Utilization of Biogas in Glass Melting Applications

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Abstract:

Natural gas is the most dominant fuel to provide process heat in many thermal processing applications, for example in the glass, ceramics or metals industries. However, here as well there is increasing pressure to reduce both fuel costs and carbon dioxide (CO_2) emissions. One possible approach in this regard is the use of mostly untreated biogas from fermentation processes as a fuel, either to completely substitute natural gas, or for co-firing. But while the use of such biogas can decrease both natural gas consumption and overall CO_2 emissions (biogas is considered to be a CO_2-neutral fuel), there is concern how this change of fuel will affect product quality, combustion behavior and the refractory material. Trace contaminations in the biogas are one aspect in this context which might have a negative impact on product quality or the durability of the refractory of industrial furnaces. In the course of a German research project, these topics were investigated both experimentally and numerically for glass melting applications. In addition to analyses of the firing process itself, a custom-built mobile test rig was used to look into the effects of the combustion of untreated biogas on the properties of samples of glass and refractory material directly exposed to the flue gases.
It was found that trace elements in the untreated biogas do not cause prohibitive quality issues with neither the glass nor the refractory samples, so that in principle, biogas can be used to provide process heat for glass melting applications. CFD simulations of a glass melting furnace show, however, that due to the significantly different physical properties of biogas compared to natural gas, the flow fields and temperature distributions in the furnace change quite drastically, so that for existing plants, a co-firing approach seems to be the appropriate solution.

Keywords:
Biogas, Combustion, Glass manufacturing, Co-firing, CO_2 Emissions, Refractory Material

1. Introduction

About 85 % of the process heat used in German thermal processing applications is generated by the combustion of natural gas [1] while industry accounts for about 40 % of the German consumption of natural gas [2]. Given the ambitious goals of the German federal government to reduce overall CO_2 emissions by 40 % (compared to 1990) while also increasing the contribution of renewable energy sources to the energy supply to 18 % by 2020 [3], the question how industrial energy consumers can do their part to achieve this goal has yet to be answered.

One obvious approach to reduce industrial CO_2 emissions is to increase plant efficiency since reduced fuel consumption is directly connected to a decrease of carbon dioxide emissions. In many thermal processing industries, a lot of effort has already been put into increasing plant and process efficiency in the last decades, since this will also lead to reduced fuel costs and hence higher profitability. In the glass industry, measures like recuperative and regenerative air-preheating, oxy-fuel combustion and optimized process control such as very low air ratios, but also batch preheating and extensive use of cullets as well as improved refractory materials have found widespread application. There are however, physical and technological limits since the melting process always

requires large amounts of energy. The physical minimum energy requirement for the melting of container glass is around 650-750 kWh/t_{glass} while the technologically realizable minimum requirements range between 800 and 1200 kWh/t_{glass}. Optimized furnaces today require between 1000 and 1450 kWh/t_{glass} [4], [5], [6], depending on the glass product, furnace type and age, to name just a few factors. In this context, the technologically realizable minimum requirement refers to a theoretical value, while the values for optimized furnaces are based on operational data from state-of-the-art plants. Studies such as [6] indicate that the means to reduce CO_2 emissions by increasing furnace efficiencies have for the most part already been exploited in modern furnace designs. If additional CO_2 emissions reduction is to be achieved, it has to be done by changing the fuel itself, from a fossil fuel such as natural gas to a CO_2-neutral fuel such as biogas, either completely or with a co-firing approach.
In Germany, there are currently about 150 biogas plants in operation where biogas is conditioned to natural gas quality and then injected into the natural gas grid. Additionally, there are about 7,000 plants which use biogas to generate electricity by means of gas engines or turbines [7]. However, biogas could in theory also be used to provide process heat for many industrial applications. The suitability of biogas in glass melting applications as well as its impact on glass quality and refractory properties were therefore the focus of a joint research project [8] carried out by "Gas- und Wärme-Institut Essen e.V." (GWI), „Hüttentechnische Vereinigung der Deutschen Glasindustrie e.V. (HVG)" and „Forschungsgemeinschaft Feuerfest e.V." (FGF).

