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## COMPARISON OF CHEMICAL KINETIC MECHANISMS FOR COMBUSTION SIMULATION OF TREATED BIOGAS

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Living on a planet with limited resources, more efficient and cleaner combustion is highly desired. Moreover, focus is now on renewable energy. The development of internal combustion engines fuelled by biogas requires both CFD and chemical kinetic simulations. Several detailed chemical kinetic models dealing with the combustion of C1–C3 fuels have been published already. This work uses a selection of these models in COSILAB software assuming treated biogas as methane enriched with ethane and propane, under engine-relevant, lean conditions. The models are compared to each other regarding their performance in laminar flame speed obtained from a one-dimensional freely propagating flame model, and ignition delay time obtained from a zero-dimensional homogeneous ignition process in a batch reactor.

**Key words:** chemical kinetic, combustion, biogas.

**Usporedba mehanizama kemijske kinetike za simulaciju izgaranja obrađenog bioplina.** Za življenje na planeti s ograničenim resursima poželjno je učinkovitije i čišće izgaranje. Osim toga, danas je naglasak na obnovljivim izvorima energije. Razvoj motora s unutarnjim izgaranjem koji koriste bioplin zahtijeva i računalnu simulaciju dinamike fluida (CFD) i simulaciju kemijske kinetike. Objavljeno je već nekoliko modela kemijske kinetike koji se bave izgaranjem C1-C3 goriva. U ovom radu izbor tih modela proveden je u COSILAB programskom paketu uz pretpostavku da je bioplin metan obogaćen s etanom i propanom pri blagim, ali za rad motora važnim uvjetima. Modeli su međusobno uspoređeni glede performansi u brzini laminarnog plamena dobivenih iz jednodimenzionalnog modela slobodno rasprostirajućeg plamena, a vrijeme odgode paljenja dobiveno je iz bezdimenzionalnog modela homogenog procesa paljenja u kotlastom reaktoru.

**Ključne riječi:** kemijska kinetika, izgaranje, bioplin.

### INTRODUCTION

With the ongoing increase in calculation power of computers and the increasing focus on more fuel-efficient and less polluting engines, detailed chemical kinetic mechanisms for the simulation of C1-C3 gaseous fuel combustion also covering NO<sub>x</sub> formation have evolved. For instance, the well-known GRI-Mech 3.0 [1] published in 1999 covers 53 species in 325 reaction equations. Ranzi et al. [2] published a

mechanism that uses 113 species in 1909 reaction equations in 2012. In this paper, the laminar flame speed  $s_L$  and the ignition delay time  $\tau$  [3] were selected as criteria for comparing the overall performance of those mechanisms. They were originally developed for natural gas combustion but are suitable for the simulation of the combustion of treated biogas as well. After all, biogas cleaned to >96% v/v CH<sub>4</sub> can be fed into the

already existing gas grid. Heating value and Wobbe index are adapted to the gas grid standard by adding propane. [4]

Despite high performance of modern computers, it is still impossible to use large detailed chemical kinetic mechanisms for CFD simulation because solving detailed mechanisms for each cell results in extremely long computation times. For this reason reduced chemical kinetic mechanisms are used. They behave similarly within boundary conditions regarding defined

criteria. Reduction can be performed heuristically or systematically by eliminating species and reactions, lumping, i.e. the replacement of several similar species and their reactions with a species class and class reactions, and solution mapping, i.e. the use of a solution library. [5] The development of such a reduced mechanism is a long-term objective of this project, beginning with the choice of a suitable detailed mechanism for adaptation and reduction.

## SIMULATION EXPERIMENTS

For the simulation of  $\tau$ , a zero-dimensional isochoric homogeneous batch reactor model was used. The value of  $\tau$  was obtained by the maximum increase of pressure over time.  $s_L$  was modelled by a one-dimensional freely propagating flame. The temperature was 900K and the pressure was 150bar, conditions where engine knock is likely to occur. The equivalence ratio  $\phi$  was 0.55 for technical air, i.e. 21% v/v O<sub>2</sub> and 79% v/v N<sub>2</sub>. The gas mixtures used for

simulation are shown in Table 1. Data for the mechanisms chosen are shown in Table 2. Simulations were performed using COSILAB software version 3.3 6652 on a PC using Windows® XP 32-bit. The ignition delay times obtained are presented in Figure 1; Figure 2 shows the laminar flame speeds. It was not possible to calculate laminar flame speeds with the NUIG mechanism because the required transport data were not available.

