COMBUSTION OF HYDROGEN-NATURAL GAS MIXTURES APPLIED TO CERAMICS FIRING: EMISSIONS AND FLAME PROPERTIES

S. Ferrer(1), E. Monfort(1), R. Pereira(2),M. Gallagher (2), J. Viduna(2), J. Montolio(1), A. Mezquita(1), J. Vedrí(1)

(1) Instituto de Tecnología Cerámica.
Asociación de Investigación de las Industrias Cerámicas.
Universitat Jaume I. Castellón. Spain
(2) Sociedad Española Carburos Metálicos.
Commercial Technology
Av de la fama, 1. Cornellà de Llobregat, Barcelona. Spain

ABSTRACT:

In the coming years, high-temperature industries will have to face very significant challenges in order to meet planned requirements in terms of reduced CO_2 emissions, and such adaptation will only be possible by implementing major technological changes, as well as by using alternative energy sources. One way of contributing to decarbonisation is to use green hydrogen as a fuel to produce the heat required for drying and firing by direct combustion. The great advantage of such a process is that hydrogen combustion does not generate CO_2 emissions but, in contrast, hydrogen is not a primary source of energy.

This paper presents a purely technical study, without considering the economic issues of using hydrogen as a fuel. The first part provides a theoretical study of the combustion of hydrogen/natural gas mixtures, while the second part presents the experimental results from preliminary hydrogen-oxygen combustion tests using an oxy-fuel burner specifically adapted for this research.

To study the process in greater detail, a combustion chamber was designed that makes it possible to define the principal combustion parameters: geometric characteristics and temperature profile of the flames, heat transmission coefficients, and the composition of flue gases. The results obtained will be key to future work focusing on the technical-economic feasibility of using this fuel in ceramic industry kilns.

1. INTRODUCTION

The ceramic industry is an intensive user of thermal energy, obtained mostly by the combustion of natural gas, which in turn generates CO_2 emissions. It is well known that CO_2 is a greenhouse gas (GHG), so its emissions are the subject of international monitoring and control given its connection with global warming and consequently climate change.

The process technologies currently used to manufacture ceramic products have a high degree of maturity, so the margin to reduce direct emissions from the process is unquestionably limited. As a result, the sector will have to radically alter the technologies and energy sources it currently uses in its production process if it is to meet the ambitious emission reduction targets set at European level.

One of the most prominent options for decarbonisation available to the European high-temperature processing industries is the use of hydrogen as a fuel (either alone or mixed with natural gas), specifically what is known as 'green hydrogen', which is generated by electrolysis of water using electrical power from renewable sources. The economic feasibility of the process relies on the energy source being the surplus of renewable electricity that is mainly produced by the numerous episodes of decoupling that occur between energy production and demand.

In the specific case of the ceramic industry, the hydrogen generated could be completely or partially used as a fuel to replace natural gas as a means of generating high-temperature heat. The great advantage of the process is that hydrogen combustion only produces water vapour, so when the energy used to produce it comes from a renewable source, the direct CO_2 emissions associated with it would be null or very low, and thus it is of significant interest as a way of achieving intended decarbonisation goals.

However, the use of hydrogen as a fuel in industrial processes is technically an immature technology and so detailed studies are required to ascertain how such a change of fuel might affect the physical and chemical reactions taking place in the processed materials, the possible consequences it may have on the construction materials used in industrial equipment, and its influence on process variables and atmospheric emissions.

This paper is part of a series of ongoing studies to analyse the viability of different decarbonisation options open to the ceramic industry.

2. OBJECTIVE AND SCOPE

The aim of this work is to define theoretical combustion parameters for mixtures of hydrogen with natural gas, and their impact on heat generation and transmission, on the composition of the resulting flue gases, and the changes in flame profile required to achieve energy-efficient and high-quality firing, with special attention paid to the emissions thus generated.

The financial and economic considerations lie outside the scope of this paper, although they will be looked at in subsequent papers within the overall project.

3. THEORETICAL STUDY OF NATURAL GAS AND HYDROGEN COMBUSTION

3.1. PROPERTIES OF HYDROGEN AS A FUEL COMPARED TO NATURAL GAS

Depending on the origin of the raw materials used, one can distinguish between blue or grey hydrogen, obtained from fossil sources, and green hydrogen, which comes from water using electricity from renewable sources. This latter option is the only one that makes sense from the point of view of decarbonising the ceramic manufacturing process.

