PROCESS SAFETY AND ENVIRONMENT PROTECTION 86 (2008) 315–320

Contents lists available at ScienceDirect

Process Safety and Environment Protection

journal homepage: www.elsevier.com/locate/psep

Harnessing methane emissions from coal mining

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ABSTRACT

Methane emissions associated with coal-mine ventilation pose a tremendous environmental problem and lead to inadvertent loss of a valuable energy source. The proportion of methane released through underground ventilation is as high as 70% of all the coal-related emissions. Additionally, the CH_4 Global Warming Potential is 21 (for a timescale of 100 years), compared with 1 for carbon dioxide. If the heat of combustion of the methane could be usefully employed, this would bring a twofold benefit of avoiding both CH_4 release and CO_2 emission from the production and use of the fuel thereby displaced. The projects carried out in the Institute of Chemical Engineering, Polish Academy of Sciences explored three major routes for utilizing ventilation air methane (VAM): (1) using VAM as combustion air in conventional boilers, (2) oxidizing VAM in reverse-flow reactors (either catalytic or non-catalytic) to produce heat, (3) enriching VAM (via pressure-swing adsorption or membrane separation) to concentration levels suitable for subsequent use (in, say, reverse-flow reactors). The investigations have now been focused upon homogeneous combustion of VAM in reverse-flow reactors.

Keywords: Ventilation air methane; Combustion air; Reverse-flow reactors; Pressure-swing adsorption; Membrane separation

1. Introduction

Methane is a greenhouse gas that exists in the atmosphere for approximately 9–15 years. As a greenhouse gas, CH_4 is over 20 times more effective in trapping heat in the atmosphere than carbon dioxide over a 100-year period and is emitted from a variety of natural and human-influenced sources. Human-influenced sources include landfills, natural gas and petroleum systems, agricultural activities, coal mining, stationary and mobile combustion, wastewater treatment, and certain industrial processes. Methane is also a primary constituent of natural gas and an important energy source. As a result, efforts to prevent or utilize methane emissions can provide significant energy, economic and environmental benefits.

Methane gas and coal are formed together during coalification, a process in which biomass is converted by biological and geological processes into coal. Methane is stored within coal seams and also within the rock strata surrounding the seams. Methane is released when pressure within a coalbed is reduced as a result of natural erosion, faulting, or mining. Deep coal seams tend to have a higher average methane content than shallow coal seams, because the capacity to store methane increases as pressure increases with depth. Accordingly, underground mines release substantially more methane than surface mines, per tonne of coal extracted. Estimates suggest that as much as 200 m^3 of methane per tonne of coal may be generated during the process of coalification. Some methane may also be generated by later biogenic action, particularly in coal seams which are relatively close to the surface. Whatever its source, most of this methane is subsequently lost by migration through the surrounding rock strata. However, undisturbed coal seams may still contain up to 25 m^3 per tonne of coal, adsorbed within the pore structure of the coal. This residual methane is emitted when the coal is mined and used.

Considerable amounts of methane are released into the atmosphere with coal-mine ventilation air (VAM). A single ventilation shaft may discharge several hundred thousand cubic metres of VAM per hour, and although the concentration of methane in these gas streams is rather low (usually below 1 vol.%), the emissions thus generated pose an environmental threat and lead to the loss of a potential source of energy.

There are several ways in which methane emissions from ventilation air could be reduced. The first is to use the ventilation air as the combustion air in surface installations at the

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Received 10 March 2008; Accepted 9 April 2008

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doi:10.1016/j.psep.2008.04.003

