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To cite this article: Y Muharam et al 2018 IOP Conf. Ser.: Earth Environ. Sci. 105 012089

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Prediction of ignition delay time of Liquefied Gas for Vehicle (LGV)

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Abstract. Ignition delay time of liquefied petroleum for vehicle (LGV) fuel was predicted in this research. The method was using a detailed kinetic model of oxidation and combustion of propane/n-butane mixture. The validation of the model used experimental data in shock tubes in the temperature range from 1300 K to 1500 K and the pressure range from 2.5 bar to 10 bar for pure propane and pure n-butane. Calculated results of ignition delay time using the model have good agreement with experimental results indicating that the model may be used for LGV fuel. Simulation results of the model of LGV fuel show that the ignition delay time is faster when the n-butane fraction in the fuel is higher. The switchover of the ignition delay time order among different compositions of the fuels takes place at the initial temperature of 1200 K for the equivalence ratios of 1 and the initial pressure of 10 bar.

1. Introduction

Liquefied gas for vehicle (LGV) is liquefied petroleum gas (LPG) used as a fuel in internal combustion engines as well as in stationary applications such as generators. It is a mixture of propane and butane. It is a green fuel since it reduces CO₂ exhaust emissions. It has an octane rating (RON) that is between 93.5 and 109.4 [1] and an energy content (higher heating value—HHV) that is between 25.5 MJ/L (for pure propane) and 28.7 MJ/L (for pure butane) depending upon the actual fuel composition.

One of combustion characteristics in internal combustion engines is autoignition. In diesel engine autoignition of a fuel is desired when the fuel injected into combustion chamber. The autoignition is caused by the high temperature which the air achieves when it greatly compressed. There is a period between the start of injection and the start of combustion, which is called delay time. In diesel engines, the delay time consists of physical delay wherein atomization, vaporization and mixing of air-fuel occur, and of chemical delay attributed to pre-combustion reactions [2]. The latter is caller ignition delay time. In spark-ignition engines which use spark plugs to ignite an air-fuel mixture autoignition is unwanted. The autoignition occurs because the increases in temperature and pressure of the unburned end gas cause it to ignite before it has been consumed by the propagating flame. This raises audible knocking. This malfunction is a serious limitation to the power developed and could lead to engine damage [3].

Research on the oxidation and combustion of LPG has been carried out by Kim et al. in a rapid compression machine [4]. It used pure butane and propane/butane mixture as the fuel. It investigated the ignition delay times of the fuel in the temperature ranging from 720 K to 900 K, the pressure range of 16 bar – 18 bar and equivalence ration of 1. The autoignition of LPG in spark-ignition engines was
investigated by Morganti et al. [5]. The experiments examined four species which are the primary constituents of LPG, i.e. propane, propylene (propene), n-butane and iso-butane.

Experimental and detailed kinetic study of the gas-phase oxidation of LPG (propane/n-butane/iso-butane) were performed in a jet-stirred reactor by Dagaut and Ali [6] at 1 bar, over the temperature range of 950 K – 1450 K and for equivalence ratios of 0.25, 0.5, 1, 1.5, 2 and 4. Mole fraction profiles as a function of temperature were obtained for molecular species. These experimental data were used to validate the detailed kinetic reaction mechanism consisting of 112 species and 827 reactions. Overall, the model is in very good agreement with the experimental data.

The recent research is intended to predict the ignition delay time of LGV using a kinetic model of detailed reaction mechanism of the fuel. The effects of propane/butane ratio, initial temperature, initial pressure and equivalence ratio on the ignition delay time were studied.

2. Method

Liquefied gas for vehicle considered in the research consists of propane and n-butane. The detailed reaction mechanism of LGV was derived from the detailed reaction mechanism for large aliphatic hydrocarbons developed by Muharam [7]. The validation was performed by comparing the calculated results of ignition delay time with the experimental data of ignition delay time for pure propane and pure n-butane. The data was obtained from Burcat and Radhakrishnan using a shock tube in the temperature range from 1300 K to 1500 K and the pressure range from 2.5 bar to 10 bar [8].

3. Modelling

In chemistry, a reaction mechanism is the step by step sequence of elementary reactions by which overall chemical change occurs [9]. If there are many elementary reactions, the net amount of a reactant consumed or a product produced will arise from the addition of the contributions of each elementary reaction. In general, species will take part in the reaction as a reactant and as a product on the other. The rate of production and consumption is a net result of all elementary reactions.

For a mechanism consisting of R elementary reactions of S species, which is given by

\[
\sum_{i=1}^{8} v_i(c_i A_i) \rightarrow \sum_{i=1}^{8} v_i(p_i A_i)
\]

where \( r = 1, 2, \ldots, R \), \( v_i(c) \) and \( v_i(p) \) indicate the stoichiometric coefficients of reactants and products, respectively, the rate of formation of a species \( i \) is obtained from the addition of the whole rate equations where the species \( i \) is involved,

\[
\left( \frac{\partial c_i}{\partial t} \right)_{chem} = \sum_{r=1}^{8} k_r \left( v_i^{(p)} - v_i^{(c)} \right) \prod_{s=1}^{8} c_s^{(c)}
\]

where \( i = 1, 2, \ldots, S \).