2. Biogas for Industrial Applications

Biogas is usually produced either by gasification or fermentation from biomatter feedstock. The chemical composition of the biogas is to a great extent dependent on the production process. While biogas from gasification plants only contains small quantities of methane and is chemically similar to coke oven gas (COG) or generator gas, biogas from a fermentation process can consist of up to 70 vol.-% of methane, depending on the feedstock being used. The research work presented here focussed on the use of this latter form of biogas, since there is already a lot of operational experience of using coke oven gas, town gas or generator gas in glass melting furnaces. Table 1 [9] shows a comparison of various properties of untreated biogas from feedstock that was specifically grown to be used in biogas production (corn, for example), biowaste recycling plants and the properties of natural gas according to German Codes of Practice DVGW G 260/262 [10], [11]. In this context, untreated means that the biogas was roughly de-sulphurized but not conditioned to natural gas quality. As can be seen in the table, there are significant differences between biogas from dedicated feedstock production and recycled biowaste. In particular, there are often more impurities and trace elements in biogas from recycled biomass due to the greater heterogeneity of the feedstock.

As can be seen in the table, the main difference between biogas and more conventional fuels such as natural gas is the much larger content of inert species such as CO_2 in the fuel gas, which leads to much lower calorific values. For the same reason, the densities of biogases are usually higher. Thus, in order to provide the same amount of energy, much higher mass flows of fuel gas have to be realized while at the same time, the amount of oxidizer changes as well due to the reduced specific air requirements of biogases which usually contain only about 50 - 60 vol.-% of methane. All this leads to drastically different flow fields (and hence flame shapes, heat transfer characteristics, etc.) in a furnace if natural gas is completely substituted with biogas.

Another aspect is the possible existence of contaminants in the biogas. While natural gas is usually reasonably clean with regards to trace elements, biogas, especially if produced from bio wastes, can contain various trace elements (e.g. sulphur, nitrogen and silicon compounds) which might impact glass quality but also lead to chemical interactions with the refractory materials. One aim of the research project was therefore to investigate the effects of the combustion of untreated biogas on both glass quality and refractory materials.

While these factors will in the end decide whether biogas is industrially applicable in an economic manner or has to be upgraded to natural gas quality in order to be usable in industrial furnaces, thermal processing industries are definitely interested in this potential alternative fuel source, as the ongoing research activity, for example in Germany and in France, [8], [12], [13] shows.

Table 1: Comparison of biogases (from different feedstocks) with the requirements of the German natural gas quality regulations DVGW G 260 / 262 [10], [11] (taken from [9])

Property	Unit	Typical values (biogas from plants such as corn)	Typical values (recycled biowaste)	Requirements DVGW G260/262
gross calorific value*	kWh/m^3	5.5 - 6.5	6.6 - 7.8	8.4 - 13.1
	MJ/m^3	19.8 - 23.4	23.8 - 28.1	30.2 - 47.2
relative density	-	0.99 - 1.04	0.85 - 0.94	0.55 - 0.75
Wobbe Index*	kWh/m^3	5.4 - 6.1	6.8 - 8.4	H-Gas: 10.8 - 15.7
	MJ/m^3	19.4 - 22.0	24.5 - 30.2	49.0 - 56.5
	kWh/m^3			L-Gas: 10.5 - 13.0
	MJ/m^3			39.6 - 46.8
dew point water	°C	saturated at $T_{fermenter}$, $p_{fermenter}$	saturated at $T_{fermenter}$, $p_{fermenter}$	maximum at T_{ground}, $p_{pipeline}$
CH_4	Vol.-%	50 - 55	60 - 70	-
CO_2	Vol.-%	43 - 50	30 - 40	6
O_2 (dry grid)	Vol.-%	0 - 2	0 - 1	3
O_2 (wet grid)	Vol.-%	-	-	0.5
carbon acids	mg/m^3	<220	traces	-
alcohols	mg/m^3	traces	<22	-
BTEX	mg/m^3	traces	<10	-
C_xH_y, rest	mg/m^3	<2	<1,250	condensation @ T_{ground}
H_2S	mg/m^3	<600 (rough desulphurization)	<30,000	5
mercaptanes	mg/m^3	<10	<5	6
COS	mg/m^3	<8	<0.6	-
NH_3	mg/m^3	<10	<10,000	-
H_2	Vol.-%	<0.3	<1	5
Si_{total}	mg/m^3	<15	5	-

* @German reference temperatures 25 °C / 0 °C

3. Investigations at Gas- und Wärme- Institut (GWI)

In a first step, the consequences of the utilization of biogas on the combustion process in glass melting furnaces were investigated both experimentally and by means of computational fluid dynamics (CFD). Using various mixtures of natural gas and CO_2, various rates of biogas co-firing (or exclusive biogas firing) were analyzed. Admixing of 25 % CO_2 would correspond to a biogas co-firing approach while a mixture of 50 vol.-% natural gas and 50 vol.-% CO_2 approximates the combustion of biogas only.

