SYNGAS EXPLOSION REACTIVITY IN STEAM METHANE REFORMING PROCESS

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ABSTRACT

During the synthesis of hydrogen by methane steam reforming, mixtures composed of H_2, CH_4, CO and CO_2 are produced in the process. In this work, the explosion reactivity of these mixtures, on the basis of detonation cell size and laminar flame speed, is calculated using a reactant assimilation simplification and a kinetic approach. The detonation cells width are calculated using the Cell_CH Kurchatov institute method and the laminar flame velocities are calculated with Chemkin Premix using different detailed chemical kinetic mechanisms. These calculations are used to define if these mixtures could be considered having a medium or a high reactivity for risk assessment in case of leak in the hydrogen plants.

1.0 INTRODUCTION

Hydrogen can be produced from diverse domestic feedstocks using a variety of process technologies. Thermochemical processes (reforming or gasification) can be used to produce hydrogen from biomass and from fossil fuels such as coal, natural gas and petroleum.

Power generated from sunlight, wind and nuclear sources can be used to produce hydrogen by electrolysis. Sunlight alone can also drive photolytic production of hydrogen from water, using advanced photoelectrochemical and photobiological processes.

At the time being, most of the hydrogen in the world is produced by steam reforming of natural gas (SMR). For the near term, this production method will continue to dominate.

In this process, in a first step, the natural gas (30 bars) mixed with hot steam reacts on a catalyst in a multi tubular reformer furnace following the endothermic reaction: $CH_4 + H_2O \rightarrow CO + 3\ H_2$ *(1).* Due to equilibrium consideration, all the methane is not converted by the reaction (1).

In a second step, the carbon monoxide is partially converted into hydrogen in a water gas shift reactor according to the exothermic reaction: $CO + H_2O \rightarrow CO_2 + H_2$ *(2)*

In a last step, the stream composed of H2, CO_2, CO and CH_4 (by order of importance) purified using a pressure swing adsorption (PSA) unit. This unit produces a pure high pressure hydrogen stream and a atmospheric offgas composed on hydrogen and process by products.

The table 1 shows a typical dry composition (in %vol.) of the gas mixtures along the SMR process. The PSA off gas is not considered due to its low pressure (small flammable cloud formation in case of leak).

Table 1. SMR stream composition (in % dry)

%	Reformer outlet	Shift outlet
CH_4	7.5	6.5
H_2	70	74
CO	16,5	3
CO_2	6	16,5

It is well known from nuclear industry research that steam has a strong effect on combustion properties, decreasing global reactivity by dilution and chemical effects (reducing laminar flame speed and increasing cell size). In real SMR loss of containment accidents, the leaking syngas cloud is charged with steam; this steam will condense in the dispersion cloud and will rain out. However, it is very complex to take into account this effect in dispersion and combustion modelling (steam and small water aerosol decrease reactivity but large droplet could improve it); it has been decided, on a conservative way, to exclude steam, and to consider combustion properties on a dry basis.

In consequences assessment using multi energy method (MEM) or Baker Strehlow Tang method (BST) [21], the reactivity of a fuel in part determines the severity of a Vapour Cloud Explosion (VCE). It is generally accepted that the fuel reactivity is dependent to the laminar flame speed and to the detonation cell size [21] [25]. A fuel with a laminar flame speed higher than 0.75 m/sec or with a detonation cell size lower than 50 mm is considered having a high reactivity. On the other hand, a fuel with a laminar flame speed lower than 0.75 m/sec and a detonation cell size higher than 50 mm is considered having a medium reactivity.

2.0 BINARY MIXTURE APPROACH

Because, SMR gases are composed of mainly 4 gases (H_2, CH_4, CO, CO_2), to compare with binary mixtures, it is needed to make some simplification assumptions.

Different simplification approaches are described in Table 2. Three different simplification approaches are evaluated:

1. All non-H_2 gases act as CO (conservative approach)
2. CO acts as H_2 and CO_2 acts as CH_4 (also conservative)
3. CO acts as H_2 and CH_4 acts as CO_2 (could minor the reactivity)

The influence of gaseous additives (methane, carbon monoxide and carbon dioxide) on the fundamental combustion properties (laminar flame speed and detonation cell size) of a H_2 - air mixture has been studied in the literature. The figure 1 and 2 presents the influence of CH_4, CO and CO_2 on the laminar flame speed and the detonation cell size.

