INNOVATIVE TECHNOLOGIES TO REMOVE CHLORINATED HYDROCARBONS AND CO_2 FROM LFG

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ABSTRACT
New technologies are being developed to process landfill gas (LFG) for use as a fuel. Two technologies currently under development by GCE and the Reaction Engineering and Transportation Group at the University of Southern California (RETG/USC) are biofilters to remove chlorinated hydrocarbons and sulfur compounds and high temperature ceramic polymer membranes for CO_2 removal.

These technologies show promise as potential low cost alternatives for gas treatment. One particularly intriguing aspect of these technologies is their simplicity of operation.

A demonstration project has been set up at a southern California landfill to test the biofilters. This demonstration project follows on the heels of a highly successful laboratory study that proved the viability of this process to remove chlorinated hydrocarbons.

The membrane development is being funded by the Department of Energy and the California Trade and Commerce Agency Office of Strategic Technology (OST). The membranes show significant promise as a preferred technology of the future. This is a two year grant and includes optimizing the membrane design and performing field testing.

A third process that has already been developed by is a hydrotreater to convert chlorinated hydrocarbons to HCl for easy removal using an absorbent.

INTRODUCTION
Landfill gas (LFG) is generated by the decomposition of waste materials by anaerobic bacteria. This gas typically consists of approximately equal amounts of methane and carbon dioxide. It also contains traces of non-methane organic compounds (NMOCs), sulfides and chlorinated hydrocarbons. Federal regulations, promulgated in March 1996, require hundreds of additional landfills across the country to collect and combust their landfill gas to reduce NMOC emission to the air. (LMOP, 1996.) However, the LFG, due to its methane content, is also a valuable source of energy. Once the landfill gas is collected, it can be used as a natural gas substitute.

There are several potential problems that can be caused by some of the contaminants in LFG.

Organic chloride when oxidized form hydrogen chloride. When in aquaous phase the resulting hydrochloric acid can be corrosive to equipment. Chlorine can also be a poison to hydrogen reforming catalysts in fuel cells, hence in this application its removal is essential. Sulfur hydrogen sulfide also has the potential of being a problem because of similar acid formation problems. Furthermore, LFG in its raw state is not always a suitable gas for all fired equipment LFG utilization would be considerably simpler if the resulting product gas was nearly identical to natural gas so that no burner modifications were required. This is especially important at plants that have many burners distributed around the facility. This goal can be partially met by removing CO_2 from the gas.

There are a number of processes that can be used to treat LFG to improve its quality as a fuel. This paper briefly discusses three novel processes that are at various stages of development by the RETG/USC that can be used to improve LFG quality. These are:

1. Biofilter	Selective removal of chlorinated hydrocarbons and NMOCs.
2. Carbon molecular sieve membranes (CMSMs)	Carbon dioxide removal.
3. Hydrotreater	Selective removal of chlorinated and sulfided compounds.

BIOFILTER

Biofilters remove contaminants from gaseous streams by passing them through a wet porous medium that supports a vigorous culture of microorganisms, which biodegrade the contaminants after they are dissolved in the water phase. Biofiltration is typically used to degrade compounds present in concentration ranging from the ppb level to upwards of 1000 ppm. Biofilters have been commonly used to treat trace contaminants in air, and have employed aerobic microorganisms, which use oxygen as the terminal electron acceptor. In preliminary studies utilizing a laboratory scale biofilter (length=1m, d_{int}=7.6cm), biofiltration was used to remove tetrachloroethylene (PCE) from an anaerobic gas (equimolar mixture of CO_2 and CH_4 plus 30-100ppm PCE), which simulates a LFG, by reductive dehalogenation. (Schwarz, et al., 1999.) The biofilter uses granular activated carbon as the support material for the biomass, which only during the first (46) days contributes to the elimination of the PCE by adsorption, after which time the removal of the PCE is completely due to the biodegradation process. After a 13 month period the conversion (i.e., PCE degradation efficiency) that the reactor attained was higher than 98%. To enhance the biofiltration process several steps were taken. These included:

To test the technology in the field a dual-bed biofilter pilot project is being performed at the West Riverside landfill in Riverside County, California. The first bed acts as an aerobic biofilter and the second bed acts as an anaerobic biofilter. Oxygen in LFG at the inlet to the pilot plant is sufficient for the aerobic bacteria. This oxygen is scavenaged in the first bed resulting in anaerobic conditions. Test results have so far been encouraging, and will be reported in future presentations. A schematic of this test facility is presented in **Figure 1.**