**Table 1.** Gas mixtures used for simulation

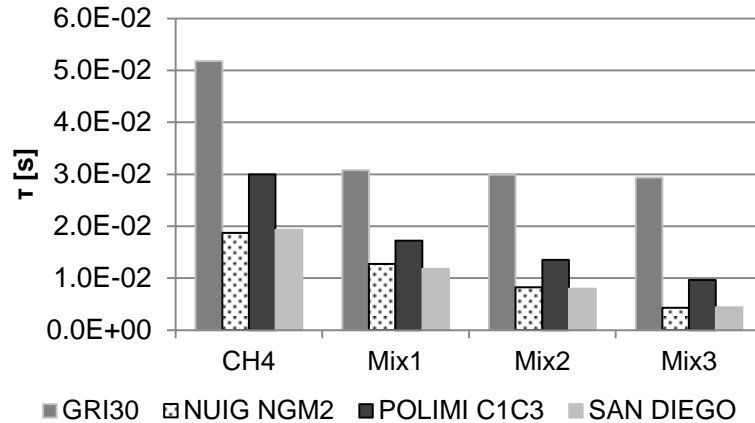
**Tablica 1.** Smjese plina korištenog za simulaciju

<b>Mixture Name</b>	CH4	Mix1	Mix2	Mix3
<b>CH<sub>4</sub> [% v/v]</b>	100	97.24	94.98	87.94
<b>C<sub>2</sub>H<sub>4</sub> [% v/v]</b>	0	2.16	2.11	1.94
<b>C<sub>3</sub>H<sub>8</sub> [% v/v]</b>	0	0.60	2.91	10.12

**Table 2.** Chemical kinetic mechanisms used for simulation

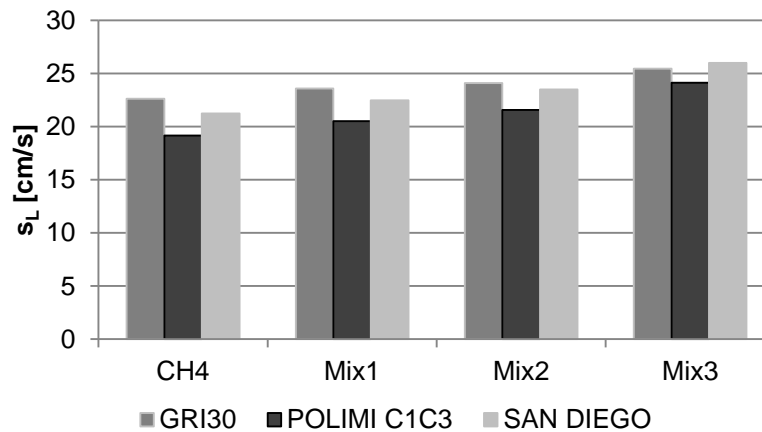
**Tablica 2.** Mehanizmi kemijske kinetike korišteni za simulaciju

<b>Mechanism</b>	<b>Species</b>	<b>Equations</b>	<b>Scope</b>	<b>NO<sub>x</sub> covered</b>
GRI-Mech 3.0 [1]	53	325	C1-C2, propane: traces	yes
NUIG NGM2 (nC5_44) [6]	289	1580	C1-C5	no
POLIMI CRECK C1C3 [2]	113	1909	C1-C3	yes
SAN DIEGO + NO <sub>x</sub> [7]	63	297	C1-C3	yes