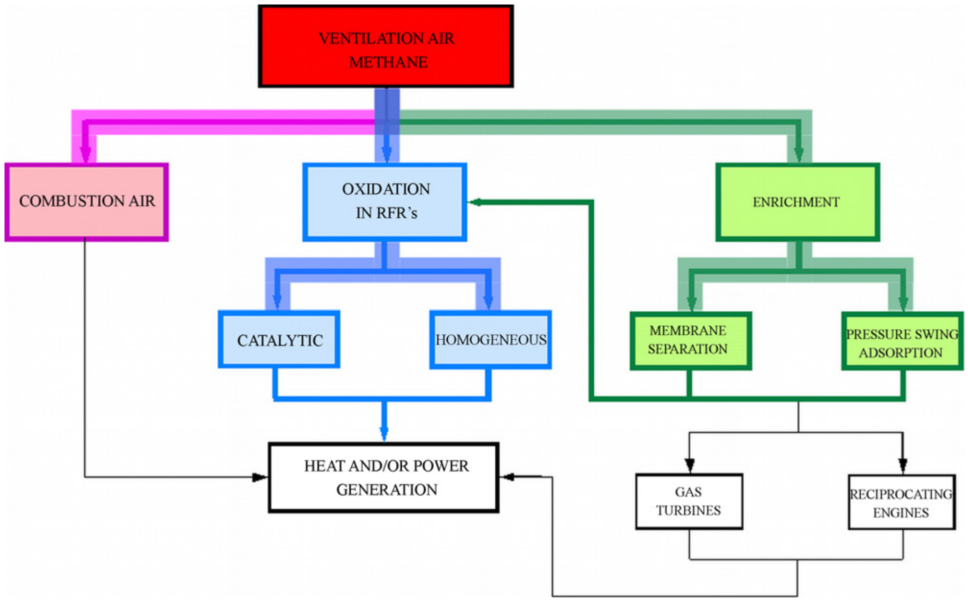

Fig. 1 – A graphical representation of the options studied for the utilization of VAM.

mine site. However, this approach is unlikely to use more than a small proportion of the total available. A second approach is to oxidise the methane to CO_2. Simple flaring is not viable, since the concentration of methane in ventilation air is too low to support combustion. Addition of further fuel would remedy this but the overall effect would be to increase the total emission of greenhouse gases. Thermal incineration may be more practical, although the calorific value of ventilation air is typically around the minimum required for self-sustaining operation. The more recent technology of catalytic incineration could ease this by reducing the required operating temperature, although catalyst poisoning may be a problem. Finally, the methane content of the ventilation air could be enhanced by one of several membrane or adsorption based techniques. Unfortunately, methane is not strongly adsorbed on any of the substrates currently in use. The technique could, however, be considered as a means of obtaining the relatively small increase in concentration required for stable incineration.

The principal objective of the present study is to show in more detail the various options for utilizing VAM and to assess these options in terms of technical feasibility and economic viability (Fig. 1).

2. The utilization of ventilation air methane in existing boilers

One of the obvious alternatives for the utilization of VAM is combustion in existing boilers situated at a reasonable distance form a ventilation shaft (Warmuzinski et al., 2004). An additional amount of energy thus introduced decreases the amount of primary fuel that would otherwise be used to carry out the combustion. The method discussed does not require any special upgrading technique or complex equipment. The principal elements of the system include a blower/compressor and an insulated pipe connecting the source to the boiler.

This mode of utilization becomes profitable once the cost of the fuel replaced (say, coal) exceeds the total cost of the system. Fig. 2 shows the break-even curves as VAM flow rate vs. length of the pipeline. (The discontinuity is due to a step change in the cost resulting from a step increase in the pipe thickness for diameters in excess of 2 m). The area to the left of the curves shows parameters for which the whole exercise is actually profitable. Using such a graph is therefore a rapid and fairly accurate way for assessing the limiting values of the basic parameters involved (VAM flow rate, length of the pipeline and methane concentration) for which the use of VAM as combustion air becomes economically viable.

3. Oxidation of VAM in reverse-flow reactors

An interesting option for the utilization of VAM with the simultaneous production of heat is the oxidation in reverse-flow reactors, either catalytic or non-catalytic (Warmuzinski et al., 2006). So far, the most attractive option has seemed to be that based on catalytic combustion in a CFRR (catalytic flow-reversal reactor) (Gosiewski and Warmuzinski, 2007; Gosiewski et al., 2008). (The relevant studies were also carried out at National Resources Canada (Sapoundjiev, 2001) and in the Institute of Catalysis, Russian Academy of Sciences). However, the large-scale implementation of this technique may prove problematic. The concentration of methane in ventilation air may reach 1% and, with the use of the manganese catalyst, the temperature of the catalytic bed may exceed

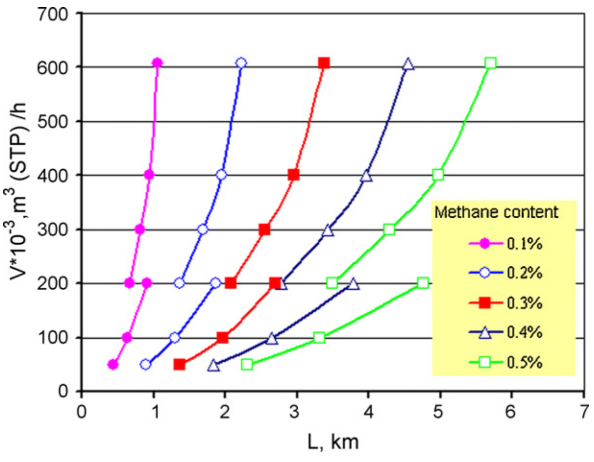

Fig. 2 – Break-even curves for the utilization of VAM as combustion air.

