

Membrane Systems for the Recovery of Hydrogen from Multicomponent Gas Mixtures Obtained in Biomass Gasification

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This work first generally reviews possible membrane materials for the hydrogen enrichment of biomass gasification producer gas mixture. Subsequently two permeator arrangements (single stage and two-stage with sweep) equipped with a glassy membrane material are evaluated through numerical modelling. The evaluation of the permeator systems focuses on critical hydrogen upgrading parameters like achievable hydrogen purity, hydrogen recovery and compression energy requirement. It is shown that the two-stage arrangement with sweep allows production of hydrogen with relatively high purity (above 98 % v/v) and recovery.

1. Introduction

Processing of the gas obtained in biomass gasification is one of several possible ways to produce renewable hydrogen (Pfeifer et al., 2009; Miltner et al., 2010a). For example gases produced in biomass steam gasification processes are multicomponent mixtures that consist typically of hydrogen (35-45 % v/v), carbon monoxide (19-23 % v/v), carbon dioxide (20-24 % v/v), methane (7-10 % v/v) and longer hydrocarbons (up to 4 % v/v) (Pfeifer et al., 2009). Furthermore producer gas typically contains air components and malicious components like hydrogen sulphide or ammonia. As for the energy utilisation, the gases of interest are hydrogen, methane with longer aliphatic hydrocarbons and carbon monoxide. If effectively processed, the first one can be used for the production of renewable hydrogen and the second one with longer hydrocarbons can be utilised for the production of renewable synthetic natural gas. Due to its toxicity carbon monoxide is most likely to be converted into electricity and heat or used for chemical syntheses.

This work focuses on the application of (non-porous) membrane gas permeation systems for the recovery of hydrogen from producer gas produced in biomass gasification. First a number of membrane materials for the hydrogen enrichment are generally reviewed based upon the information from the literature. Subsequently, a single and a two-stage configuration for the hydrogen recovery from biomass gasification gas using glassy polyimides are proposed and evaluated using numerical modelling. The evaluation focuses on critical gas processing parameters like achievable hydrogen recovery, purity and energy requirement.

2. System Design and Evaluation Methods

Several membrane gas transport mechanisms are possible for the process of H₂-recovery from gas mixtures. In porous membranes, gas transport phenomena like Knudsen-diffusion, molecular sieving or surface diffusion, in metallic membranes, H₂-ion-transport mechanism and, in the continuous polymeric membrane, solution-diffusion mechanism can be exploited. Due to their intrinsic advantages like relatively easy membrane engineering, operability in wide ranges of temperatures and pressures, non-porous polymeric membranes are likely to be utilised in a considerable number of H₂-enrichment processes.

Table 1: Gas feed composition that is assumed for the evaluation of configurations.

component	content [% (v/v)]
H ₂	39.8
CO	22.3
CO ₂	22.4
CH ₄	10.3
C _x H _y	3.2
N ₂	2.0

Table 2: Assumed ideal membrane gas selectivities versus H₂ used in the evaluation of configurations.

component	generic polyimide [-]	crosslinked polyimide [-]
CO	45.0	75.0
CO ₂	2.7	9.0
CH ₄	100.0	225.0
C _x H _y	470.0	750.0
N ₂	66.7	150.0

In H₂-recovery from biomass gasification products, glassy polymers, whose gas selectivities are based mainly upon diffusivity-selectivity, exhibit favourable gas selectivity order. As H₂ is the smallest molecule among the other gasification product components, it shows the highest permeation rates. The contemporary disadvantage of the glassy polymers in the H₂-enrichment is the relatively low H₂/CO₂-selectivity, which, for example, does not exceed the value of three in typical polyimides. However, recent investigations have proved that the H₂/CO₂ selectivity can be considerably increased through application of polymer blends or chemical crosslinking in the membrane manufacture (Shao et al., 2009). A very promising technique is the later one, as ideal selectivities of above 50 were reported in the literature for this type of polymer modification. The growth of the selectivity is influenced by the type of crosslinking diamine, temperature and length of the crosslinking process and is typically associated with a decrease in the membrane permeability (Shao et al., 2009).

Rubbery polymers are also a possible choice for the application in H₂-enrichment processes. These polymers exhibit so called inverse selectivity, as, through these

polymers, CO₂ typically permeates faster than H₂. This has very positive consequences for the H₂/CO₂ separation processes since higher H₂-purities may be achieved with less effort and the produced gas leaves the system at high pressure. However, the rubbery polymers are rather unlikely to be applied in the H₂-recovery from producer gas as in the rubbery polymers CO exhibits lower permeation rates than H₂ and is enriched in the retentate.

Table 1 shows the composition of a representative biomass gasification mixture that is used for the evaluation of the permeator configurations. Table 2 lists the ideal membrane selectivities versus H₂ for each of the considered gas components. Polyimides with two assumed selectivity-sets were investigated: an unmodified with H₂/CO₂ selectivity of 2.7 and one crosslinked with H₂/CO₂ selectivity of 9.