GWI's high-temperature burner test rig allows for burner investigations in a semi-industrial setting. For this campaign, the burner load was set to 650 kW, with air ratios of about 1.05. Air pre-heat temperatures were about 1200 °C. Pre-heat temperatures, burner load and air ratios were kept constant for all experiments and close to the boundary conditions found in glass melting furnaces.

The burner was installed in a so-called underport configuration which is quite common on end-fired glass melting furnaces. The test rig is specifically designed for optimum access with measurement probes so that 2D field measurements of temperatures and species can be carried out, using thermocouples and suction probes respectively. Figure 1 shows an image of the furnace.

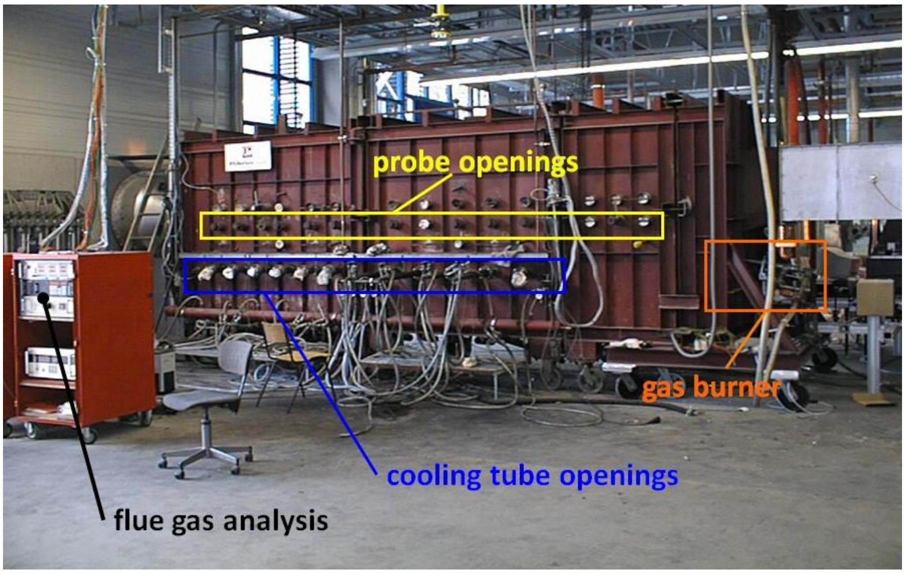

Figure 1: GWI's high temperature test rig

Figure 2 shows a comparison of measured temperature distributions in the burner plane of the test rig for different natural gas (NG) and CO_2 mixtures. These measurements were carried out using IFRF-type water-cooled suction probes which take a small flue gas sample at the tip of the probe, quickly quench it to prevent further chemical reactions in the body of the probe and then lead the gas sample to a flue gas analyzer. According to the equipment manufacturer, measurement uncertainties with regards to species concentrations are less than 1% of the maximum scale range. Temperature profiles were measured using type S thermocouples.

It is interesting that although "pure" natural gas has the highest adiabatic temperature of the three investigated fuel mixtures, the mixture with 25 vol.-% CO_2 was found to have the highest furnace temperature in the measurement campaign. This result was corroborated by simulation results. This is most probably due to increased mixing efficiency in this case caused by different mass flows for both fuel and oxidizer. Burners for glass melting applications are generally designed for inefficient mixing in order to obtain long, highly luminous flames. Since the burner used in these experiments was originally designed for natural gas and not adapted for biogas utilization, the changing mass flows and hence momenta can very well have this effect. In the case of a 50/50 mixture, however, the amount of chemically inert CO_2 is too high to be compensated by improved mixing.

The measured NO_X emissions follow the trend of maximum temperatures, i.e. the mixture with 25 vol.-% CO_2 also showed the highest NO_X emissions. It should be pointed out though that in these experiments the biogas was generated synthetically which means that the dominant formation pathway for NO_X was the thermal Zeldovich mechanism. This is comparable to natural gas combustion in high-temperature industrial furnaces. Real biogas, on the other hand, can contain nitrogen compounds such as HCN or NH_3 (cf. table 1) in which case the fuel-NO_X pathway may well become the dominant pathway. This was already shown in a previous investigation [14].