MEMBRANES AS A SEPARATION TOOL

To upgrade pure LFG to natural gas quality, it is necessary to remove impurities and CO_2. A good separation process that can be used to remove CO_2 is based on carbon molecular sieve membranes (CMCMs). These membranes offer significant advantages over other types because of their higher separation factor and permeance. For all membranes there is a tradeoff between permeance and separation factor. Polymeric membranes offer very good separation factors, but their permeance is very low. On the other hand, porous inorganic membranes offer higher fluxes but low separation factors. This has motivated the development of microporous inorganic membranes, made from a variety of crystalline zeolitic materials by hydrothermal routes, and also from silicas made via sol-gel and chemical vapor deposition (CVD) techniques, that offer improved separation factor and permeance.

Carbon molecular sieve membranes, prepared by the carbonization of polymeric precursors, have been studied in the past few years as a promising alternative to both inorganic and polymeric membranes. These membranes have been shown to have, for many commercially interesting separations, equal or higher permselectivity than polymeric membranes, and a high enough permeability so as to be comparable with the microporous inorganic membranes. A very recent study (Sedigh, et al., 1999) by TERG/USC shows promising results using CMSM prepared by carbonization of polyetherimide-coated mesoporous tubular membranes. The membranes show higher permeance and better separation factors than other supported CMSMs reported in the literature for the CO_2/CH_4 and H_2/CH_4 binary mixtures as well as for the $CO_2/H_2/CH_4$ ternary mixture. CO_2/CH_4 separation factors as high as 145 for the equimolar binary, and 155 for the ternary mixture were obtained with a CO_2 permeance of about 0.15 cm^3/cm^2 psi min. This compares favorably to cellulose acetate membranes which typically have a separation factor of less than 10. It is envisioned that the new membranes will be able to efficiently remove carbon dioxide from LFG at pressures as low as 40 psig.

With this promising result an economic evaluation of the use of the membranes to upgrade high quality LFG to pipeline quality gas or poor quality LFG to a level suitable for use in an internal combustion engine (IC) (Prosser, et al., 1999) was recently undertaken by GCE in collaboration with TERG/USC, and Media & Process Technology, Inc. (M&PT) of Pittsburgh, PA. In this study the focus was on the performance and economics of the CMSMs application in LFG energy recovery projects in small landfills, holding from 1 to 5 million tons of municipal solid waste. The goal was to understand the conditions and economics that would allow the CMSM be used to upgrade poor quality LFG to a suitable quality for use in IC engines use or to upgrade high quality LFG to pipeline quality methane gas. The study concluded:

1. That the use of CMSM shows significant promise as a future technology to remove CO_2 from LFG.
2. Future work is needed to prove the long-term effectiveness of the membranes in a field test using LFG. This work is scheduled by GCE and M&PT for the year 2000 at a landfill in Southern California. A flow diagram of the test system is presented in **Figure 2.**

HYDROTREATER

Hydroprocessing is a mature technology used for many years in the petroleum industry for the removal of heteroatoms, like oxygen, nitrogen and sulfur. More recently, the technology has been tested in the dehalogenation of various chlorinated NMOCs. The new process is called catalytic-sorption hybrid process (CSHP), which has been developed jointly by RETG/USC and EPRI (Electric Power Research Institute) and tested in the field. (He, et al. 1997.) The process for hydrotreating LFG consists of:

1. A catalytic hydrotreatment step to convert the halogenated and sulfided compounds into HCl, HF, and H_2S.
2. Sorption of the HCl/HF and H_2S produced on a suitable sorbent or removal of the HCL/HF by dissolving them in water, which can then be neutralized using caustic soda to form sodium chloride or sodium fluoride. A significant advantage of this process is that the halogenated/sulfided hydrocarbons are not merely separated from LFG but are transformed completely to mineral compounds, which are then easily removed. Because this process is selective, other NMOCs that contribute to the BTU value of the gas are not removed.