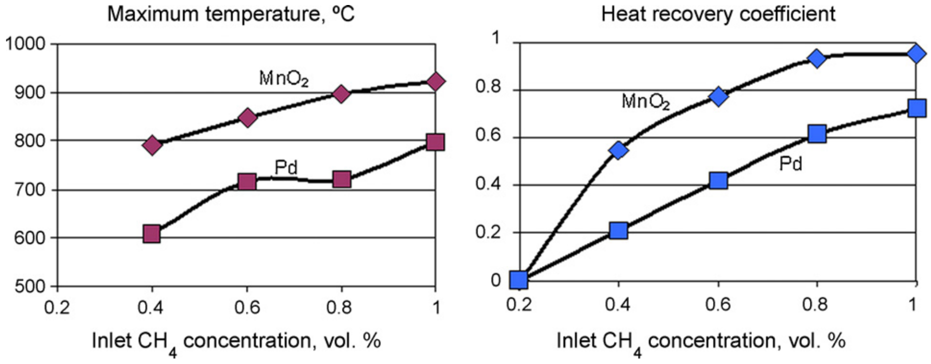

Fig. 3 – Maximum catalyst temperature and heat recovery vs. methane concentration for the two catalysts studied.

900 °C for CH_4 concentrations above 0.8%, even for highly efficient removal of heat from the reactor. Thus, the relatively cheap Mn catalyst may undergo rapid destruction. If the more expensive palladium catalyst is employed, the temperature can be kept at a level lower by about 100 °C. Unfortunately, the heat recovery also becomes considerably lower and the cost of the Pd catalyst leads to a payback period of almost 7 years for an industrial plant. The relation between the maximum temperature and the heat recovery can be seen from the graphs below (Fig. 3).

The excessive temperature results mainly from a considerable share of homogeneous combustion in the gaseous phase, within both the catalytic bed and inert material whose sole purpose is the accumulation of heat. Thus, non-catalytic flow-reversal combustors (TFRR) offer a clear advantage over catalytic flow-reversal reactors (CFRR), although the materials of construction will be more expensive. An important upper limit of temperature is associated with the formation of NO_xs; these, however, do not appear in large quantities below 1300 °C, at which temperatures the reactor will operate.

The simulation of the TFRR operation requires the knowledge of reliable kinetic equations for the homogeneous combustion in the gaseous phase. The available data lead to divergent results, in terms of both temperature profiles and conversion degrees. Therefore, the calculations done in the present study are based on independent experiments carried out in our laboratory, both in a unidirectional tubular reactor and in a flow-reversal system. The principal objective of the unidirectional experimental studies was to provide general characteristics of the non-catalytic combustion of methane. The flow-reversal experiments were carried out for air–methane mixtures of CH_4 concentrations similar to those in mine ventilation air. It is shown that even for a relatively short inert bed (30 cm) it is possible to attain an almost complete conversion of methane at a temperature as low as 950 °C.

Based on our experimental data along with those available in the open literature simulations were performed for the TFRR. Although the numerical results obviously depend on a kinetic equation employed (cf. Fig. 4), they clearly show that it is possible to conduct flow-reversal combustion at temperatures that do not lead to excessive formation of NO_x. Both the experiments and simulations suggest that a high conversion of methane can be reached at temperatures below 1000 °C. Also, the temperatures higher than those associated with catalytic combustion should safeguard more efficient heat withdrawal from the system.

An important problem in the modelling of methane combustion in TFRRs is the formation of carbon monoxide. The studies carried out so far in our laboratory reveal that if the oxidation occurs in an empty space of the reactor (rather than over a monolith packing), considerable amounts of CO may indeed appear over some temperature ranges. Only at higher temperatures does the reaction lead to carbon dioxide. The formation of CO over a monolith packing seems to be negligible, probably due to the presence of oxidizing radicals activated by the monolith surface.

The experiments are now conducted in a large laboratory reverse-flow vessel packed with non-catalytic monolith blocs, at an inlet flow rate of 200–400 m^3/h (Fig. 5).

