**ABSTRACT:**

This study gives an overview of processes used to produce hydrogen from LPG. The different possible ways to reform LPG are presented. Their specification for an use in stationary fuel cells are compared. Key players in that field are reviewed.

**KEYWORDS:** Hydrogen production, LPG, reforming, Stationary fuel cells

1. **INTRODUCTION**

Natural gas is the most common fuel considered to be used in stationary fuel cells. Natural gas distribution network is well established. This fuel is mainly composed of methane. Energy cost to reform alkanes in CO and H₂ decreases when the length of the carbon chain increases. Therefore, methane is the alkane that needs the highest supply of energy to be reformed. However, a high reforming temperature assists the removal by oxidation of carbon deposits. The reformer does not convert 100 % of the methane in hydrogen rich gas. The remaining methane in the reformate is not a poison for the fuel cell.

Heavier hydrocarbons can also be transformed in hydrogen rich gas. The catalysts and test conditions have to be judiciously chosen in order to limit the formation of products that could affect catalyst activity and/or performances of the fuel cell. Liquid Petroleum Gas (LPG) could be an interesting alternative to natural gas in stationary fuel cells applications, more especially in areas disconnected from the natural gas distribution network.

The study gives an overview of worldwide activities concerning hydrogen production from LPG for stationary fuel cells. Key players involved in the field (fuel processors developers, fuel cell systems manufacturers, laboratories and other various organizations) are presented. The systems specifications (type of process, dimensions of the systems, type of catalysts used, type of fuel cell supplied by LPG…) and the on-going projects are also reviewed.

2. **DIFFERENT GRADES OF LPG**

LPG is composed of butane and propane or of a mix of both. Its composition is very different from region to region. Three different LPG types are commercially available (table 1)

<table>
<thead>
<tr>
<th>compound</th>
<th>Propane HD-5</th>
<th>Commercial Propane</th>
<th>Commercial mix Butane/propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>propane</td>
<td>content &gt; 90 % vol.</td>
<td>Propane + propylen &gt; 90 % vol.</td>
<td>Propane + propylen ~ 50 % vol.</td>
</tr>
<tr>
<td>propylen</td>
<td>5 % vol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butane and heavier hydrocarbon</td>
<td>2,5 % vol. liquide</td>
<td>2,5 % en volume</td>
<td>Butane + butylen ~ 50 % vol.</td>
</tr>
<tr>
<td>Pentane and heavier hydrocarbon</td>
<td></td>
<td></td>
<td>Max. 2,5 % vol.</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>123 ppm (mass)</td>
<td>185 ppm (mass)</td>
<td>140 ppm (mass)</td>
</tr>
</tbody>
</table>

Table 1 : commercially available LPG
Coking risk is higher when reforming LPG instead of natural gas because propane and butane are heavier than methane. Moreover, high sulphur content of LPG has to be reduced because sulphur can reduce catalysts activity. Reduction of olefins content (propylene, butene) is also necessary.

3. DIFFERENT PROCESSES TO REFORM LPG

Table 2 gives an overview of the different processes to reform LPG:

<table>
<thead>
<tr>
<th>Process</th>
<th>Operating temperature</th>
<th>H$_2$ content before purification</th>
<th>Advantages/drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming</td>
<td>900 °C (prereforming step : 500 °C)</td>
<td>~ 75 %</td>
<td>Advantage: • Good H$_2$ efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Drawbacks: • High energy consumption</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>650-700 °C</td>
<td>~ 27 %</td>
<td>Advantage: • Exothermal reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Drawbacks: • Need O$_2$ supply (production of NOx if air is used)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autothermal</td>
<td>400 °C</td>
<td>~ 45 %</td>
<td>Advantage: • Energy produced is autoconsumed</td>
</tr>
<tr>
<td>reforming</td>
<td></td>
<td></td>
<td>Drawbacks: • Need O$_2$ supply (production of NOx if air is used)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cracking</td>
<td>900 °C</td>
<td>&gt; 90 %</td>
<td>Advantages: • No CO formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Very good H$_2$ efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Drawbacks: • High energy cost</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Need two reactors (one to remove coke)</td>
</tr>
</tbody>
</table>

Table 2: comparison of the various processes to produce hydrogen from LPG

The described processes have all advantages and drawbacks. To get a high hydrogen content in the reformate, cracking and steam reforming are the best processes. For the steam reforming process, a prereforming unit is needed to transform heavier hydrocarbon than methane in a mix of methane, H$_2$ and CO. The cracking process has the drawback that two reactors are needed in order to regenerate the catalyst bed. This implies an overcost when compared to the other processes. Moreover, the high operating temperature of the cracking process increase operation costs. This process is not really envisaged by developers.

Partial oxidation and autothermal reforming consume less energy but hydrogen has a low partial pressure in the reformate. Partial oxidation could be an interesting process to produce hydrogen if the catalytic reaction was coupled to a membrane separation (membrane catalysis).

