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Fuel processing of biogas for small fuel cell power plants

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Abstract

Biogas has a huge potential as fuel for fuel cell power plants. In the present work developments in fuel processing of biogas for a phosphoric acid fuel cell power plant to be located in rural India are described. Experimental work including steam reforming and shift conversion of biogas and methane has been carried out in a laboratory development unit. It is confirmed that biogas is not only a useful fuel but also that the carbon dioxide in biogas has a positive effect on methane conversion. The biogas fuel cell power plant will give a high electrical efficiency on the small scale of biogas units.

Keywords: Phosphoric acid fuel cells; Biogas

1. Programme outline

This Indo–Swedish research programme will result in a specification of competitive fuel cell power plants for rural India and elsewhere. Primary fuels are renewable sources such as animal dung, agricultural wastes and energy crops. A typical size for such village power plants is 500 kW.

Two laboratory development units, LDU 1 and LDU 2, have been designed and built within the programme. LDU 1 is intended for biogas with a phosphoric acid fuel cell (PAFC) generator and LDU 2 for producer gas, from thermal gasification of biomass, with an alkaline fuel cell (AFC) generator. This paper describes results from experimental work with the LDU 1 fuel processor. LDU 1 is now in operation in India operating with biogas produced locally.

The programme is carried out in collaboration between the Royal Institute of Technology (KTH) in Stockholm, Sweden, and three Indian Universities. The Indian partners are the Punjab Agricultural University in Ludhiana, The Tamil Nadu Agricultural University in Coimbatore and the Central Institute of Agricultural Engineering in Bhopal.

2. Power plant outline

The biomass fuel cell power plant consists of four major blocks, Fig. 1. In the primary conversion step animal wastes and/or biomass are converted to a fuel gas by anaerobic digestion or thermal gasification.

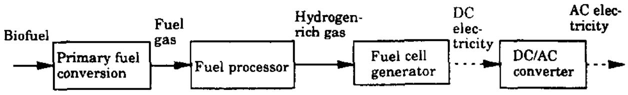

Fig. 1. Block diagram for a biomass fuel cell power plant.

The fuel processor removes impurities and converts the fuel gas to a hydrogen-rich gas. The detailed flow sheet for this step depends on the composition of the fuel gas and the requirements of the fuel cell generator.

Different types of fuel cell generators can be used in these power plants. In the present programme phosphoric acid fuel cells and alkaline fuel cells were selected for further evaluation.

The final block of the power plant is an inverter for conversion of fuel cell direct current (d.c.) to alternating current (a.c.) for the grid or equipment requiring a.c. power.

3. Laboratory development unit 1

LDU 1 is a 1.5 kW PAFC power plant constructed for laboratory runs. The fuel processor of LDU 1 converts biogas to a hydrogen-rich gas for the PAFC generator. Typical composition of biogas is 60% methane and 40% carbon dioxide with up to 1% hydrogen sulfide.

LDU 1 is a laboratory version of a PAFC plant and is described in detail in Section 4. The final design will be different in many ways. Hydrogen sulfide removal will, for example, be accomplished in two steps, one for bulk removal, with a cheap absorbent, and one for final clean up. The steam

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reformer will be heated by a gas burner and not electrically as in LDU 1. Heat exchangers will be used to recover waste heat to be used in the process, etc.

4. Equipment and process details

Fig. 2 shows the LDU 1 fuel processor setup. Synthetic biogas is first desulfurized in a zinc oxide bed at 400 °C. This is because sulfur poisons the catalyst in the fuel cell anodes. Most steam reforming and shift conversion catalysts are also poisoned by sulfur. The hydrogen sulfide content in the gas is reduced to less than 0.1 ppm in the zinc oxide bed.

Methane is reacted with steam in the reformer to hydrogen and carbon monoxide over nickel catalyst at 600 to 800 °C and atmospheric pressure:

$$CH_4+H_2O \longleftrightarrow CO+3H_2 \qquad \Delta H^0=206.2 \text{ kJ/mol}$$

This highly endothermic reaction is enhanced by high temperature, low pressure and excess of steam. Some of the carbon monoxide produced in the reformer is converted to carbon dioxide in the shift reaction simultaneously taking place in the reformer.