This process was initially tested in the RETG/USC laboratory with promising results, after which it was scaled-up and tested by EPRI in a pilot-plant scale unit (as a part of a fuel cell demonstration project) using LFG generated by the Anoka Landfill in Minnesota **(Figure 3).** The CSHP system was tested as the second stage to a more conventional LFG treatment system, where in the first stage a sorbent was used for the removal of sulfide compounds, and then a packed bed containing activated carbon removed NMOCs and halogenated compounds. The CSHP unit operated to reduce chlorinated hydrocarbons that escaped past the activated carbon beds. The results, after 1000 hr of operation, showed that the new process was highly effective in converting and removing halocarbon and sulfur compounds from LFG. The process had very little effect on other NMOCs present in the LFG. The conclusions of the study were:

1. The CHSP process is feasible to clean LFG of halogen and sulfur containing compounds.
2. The CHSP system could be utilized as a stand-alone system or in combination with more conventional LFG clean-up schemes, as demonstrated at the Anoka test site.
3. The system would be applicable to any power-generation device or process, where chlorinated hydrocarbons are destructive to the equipment or potentially harmful to the atmosphere.

This process is licensed by the Electric Power Research Institute.

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FIGURES

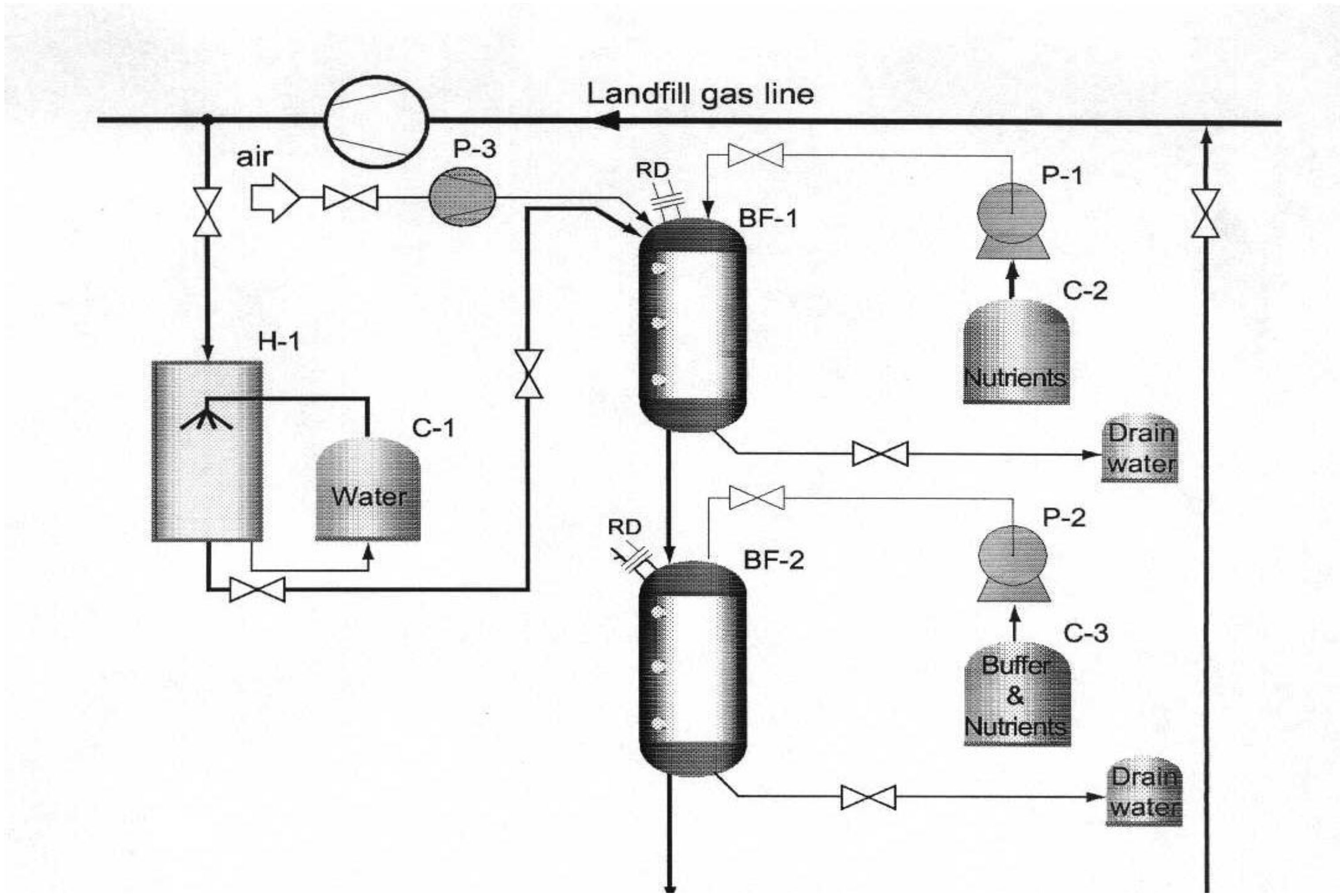
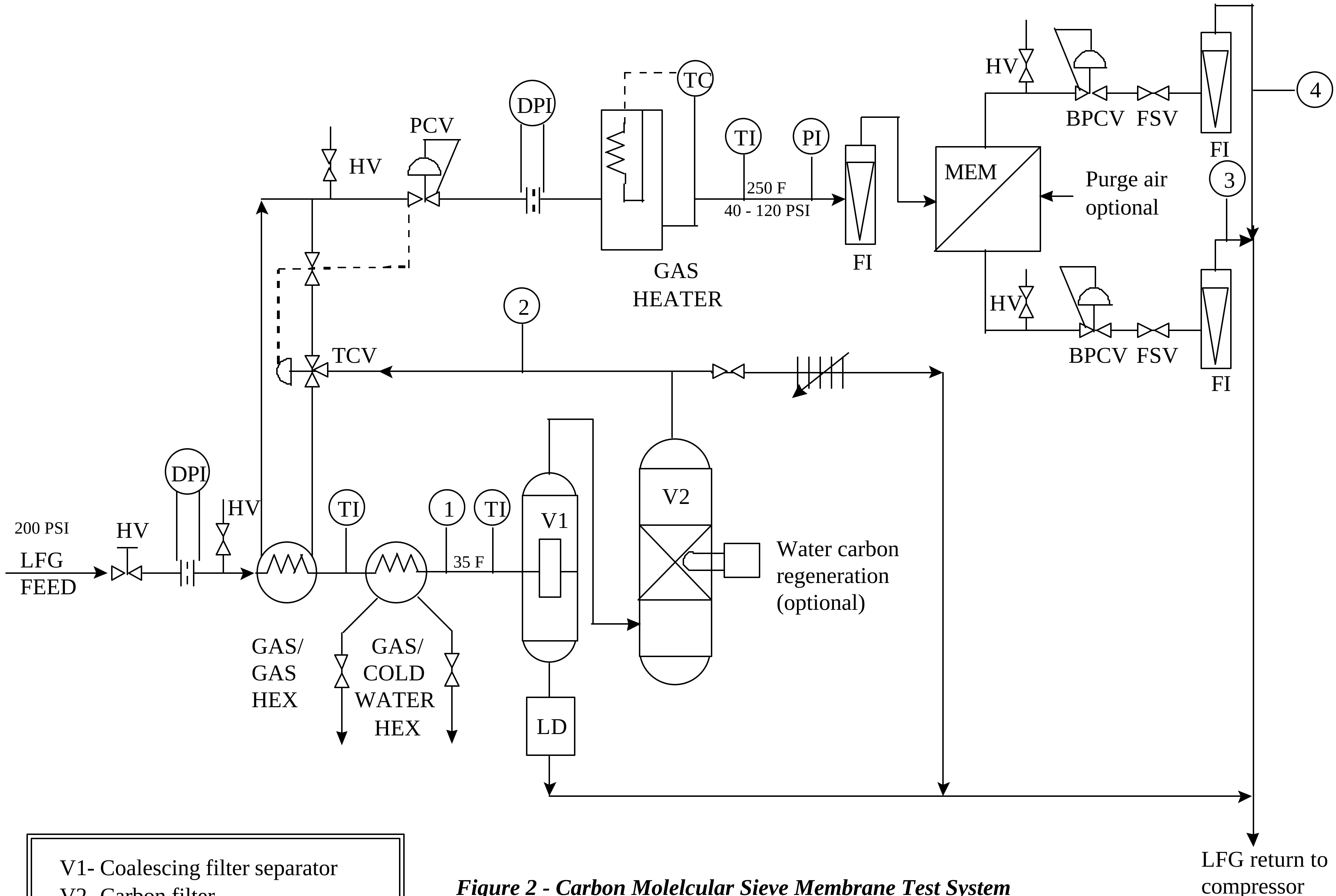


