fluxes, i.e., ratios of average permeate flux to deionized water flux at operational transmembrane pressure, and relative deionized water fluxes, i.e., ratios of deionized water flux measured after the process to deionized water flux measure before the process, were calculated (Figure 5). Calculated relative permeate fluxes showed, that the highest process capacity was obtained for MK membrane, for which wastewater filtration corresponded to 10% of deionized waster

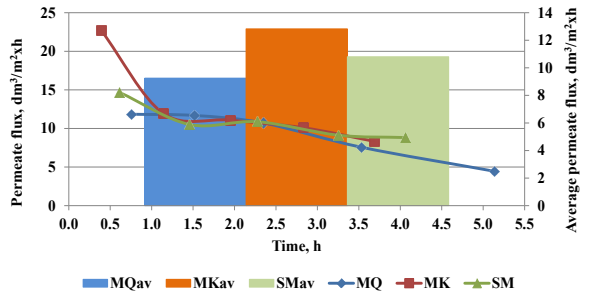

Figure 4: The change and the average capacity of gasification wastewater ultrafiltration.

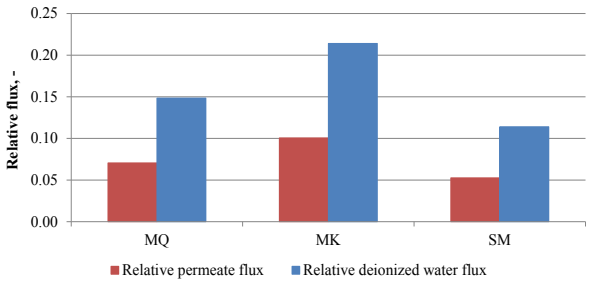

Figure 5: Comparison of relative permeate flux and relative deionized water flux.

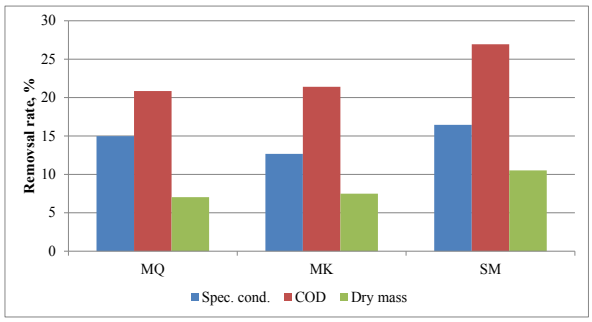

Figure 6: Removal rates of particular contaminants indicators.

Parameter	Feed	Permeates			Condensates		
		MQ	MK	SM	MQ	MK	SM
pH, -	8.96	9.10	9.08	9.01	8.73	8.84	8.86
Spec. cond., mS/cm	47.63	40.50	41.60	39.8	45.1	41.6	41.6
COD, g/dm³	36.13	28.60	28.40	26.40	33.5	37.3	39.5
Dry mass, g/dm³	28.70	26.68	26.55	25.68	32.0	35.6	31.4

Table 1: Process streams parameters.

flux measured for clean membrane. In case of this membrane also the highest recovery of initial membrane capacity equal to 21% was noted. Additionally, it was found that SM membrane fouling was the most severe, as both permeate and deionized water relative fluxes calculated for this membrane were the lowest ones. It was explained by the fact of formation of the most dense filtration cake on the SM membrane surface, which affected process capacity during wastewater treatment and increased flow resistances during deionized water filtration. To sum up, obtained results indicated that gasification wastewater ultrafiltration process was the most efficient in case of MK membrane.

Removal of contaminants

The effectiveness of contaminants removal is also an important factor taken into account, when selecting the optimal treatment process. In Table 1 comparison of process stream parameters is shown, while in Figure 6 removal rates of particular contaminants indicators are presented. As it could have been supposed, membrane of the smallest cut off, i.e., SM, characterized with the highest removal rates of particular contaminants indicators. The most effective rejection was observed for compounds indicated as COD, removal rate of which varied from 20.8 to 26.9%. On the other hand, it was the content of dry mass, the reduction of which was found to be the poorest and varied from 7 to 10.5%. Nevertheless, if costs of further utilization of filtrate were based on COD level, what was a common practice in case of industrial wastewater plants, which accepted external wastewater to treatment, even 20% decrease of the parameter value would generate significant savings. Additionally, in case of all process, retentate enriched in organic compounds was obtained, which was an advantage considering its further application as a fuel remoistening agent, i.e., recirculation of organic substances to gasification process. Finally, it was concluded that among all tested membranes, the treatment of gasification wastewater at MK membrane would be preferable due to its capacity, lowest fouling affinity and contaminants removal efficiency comparable to SM membrane.