The laboratory reformer is a single tube with a length of 660 mm and an inside diameter of 21 mm. The height of the catalyst bed was 220 mm in the experiments reported here. The steam reformer is heated electrically with two separate furnace units. The temperature in each furnace is kept constant by means of proportional integrating derivating regulation. Steam is produced in a steam generator.

Carbon monoxide and steam are then shifted to additional hydrogen and carbon dioxide in the shift converters:

$$CO+H_2O \longleftrightarrow CO_2+H_2 \qquad \Delta H^0=-41.2 \text{ kJ/mol}$$

Carbon monoxide is harmful to the PAFC generator and the carbon monoxide content in the anode gas should not exceed 1.5% [1]. To reach this level the shift reaction is accomplished in two steps. The high-temperature shift works at 330 to 450 °C with an iron chromium oxide catalyst. The low-temperature shift uses a catalyst containing copper oxide and zinc oxide at 200–250 °C. The shift converters are 540 and 590 mm long tubes, respectively, with an inside diameter of 40 mm. The tubes were filled completely with catalyst.

Residual water in the gas stream is removed in a condenser. The composition of the dry gas leaving the system is analysed in a gas chromatograph with a thermal conductivity detector.

5. Experimental

A first series of experiments included steam reforming of synthetic, sulfur-free biogas (60% methane and 40% carbon dioxide) and of pure methane at atmospheric pressure. The intention was to get quantitative evidence regarding the effect of carbon dioxide in biogas on the hydrogen yield. The reforming step was studied under different conditions. Factors varied were the temperature in the reformer, the steam-to-carbon ratio, the space velocity and the carbon dioxide content of the fuel gas (biogas or pure methane). The gas leaving the reformer was analysed and the conversion of methane determined for different conditions.

The second series of experiments included shift conversion of reformed gas in the two shift converters. Synthetic biogas was used as feed. The temperature in the reformer and the steam-to-carbon ratio were varied.

6. Results and discussion

Reforming of biogas has received little attention in the past [2–4]. Few experimental studies have been reported in the literature. Reforming of methane and higher hydrocarbons, on the other hand, is a well-established industrial process that has been studied by many researchers [5].

In the USA operation of a 40 kW PAFC plant on landfill gas has been demonstrated [6,7] with almost the same system's efficiency as with natural gas. Work on the preprocessing of landfill gas for use in commercial PAFC power plants is in progress [8].

Table 1 gives conditions and results from the steam reforming experiments. The conversions obtained in all reforming experiments are shown in Figs. 3 and 4. Tests K1 to K8

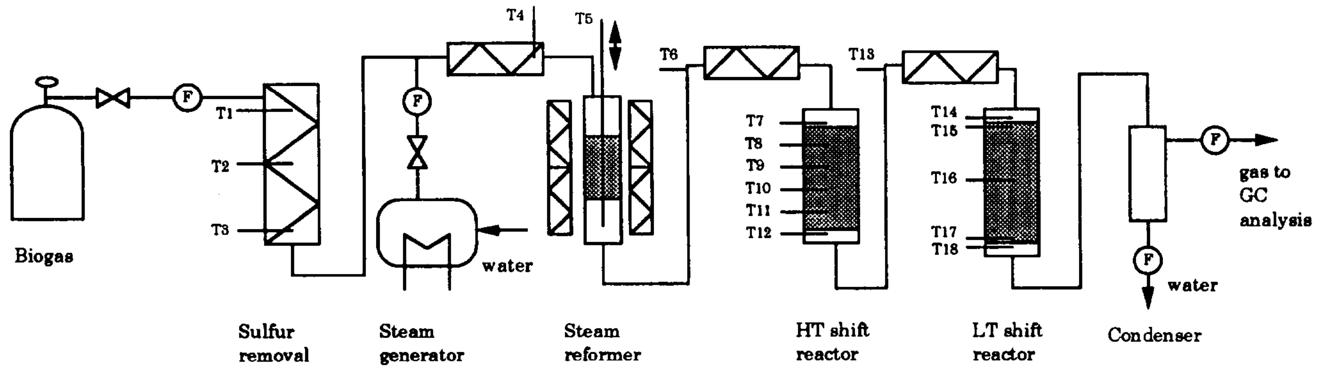

Fig. 2. Laboratory fuel processor of LDU 1. T1–T18 = thermocouples; Ⓕ = flow meter.