The rate laws for a reaction mechanism consisting of R reactions among S species can be written as a system of first order ordinary differential equations,

\[
\frac{dc_i}{dt} = F_i(c_1, \ldots, c_S, k_1, \ldots, k_R) \quad i = 1, 2, \ldots, S
\]

with initial conditions

\[
c_i = c_i^0 \text{ at } t = t_0
\]

For many elementary reactions, a change in the parameters of the system (the rate coefficients) has nearly no effect on the time-dependent solution. Even if the reaction is included explicitly in the mechanism, it does not need a highly accurate rate coefficient. On the other hand, for a few of the elementary reactions, changes in the rate coefficients have really large effects on the outcome of the system. Accordingly, accurate rate coefficients are demanded. These few important reaction steps are
rate-determining steps or rate-limiting steps. The dependence of the solution $c_i$ on the parameters $k$ is called sensitivity and sensitivity analysis is a procedure to validate the kinetic model of detailed reaction mechanism.

4. Validation
The detailed reaction mechanism for the oxidation and combustion of propane/n-butane mixture consists of 155 species involving in 689 elementary reactions. Each elementary reaction is equipped with Arrhenius parameters which are pre-exponential factor ($A$), temperature exponent ($n$) and activation energy ($E_a$). Figure 1 and Figures 2 show the experimental and calculated ignition delay times of propane and n-butane. In general, the calculated ignition delay times are in good agreement with the experimental ones.

![Figure 1](image1.png)

**Figure 1.** Experimental and calculated ignition delay times of propane.

![Figure 2](image2.png)

**Figure 2.** Experimental and calculated ignition delay times of n-butane.

5. Simulation
The valid model was then used to predict the ignition delay times in various fuel compositions, initial temperatures, initial pressures and equivalence ratios.

5.1. Fuel composition and initial temperature

Variations in fuel compositions were performed for the equivalence ratios of 1 and the initial pressure of 10 bar. The fuel compositions are: 0% propane and 100% n-butane (LGV-1), 20% propane and 80% n-butane (LGV-2), 40% propane and 60% n-butane (LGV-3), 50% propane and 50% n-butane (LGV-4), 80% propane and 20% n-butane (LGV-5) and 100% propane and 0% n-butane (LGV-6).

The fuels are burned with oxygen from the air so that there is nitrogen in the mixture as diluent.

Figure 2 illustrates the ignition delay times for various fuel compositions in the temperature range from 1100 K to 1500 K. It can be seen in the figure that the ignition delay time is faster when the n-butane fraction in LGV is higher. LGV-1, which is pure n-butane is the fastest, while LGV-6, which is the pure propane is the slowest. This is because carbon-carbon bonds and carbon-hydrogen bonds in longer hydrocarbon molecules, such as n-butane in this case, are weaker than the same bonds in propane molecules, making them easier to break off by radical attacks.

The figure shows an interesting phenomenon, i.e. there is a switchover of the ignition delay time order among different compositions of the fuels. When the temperature decreases to below 1200 K, LGV-1, LGV-6 and other LGVs switch their position. The ignition delay time of LGV-6 becomes the fastest, and that of LGV-1 becomes the slowest. This occurs because in the temperature range below 1200 K, oxidation reactions begin to play their role in ignition delay times.

![Graph showing ignition delay times for various fuel compositions and initial temperatures.](image)

**Figure 3.** Ignition delay times for various fuel compositions and initial temperatures.

5.2. Initial pressure

Variations in initial pressure were carried out for the equivalence ratio of 1 and the fuel composition of 50% propane and 50% n-butane. The simulated initial pressures are 2 bar, 10 bar, and 18 bar.

Figure 4 shows the relationship between the ignition delay time and the initial pressure. It can be seen in the figure that the fuel with the initial pressure of 2 bar has the slowest ignition delay time. When the initial pressure increases to 10 bar, the ignition delay becomes faster. Similarly, when the initial pressure increases to 18 bar, the fuel becomes more combustible. This phenomenon is caused by the involvement of third bodies in a number of chemical reactions. Third body which is a collection of species other than the species expressed in a reaction equation provides energy to the collisions between the reactants so as to speed up the reaction.
5.3. Equivalence ratio
Equivalence ratio varies at the initial pressure of 10 bar and the fuel composition of 50\% propane and 50\% n-butane. The three selected variants represent the mixture types, which are 0.5 (fuel lean), 1 (stoichiometric), and 2 (fuel rich).

The relationship between the ignition delay time and the equivalence ratio is exhibited in Figure 5. It can be seen in the figure that the fastest ignition delay time occurs for fuel lean mixture. This happens because in fuel lean mixture, although the reaction is slow, excess oxygen is able to initiate chain reactions by abstracting more H atoms from more fuel molecules so that the formation of radical pool is faster than that in stoichiometric mixture or fuel rich mixture. As a result, the ignition delay time is faster.

An interesting phenomenon takes place when the temperature decreases to below 1100 K where the fastest ignition delay time occurs for fuel rich mixture. This happens because at the temperatures below 1100 K, chain branching reactions are the decompositions of stable peroxide molecules. The formation of these molecules is preceded by the reaction of oxygen addition to radicals. Indeed, fuel rich mixture provides more fuel, and more fuel provides more alkyl radicals to be oxidized.

Figure 4. Ignition delay times at various initial pressures.

Figure 5. Ignition delay times at various equivalence ratios.
6. Conclusion
Calculated results of ignition delay time using the model have good agreement with experimental results indicating that the model may be used for LGV fuel. Simulation results of the model of LGV fuel show that the ignition delay time is faster when the n-butane fraction in the fuel is higher. The switchover of the ignition delay time order among different compositions of the fuels takes place at the initial temperature of 1200 K for the equivalence ratios of 1 and the initial pressure of 10 bar.

7. Acknowledgement
We express our gratitude to the University of Indonesia, which funded this research through the scheme of Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa No 863/UN2.R3.1/HKP.05.00/2017.

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