4. KEY PLAYERS
4.1. NORTH AMERICA

In North America, The PERC (Propane Education Research Council) promotes clean use of LPG. 10 development projects of LPG residential fuel cell systems have been funded by this organization. These projects were also received funding from DOE (Department Of Energy).

Table 3 gives few examples of companies involved in the field of LPG stationary fuel cells in the US.
Table 3: North America players

In North America, the potential to use LPG in fuel cells is assumed important in remote areas and in places not connected to the natural gas network.

TOTAL test an IDATECH LPG fuel cell systems in Belgium.

4.2. JAPAN

Japan seems also to be very involved in the development of LPG fuel cells. LPG is often used to heat houses in this country.

During 1995 and 2002, 8 stationary PAFC systems of FUJI ELECTRI (50 kW each) have been field tested.

Today, LPG residential fuel cells (nearly 1 kW) are developed in Japan. A 5 year and 16 M€ national project has been recently launched by the LPGC (Liquified Petroleum Gas Center). It is funded by NEDO.

The projects partners are NIPPON OIL CORPORATION, MITSUBISHI, IDEMITSU KOSAN, MATSUSHITA ELECTRIC, AIR WATER INC et IWATANI INTERNATIONAL CORPORATION.

Table 4 gives an overview of key Japanese players in the field:

<table>
<thead>
<tr>
<th>Company name</th>
<th>Activity</th>
<th>Process</th>
<th>Other information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ACUMENTRIC</strong>S</td>
<td>SOFC</td>
<td>Internal reforming</td>
<td>− 5 kW and 10 kW systems (residential application) &lt;br&gt;− 5 to 100 kW (industry applications) &lt;br&gt;− standard fuel is natural gas but propane is possible in option</td>
</tr>
<tr>
<td><strong>CHEVRON TEXACO ENERGY VENTURES</strong></td>
<td>Reformer manufacturer</td>
<td>Steam reforming</td>
<td>− prototype presented in 2003 &lt;br&gt;− hydrogen production = 120 NL/min. &lt;br&gt;− efficiency = 75 % &lt;br&gt;− cold start time = 60 minutes &lt;br&gt;− hydrogen purity &gt; 40 %</td>
</tr>
<tr>
<td><strong>HYRADIX</strong></td>
<td>Reformer manufacturer</td>
<td>Autothermal</td>
<td>− Prototype operate with natural gas or LPG ; &lt;br&gt;− hydrogen production = 5 Nm3/hr &lt;br&gt;− energetic efficiency = 80 % &lt;br&gt;− Dimensions = 1,3 <em>0,5</em>1,2 m3 ; &lt;br&gt;− Conversion efficiency = 45 % ; &lt;br&gt;− Electricit needs = 500 W.</td>
</tr>
<tr>
<td><strong>IDATECH</strong></td>
<td>PEM fuel cells</td>
<td>Steam reforming</td>
<td>− A 5 kW system presented at Fuel Cell Seminar 2003</td>
</tr>
<tr>
<td><strong>NUVERA</strong></td>
<td>PEM fuel cells</td>
<td>Steam reforming, autothermal, partial oxidation</td>
<td>− 500 W to 75 kW systems designs, built and tested to operate with Natural gas and propane.</td>
</tr>
<tr>
<td><strong>PLUG POWER</strong></td>
<td>PEM fuel cells</td>
<td></td>
<td>− LPG fuel cell prototype : 2 units testesd with AGWAY ENERGY PRODUCTS. &lt;br&gt;− an HYRADIX reformer intégrated in a PLUG POWER system</td>
</tr>
<tr>
<td><strong>SOFC</strong></td>
<td>Reformer manufacturer</td>
<td>Partial oxidation</td>
<td>− development of an hydrogen production unit for 10 kW SOFC ; &lt;br&gt;− energy efficiency : 70 % ; &lt;br&gt;− conversion efficiency &gt; 80 %</td>
</tr>
<tr>
<td><strong>TMI</strong></td>
<td>Piles SOFC</td>
<td>Multi fuel steam reforming</td>
<td>− 1 kW SOFC operating with various fuels including propane</td>
</tr>
<tr>
<td><strong>UTCFC</strong></td>
<td>PEM fuel cells</td>
<td>Catalytic partial oxidation</td>
<td>− 5 kW prototypes operating with natural gas or propane ;</td>
</tr>
</tbody>
</table>
AIR WATER INC  
- PEM fuel cell  
- Development of 1 kW LPG Unit  
- Tests have been performed since 2003

IDEMITSU KOSAN  
catalysis  
- Development of a desulphurisation catalyst for LPG PEM fuel cell

IHI  
LPG reformers  
- Development of LPG fuel processors

IWATANI  
PEM fuel cells  
- Development of a propane reformer ;  
- 1 kW LPG reformer for fuel cells tested  
- hydrogen content = 75 %

Universités de Kyoto et de Kyushu  
Reformer manufacture  
autothermal  
- hydrogen content = 50 %

MATSUSHITA ELECTRIC WORKS  
PEM fuel cells  
- Development of a 1 kW LPG reformer for fuel cell

MHI  
PEM fuel cells  
- Development of a 1 kW LPG fuel cell system which can operate with natural gas, LPG, kerosene, naphta, DME and methanol

NIPPON OIL CORPORATION  
PEM fuel cells  
- 1 kW PEM residential fuel cells;  
- system cost < 3800 € ;  
- Installation of LPG fuel cells on 100 different sites différents.