Conclusion

Proper utilization of gasification wastewater is one of the most important issue considering popularization and commercialization of the process. The formation of wastewater is a result of process gas cleaning, nevertheless the presence of contaminants in the liquid side stream results of incomplete gasification, too short retention time or kidnapping of compounds by gas stream leaving the gasifier. Hence, their recirculation to the process, in order to increase the overall fuel to gas conversion rate, is desired. In the presented study, the use of ultrafiltration for preliminary treatment of gasification wastewater was discussed. Three type of polyethersulphone membrane of cut off 50 kDa, 30 kDa and 20 kDa were used. The study revealed that gasification wastewater filtration affected membrane capacity, and the main role was played by membrane fouling. On the other hand, in case of more open membrane fouling was caused by deposition of contaminants inside membrane pores, while in case of 20 kDa membrane formation of dense filtration cake was of the highest consideration.

To conclude, evaluation of both, process capacity and contaminants removal effectiveness indicated, that if tested membrane were considered, the process with the use of 30 kDa membrane would be preferable. Additionally, in case of all filtrations, retentate enriched in organic compounds, which could be used for gasification fuel remoistening, was obtained. Hence, the partial recirculation of organic compounds appearing in the wastewater was approached.

Acknowledgement

The results presented in this paper were obtained during the research project IChPW no 11.16.008, financed by the Ministry of Science and Higher Education.

References

1. Kotowicz J, Sobolewski A, Iluk T (2013) Energetic analysis of a system integrated with biomass gasification. Energy 52: 265-278.
2. Stelmach S, Wasielewski R, Figa J (2008) Gasification of biomass – Examples of novel technologies. Archives of Waste Manage and Environ Protection 7: 9-20.
3. Sobolewski A, Kotowicz J, Matuszek K, Iluk T (2011) Biomass gasification reactors in CHP systems – The future for renewable energy in Poland. Polish Energy 14: 349-360.
4. Ruiz JA, Juarez MC, Morales MP, Munoz P, Mendivil MA (2013) Biomass gasification for electricity generation: Review of current technology barriers. Renewable and Sustainable Energy Rev 8: 174-183.
5. Pytlar Jr. TS (2010) Status of existing biomass gasification and pyrolysis facilities in North America. Proceedings of 18th North American Waste-to-Energy Conference.
6. Mishra AK, Singh RN, Mishra PP (2015) Effect of biomass gasification on environment. Mesopotamia Environ J 1: 39-49.
7. Sulc J, Stojdl J, Richter M, Popelka J, Svobooda K, et al. (2012) Biomass waste gasification - Can it be the two stage process suitable for tar reduction and power generation? Waste Manage 32: 692-700.
8. Han J, Kim J (2008) The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. Renewable and Sustainable Energy Rev 12: 397-416.
9. Hernandez JJ, Ballesteros R, Aranda G (2013) Characterization of tars from biomass gasification: Effect of the operating conditions. Energy 50: 333-342.
10. Tripathi L, Dubey AK, Sandip G, Singh PL (2013) Waste water treatment of biomass based power plant. Int J ChemTech Research 5: 761-764.
11. Chiranjeeva Rao S, Vinod Babu CH, Vykunta Rao M (2015) Techniques of tar removal from producer gas – A review. Int J Innovative Res Sci Eng Technol 4: 258-266.
12. Bodzek M (2013) Inorganic micropollutants removal by means of membrane processes - State of the art. Ecological Chemistry and Eng S 20: 633-658.
13. Konieczny K (2008) Analysis of the reliability of the water treatment plants based on membrane. Technologies. Chemical Industry 87: 485-488.