Regardless of its source, hydrogen could be used as a fuel in those processes in the ceramic industry where natural gas is currently employed. Table 1 the characteristics of both gases for use as fuels.

Parameters	H_2	Natural gas
Composition considered	100%	90% methane 7.5% ethane 1.5% propane 0.4% butane 0.6% N_2
LHV (kWh/Nm³)	2.997	10.617
Gas density (kg/Nm³)	0.0899	0.7955
Flammability range (% vol.)	4-75 (Air)	5-15 (Air)
	4-94 (Oxygen)	5-61 (Oxygen)
Laminar flame velocity (cm/s)	270 (Air)	35 (Air)
	290 (Oxygen)	330 (Oxygen)
Adiabatic flame temp. (ºC)	2045 (Air)	1875 (Air)
	2805 (Oxygen)	2780 (Oxygen)
Flame visibility	No	Yes

Table 1. *Main characteristics of natural gas and hydrogen.*

The main **advantage** of hydrogen combustion compared to the combustion of fossil fuels is that it **does not produce CO_2 emissions**, as can be seen in the combustion reactions detailed in Table 2.

Combustion reactions	Stochiometric relationship
$H_2(g) + 0.5\ (O_2\ (g) + 3.76\cdot N_2)\ (g) \rightarrow H_2O(g) + 1.88\cdot\ N_2\ (g)$	**Volume** 2.38 Nm^3 air/Nm^3 H_2
$H_2(g) + 8\cdot O_2\ (g) + 26.5\cdot N_2\ (g) \rightarrow 9\cdot H_2O(g) + 26.5\cdot N_2\ (g)$	**Mass** 34.5 kg air/kg H_2

Table 2. *Combustion reactions of hydrogen with air*

It is important to note that the combustion of air with hydrogen can generate a greater amount of thermal NO_x, since flame temperature is higher (about 170°C higher); this parameter is critical at temperatures of around 1400ºC and higher. NO_x emissions are bound by emission limit values in integrated environmental permits (variables that depend on the stage of the process in question).

Indeed, developing burners and/or operating conditions that bring down the formation of NO_x in combustion is one of the designated aims of this project.

3.2. THEORETICAL STUDY OF NATURAL GAS AND HYDROGEN COMBUSTION WITH AIR

Table 3 and 4 show the combustion products from combusting natural gas with air and hydrogen with air, respectively, for different stochiometric air-fuel ratios (n).

n	Composition of wet fumes			
	CO_2 (%)	H_2O (%)	O_2 (%)	N_2 (%)
1	9.78	18.53	0.00	71.69
1.2	8.28	15.68	3.22	72.81
1.4	7.18	13.60	5.59	73.64
1.6	6.33	12.00	7.40	74.27
1.8	5.67	10.74	8.83	74.76
2	5.13	9.72	9.99	75.17

Table 3. *Combustion products (in %) from natural gas with air per different excess air rates. Calculation base: 1 Nm^3 of natural gas.*

n	Composition of wet fumes			
	CO_2 (%)	H_2O (%)	O_2 (%)	N_2 (%)
1	0	34.71	0	65.29
1.2	0	29.79	2.98	67.23
1.4	0	26.09	5.22	68.70
1.6	0	23.20	6.96	69.83
1.8	0	20.90	8.36	70.75
2	0	19.00	9.50	71.49

Table 4. *Combustion products (in %) of hydrogen with air per different excess air rates. Calculation base: 1 Nm^3 of hydrogen.*

Table 4 shows that, in the combustion of hydrogen with air, the percentage of water vapour present in the flue gases increases significantly, almost doubling the amount produced by natural gas combustion. For example, at a stochiometric combustion (n=1) of natural gas and hydrogen, water vapour values are 18.53% and 34.71% respectively (Table 3 and table 4).

3.3 COMBUSTION OF METHANE-HYDROGEN MIXTURES WITH AIR

When hydrogen is added to natural gas, the properties of the resulting mixture are significantly different. The table below shows the results obtained when the energy properties of natural gas and hydrogen mixtures are varied to attain a hydrogen concentration of 100% by volume. The calculations were performed at standard pressure and temperature (P=1 atm, T=273.15 K).