Figure 1 - Biofilter Test Facility Schematic



V1- Coalescing filter separator
V2- Carbon filter
MEM- Carbon/Ceramic membrane

Figure 2 - Carbon Molelcular Sieve Membrane Test System

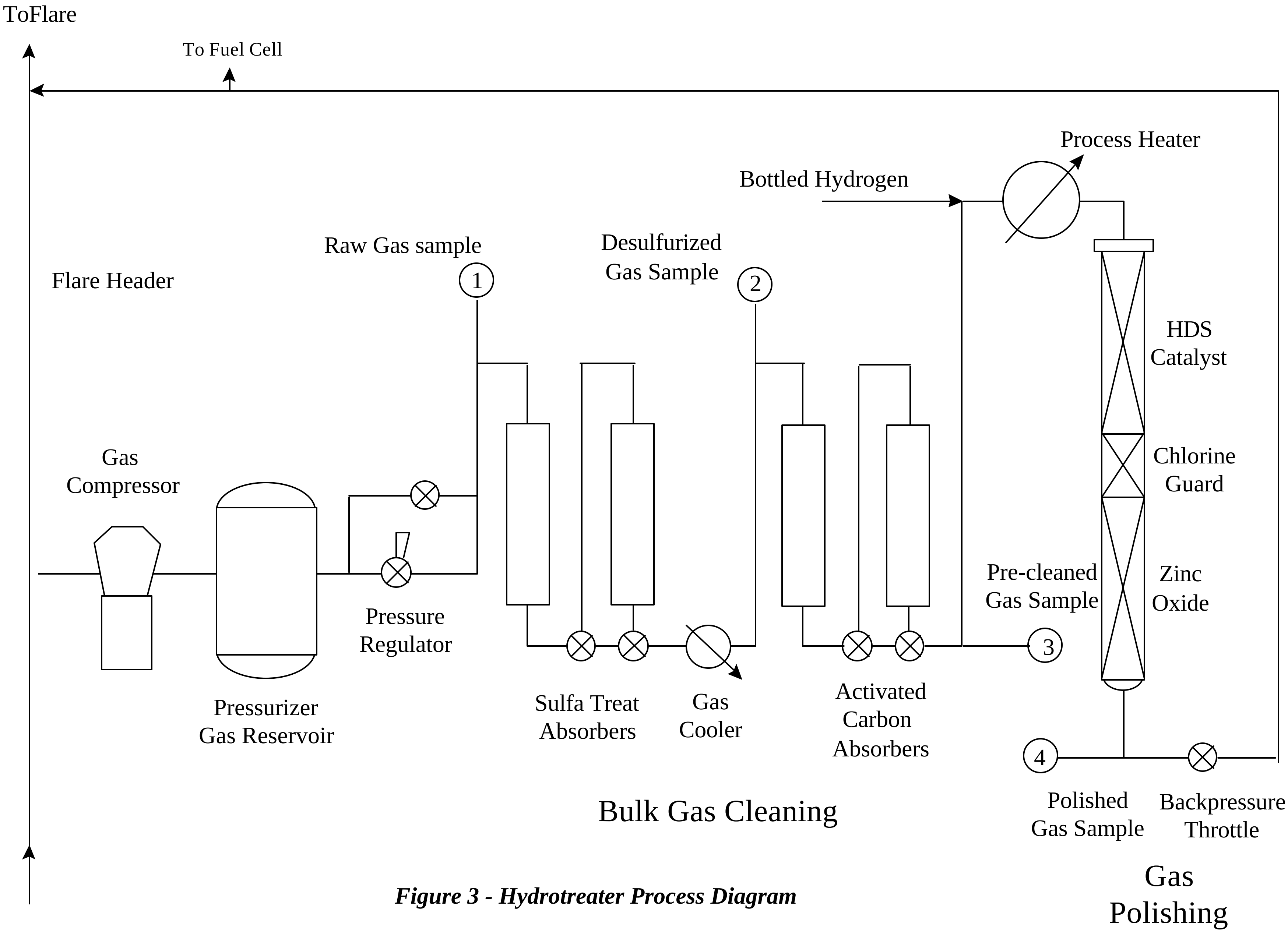


Figure 3 - Hydrotreater Process Diagram