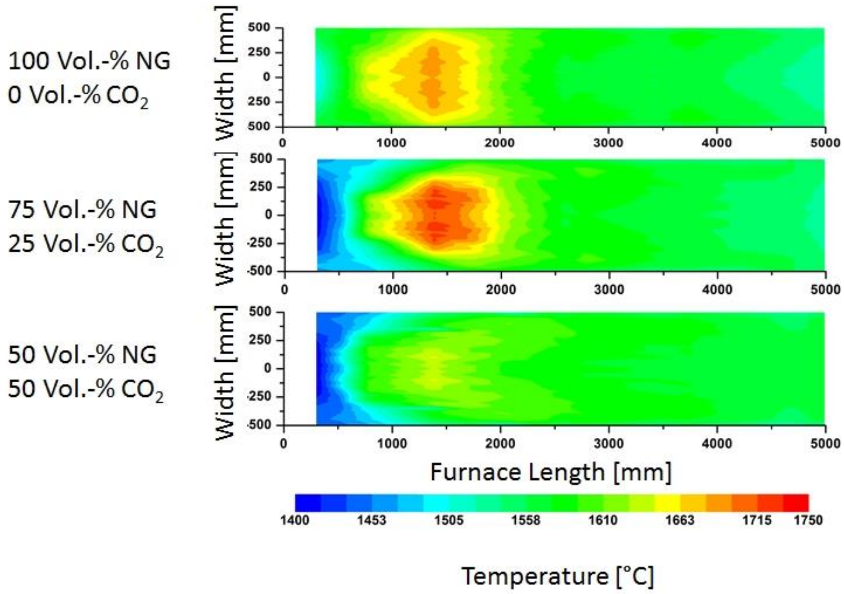

Figure 2: Measured temperature fields in the burner plane for different natural gas / CO_2 mixtures

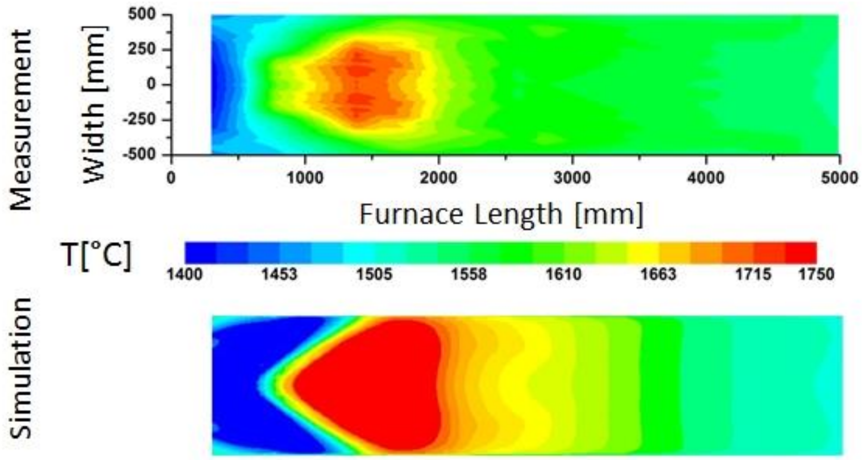

Figure 3: Comparison of measured and simulated temperature fields in the burner test rig

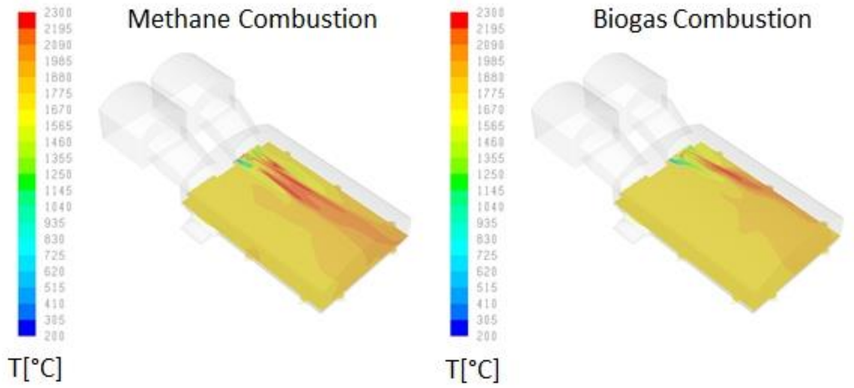

Figure 4: Temperature fields in the burner plane for combustion of pure methane and biogas in an end-fired furnace

The measurement campaign also served to validate simulation efforts to look into the use of biogas in industrial combustion processes. The CFD studies were carried out using the ANSYS FLUENT package (v13), a commercially available CFD code. Based on previous extensive experience of modeling glass melting applications, the CFD simulations used the realizable k-ε turbulence model and the Discrete-Ordinates Model for radiative heat transfer. Combustion was described by means of the Westbrook-Dryer 2-step reaction mechanism in combination with an eddy dissipation / finite rate formulation.