Table 5 upper and lower heating values from the resulting mixture per unit volume, Wobbe index and its variation, for the different mixtures of natural gas and hydrogen.

Calculating the Wobbe index was considered of interest as it is a key parameter when determining the interchangeability of combustible gases. Two gases are interchangeable when, for a given burner with the same feed conditions (P and T), the combustion characteristics - heat flow and flame behaviour – remain unchanged.

The Wobbe index is used to compare the energy provided by different compositions of gas fuels in the same burner. Two fuels that have the same Wobbe index can be used in the same burner without altering the operating conditions. Variations of up to 5% are acceptable without any need to make changes to the burner, but greater variations require the equipment to be adjusted or even replaced.

Natural gas (% vol.)	Hydrogen (% vol.)	UHV (kWh/Nm^3)	LHV (kWh/Nm^3)	Wobbe Index (kWh/Nm^3)	% Variation Wobbe Index
100	0	11.783	10.617	54.158	-
90	10	10.959	9.855	52.764	2.57
80	20	10.135	9.093	51.359	5.17
70	30	9.311	8.331	49.951	7.77
60	40	8.487	7.569	48.557	10.34
50	50	7.663	6.807	47.205	12.84
40	60	6.839	6.045	45.946	15.16
30	70	6.015	5.283	44.884	17.12
20	80	5.191	4.521	44.249	18.30
10	90	4.367	3.759	44.651	17.55
0	100	3.543	2.997	48.357	10.71

***Table 5**. Higher and lower heating values per unit volume, Wobbe index and its variation, for different mixtures of natural gas and hydrogen.*

One can see that the heating value of the mixtures decreases as the amount of hydrogen increases, i.e., the energy contained per unit volume progressively decreases, as hydrogen has a lower heating value per unit volume table 1.

For example, under standard conditions, when 10% hydrogen by volume is reached in the mixture, it is seen to cause a 7% drop in heating value. When that proportion is increased to 50% hydrogen by volume in the mixture, the heating value is reduced by 35%.

In regard to interchangeability, on the basis of the values shown in the table and taking a tolerance criterion in Wobbe index variation of 5%, adding up to 20% hydrogen by volume to natural gas would still make operating with the same burners and combustion system possible. At higher proportions of hydrogen, adjustments need to be made and even the design of the burners changed.

3.4 VARIATION IN COMBUSTION GAS COMPOSITION FROM THE KILN DEPENDING ON THE PROPORTION OF HYDROGEN IN THE MIXTURE

When natural gas-hydrogen mixtures are used, the resulting flue gas composition is significantly altered. Figure 1 shows how the composition of gases formed in the full combustion (CO_2, H_2O) of different mixtures of natural gas and hydrogen varies.