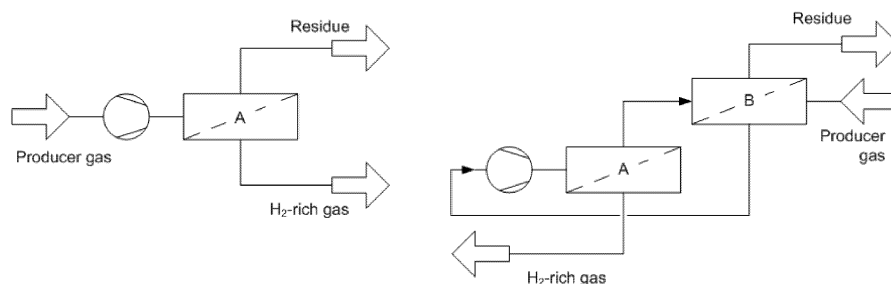


Figure 1: Single-compressor permeator configurations that are considered in this work; single stage (left) and two-stage with sweep (right).

This work investigates two single-compressor permeator arrangements: a single stage and a two-stage with sweep, both are schematically visualised in Figure 1. For the evaluation of the permeator systems the recently developed numerical algorithm and model were used (Makaruk and Harasek, 2009). The modelling approach has been validated against experiments showing good agreement. Within this work it is assumed that the transmembrane flow is ruled by the solution-diffusion mechanism only. Pressure effects, pressure losses and flux-coupling were neglected. Permeators are assumed to be hollow-fibre modules operated in countercurrent mode. Moreover, the gas mixture is assumed to fulfil ideal gas laws.

3. Results

Figure 2 shows modelling results on the achievable H₂-purities for the single permeator and aforementioned membrane selectivities. Both the increasing pressure and the lowering of stage cut have positive effect on the H₂-content in the permeate. This, however, results in higher energy consumption and lower H₂-recovery, respectively. Furthermore, in the single stage permeation, the crosslinked polyimide would yield the H₂-purity of 92 % (v/v) at best, while ordinary polyimides are not likely to produce higher H₂-contents than 80 % (v/v). Hence, it can be noted that single stage systems using the investigated membranes are hardly able to reach very high H₂-purities.

In the investigated two-stage system, the permeate of the second stage is swept with the system inlet gas. This allows to significantly increase the H₂-content in the first stage feed and, as a result, also the H₂-purity in the produced permeate. In Figure 3 the dependence of the H₂-content in permeate on the increase of membrane area ratio B/A is diagrammed. The area ratio variation is done for the constant H₂-recovery of 75.8 % and absolute feed pressure of 16 bar. For higher area ratios and membranes with augmented selectivities the system is able to produce relatively high H₂-purities of above 98 % (v/v). The ordinary polyimides are expected to yield H₂-purities of above 90 % (v/v).

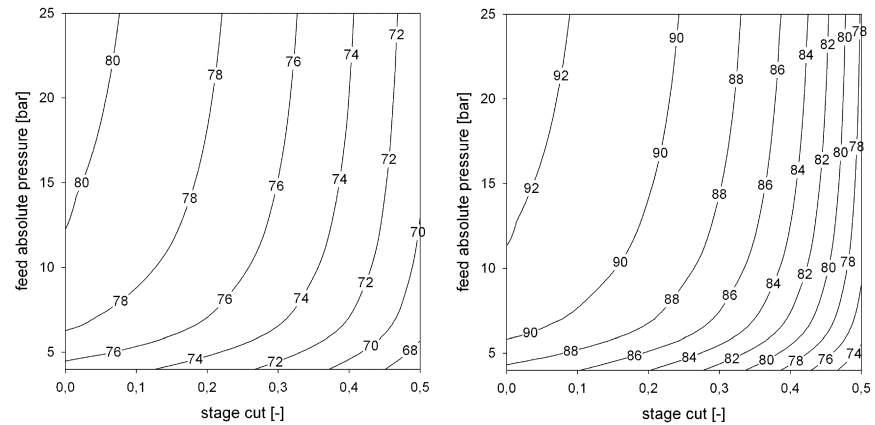


Figure 2: Isolines of H₂-content [% (v/v)] in the permeate of the single-stage configuration for different stage cuts and feed pressures; on the left generic polyimide, on the right crosslinked polyimide with augmented selectivities.