The comparison between numerical and experimental results showed a reasonably good agreement. Figure 3 shows a comparison of measured and calculated temperature fields in the horizontal burner plane of the test rig for the case with 75 vol.-% natural gas, 25 vol.-% CO_2. The principal shape and location of the reaction zone in the CFD simulation corresponds quite well with the measured data. Temperatures and predicted NO_X emissions show the same trends that was found in the measurements, i.e. the highest maximum temperatures and NO_X emissions were found in the case with a fuel gas consisting of 75 vol.-% natural gas and 25 vol.-% CO_2.

Based on these promising results, the effect of biogas utilization in a real glass melting furnace was also investigated using CFD. The intention of these simulations was not primarily to provide a quantitative prediction of flow, combustion and heat transfer processes in a real furnace geometry, but instead to give insight into the changes in these processes due to the changing fuel. In figure 4, a comparison of the temperature distributions in the burner plane for a typical end-fired furnace can be seen. The image on the left hand side shows the result for the combustion of pure methane (as a substitute for natural gas), the image on the right hand side was generated for the combustion of a biogas consisting of 65 vol.-% CH_4 and 35 vol.-% CO_2 which corresponds quite well to biogas from biowaste feedstock. In both simulations, the furnace was operated with a burner load of 11 MW, an air ratio of 1.07 and an air pre-heat temperature of 1,400 °C, common operational conditions for such a furnace. The same burner geometry was used for both fuels.

As was to be expected, the impact of the fuel on the temperature distributions is quite profound. The size and shape of the hot region, crucial for heat transfer in glass melting furnaces and hence the quality of the product, changes completely. A comparison of the energy balances for the two cases indicates that about 10 % less energy were transferred to the glass melt, resulting in an inacceptable decrease of overall efficiency compared to the reference gas with natural gas. This means that for already existing furnaces, it appears to be more sensible to use biogas in a co-firing approach. If biogas is to be used exclusively, the burner and furnace geometries will have to be adapted accordingly.

4. Mobile Test Rig Experiments

The experiments carried out at GWI gave important first insights into the effects of biogas utilization in industrial combustion processes. The “biogas” used in these experiments, however, was synthetically generated so that many questions pertaining to the applicability of biogas in industrial furnaces remained unanswered. Compared to natural gas, biogas - especially when produced from biowaste feedstock such as kitchen waste - is subject to significant variations in its composition and properties. Also, it may well contain trace elements which can interact with either the glass melt or the refractory material of the furnace, potentially causing decreased glass quality or reduced refractory lifetime.

In order to investigate the possible effects of biogas utilization on both glass quality and refractory properties, a mobile combustion chamber test rig with a flue gas duct was designed, built and equipped with the necessary safety and control technology. This test rig can be moved to different biogas plants and then use the locally available, only roughly de-sulphurized biogas for the experiments. During the research project, three measurement campaigns at different sites were carried out: one at a biogas plant which uses renewable resources; the second plant used bio and food waste with additional packaged foodstuff as feedstock, while the third campaign was a reference run with natural gas at GWI.

A sketch of the test rig with the various measurement positions can be seen in Figure 5 (left), while the image on the right hand side shows an image of the actual test rig installed at one of the biogas plants. One peculiarity of the test rig is that it was specifically designed to allow for the insertion of both glass and refractory material samples at various positions in combustion chamber and flue gas duct without interrupting operations (cf. Figure 6). A 100 kW burner was installed in the test rig while air ratios where controlled by a lambda probe in the exhaust gas duct. The furnace was operated at air ratios commonly found in glass melting furnaces ($\lambda \approx 1.05$). The biogas was directly drawn from the fermenter plant and only roughly de-sulphurized. The measurement equipment, in particular the flue gas analyzer, was basically the same as the one used in the experiments at the larger GWI semi-industrial test rig.