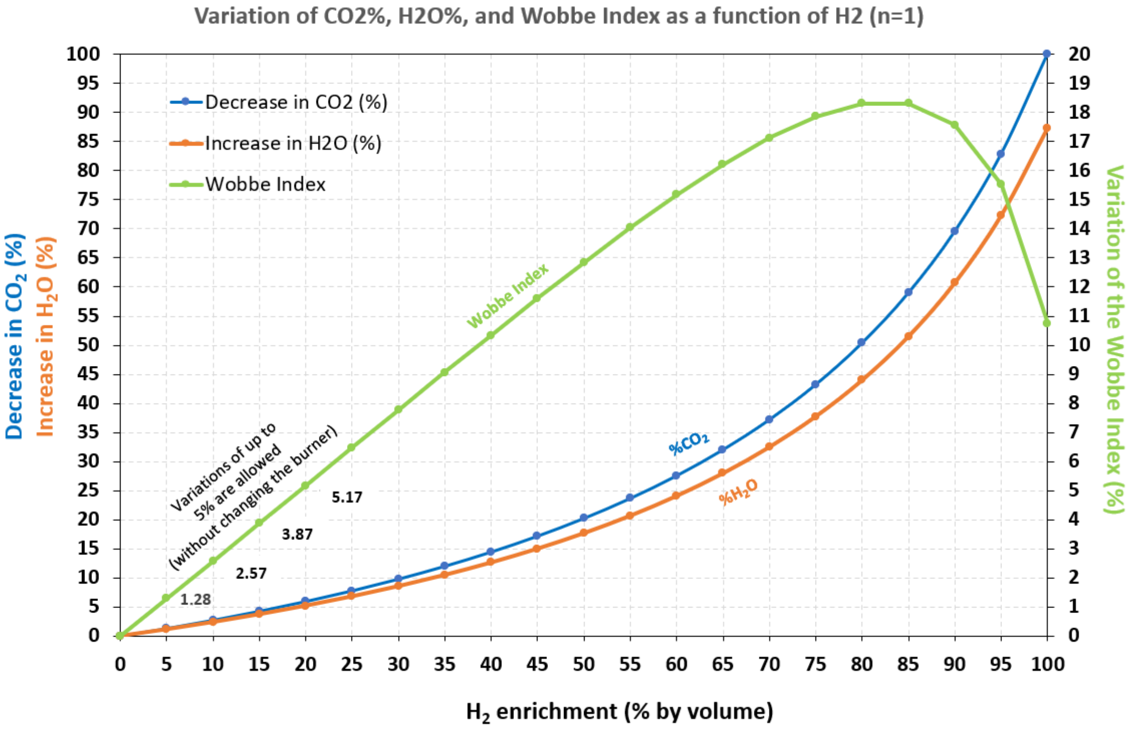


Figure 1. *Variation in the composition of complete combustion products (CO_2, H_2O) and in Wobbe Index for different mixtures of natural gas and hydrogen.*

Based on the above diagram, the following may be noted:

- To significantly reduce CO_2 emissions, very rich mixtures of hydrogen need to be used, given its low heating value. For example, one can see that adding 10% hydrogen by volume to the natural gas mixture only reduces generated CO_2 by 2.52%. To achieve a reduction in CO_2 of around 50%, it is necessary to use mixtures with more than 80% hydrogen.

- Another important issue to consider is the variation in the percentage of H_2O vapour in the combustion chamber. The use of hydrogen-rich mixtures leads to an enrichment of water vapour in the flue gases. For example, with a 50% hydrogen mixture, water vapour increases by 17.67% compared to the water vapour generated during the combustion of natural gas. When operating with 100% hydrogen, the increase in the proportion of water vapour in the combustion products would reach 87.34%.

- The consequences that such an increase in the amount of water vapour would have on both the product and the refractory lining are difficult to predict theoretically and, therefore, experimental studies are called for to assess its effect.

4. PRELIMINARY EXPERIMENTAL STUDY OF THE COMBUSTION OF NATURAL GAS AND HYDROGEN MIXTURES

4.1. CLEANFIRE® HRX™ HYDROGEN BURNERS

This project has involved adapting Air Products' Cleanfire® HR$_x$™ burner to operate with hydrogen, for use both in the ceramic and frit sectors. It is a flat-flame oxy-fuel burner that was originally designed for the glass industry (Figure 2). It has several key features, including up to 95% oxygen staging capacity, a foam reduction mode to improve heat absorption in melting furnaces, low NO_x emissions, and optional sensors for remote performance monitoring.

