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# Rapid compression machine studies on ignition delay changes in a methyl butanoate/*n*-heptane mixture by hydrogen addition

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## ABSTRACT

The use of alternative energy is increasing with the concerns about global warming and the dwindling reserves of fossil fuels. Biodiesel and hydrogen are promising alternative fuels, and engine research has investigated the use of biodiesel/hydrogen mixtures. However, no study has examined the chemical kinetics of biodiesel and hydrogen mixtures. This study investigated the effects of hydrogen on the ignition delay of a methyl butanoate/*n*-heptane mixture. An experiment was conducted using a rapid compression machine (RCM) at 15 bar while varying the temperature (716–858 K) and hydrogen fraction in the fuel mixture (0, 25, 50, and 75%), and a numerical analysis was performed using CHEMKIN-PRO software to understand how the combustion process changes. The experimental and numerical analyses showed that, with hydrogen addition, the ignition delay increased.

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## Introduction

The use of alternative fuels is increasing due to concerns over fossil fuel depletion and carbon dioxide emissions. Extensive studies of biofuels have been conducted to reduce dependence on fossil fuels. Biodiesel, one of the most widely used biofuels, has the advantages of less carbon monoxide (CO), unburned hydrocarbon (UHC), and soot emissions. It is also considered a carbon-neutral fuel. One of the biggest structural differences between biodiesel and diesel is that biodiesel contains oxygen atoms, such that the combustion reaction path of biodiesel differs considerably to that of diesel. Therefore, research on the reaction pathway of oxygenated fuels, especially methyl

esters, is essential for understanding biodiesel combustion. Some researchers have studied the auto-ignition pathway of methyl butanoate (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>) using diverse types of experimental equipment and kinetic analyses [1–7]. In addition, kinetic analyses on large methyl esters such as methyl decanoate (C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>), methyl palmitate (C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>), and methyl linolenate (C<sub>19</sub>H<sub>32</sub>O<sub>2</sub>) have been conducted [5,6,8–11]. However, these studies are challenging because the components require large mechanisms. Brakora et al. suggested a fuel mixture of 1 mol of methyl butanoate and 2 mol of *n*-heptane as a biodiesel surrogate [12]. This fuel mixture not only has similar physical properties to soy-based biodiesel fuel, but includes a methyl ester component similar to that of biodiesel fuel. Also, methyl butanoate and *n*-heptane molecules are

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large enough to be isomerized, which is an important reaction with respect to the low-temperature chemistry of diesel fuel [3]. In addition, this fuel mixture is easy to analyze due to its simple chemical structure. Several kinetic studies on biodiesel fuels have been executed using this surrogate fuel [13–15].

Hydrogen has been attracting attention as a fuel additive due to its superior ignition and emission characteristics. It can reduce CO, CO<sub>2</sub>, and soot emissions, and has a high flame propagation speed, high diffusivity, wide flammability range, and high heating value on a mass basis. Due to these advantages, the effects of hydrogen blending on the combustion of diverse types of fuels have been extensively investigated by many researchers using various types of equipment such as an internal combustion engine, a rapid compression machine, a flow reactor, and a shock tube [16–27]. Effects of hydrogen on the combustion of biodiesel or mixed fuels including biodiesel have also been investigated [28–31].

All of the studies of the effects of hydrogen on biodiesel combustion have mainly involved compression-ignition engine experiments. Biodiesel and biodiesel/diesel mixtures have been researched in homogeneous charge compression ignition (HCCI) combustion, but the effect of hydrogen addition on biodiesel has not been investigated. Therefore, the chemical kinetic effects of hydrogen on biodiesel combustion are not well-known and thus should be investigated further.

This study investigated the effects of hydrogen on ignition delay of a methyl butanoate/*n*-heptane mixture, a simple biodiesel surrogate. Ignition delay time was measured through an RCM experiment using various temperatures and chemical compositions. Sensitivity and rate of production analyses were conducted using CHEMKIN-PRO software to determine how added hydrogen changes the auto-ignition reaction of the methyl butanoate/*n*-heptane mixture.