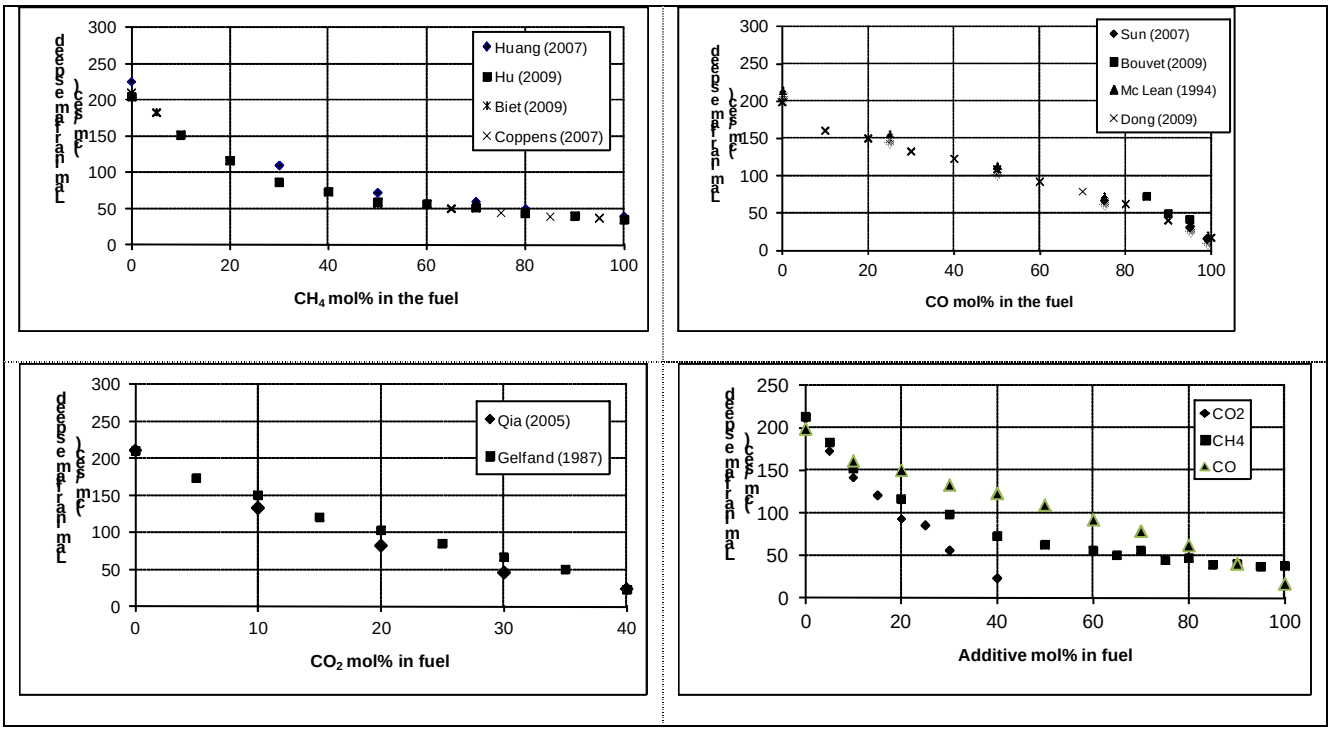

Figure 1. Laminar flame speed for H_2/CH_4, H_2/CO, H_2/CO_2 mixtures for ambient stoechiometric air conditions, against the rate of additive in the fuel from different authors [1] to [11]