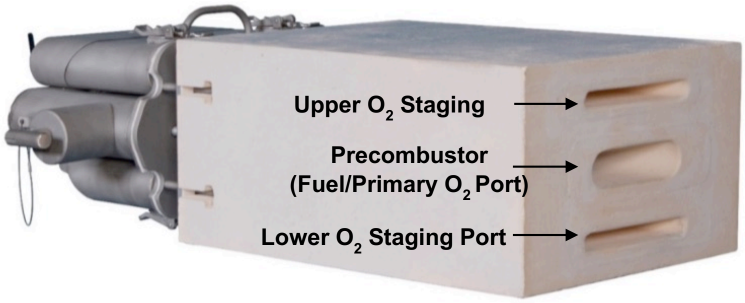
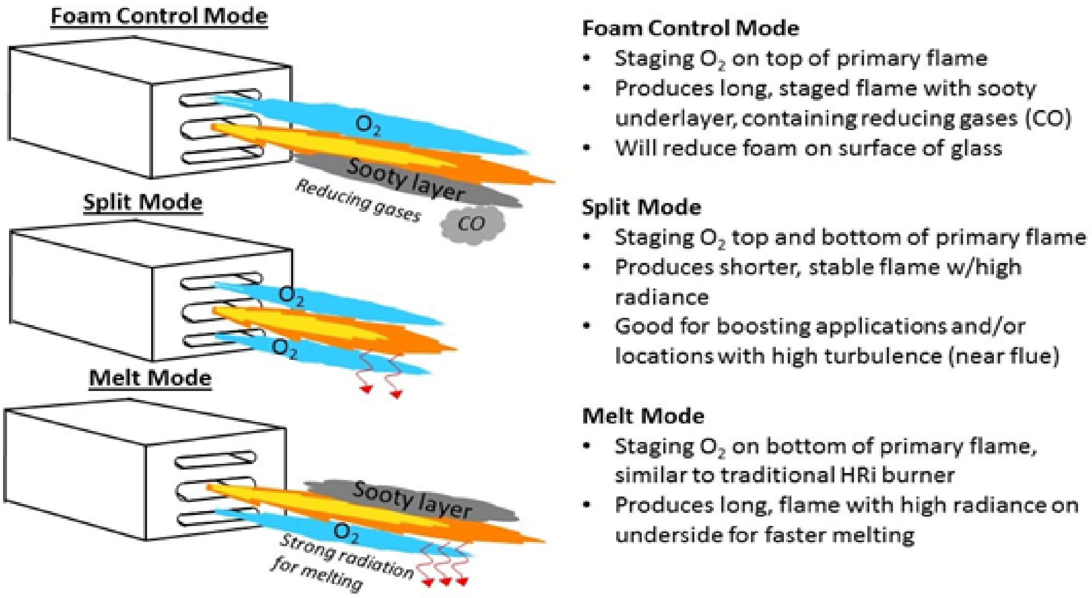


Figure 2. *The Cleanfire® HR$_x$™ burner with details of the hot face on the burner block*

The HRx burner block has three output ports: a central pre-combustion port where fuel and primary oxygen initiate combustion and the flame is formed and stabilised, and two top and bottom oxygen staging ports.

One of the features of this burner is that it can control oxygen staging directionally, which enables oxygen to be fed through the top or bottom ports (or split between the two) that surround the primary pre-combustor. Oxygen staging modes include "Foam Control" mode, "Melt" mode for glass melting, and "Split" mode to divide oxygen staging. This directional oxygen staging control offers several benefits, including adjustment of the length, radiation, and luminosity of the flame.

Figure 3 shows the HR_x burner's different operating modes.



Foam Control Mode

- Staging O_2 on top of primary flame
- Produces long, staged flame with sooty underlayer, containing reducing gases (CO)
- Will reduce foam on surface of glass

Split Mode

- Staging O_2 top and bottom of primary flame
- Produces shorter, stable flame w/high radiance
- Good for boosting applications and/or locations with high turbulence (near flue)

Melt Mode

- Staging O_2 on bottom of primary flame, similar to traditional HRi burner
- Produces long, flame with high radiance on underside for faster melting

Figure 3. *Different operating modes for the Cleanfire® HR_x™ burner*

The purpose of 'staging' the oxygen flow is to prevent the formation of NO_x, by delaying the mixing of oxygen and fuel, thus producing a lower maximum flame temperature in the areas where most of the thermal NO_x is generated. The burner is equipped with a valve, called a primary O_2 valve, which controls the amount of primary oxygen flowing through the main burner port, as well as the secondary oxygen that is fed selectively and directionally, so that it is distributed independently to the various ports on the burner block.

- **Split mode**. In "Split" mode, an equal amount of oxygen is directed to the top and bottom oxygen outlet ports. This results in a shorter, brighter and more stable flame. "Split" mode can be especially useful in turbulent locations in oxy-fuel furnaces (e.g., near the stack) and for oxy-fuel boosting applications.
- **Melt mode**. In melt mode, oxygen is directed through the bottom oxygen port on the burner block, which is located below the main flame. The flame will therefore develop a bright under-surface because of thermal radiation caused by the localised combustion of oxygen fed with the gases on the lower surface of the flame. The high radiation produced in Melt mode is directed downwards, towards the surface of the material, and has been shown to speed up the glass melting process.
- **Foam Control mode**. In foam control mode, oxygen is directed through the top oxygen outlet port on the burner block, which is above the main flame. The resulting flame appears to be covered in soot on its lower edge, which contains reducing gases with significant concentrations of CO. The reducing atmosphere created by the flame extends above the surface of the material and serves to reduce foam on the surface of the glass.