Table 1
Results from steam reforming experiments

Test no.	Temperature at reformer exit (°C)	Feed steam:carbon ratio	Feed gas (% CH_4)	Space velocity (l/l cat,h)	Reformed gas composition (mol/mol CH_4 in feed)					Conversion of CH_4 (%)
					CH_4	CO_2	H_2O	CO	H_2	
F1	808	4.0	60	1000	0	0.975	2.807	0.874	3.437	100
G1	796	4.0	60	1000	0	0.815	2.752	0.714	2.905	100
G2	699	4.0	60	1000	0.011	0.917	2.609	0.604	2.968	98.9
F2	596	4.0	60	1000	0.152	1.006	2.722	0.344	2.605	84.8
F3	803	2.0	60	1000	0.003	0.508	1.018	0.969	2.570	99.7
F4	600	1.9	60	1000	0.313	0.757	1.049	0.473	1.977	68.7
H2	679	8.2	60	2000	0.008	1.402	6.136	0.516	3.950	99.2
G3	708	4.0	60	2000	0.021	0.904	2.709	0.605	2.884	97.9
K12	700	3.9	60	2000	0.014	0.931	2.721	0.854	3.393	98.6
K2	694	4.0	60	2000	0.022	0.911	2.627	0.744	3.202	97.8
H1	675	4.0	60	2000	0.026	0.969	2.578	0.737	3.189	97.4
K16	597	3.9	60	2000	0.158	1.001	2.611	0.533	3.133	84.2
K6	595	4.0	60	2000	0.167	1.043	2.693	0.436	2.851	83.3
K4	698	2.0	60	2000	0.040	0.545	0.974	0.978	2.700	96.0
K8	599	2.0	60	2000	0.295	0.738	1.138	0.508	2.102	70.5
K1	693	3.8	100	2000	0.027	0.465	1.970	0.579	3.706	97.3
H3	674	3.9	100	2000	0.026	0.513	2.086	0.558	3.639	97.4
K5	593	3.8	100	2000	0.240	0.560	2.096	0.325	3.256	76.0
K3	700	1.9	100	2000	0.072	0.205	0.559	0.696	2.910	92.8
K7	601	1.9	100	2000	0.361	0.306	0.780	0.335	2.286	63.9

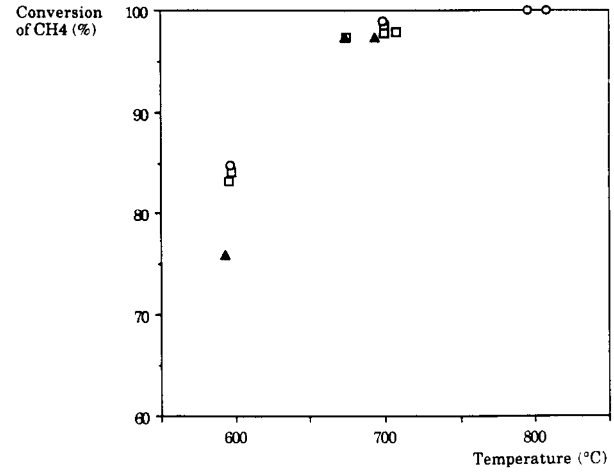

Fig. 3. Conversion of methane from experiments with steam reforming of biogas and of pure methane at different temperatures. Steam-to-carbon ratio = 4:1. (○) biogas, space velocity 1000 l/l cat,h, (□) biogas, space velocity 2000 l/l cat,h, and (▲) methane, space velocity 2000 l/l cat,h.

constitute a 2^3 factorial design with the three variables: reformer temperature, steam-to-carbon ratio and carbon dioxide content in the feed gas. It is well known [5] that temperature and steam-to-carbon ratio have strong influence on the conversion of methane.