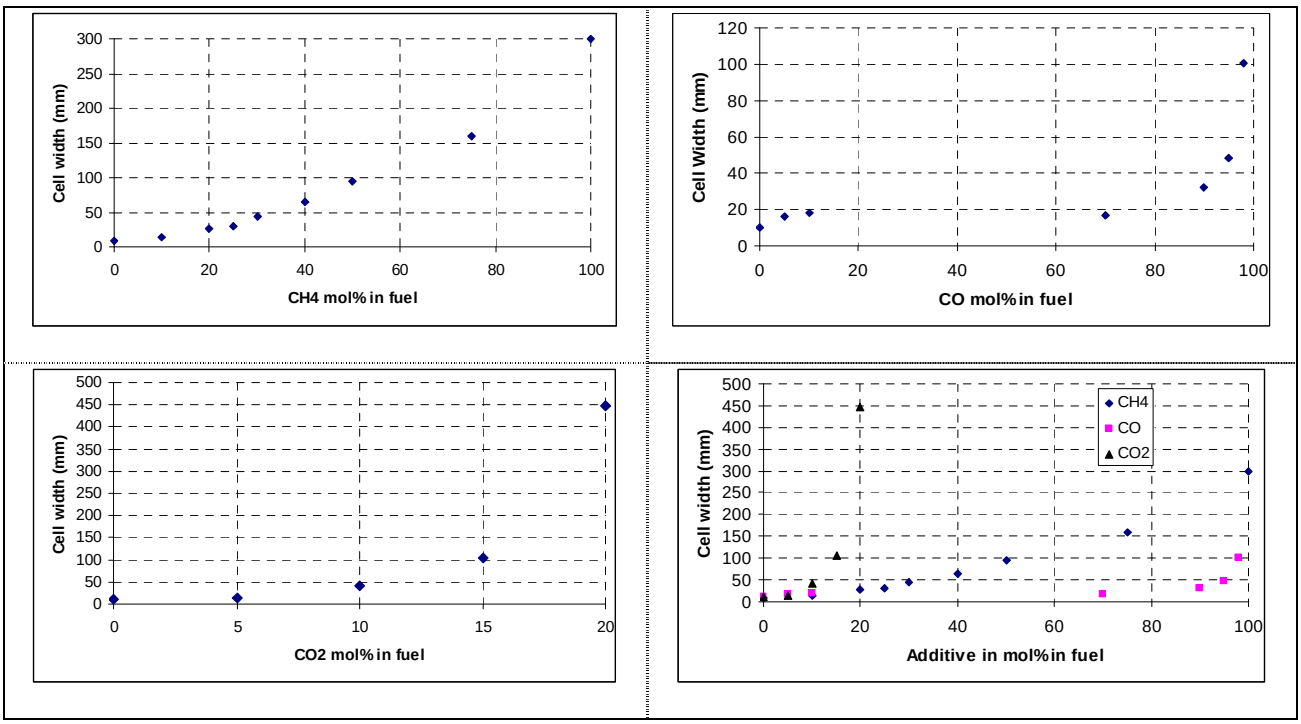

Figure 2. Detonation cells width for H_2/CH_4 – H_2/CO and H_2/CO_2 with air in stoechiometric conditions [12] to [20].

As shown of figure 1, introduction of CO_2, CO and CH_4 in H_2 induces a strong decrease of the stoechiometric laminar flame speed (S_L). The most efficient additive for S_L reduction is CO_2 because it is non-flammable and then acts by simple dilution. For CO_2 percentage larger than 40%, ignition becomes difficult and flame speed determination is impossible. Concerning the other additives, the laminar flame speed reduction is the largest with CH_4 compared with CO. Surprisingly, CO appears to have a poor flame speed reduction capacity.

Concerning detonation, as shown on figure 2, addition of CO_2 strongly increases the detonation cell size. Above 20% CO_2 in H_2, detonation is not experimentally observed even if initiated with strong condensed explosive. In a lower extent, methane addition leads also to an increase of the detonation cell size. As already observed for flame speeds, carbon monoxide addition has a very small impact on cell size. A percentage higher than 80% is needed to reach an observable impact on the cell size.

Using figure 1 and figure 2, the laminar flame speed and detonation cell size of the lumped compositions are calculated in table 2.

Table 2. Laminar flame velocities and detonation cell sizes for different lumping assumptions.

Simplification approach 1		Reformer outlet	Shift outlet
CH_4 # CO_2 # CO	H_2 (%)	70	74
	CO (%)	30	26
	S_L (Φ = 1) (cm/sec)	134	141
	λ (Φ = 1) (mm)	13	12
Simplification approach 2	H_2 (%)	86,5	77
CO # H_2	CH_4 (%)	13,5	23
CO_2 # CH_4	S_L (Φ = 1) (cm/sec)	141	109
	λ (Φ = 1) (mm)	22	33
Simplification approach 3	H_2 (%)	86,5	77
CO # H_2	CO_2 (%)	13,5	23
CH_4 # CO_2	S_L (Φ = 1) (cm/sec)	129	83
	λ (Φ = 1) (mm)	86	No detonation

As can be seen on table 2 , using this binary simplification approach, no SMR mixture stream could be assess with a medium reactivity on the basis of the commonly accepted criterion (S_L < 75 cm/sec and detonation cell size > 50 mm) [21] [25].

3.0 KINETIC APPROACH

The laminar flame speeds are calculated using the CHEMKIN INTERPRETER and PREMIX software (Chemkin 2012).