4. The enrichment of VAM via pressure-swing adsorption and membrane separation

The efficiency of heat recovery in a CFRR strongly depends on the concentration of methane in the feed gas. As Fig. 6 shows, over the range of concentrations prevailing in VAM a twofold increase in CH_4 content may raise the efficiency by a factor of three. It might therefore be of interest to see whether the benefits of the enrichment outweigh the costs associated with a selected adsorptive or membrane process.

The pressure-swing adsorption process is carried out in a two-column installation packed with carbon molecular sieves 5A (Warmuzinski et al., 2001). The simple pressure-swing cycle takes 26 min to complete and includes pressurisation, adsorption, blowdown and purge. Methane is recovered as a low-pressure product during the countercurrent desorption step, and its concentration in the product is assumed to be twice that in the feed gas (supplied at a rate of 0.49 m_N^3/s).

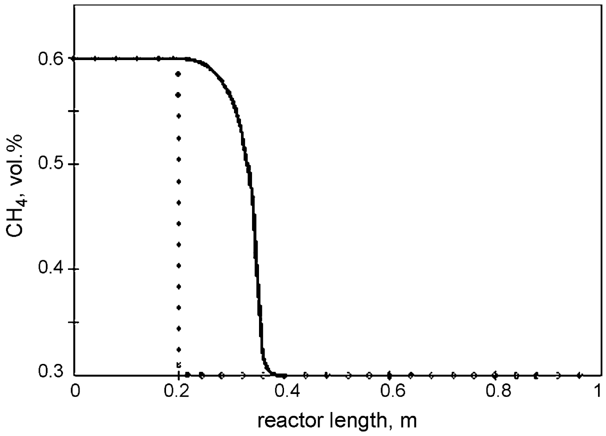

Fig. 4 – Methane concentration in a stable cyclic steady state for an inlet CH_4 content of 0.63 vol.% and for two different kinetic equations.

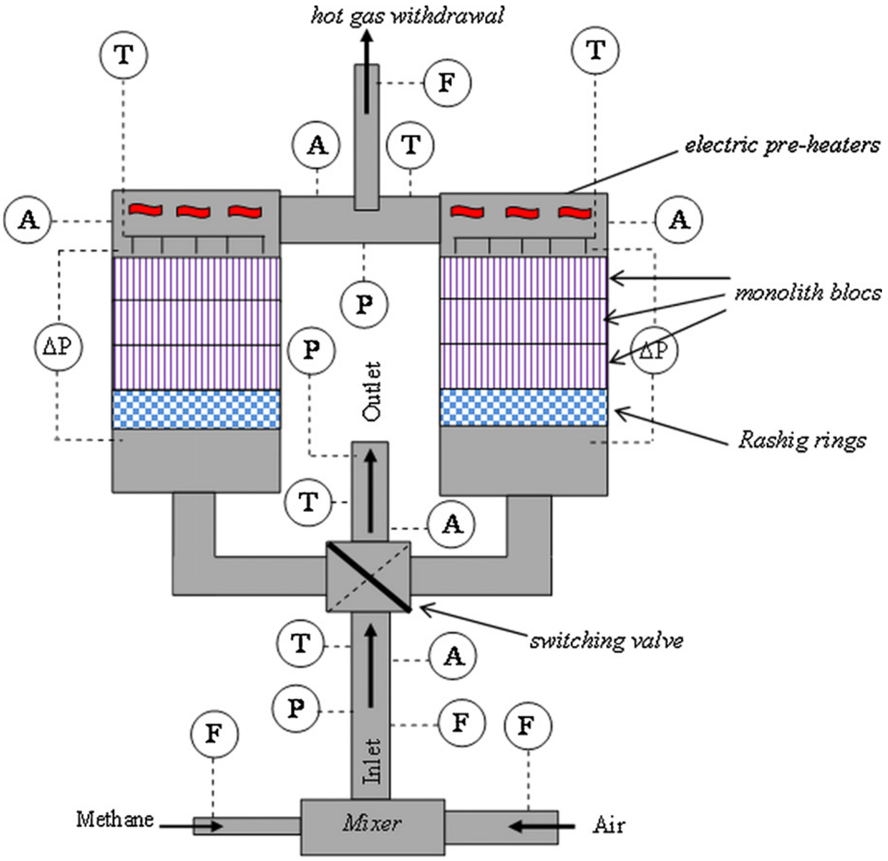

Fig. 5 – Scheme of an experimental non-catalytic reverse-flow reactor.