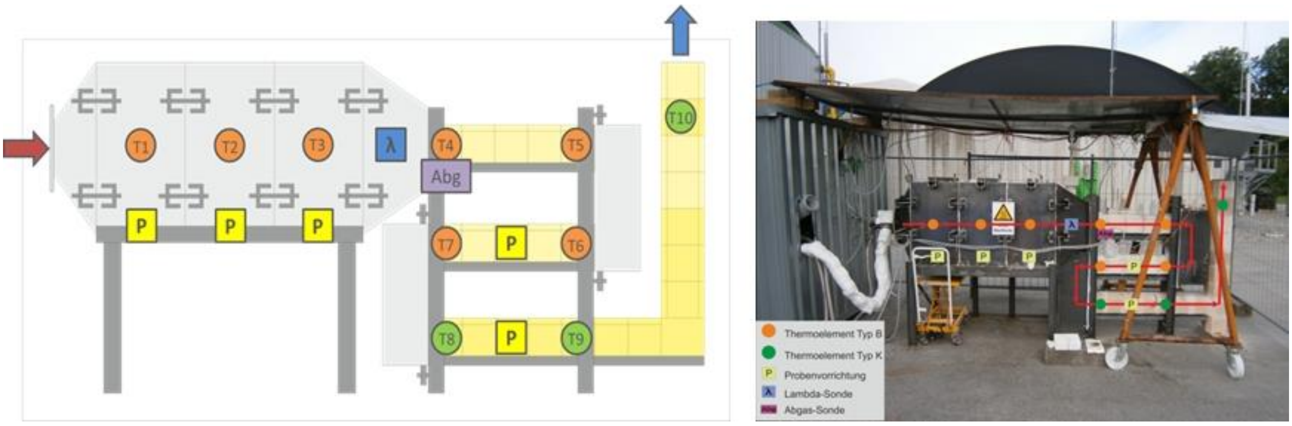

Figure 5: Measurement positions of the mobile test rig and the actual test rig on-site

Figure 6: A crucible containing a glass batch sample is inserted into the test rig

Figure 7 shows the evolution of furnace temperatures, as measured by thermocouples, during one day of operations. The dips in the curves are due to the opening of the access ports in order to introduce samples into the furnace. In addition to temperature measurements, relevant species in both the fuel and the exhaust gas are also continuously monitored (cf. Figure 8).

Using this mobile test rig, it was possible to investigate the impact of untreated biogases of various sources on furnace operation, pollutant emissions, glass quality and refractory material. One aspect of concern when using untreated biogas may be its sulphur content. While the SO_2 emissions due to biogas combustion are relatively small compared to other SO_2 emission sources in the glass manufacturing process such as refining, the overall increase of SO_2 emissions however may make the installation of a desulphurization plant necessary, putting the overall economic feasibility of biogas utilization in question.

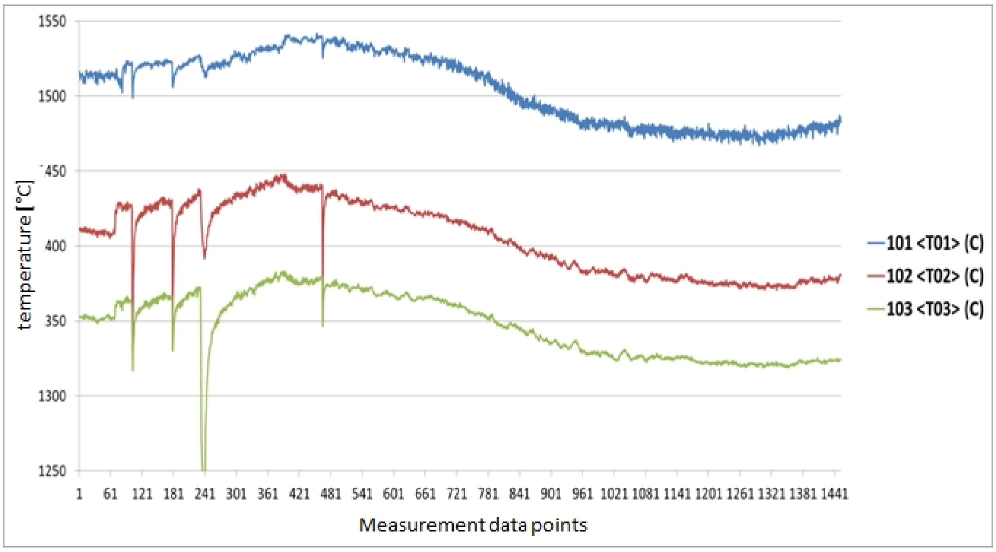

Figure 7: Typical temperature measurements in the test rig during one day of operation