Two different kinetic mechanisms are investigated:

- GRI-Mech 3.0 [22]. This mechanism (34 species and 225 reactions) has been developed by the Gas Research Institute (USA). It is an optimized mechanism designed to model natural

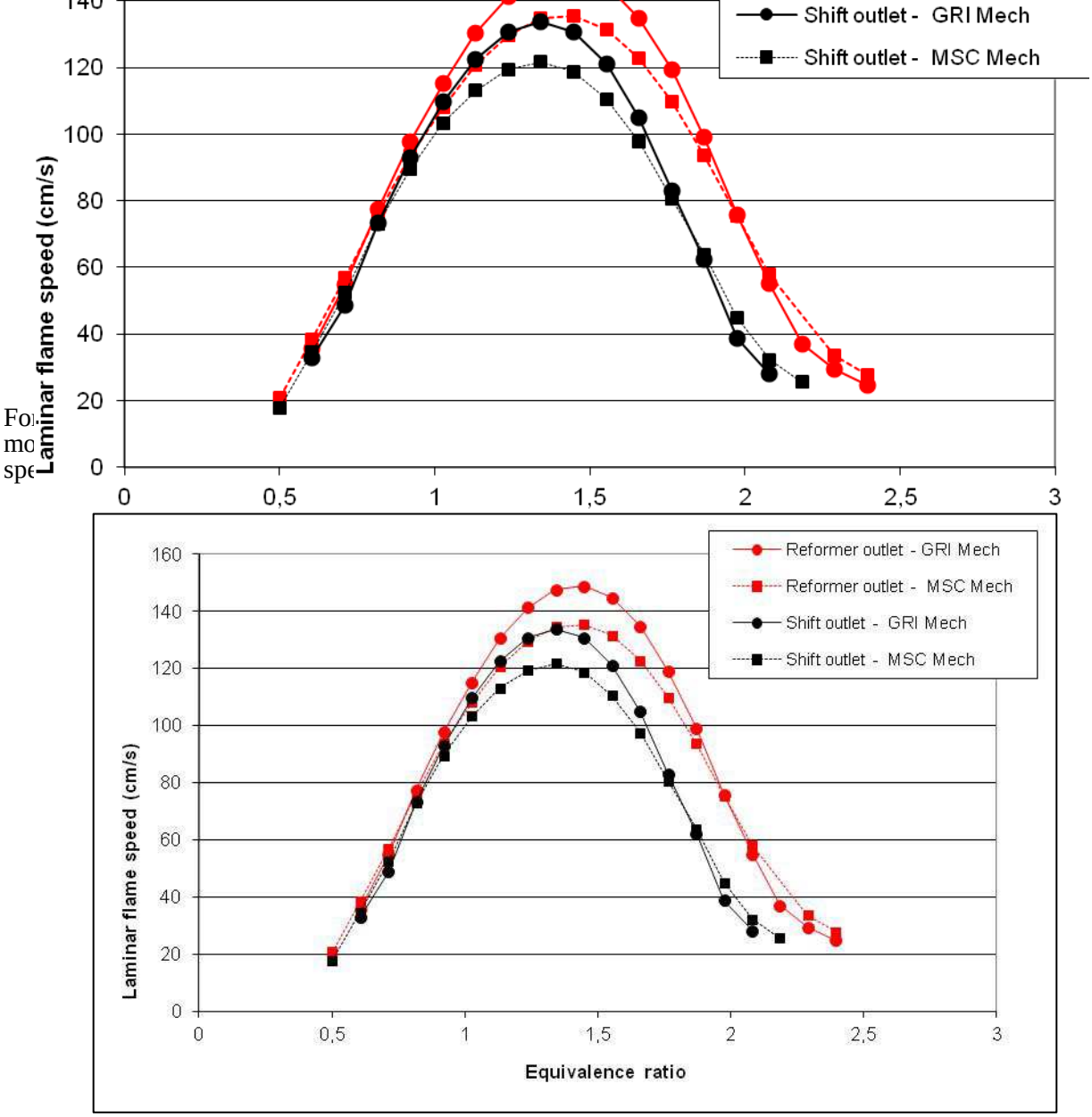

Figure 2. Laminar flame speed as a function of equivalence ratio calculated for the reformer outlet and shift outlet streams using Gri-Mech3.0 and USC-Mech2.0 mechanisms.

The table 4 shows the laminar flame speeds calculated with the two models for the SMR streams.

Table 3. Laminar flame speeds for the two SMR streams

	Reformer outlet	Shift outlet
GRI-Mech3.0	1.15 m/sec	1.10 m/sec
USC-Mech2.0	0.94 m/sec	0.90 m/sec

As shown on table 3, the SMR streams have laminar flame speeds higher than 0.75 m/sec and then have to be considered regarding this criterion as highly reactive. A good agreement is also obtained between the two models.

Gavrikov et al. [24] have proposed a semi-empirical correlation for detonation cell size based on the relation between the multidimensional structure of the detonation waves and their stability.