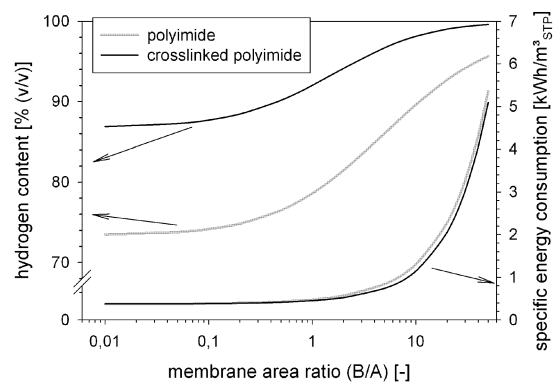


Figure 3: H₂-content in the permeate and the specific isentropic compression energy consumption for variable area ratios of the two-stage configuration with sweep. The design H₂-recovery equals 75.8 % and the absolute operating pressure equals 16 bar.

As it can be noted in Figure 3, increase in the area ratio is accompanied by increase in the specific compression energy consumption (calculated here as isentropic compression energy over the volumetric flow of pure H_2 in permeate). For example, for the investigated crosslinked polymer and the area ratio of 10 the system produces H_2 with the purity of 98.1 % (v/v) and the required specific compression energy equals 1.14 kWh/m³_{STP}. One should note that the upper heating value of a standard cubic meter of H_2 equals 3.55 kWh/m³_{STP} and that the calculated compression energy requirement does not include compression efficiencies. This suggests that the energy conversion efficiency for the production of bio-hydrogen from biomass gasification products is still low for energy production systems.

The possible applications for the enriched H_2 -stream will largely depend on the presence of other gas components. Figure 4 presents results on the composition of the permeate for the two-stage system with crosslinked polyimide and the process conditions as described above. The second most abundant component in permeate is CO_2 followed by CO , CH_4 , N_2 and longer hydrocarbons in decreasing order. The content of the toxic CO for the higher membrane area ratios falls below 1000 ppmv which makes the stream more suitable for the use in proton exchange fuel cells.

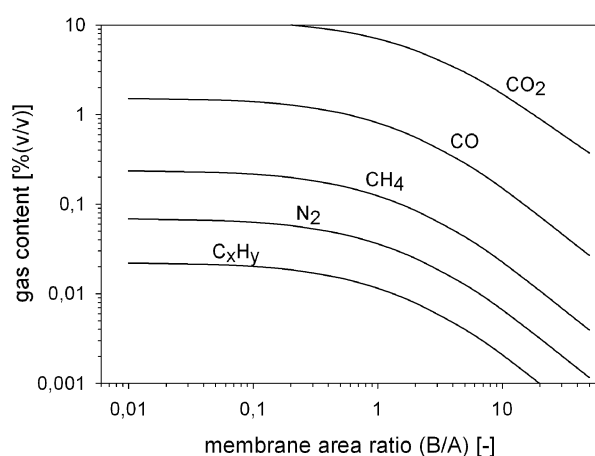


Figure 4: Gas composition for variable membrane area ratio using the two-stage configuration with sweep and crosslinked polyimide. H_2 is the balance. The design H_2 -recovery equals 75.8 % and absolute operating pressure equals 16 bar.

4. Conclusions and Future Work

The recent investigations point out that membrane gas permeation can be an adequate technology for the production of renewable gaseous fuels (Mayer et al., 2010; Miltner et al., 2010b). The two-stage process is able to deliver a H_2 -stream with high purity and adequate recovery provided that membranes with improved selectivities are used. However for the possible renewable hydrogen applications like fuel cell or fuel for

mobility, the main problems include relatively low energy conversion efficiency. Further theoretical and experimental studies are required to develop the hydrogen production processes from biomass gasification gas. Future work includes further optimisation and evaluation studies on single compressor and multicompressor stage arrangements as well as field experiments (Figure 5), membrane polymer tests and module-sweep engineering.

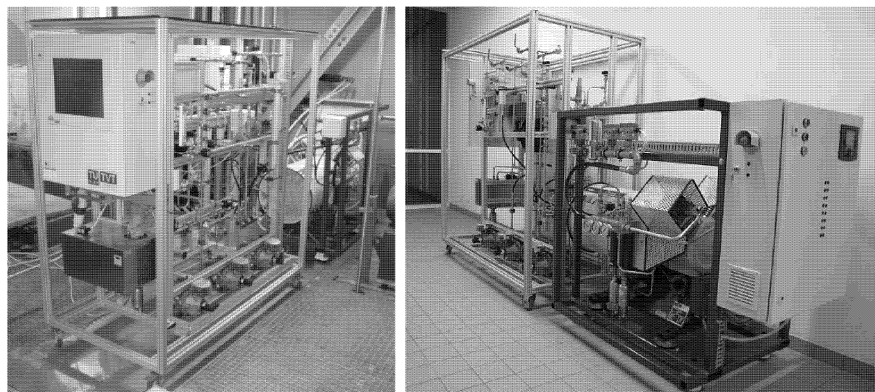


Figure 5: Multistage permeator test-rig during experiments on H_2 -upgrading from producer gas.

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