**Figure 1.** Ignition Delay Times at 900K, 150bar,  $\phi=0.55$

**Slika 1.** Vremena odgode paljenja na 900K, 150bar,  $\phi=0.55$

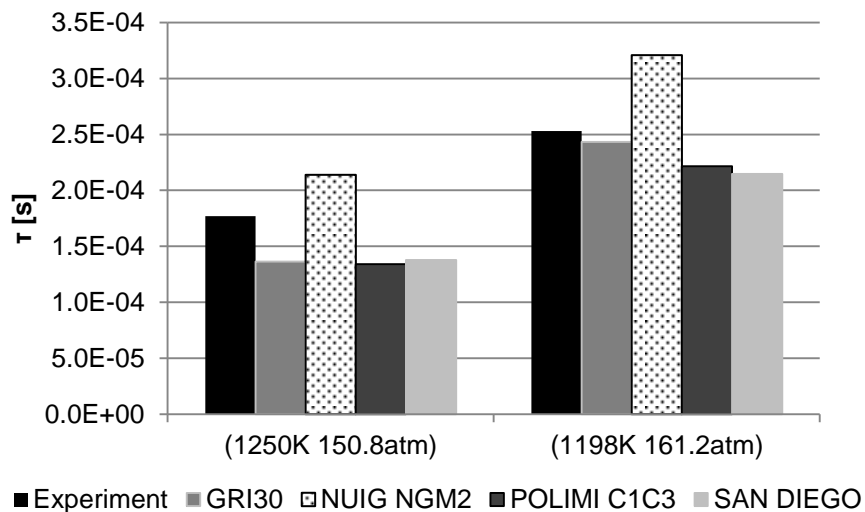


**Figure 2.** Laminar Flame Speed at 900K, 150bar,  $\phi=0.55$

**Slika 2.** Laminarna brzina plamena pri 900K, 150bar,  $\phi=0.55$

For CH<sub>4</sub> ignition delay times from high-pressure shock tube experiments [8] were published for a lean mixture with  $\phi=0.4$  and N<sub>2</sub> replaced by Ar. These two experiments at 1250K and 150.8atm, resp.

1198K and 161.2atm were also modelled with the four mechanisms shown in Table 2. Figure 3 presents a comparison of the simulated ignition delay times to the experimental data.



**Figure 3.** Ignition delay times from shock tube experiments and their simulation  
**Slika 3.** Vremena odgode paljenja iz eksperimenata i njihova simulacija

## DISCUSSION

In general, the opposing trends of  $s_L$  and  $\tau$  with increasing propane content of the fuel mixture could be observed very well. GRI-Mech 3.0 was incapable of handling higher propane contents in the calculation of  $\tau$ , a behaviour that is pointed out on the GRI-Mech website. Figure 1 shows that this mechanism also calculated larger values for  $\tau$  than the other three mechanisms even for pure  $\text{CH}_4$ . NUIG NGM2, POLIMI C1C3 and SAN DIEGO performed similarly. NUIG NGM2 and SAN DIEGO delivered nearly the same results in Figure 1. Considering the simulation of the  $\text{CH}_4$  shock tube experiments, all four mechanisms perform very well with NUIG NGM2 slightly

overestimating  $\tau$ , whereas the other three calculate values slightly lower than the experiment. GRI-Mech 3.0 also shows good agreement with the measurements. It is interesting to see that a 350K temperature increase from 900K to 1250K results in a drop of  $\tau$  from approx. 30ms to approx. 0.15ms.  $s_L$  increased with higher propane content of the fuel mixtures with all three mechanisms showing very similar values.

In the simulations this trend is not as pronounced as the decrease of  $\tau$ . This shows that  $s_L$  has a lower sensitivity to the fuel composition than  $\tau$ .

## CONCLUSION

Ignition delay times and laminar flame speeds were simulated with different detailed chemical kinetic mechanisms for methane and three methane/ethane/propane mixtures with propane contents of up to

10.2% v/v as model mixtures for treated biogas. The simulations were performed at 900K, 150bar and  $\phi=0.55$ , conditions where engine knock is likely to occur. All mechanisms showed the opposing trends of

$s_L$  and  $\tau$  with increasing propane content, with  $\tau$  being more sensitive to the propane content of the fuel mixture than  $s_L$ . All mechanisms showed very good agreement with shock tube experiments for the lean combustion of methane [8]. However, further comparison with available ignition

delay time and laminar flame speed measurements for lean C1-C3 mixtures at elevated temperatures and high pressures has to be accomplished in order to choose a mechanism for further adaptation and reduction.

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