## Experiment

### RCM

The RCM was used to determine the effects of hydrogen on combustion of a methyl butanoate/*n*-heptane mixture. Fig. 1 is a schematic diagram of the RCM used in this study [24]. This machine is useful for studying combustion phasing because it can directly measure the in-cylinder pressure from which the ignition delay can in turn be directly calculated. The in-

cylinder pressure is measured by a pressure transducer (6125C; Kistler). Then, the pressure signal is amplified and converted into digital signals by data-acquisition hardware. The RCM is driven by pneumatic pressure and stopped by hydraulic pressure. The compressed temperature was approximately 650–900 K, and changes with the compression ratio and initial temperature of the mixture in the premixing vessel. The compressed pressure also changes with the compression ratio and initial pressure of the premixing vessel. The clearance was 1.6 cm and the bore was 5 cm, so the clearance volume was 31.4 cc. The creviced piston is used to prevent a roll-up vortex [32]. In this study, the compression time was 31 ms and the compression ratio was 16.375.

Fuels are mixed with air in the premixing vessel. The inside of the vessel is brought to a high vacuum state (<0.1 Pa) using an oil diffusion pump (VPC-050; ULVAC). Then, methyl butanoate and *n*-heptane are injected into the vessel using a microsyringe and are vaporized immediately due to the extremely low pressure, and 99.999% purity hydrogen and air directly enter into the vessel through the gas line. During this process, the partial pressure of the premixing vessel is monitored continuously with a pressure gauge (626 Baratron; MKS Instruments), and the amount of gas entering is regulated by a metering valve (SS-4BMW-VCR; Swagelok). The inside temperature of the vessel can be set by wrapping the vessel with three heating jackets controlled by a thermostat. The magnetic stirrer is used to make a homogeneous charge in the vessel. Fig. 2 describes the experimental setup for this study.

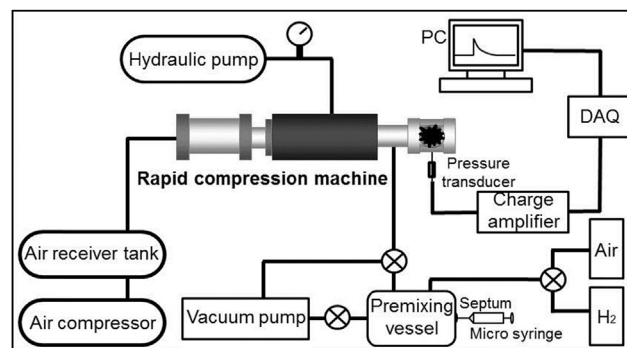


Fig. 2 – Schematic diagram of the experimental setup [24].

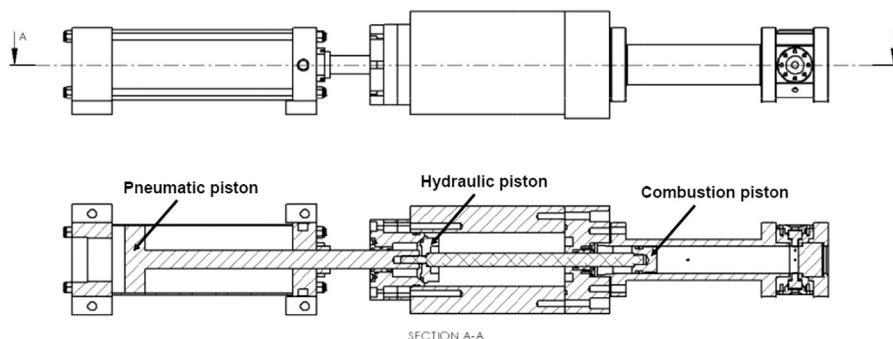


Fig. 1 – Schematic diagram of the rapid compression machine [24].

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