4.2 HYDROGEN TESTING

Experimental tests were carried out with the Cleanfire® HR$_x$™ burner using different mixtures of hydrogen with natural gas, from 100% natural gas to 100% H_2, mainly using oxygen as the oxidiser.

In order to work with hydrogen, small adjustments were made to the burner settings and the characteristics of the flame, such as its shape and luminosity, were observed. Figure 4 shows an example of how the natural gas/H_2 mix ratio affects those characteristics.

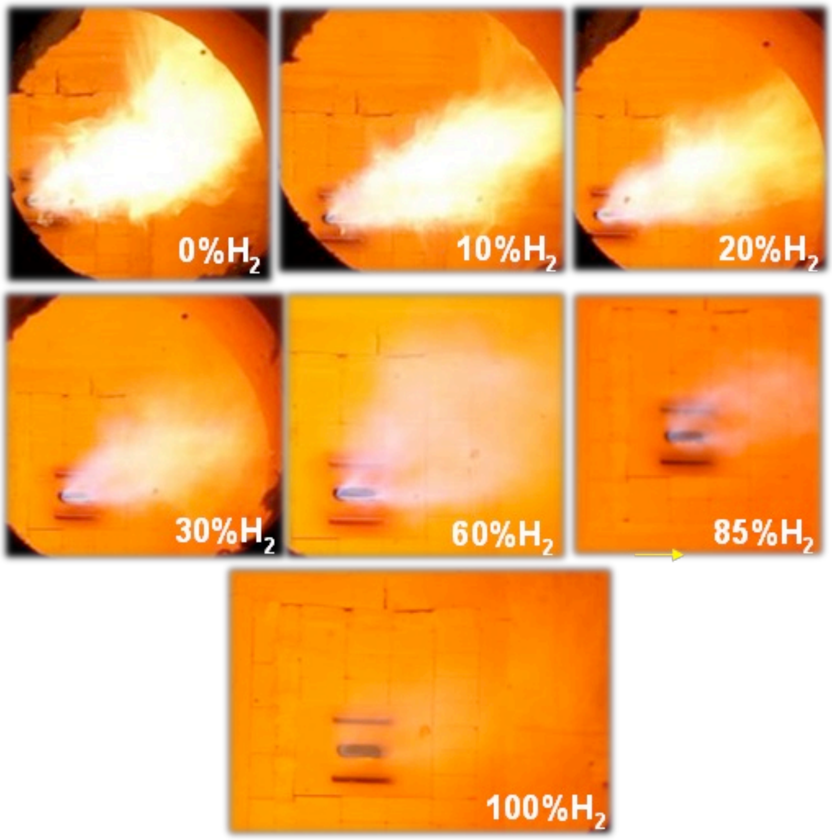


Figure 4. *Images of the flame in the Cleanfire® HR$_x$™ burner with mixtures containing different volume proportions of hydrogen-natural gas.*

As figure 4 when the hydrogen content in the mixture is increased, the luminosity of the flame decreases. When it reaches 100% hydrogen, the flame seems almost invisible.

The shape of the flame also changes as hydrogen increases. In this case, flame length decreases, due to the higher combustion reaction rate. The impact that this new heat release profile with shorter flames has needs to be taken into consideration to ensure optimal heat transfer to the product.

It is worth noting that, during our experimental tests, no degradation effects from the different atmospheres generated were seen in the combustion chamber, and no hot spots were found on the face of the burner block.

5. CONCLUSIONS

The results of this study show that **replacing natural gas with hydrogen** will involve adapting and/or replacing current burners and equipment, given the special characteristics of hydrogen.

Therefore, future research should:

- Invest in developing **new hydrogen burners** of the size and power ratings required by the ceramic industry.
- Work on **minimising NO_x formation** during the combustion of hydrogen with air.
- Study its **adaptation to process characteristics.** It will be necessary to carry out in-depth research to ascertain how the **processed ceramic materials,** as well as the **kiln construction materials, behave** with the new atmosphere generated in the kiln when natural gas is replaced by hydrogen.
- Pay special attention to **end product quality,** because in the firing of ceramic tiles, that is greatly influenced by **flame shape and properties.**
- Assess the **effects of the resulting increase** in the amount of water vapour generated by combustion, which, a priori, are difficult to predict.

6. ACKNOWLEDGEMENTS

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