The calculations reveal that methane content in the feed over the range studied (0.25–1.5 vol.%) does not have any significant effect on the size of the installation. What really matters is the adsorption pressure—the higher the pressure, the lower the capital cost.

The operating costs include the costs of compression, maintenance and depreciation. Again, the principal parameter in terms of the cost is the pressure at which the feed leaves a compressor. Obviously, the operating costs increase with the pressure due to the increased cost of electricity. The total annual costs of the PSA enrichment as a function of the adsorption pressure are shown in Fig. 7.

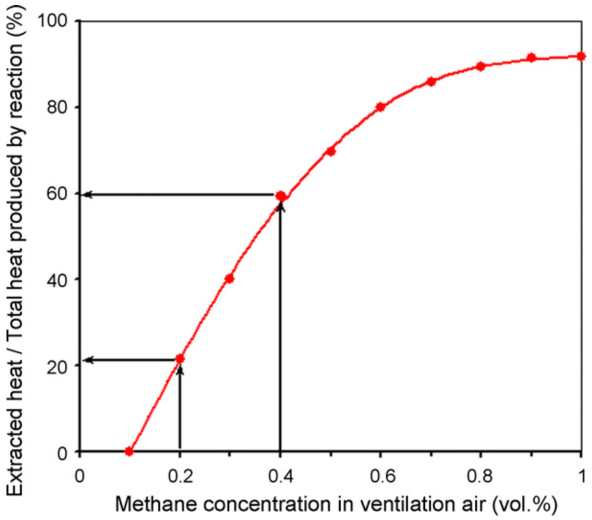

Fig. 6 – Efficiency of the heat extracted as a function of methane concentration (Sapoundjiev, 2001).

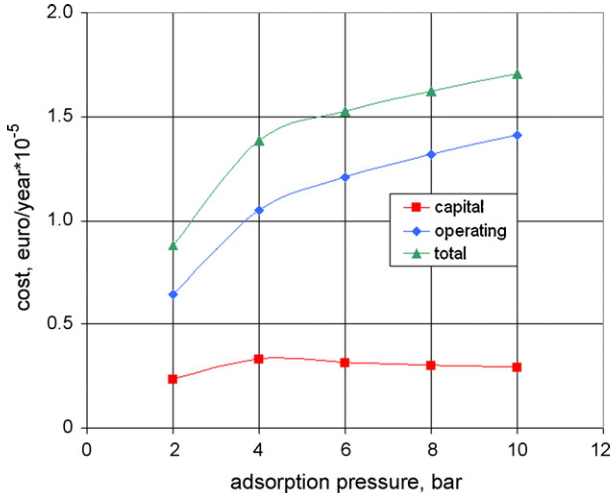

Fig. 7 – Costs of PSA enrichment vs. adsorption pressure.

If, however, the profit resulting from additional energy production in a reverse-flow reactor is compared with the costs incurred, it can be seen that these costs outweigh the profit by, roughly, an order of magnitude.

A survey of commercial membranes reveals that polydimethylsiloxane (PDMS) exhibits reasonable selectivity vis-a-vis binary mixtures of methane and nitrogen. The ratio of permeation coefficients Q_{CH_4}/Q_{N_2} is, on the average, equal to 3.2. Our own experiments for a tubular PDMS membrane on polysulphone support yield $Q_{CH_4} = 7.38 \times 10^{-11}\,\text{kmol/m}^2\,\text{s Pa}$ and $Q_{N_2} = 2.21 \times 10^{-11}\,\text{kmol/m}^2\,\text{s Pa}$. Thus, the ideal separation coefficient is 3.34, and it is this value that was employed in further calculations. The permeate flow rate was assumed to be equal to the flow rate of the low-pressure product in the PSA

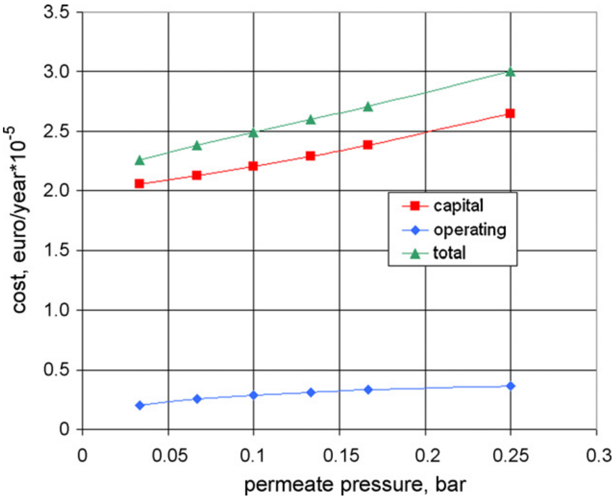

Fig. 8 – Costs of membrane enrichment as a function of permeate pressure.