NISSEKI  
PEM fuel cells  
- LPG PEM fuel cells development

OSAKA GAS  
Residential fuel cell  
Steam reforming  
- LPG reformer for a 1 kW fuel cell system

SANYO  
PEM fuel cells  
Steam reforming  
- Development of a reformer prototype for 1 kW fuel cell;  
- Conversion efficiency = 94 %

TOTO  
Micro-piles  
SOFC  
- Development of LPG and DME SOFC fuel cells

NIPPON OIL CORPORATION is a major player in that field. They want to test many LPG residential fuel cell systems in order to find a new application for LPG.

4.3. EUROPE

Very few works are done in Europe in the field of LPG fuel cells. Most fuel cell developers and operators test natural gas systems. Nevertheless, some institutes or starts-ups are developing products (Table 5).

<table>
<thead>
<tr>
<th>Company name</th>
<th>activity</th>
<th>process</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRAUNHOFER INSTITUTE (Germany)</td>
<td>Research Institute</td>
<td>Autothermal</td>
<td>LPG reformer for recreational vehicles</td>
</tr>
<tr>
<td>INTELLIGENT ENERGY (UK)</td>
<td>PEM fuel cells</td>
<td></td>
<td>Design and development of a Natural gas or LPG reformer to integrate in a fuel cell system.</td>
</tr>
</tbody>
</table>
| JOHNSON MATTHEY (UK) | Catalysis Reform development | Autothermal | Design and development of a reformer that can operate on propane  
- efficiency : 75 to 78 % ; |
| N-GHY (France) | Reformer development | High temperature and non catalytic reformer | Development of a multifuel reformer (diesel, biofuels, éthanol) that can also operate on propane |
The only LPG fuel cell system tested in Europe is an IDATECH 5 kW system operated by TOTAL in a service station in Belgium.

VAILLANT and SULZER do not field test LPG fuel cell systems.

5. CONCLUSIONS

Japan and North America are the most active regions involved in LPG fuel processors for stationary fuel cells. The PERC (PROPANE EDUCATION RESEARCH COUNCIL) has been funding LPG fuel cells projects in North America over the past few years and encourages the development of these systems. However, there are very few LPG fuel cell systems projects comparing to those fuelled with natural gas. Moreover, several important North American fuel cell manufacturers (BALLARD and HYDROGENICS for instance) have not been developing LPG fuel cell systems.

In Japan, the LPGC (LIQUEFIED PETROLEUM GAS CENTER) also funds japanese companies to develop LPG fuel cell systems. For instance, NIPPON OIL CORPORATION has announced the field-trials of LPG fuel cell systems on 100 different sites. These units are controlled from a refinery located in Yokohama (Japan). The company also recently announced starting to lease 750 W LPG-fed fuel cell systems in Japan.

Europe seems to be less involved than Japan and North America. Indeed, VAILLANT and SULZER, the main stationary fuel cell systems developers in Europe, do not forecast to test LPG fuel cell systems.

Most fuel processors developers use a pre-reforming step to convert LPG into a methane rich gas. The latter is then converted at higher temperature into a hydrogen rich gas. This two step process generates less coke than the direct reforming of LPG in a hydrogen rich gas. The LPG fuel cell systems seem to be as performant as conventional natural gas fuel cell systems. For instance, the performances of a LPG SOFC system tested by CERAMIC FUEL CELL LIMITED were similar to those of the equivalent SOFC system using natural gas. However, the lifetime of LPG reformers seems to be lower. This is mainly due to a higher coke formation and a higher sulphur poisoning. While LPG contains in average more sulphur than natural gas, LPG has to be further desulphurised than natural gas before being used in a fuel cell. Moreover, in the LPG hydodesulfurization process, a hydrogen overconsumption has to be forecasted due to the secondary hydrogenation reaction of olefins (propylene and butylene).

The remote sites disconnected from the grid and/or the natural gas distribution networks are the main potential market of LPG fuel cell systems.

REFERENCES

5 Karl Fröger, karlf@cfcl.com.au
7 Saint-Just J.; Sioui D.; Catalytic autothermal reforming for smale scale hydrogen generation, EHEC 2003, 5 p.
8 Hess-Mohr N.; Schmidt V.M.; Trägner U.K.; Liu Z.X.; Mao Z.Q.; J.M Xu, Autothermal reforming of propane for fuel cell systems, 55th annual meeting of electrochemistry, September 2004, Thessaloniki, Greece


14 White E.; Fuel cell thermal management system, PLUG POWER, US PATENT 2003087139


17 Fuji and Al; Development of a 1 kW propane gas fuel processor for application to residential PEFC; Fuel Cell Seminar 2002; 616-619