Knowing the detonation velocity (Chapman Jouguet CJ velocity) and using a detailed kinetic model for calculating the ignition delays behind the detonation shock wave, the detonation cell sizes are calculated.

Gavrikov et al. has validated the model using H_2/air mixtures (from 300 to 650 K, with and without steam or CO_2), H_2/O_2/Ar mixtures and hydrocarbons – air mixtures (CH_4, C_2H_6, C_2H_4 and C_2H_2). The method predicts the size by a factor 2 [24].

These cell size calculations were performed using CELL-CH. The CJ velocities are calculated with the GASEQ software [27].

Before using the Cell_CH software, a validation against experimental data was performed.

In the frame-work of the Hydromel ANR project, detonation cell size has been measured by the Laboratory of Combustion and Detonics (Poitiers France) [15].

These experimental data are compared to the CELL_CH results in the figure 4.

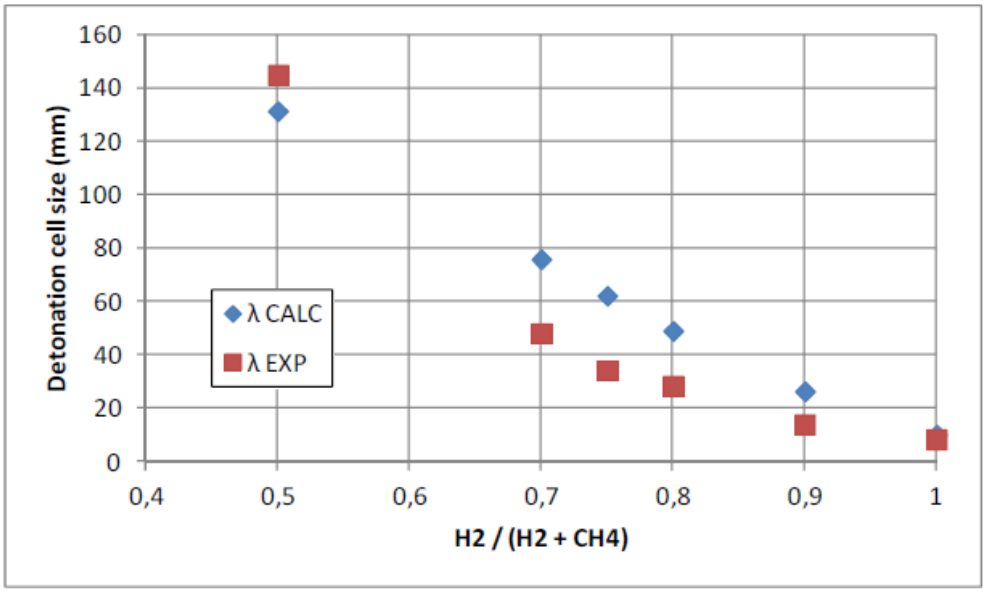

Figure 4. Comparison of the measured and calculated cell size with air in stoechiometric conditions

As shown of figure 4, the agreement is relatively good with a absolute average deviation of 50%.

The table 4 shows the detonation cell size for the SMR streams.

Table 4. Calculated detonation cell size for SMR mixtures

	Reformer outlet	Shift outlet
Cell size (mm)	29.92	42.10

As shown on table 4, the SMR streams have detonation cell size smaller than 50 mm and then have to be considered regarding this criterion as highly reactive.

4.0 CONCLUSIONS

The aim of this study is to assess the reactivity of SMR syngas streams composed H_2, CO, CH_4 and CO_2 on the basis of detonation cell size and laminar flame speed regarding vapour cloud explosions in industrial sites.

For this purpose, two approaches have been compared. On the first hand, some assimilation simplification rules have been assumed on the reactant chemical composition. Then, the laminar flame speeds and detonation cell sizes of the obtained simplified binary mixtures are determined from the literature. Using the approach with three different simplification assumptions, on the basis of the commonly accepted criterion (i.e. $S_L < 75$ cm/sec and detonation cell size > 50 mm) these SMR streams could not be considered having a medium reactivity.

On the second hand, the laminar flame velocities and detonation cell sizes on the exact syngas compositions have been calculated using recent methods based on detailed chemical kinetic mechanism. Even with this more precise method, these SMR streams could not be considered having a medium reactivity. Nevertheless, when possible, this approach should be preferred.

As a perspective, it should be interesting to apply this methodology to syngas compositions produced by others processes (POX, ATR and coal gasifier) having different compositions (more CO after the first oxidation step, and more CO_2 after shift).

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