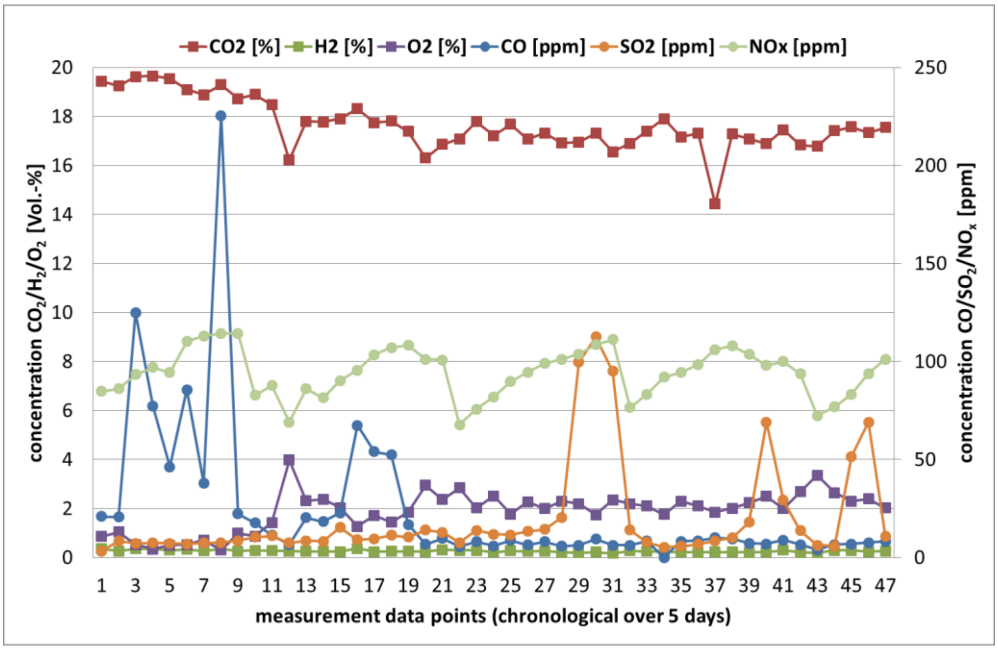

Figure 8: Flue gas analysis for a 5-day interval

A second goal of the measurement campaign with the mobile test rig was to investigate the influence of firing with pre-cleaned biogas on the color (which is a sensitive test criterion for changes in the production parameters) and quality of the molten glass using microscopy and chemical analysis. In addition to the tests carried out during the measurement campaigns, the batch and glass samples were tested in an electric furnace of the HVG to determine the properties of the samples with a standard heating, which were thenused as a baseline. In Figure 9, the industrial batches (raw materials) are shown as well as the molten glass samples from two field measurement campaigns.

The firing with the roughly pre-cleaned biogas from both biogas plants (renewable resources or bio waste) had no impact on the color and quality of the glass. The furnace temperature in the second section during melting varied between 1450 and 1530 °C. The melting time was adapted to this temperature and varies between 1 and 3 hrs. The batch was preheated up to 200°C to avoid steam explosion when entering the hot combustion chamber. The melting time was adjusted to the melting temperature based on former experience so that no residual sand grains can be found and that only few small seeds are present in the sample. The results of the glass quality analysis show that glass quality can be maintained even when switching to a very different fuel if the process parameters such as residence times are adapted accordingly. There is no indication that trace elements in the untreated biogas do have a negative effect on the quality of the product.

In addition to glass batch samples, the effect of biogas combustion on typical refractory materials that are used in glass melting furnaces to melt soda lime silica glass were also investigated:

- fused cast Alumina-Zirconia-Silica (AZS) as side wall block of the combustion chamber,
- Silica as crown material and
- different materials for the different regions of a regenerator (first layer, condensation zone, bridge block).

The different materials were placed in an area of the mobile test rig with comparable conditions (mainly temperature and atmosphere, but also flow velocity of gaseous media) as they are in a glass melting furnace. Parts of brand-new blocks and bricks were tested as well as samples of used materials that were gathered after a glass furnace campaign. These used materials were tested to ensure that the switch to and use of biogas during a furnace campaign do not cause additional harm to the materials.

