ELSEVIER

Fuel Processing Technology 86 (2005) 1109–1126

FUEL PROCESSING TECHNOLOGY

www.elsevier.com/locate/fuproc

Evaluation of formulation strategies to eliminate the biodiesel NO_x effect

James P. Szybist[a], André L. Boehman[a,*], Joshua D. Taylor[b], Robert L. McCormick[b]

[a]*The Energy Institute, The Pennsylvania State University, 405 Academic Activities Building, University Park, PA 16802, United States*

[b]*Center for Transportation Technologies and Systems, National Renewable Energy Laboratory, 1617 Cole Blvd., MS1633, Golden, CO 80401, United States*

Abstract

In this paper, we explore the efficacy of (1) reducing the iodine value of soy-derived biodiesel fuels through increasing the methyl oleate (methyl ester of oleic acid) content and (2) addition of cetane improvers, as strategies to combat the biodiesel NO_x effect: the increase in NO_x emissions observed in most studies of biodiesel and biodiesel blends. This is accomplished by spiking a conventional soy-derived biodiesel fuel with methyl oleate or with cetane improver. The impact on bulk modulus of compressibility, fuel injection timing, cetane number, combustion, and emissions were examined. The conventional B20 blend produced a NO_x increase of 3–5% relative to petroleum diesel, depending on injection timing. However, by using a B20 blend where the biodiesel portion contained 76% methyl oleate, the biodiesel NO_x effect was eliminated and a NO_x neutral blend was produced. The bulk modulus of petroleum diesel was measured to be 2% lower than B20, yielding a shift in fuel injection timing of 0.1–0.3 crank angle. The bulk modulus of the high methyl oleate B20 blend was measured to be 0.5% lower than B20, not enough to have a measurable impact on fuel injection timing. Increasing the methyl oleate portion of the biodiesel to 76% also had the effect of increasing the cetane number from 48.2 for conventional B20 to 50.4, but this effect is small compared to the increase to 53.5 achieved by adding 1000 ppm of 2-ethylhexyl nitrate (EHN) to B20. For the particular engine tested, NO_x emissions were found to be insensitive to ignition delay, maximum cylinder temperature, and maximum rate of heat release. The dominant effect on NO_x

* Corresponding author. Tel.: +1 814 865 7839; fax: +1 814 863 8892.
E-mail address: boehman@ems.psu.edu (A.L. Boehman).

doi:10.1016/j.fuproc.2004.11.006

emissions was the timing of the combustion process, initiated by the start of injection, and propagated through the timing of maximum heat release rate and maximum temperature.

Keywords: Biodiesel; Diesel; NO_x; Fuel formulation; Bulk modulus; Injection timing; Emissions

1. Introduction

Renewable fuels continue to be of interest to achieve a sustainable energy economy and reduce the effects of fossil fuel utilization. Use of renewable transportation fuels is expanding, and a national 5% renewable fuel standard has been proposed in recently considered energy-related legislation. The primary renewable transportation fuels are ethanol and fuels derived from animal fats and vegetable oils. In the latter case, the fatty acid methyl esters from transesterified animal fats and vegetable oils, referred to as biodiesel, can provide significant reductions in particulate matter, carbon monoxide and hydrocarbon emissions [1]. However, in direct injection diesel engines there is a well-documented increase in NO_x emissions of 2–4% for "B20" blends (e.g., a blend of 20 vol.% biodiesel in diesel fuel) and as much as 10% for B100 [1]. As shown by Van Gerpen et al., the NO_x increase resulting from biodiesel fueling with certain types of injection systems is at least partly attributable to an inadvertent advance of fuel injection timing. This is caused by the higher bulk modulus of compressibility in the fuel blend, which increases the speed of sound, causing a more rapid transferal of the pressure wave from the fuel pump to the injector nozzle, and advancing needle lift [2,3]. Advancing injection timing is well known to cause an increase in NO_x emissions from diesel engines [4]. These observations have recently been confirmed and extended by Szybist and Boehman, showing through measurements of the dynamic injection timing via spray imaging that biodiesel leads to a timing advance in injection [5].

Even prior to the work of Van Gerpen noted above, a number of studies were done to examine the impact of changing fuel injection timing on biodiesel NO_x emissions. Results from two of these studies are shown in Fig. 1 [1]. Injection timing retard was successful at reducing NO_x emissions to the same or lower levels as observed for conventional diesel; however, a significant fraction of the PM emission benefit was lost. Additionally, in the United States and most other countries changing injection timing constitutes changing of an engine's emission control system and would require re-certification of the engine's compliance with emissions standards.

While the reason for the biodiesel NO_x effect largely may be attributable to the difference in bulk modulus between diesel fuels and biodiesel fuels, a strategy to overcome this effect still needs to be determined. Various techniques are possible, including detection of the presence of biodiesel in the fuel and retarding of the static injection timing [6], and blending with other fuels or with additives to prevent the NO_x increase [7]. Van Gerpen et al. have pursued a fuel sensor strategy wherein biodiesel content is detected by measuring the conductivity of the fuel and then enacting some shift to return to a NO_x neutral injection timing [6]. McCormick et al. showed a roughly NO_x neutral B20 biodiesel fuel