The present experiments show furthermore, with a statistic significance [9] of >99% that the degree of conversion is higher with biogas than with pure methane. The amount of unreacted methane in the reformed biogas is thus reduced by between 16 and 44%, compared with the runs with pure methane. The presence of carbon dioxide seems to have a positive effect on the conversion of methane. This is explained by the direct reaction between methane and carbon dioxide also taking place in the reformer [4]:

$$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 \qquad \Delta H^0 = 247.4 \text{ kJ/mol}$$

$$CH_4 + 3CO_2 \longleftrightarrow 4CO + 2H_2O \qquad \Delta H^0 = 329.8 \text{ kJ/mol}$$

The total production of hydrogen and carbon monoxide is thus higher with biogas fuel than with pure methane. Since most of the carbon monoxide will finally be converted to hydrogen in the shift reactors biogas fuel will deliver more hydrogen for the fuel cell generator based on the amount of methane in the feed. Thus biogas will produce more hydrogen

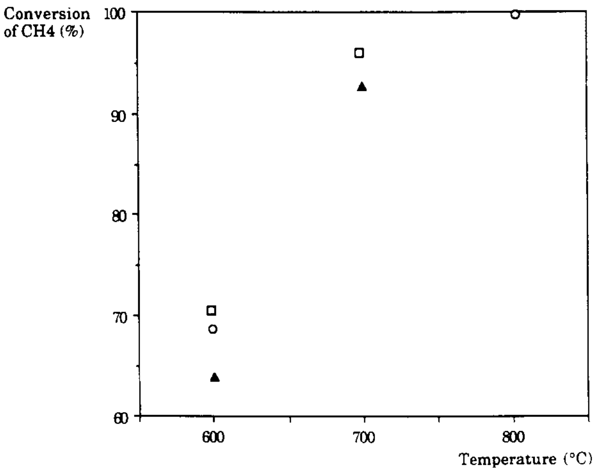

Fig. 4. Conversion of methane from experiments with steam reforming of biogas and of pure methane at different temperatures. Steam-to-carbon ratio = 2:1. (○) Biogas, space velocity 1000 l/l cat,h, (□) biogas, space velocity, 2000 l/l cat,h, and (▲) methane, space velocity 2000 l/l cat,h.

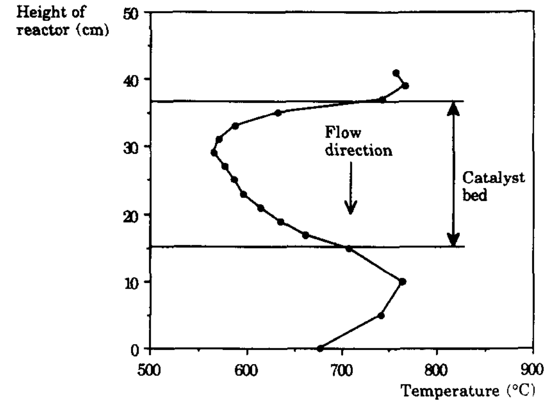

Fig. 5. Temperature profile at the centre of the reformer catalyst bed during experiment no. G3.

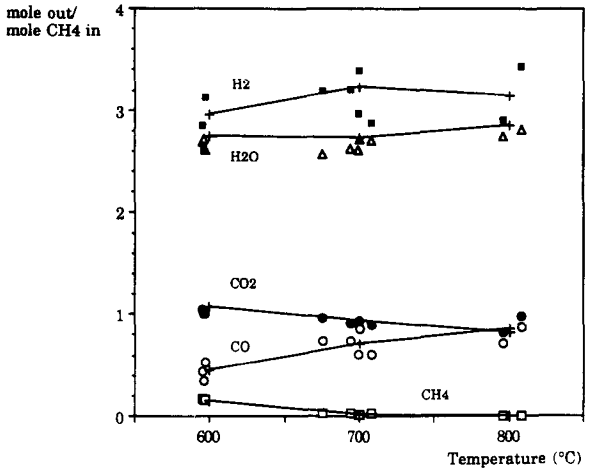

Fig. 6. Measured composition from experiments with biogas at steam-to-carbon ratio = 4:1 compared with equilibrium compositions. Experimental: (■) H_2; (△) H_2O; (●) CO_2; (○) CO, and (□) CH_4. Calculated equilibrium compositions (+).

for the fuel cells than natural gas. The dilution with carbon dioxide originated from the biogas will, however, result in a lower hydrogen concentration to the fuel cells which reduces performance slightly.