system. If, further, CH_4 concentration in VAM is 0.5 vol.% and the feed pressure is 1 bar, it is possible to calculate the membrane area necessary to effect a required separation and the associated costs for the varying methane content in the permeate and the permeate pressure. These calculations show that the total annual cost is virtually independent of the methane content in the permeate (over the range studied, 0.6–1.0 vol.%), and increase with an increase in permeate pressure (by around one third when the vacuum level increases from 33 to 250 mbar). As can be seen in Fig. 8, the total annual cost, although higher than that for the PSA enrichment, is of the same order of magnitude (provided we base our comparison on the same amount of the product and the same degree of enrichment). However, the structure of the costs is totally different, with capital cost prevailing in the case of membrane separation, and operating costs predominating in pressure-swing adsorption.

An increase in the capital cost with increasing permeate pressure (at a constant feed pressure) is due to an increase in membrane area: if the pressure is changed from 33 to 250 mbar, the membrane area rises 1.3 times, with almost the same rise in the capital cost.

The principal conclusion is much the same as in the case of the PSA process: some profit resulting from an increased heat production in a reverse-flow reactor is only a fraction of the costs associated with the preconcentration. We have to bear in mind, however, that there is an environmental advantage, however difficult to quantify, of utilizing larger amounts of methane that would otherwise be dumped into the atmosphere.

5. Summary and conclusions

Large quantities of methane are exhausted into the atmosphere with coal-mine ventilation air with very low CH_4 content (0.1–1 vol.%). The global emissions of methane from this source are estimated at, roughly, 15 Mt/year. Apart from the environmental impact, this leads to considerable energy losses, as methane is a fuel in its own right. In the studies carried out in the Institute of Chemical Engineering, Polish Academy of Sciences, three principal routes for utilizing ventilation air methane were explored: using VAM as combustion air in conventional boilers, oxidizing VAM in reverse-flow reactors (either catalytic or homogeneous) to produce heat, and enriching VAM (via pressure-swing adsorption or membrane separation) to concentration levels suitable for subsequent use.

5.1. *VAM as combustion air*

The use of VAM as combustion air in existing conventional boilers was analysed in terms of four principal parameters: net profit resulting from a decreased fuel consumption, concentration of CH_4 in VAM, the distance between the source and the boiler, and VAM flow rate. It is found that the use of VAM can still generate some profit for transportation distances as long as 4–5 km.

5.2. *Oxidation of VAM in reverse-flow reactors*

Both catalytic (CFRR) and homogeneous (TFRR) reverse-flow reactors were investigated. Simulations and experimental studies reveal that CFRRs are characterized by relatively high operating temperatures which may lead to a rapid deactivation of the catalyst. Therefore, non-catalytic oxidation in TFRRs was studied in more detail. The studies clearly demonstrate than TFRRs can become an attractive alternative to CFRRs, provided reasonable values of the operating parameters and a suitable mode of heat withdrawal are selected.

5.3. *Preconcentration of VAM*

A rise in methane content in the feed may considerably increase the efficiency of heat production in either CFRRs or TFRRs. Therefore, total annual costs were evaluated for the enrichment of mine ventilation air in methane using pressure-swing adsorption or membrane separation. A wide range of the operating parameters (including CH_4 concentration in the feed gas, flow rates, enrichment degree, adsorption pressure and permeate pressure) was analysed. It is revealed that the cost of the membrane separation is of the same order of magnitude than that of the PSA process. However, the structure of the costs is altogether different, with a much larger share of the capital cost and a much lower proportion of the operating cost in the case of membrane permeation. Finally, the profit resulting from an increased heat production in a catalytic flow-reversal reactor is found to only partly offset the cost of the enrichment.

Of the various techniques analysed it is the non-catalytic combustion of VAM in a reverse-flow reactor which seems to be the most promising one. By combining relative simplicity and cost-effectiveness with the necessary degree of operating flexibility, it is certainly an option that deserves further studies.

Acknowledgements

The contribution of K. Gosiewski, M. Jaschik and M. Tanczyk is gratefully acknowledged.

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