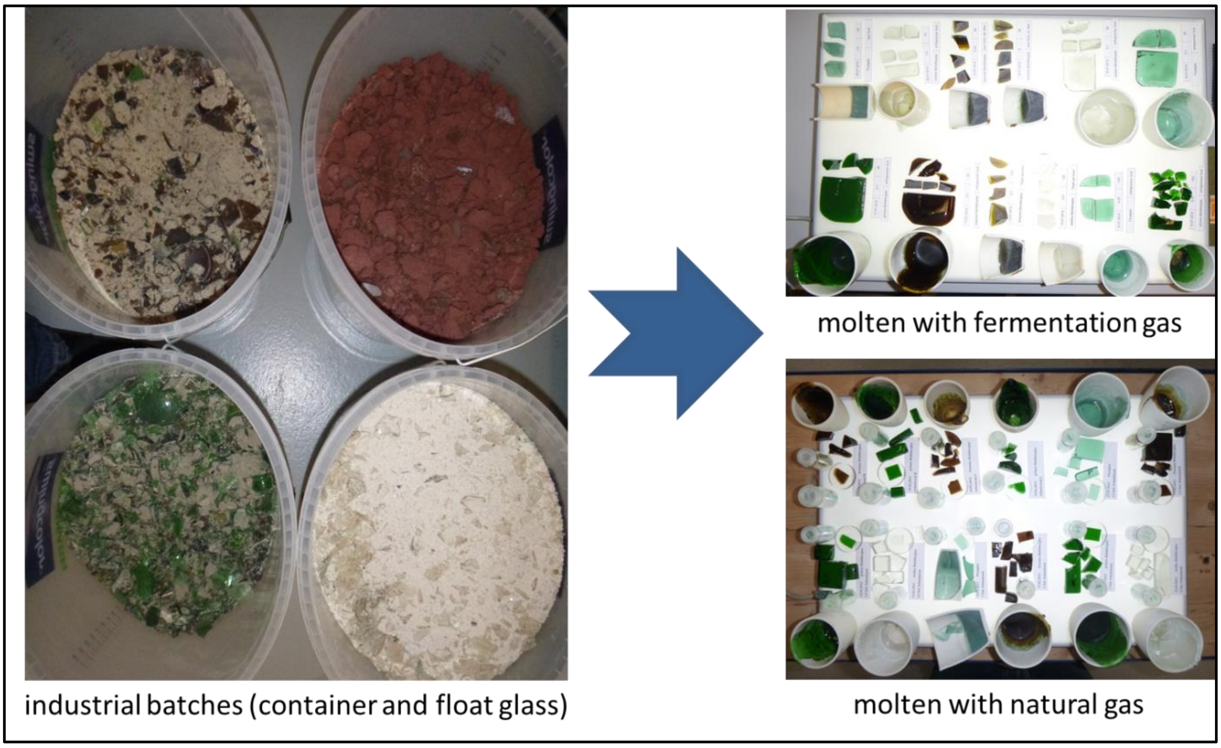

Figure 9: Raw glass material (batches) and various molten glass samples

FGF also simulated the long-term behavior (lifetimes of furnaces are up to 15 years) of samples at their test facilities. The refractory samples were exposed to synthetic atmospheres that had multiples of the concentrations of harmful trace elements in order to emulate the long term effects in a shorter time span in a laboratory scale. Furthermore, interactions of the individual trace elements were analysed in detail.

The general conclusion of the investigations of the refractory materials is that no additional and accelerated corrosion due to components of the biogas can be reported. The main effect on the tested materials of firing biogas is an increase of alkaline and alkaline earth in the surface and diffusion into the material with time. As these components are part of the glass melt and evaporate during the process, the biogas and its impurities show no impact on corrosion of the refractory during the tests.

5. Conclusions

In the course of the AiF-funded research project “Biogas Glas (AiF-Grant No. 397 ZN)”, the applicability of untreated biogas for the combustion in industrial furnaces (glass melting furnaces in this case) was investigated. In addition to experiments with synthesized biogas which were carried out to analyze the impact of the fuel change on furnace operations, the focus of this project was also on the interaction between trace elements in the untreated biogas and samples of glass batch and refractory material in order to see if the untreated fuel will cause unacceptable losses with regards to glass quality or refractory properties. The results of the two-year project show that even untreated biogas can be in fact used to produce glass without compromising the glass quality or negative impact on the refractory material. If biogas is to be used exclusively, both the furnace and the burner systems should be modified in order to compensate for the different properties of biogases and natural gas, especially with regards to densities and calorific values.

Both experiments and simulations show that a co-firing approach is probably the most suitable strategy for using biogas in existing furnaces with a minimum of modifications.

In the context of pollutant emissions, the different composition of biogas, especially with regards to nitrogen-containing compounds and sulphur, has to be taken into account. If fuel-bound nitrogen is present in the fuel, it may drastically increase overall NO_X emissions. Sulphur in the fuel also has to be considered, especially since natural gas is generally taken to be sulphur-free, at least in Germany.

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