Fig. 5 shows a typical temperature profile in the reformer. The temperature drop in the top section of the catalyst bed is explained by the reforming reaction being highly endothermic. In general, the reforming experiments gave gas compositions close to the equilibrium composition at the reformer exit temperatures.

The equilibrium compositions of biogas and methane after steam reforming at different temperatures and steam-to-carbon ratios have been calculated using the VCS-algorithm [10], Table 2. Experimental data are compared with theoretical equilibria in Fig. 6. The reaction considered in the calculations are [5]:

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H^0 = 206.2\ \text{kJ/mol}$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^0 = -41.2\ \text{kJ/mol}$$

$$2CO \longleftrightarrow C(s) + CO_2 \qquad \Delta H^0 = -172.4\ \text{kJ/mol}$$

$$CH_4 \longleftrightarrow C(s) + 2H_2 \qquad \Delta H^0 = -74.9\ \text{kJ/mol}$$

Table 3 gives the conditions and the composition of the gas leaving the fuel processor for the runs with shift conversion of reformed synthetic biogas. High steam-to-carbon ratio and low temperature in the reformer give less carbon monoxide in the gas to the fuel cell generator as expected.

7. Conclusions

Fairly high yields of hydrogen from biogas were obtained at relatively low temperatures and steam-to-carbon ratios. The large carbon dioxide content of biogas enhances hydrogen production which makes biogas a most suitable fuel for fuel cell power plants. The carbon monoxide content of the

Table 2
Equilibrium compositions for reforming of biogas or methane

Temperature (°C)	Feed steam:carbon ratio	Feed gas (%CH_4)	Reformed gas composition (mol/mol CH_4 in feed)					Conversion of CH_4 (%)
			CH_4	CO_2	H_2O	CO	H_2	
800	4	60	0.001	0.813	2.854	0.852	3.144	99.9
700	4	60	0.012	0.942	2.737	0.713	3.238	98.8
600	4	60	0.148	1.072	2.743	0.446	2.961	85.2
800	2	.60	0.004	0.504	1.167	1.116	2.825	99.6
700	2	60	0.051	0.616	1.101	1.000	2.797	94.9
600	2	60	0.331	0.793	1.204	0.542	2.132	66.9
800	4	100	0.001	0.439	2.562	0.560	3.436	99.9
700	4	100	0.013	0.521	2.491	0.466	3.483	98.7
600	4	100	0.143	0.581	2.561	0.276	3.154	85.7
800	2	100	0.007	0.207	0.800	0.785	3.185	99.3
700	2	100	0.077	0.271	0.806	0.652	3.041	92.3
600	2	100	0.278	0.311	1.132	0.245	2.312	72.2 [a]

[a] Carbon deposition.

Table 3
Results from experiments with steam reforming followed by shift conversion

Test no.	Temperature at reformer exit (°C)	Feed steam:carbon ratio	Feed gas (% CH_4)	Space velocity (1/1 cat,h)	Composition of gas leaving the shift reactors (mol/mol CH_4 in feed to reformer)					Conversion of CH_4 (%)
					CH_4	CO_2	H_2O	CO	H_2	
A1	722	4.0	60	2000	0.008	1.521	1.767	0.016	3.714	98.6
A11	697	4.0	60	2000	0.017	1.761	2.033	0.016	4.188	98.3
A12	601	4.0	60	2000	0.140	1.578	2.291	0.010	3.581	86.0
A2	595	3.9	60	2000	0.145	1.414	2.058	0.009	3.287	85.5
A4	704	2.0	60	2000	0.023	1.329	0.252	0.115	3.362	97.7
A14	700	2.0	60	2000	0.029	1.517	0.290	0.150	3.856	97.1
A3	598	2.0	60	2000	0.276	1.226	0.634	0.027	2.497	72.4
A13	596	2.0	60	2000	0.298	1.339	0.695	0.031	2.808	70.2

processed gas can also be kept at a level tolerable to the PAFC generator with two shift reactors. The biogas-based fuel cell power plant with PAFCs seems to be a technically feasible option for power generation under conditions formulated for this programme.

Preliminary system studies of a PAFC plant for biogas [11], with primary data from the experiments presented in this paper, show an electrical efficiency from biogas to d.c. well above 40% (lower heating value). This is comparable with PAFC plants using natural gas [4].

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